2004

Geminal Model Chemistry II. Perturbative Corrections

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Geminal model chemistry II. Perturbative corrections

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We introduce and investigate a chemical model based on perturbative corrections to the product of singlet-type strongly orthogonal geminals wave function. Two specific points are addressed (i) Overall chemical accuracy of such a model with perturbative corrections at a leading order; (ii) Quality of strong orthogonality approximation of geminals in diverse chemical systems. We use the Epstein–Nesbet form of perturbation theory and show that its known shortcomings disappear when it is used with the reference Hamiltonian based on strongly orthogonal geminals. Application of this model to various chemical systems reveals that strongly orthogonal geminals are well suited for chemical models, with dispersion interactions between the geminals being the dominant effect missing in the reference wave functions.   © *2004 American Institute of Physics.*
[DOI: 10.1063/1.1738110]

I. INTRODUCTION

We seek to formulate and investigate a model chemistry that is applicable to multireference systems, computationally inexpensive, and chemically accurate. It is natural to base such a model on two-electron functions, or geminals. In the framework of single-electron basis sets geminals can be represented as linear combinations of two-electron determinants. The chemical models based on geminals were introduced into chemistry by Hurley, Lennard-Jones, and Pople, along with strong orthogonality approximation in order to make the model practical.[1] The simplest variant of such a model represents wavefunctions as a single antisymmetrized product of strongly orthogonal geminals (APSG).[2–7] Sometimes this model is referred to as separated electron pair (SEP) theory.[8–12] Most prior studies focused on the total amount of correlation energy recovered by the product of strongly orthogonal geminals. It was generally concluded that the model has its limitations, primarily attributable to either lack of intergeminal correlation,[5] strong orthogonality approximation,[13] or both.[14]

In Ref. 15 one of us has introduced the antisymmetrized product of singlet-type strongly orthogonal geminal model (SSG), which is a well-defined and size-consistent version of APSG. It is important for a chemical model to be both size consistent (the energy must be an extensive property) and well defined (free from adjustable parameters specific to the system under investigation).[16] In the case of APSG the size-consistency requirement imposes a constraint on the quality of each geminal: The number of orbital pairs in each geminal must be the same in a molecule and in constituent atoms. The SSG model satisfies this constraint by optimization of the orbital pairs in each geminal. The geminals that describe fully broken bonds optimize into single determinants made of spin-unrestricted orbitals, ensuring size consistency.[15]

SSG is implemented in atomic orbital basis, with formal computational scaling of each optimization iteration similar to that of the Hartree–Fock model. The application of SSG was focused on modeling of chemical properties, using various diatomic molecules for test studies. It was found that the SSG model describes covalent bonds surprisingly well, and is deficient when bonds are formed between elements with extreme electronegativity. The primary reason for this deficiency was attributed to the absence of the intergeminal dispersion interaction in the APSG formulation. The SSG model recovers only 20%–30% of the correlation energy for many chemical bonds. To improve the accuracy of a geminal model, it is necessary to include missing electron–electron interactions. An active work in this direction is pursued by Surján's group[17–20] focused on the development of general multireference perturbation theories, with APSG being a special case. Because of this, Surján *et al.* use the projection operator techniques in the multideterminant space to define the reference Hamiltonian. Our goal is different. We analyze the strengths and shortcomings of the SSG model in terms of physical interactions that are accounted for or missing in the model. Therefore, in current work we define a reference Hamiltonian by including some two-electron interactions in addition to a one-particle mean-field Hamiltonian of the single reference theory.

Let us put the SSG model into perspective. The SSG reference wave function is similar to the generalized valence bond model with perfect pairing (GVB-PP).[21] The main difference between the two models is that in the SSG the number of orbital pairs in each geminal, or ''bond,'' is not restricted and is determined variationally. In GVB it is limited to two orbital pairs for each valence electron pair and a single orbital pair for each pair of core electrons. Another, less significant distinction is that the SSG is formulated in either spin-restricted or spin-unrestricted forms, while the GVB is usually spin restricted.

In the context of multiconfigurational theories, the PP approximation assigns a pair of virtual orbitals to a single pair of occupied ones. This approximation is assumed to be

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the most restrictive in the context of the GVB formalism. The full relaxation of the PP approximation leads to the expensive complete active space self-consistent field (CASSCF) model.[22] The main theoretical developments had been focused on some form of intermediate approximations, such as GVB-RP (restricted pairing).[23] A very promising alternative was developed by Van Voorhis and Head-Gordon, who use the coupled-cluster formalism to simplify the configuration space. They have formulated the GVB-RCC (restricted coupled cluster) model,[24] and even less restrictive imperfect pairing model (IP).[25]

The main drawback of these models is that for weakly correlated systems they are inferior to a simple Møller–Plesset perturbation theory taken to the leading order (MP2). Therefore, in order to achieve higher accuracy all these models must be augmented with additional, usually perturbative, treatment of missing excitations.

A research direction complementary to GVB and GVB-inspired models investigates a grouping of virtual orbitals into subclasses and treats various corrections to the reference wave function based on these subclasses. The classification is usually based on a spatial proximity of different orbitals to each other. These studies were pioneered by Pulay and Saebø[26–28] in the context of Møller–Plesset perturbation theory, and further developed using the coupled-cluster formalism.[29,30] The alternative localization schemes based on assignments of basis functions to individual nuclei are developed by Head-Gordon et al.[31]

The SSG theory bridges these two directions of research. The grouping of all orbitals into geminal subspaces is performed variationally, and is based on the strength of electron interactions between electrons on different orbitals. Arguably, this is the best way to subdivide the orbital space into classes. All electron interactions within each group are treated without approximations in the reference model. An important question that is addressed in the current work is the quality of such subdivision, and the nature of missing effects. In particular, it is important to compare the role of strong orthogonality (somewhat similar to perfect pairing in GVB) with the dispersion interactions that do not change identity of individual electron pairs.

II. THEORY

The SSG reference wave function is defined (assuming $n_\alpha \geq n_\beta$) as

$$\Psi_{SSG} = \hat{A}[\psi_1(\mathbf{r}_1, \mathbf{r}_2) \cdots \psi_{n_\beta}(\mathbf{r}_{2n_\beta - 1}, \mathbf{r}_{2n_\beta})$$
$$\times \phi_i(\mathbf{r}_{2n_\beta + 1}) \cdots \phi_j(\mathbf{r}_{2n_\beta + (n_\alpha - n_\beta)})],$$

$$\psi_a(\mathbf{r}_1, \mathbf{r}_2) = \sum_{k \in A} \frac{D_k}{\sqrt{2}} [\phi_k(\mathbf{r}_1)\bar{\phi}_k(\mathbf{r}_2) - \phi_k(\mathbf{r}_2)\bar{\phi}_k(\mathbf{r}_1)],$$

$$\phi_k(\mathbf{r}_1) = \sum_\lambda C_\lambda^k \chi_\lambda(\mathbf{r}_1),$$

$$\bar{\phi}_k(\mathbf{r}_1) = \sum_\lambda \bar{C}_\lambda^k \chi_\lambda(\mathbf{r}_1),$$

(1)

where $\hat{A}$ is the antisymmetrization operator. Molecular orbital (MO) coefficients C, geminal expansion coefficients D, and subspaces A are variationally optimized to minimize the energy

$$E_{SSG} = \frac{\langle \Psi_{SSG} | \hat{H} | \Psi_{SSG} \rangle}{\langle \Psi_{SSG} | \Psi_{SSG} \rangle}, \tag{2}$$

evaluated with exact Hamiltonian $\hat{H}$. The optimization of the geminal subspace is the optimization of a number of MOs assigned to a given geminal. A further constraint $\bar{C}_\lambda^k = C_\lambda^k$ for all MO coefficients yields a spin-restricted version of SSG, or RSSG. The spin-unrestricted form is labeled USSG.

For every geminal A we define four one-electron density matrices $\mathbf{P}^{\alpha,A}$, $\mathbf{P}^{\beta,A}$, $\mathbf{P}^{0,A} = \mathbf{P}^{\alpha,A} + \mathbf{P}^{\beta,A}$, and $\mathbf{P}^{e,A}$ with elements

$$P_{\lambda\sigma}^{\alpha,A} = \sum_{a \in A} (D_a)^2 C_\lambda^a C_\sigma^a,$$

$$P_{\lambda\sigma}^{\beta,A} = \sum_{a \in A} (D_a)^2 \bar{C}_\lambda^a \bar{C}_\sigma^a, \tag{3}$$

$$P_{\lambda\sigma}^{e,A} = \sum_{a \in A} D_a C_\lambda^a \bar{C}_\sigma^a.$$

Note that the last cross-spin matrix $\mathbf{P}^{e,A}$ is not symmetric in the USSG case. Open-shell orbitals ϕ_i form an additional density matrix

$$P_{\lambda\sigma}^{\alpha,I} = \sum_i^{\text{open shell}} C_\lambda^i C_\sigma^i. \tag{4}$$

We also define density matrices for the whole system $\mathbf{P}^{\alpha,T} = \Sigma_A \mathbf{P}^{\alpha,A} + \mathbf{P}^{\alpha,I}$, $\mathbf{P}^{\beta,T} = \Sigma_A \mathbf{P}^{\beta,A}$, and $\mathbf{P}^{0,T} = \mathbf{P}^{\alpha,T} + \mathbf{P}^{\beta,T}$. The two-electron integrals are contracted using these matrices as

$$J_{\lambda\sigma}^A = \sum_{\mu\nu} P_{\mu\nu}^{0,A}(\lambda\sigma|\mu\nu),$$

$$K_{\lambda\sigma}^{\alpha,A} = \sum_{\mu\nu} P_{\mu\nu}^{\alpha,A}(\lambda\mu|\sigma\nu), \tag{5}$$

$$L_{\lambda\sigma}^A = \sum_{\mu\nu} P_{\mu\nu}^{e,A}(\lambda\mu|\sigma\nu).$$

Expressions for $\mathbf{J}^T$, $\mathbf{K}^{\alpha,T}$, $\mathbf{K}^{\beta,A}$, $\mathbf{K}^{\beta,T}$ can be obtained by substituting the corresponding density matrices into the above equations. Note that the intergeminal matrix $\mathbf{L}^A$ is not symmetric in the USSG case. A global Fock matrix is defined as $\mathbf{F}^\alpha = \mathbf{h} + \mathbf{J}^T - \mathbf{K}^{\alpha,T}$, and Fock matrices for each geminal are $\mathbf{F}^{\alpha,A} = \mathbf{F}^\alpha - \mathbf{J}^A + \mathbf{K}^{\alpha,A}$ (with similar expressions for β-spin matrices). The geminal Fock matrices describe all one-electron interactions plus mean-field (i.e., Coulomb and exchange) interactions between electrons in a given geminal and all other electrons in the system.

The first step in the definition of perturbation expansion is to establish a zeroth-order reference Hamiltonian, H_0. We define it as close as possible to the one-electron Fock operator used in Møller–Plesset perturbation theory (MPPT). In order to ensure that the SSG reference wave function is the eigenfunction of the reference Hamiltonian, two-electron

terms must be included in H_0. In the context of APSG formulation it is natural to include all intrageminal interactions into H_0, as was done by Rosta and Surján.[17] This choice, however, complicates solutions for excited states of H_0 with three or four electrons in a geminal. To simplify computation of such excited states we define an auxiliary Hamiltonian $\tilde{H}_0$ as

$$\tilde{H}_0 = \sum_i F_{ii} a_i^\dagger a_i - \sum_A \sum_{i,j \in A} (ij,\overline{ij})[a_i^\dagger \bar{a}_i^\dagger a_j \bar{a}_j + (1 - \delta_{i,j}) a_i^\dagger \bar{a}_j^\dagger a_j \bar{a}_i], \qquad (6)$$

where bars indicate beta spin-orbitals, and F_{ii} are diagonal matrix elements of a Fock matrix of a geminal containing orbital i, $\delta_{i,j}$ is Kronecker delta function, and $(ij,kl) = \int \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_1)(1/r_{12}) \phi_k(\mathbf{r}_2) \phi_l(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$. The two-electron intrageminal electron repulsion part contains two terms. The first term couples doubly occupied orbital pairs to each other and is required to make the reference function an eigenfunction of $\tilde{H}_0$. The second term couples spins in open-shell orbitals within each geminal. It is included in $\tilde{H}_0$ for two reasons. First, it preserves the symmetry of Coulomb operator with respect to interchange of same-electron orbitals. Second, it describes relatively strong interactions between excited states that can be nearly degenerate, thus having a potentially significant effect on the rate of convergence of perturbation expansion.

An important and undesirable feature of $\tilde{H}_0$ is that it contains only diagonal elements of a generalized Fock matrix. The issue here is the invariance of zeroth-order Hamiltonian with respect to transformations that do not change the reference wave function. In contrast to the single determinant case, any transformation among APSG orbitals changes the wave function. The exception to this rule are the transformations among orbitals that are fully occupied in SSG wave function, such as those in uncorrelated geminals and open-shell orbitals. Therefore, one has to choose a particular set of these transformable orbitals to be used in the definition of $\tilde{H}_0$. We choose to diagonalize the global Fock matrix $\mathbf{F}$ in the subspace of fully occupied orbitals. This choice is well defined and consistent with MPPT. In future studies of open-shell systems we plan to investigate the generalization of Edmiston–Ruedenberg localization[32] of such orbitals.

The perturbative expansion of exact wave function and its energy around small perturbation $V = H - \tilde{H}_0$ leads to familiar expressions for leading corrections to wave function

$$|\Psi^1\rangle = \sum_{k=1} |\Psi_k\rangle \frac{\langle \Psi_0 | V | \Psi_k \rangle}{\langle \Psi_0 | \tilde{H}_0 | \Psi_0 \rangle - \langle \Psi_k | \tilde{H}_0 | \Psi_k \rangle}, \qquad (7)$$

and energy

$$E^2 = \sum_{k=1} \frac{\langle \Psi_0 | V | \Psi_k \rangle \langle \Psi_k | V | \Psi_0 \rangle}{\langle \Psi_0 | \tilde{H}_0 | \Psi_0 \rangle - \langle \Psi_k | \tilde{H}_0 | \Psi_k \rangle}, \qquad (8)$$

where the summation runs over all excited states Ψ_k of $\tilde{H}_0$.

Epstein–Nesbet form of perturbation expansion

An alternative formulation of perturbative expansion includes all diagonal terms $\langle \Psi_k | H | \Psi_k \rangle$ in the reference Hamiltonian

$$H_0 = \sum_{k=0} |\Psi_k\rangle \langle \Psi_k | H | \Psi_k \rangle \langle \Psi_k |, \qquad (9)$$

where the summation runs over all eigenstates of $\tilde{H}_0$. This perturbation expansion, known as Epstein–Nesbet (EN) PT,[33,34] has expressions for the leading corrections to wave function and energy similar to Eqs. (7) and (8)

$$|\Psi^1\rangle = \sum_{k=1} |\Psi_k\rangle \frac{\langle \Psi_0 | V | \Psi_k \rangle}{\langle \Psi_0 | H | \Psi_0 \rangle - \langle \Psi_k | H | \Psi_k \rangle},$$

$$E^2 = \sum_{k=1} \frac{\langle \Psi_0 | V | \Psi_k \rangle \langle \Psi_k | V | \Psi_0 \rangle}{\langle \Psi_0 | H | \Psi_0 \rangle - \langle \Psi_k | H | \Psi_k \rangle}. \qquad (10)$$

The only difference between Epstein–Nesbet and Møller–Plesset perturbation equations taken to the leading order is that ENPT denominators contain matrix elements with exact Hamiltonian, as opposed to the reference Hamiltonian in MPPT.

The main formal advantage of ENPT is that its perturbation is much weaker than in MPPT, at least in the manifold of excited states. MPPT uses ground-state mean-field potential in the expression for excited state energies. This is known to be a poor approximation,[35] as can be seen by comparing CI excitation energies with those obtained from orbital energy differences. This deficiency prompted a number of researchers to study ENPT with single-reference[35,36] and multi-reference[37] wave functions. The ENPT was found deficient for three reasons. First, it exhibits slow and oscillatory convergence for some open-shell systems.[35] Second, it is not invariant under unitary transformation of the degenerate orbitals, leading to serious artifacts in intermolecular interaction energies.[36] Third, it is very sensitive to transformations of virtual orbitals, even in the multireference case.[37]

We argue that ENPT is free from these deficiencies when used with the SSG reference wave function. It is easy to see that orbital rotation problems are irrelevant, because the SSG wave function is, in general, not invariant under any orbital transformation. Even for fully occupied orbitals the orbital rotation invariance is formally lost if the reference Hamiltonian is defined by Eq. (6) due to the presence of explicit two-electron interactions between fully occupied orbitals of the same geminal. It is important to note that the reference SSG wave function is invariant under such a rotation, and this invariance is lost by a particular choice of the reference Hamiltonian $\tilde{H}_0$. Optimized SSG orbitals are localized in space, and ENPT works better with localized orbitals.[36]

The oscillatory and slow convergence problem requires a more careful analysis. It is apparent that the source of convergence problem in the single reference case is nearly vanishing energy denominators. In order to understand the difference between excited state energies in single determinant and SSG cases, let us consider a geminal calculation of helium atom with 6-31G($2p$) basis set as an example. In particular, let us focus on p orbitals. There are two of them for

TABLE I. Comparison of different forms of perturbation theory for NH_2 radical with 6-31G basis. The MPPT and ENPT results (labeled "UMP" and "EN") are taken from Ref. 35. Each row shows an increment of total energy at a given order of perturbation expansion. In coupled-cluster case (labeled "CC"), second row shows the result of CCSD calculation, and third row shows CCSD(T) calculation. The SSG data demonstrates EN theory results applied to SSG reference wavefunction. All values are in hartrees.

Order	UMP	EN	CC	SSG(EN)
$0+1$	-55.38193	-55.18159	-55.38193	-55.39486
$\Delta 2$	-0.03154	-0.35890	-0.05360	-0.04094
$\Delta 3$	-0.00621	$+0.23848$	-0.00254	
$\Delta 4$	-0.00251	-0.32636		
$\Delta 5$	-0.00123	$+0.38697$		
$\Delta \infty$	-0.01751		-0.00286	-0.00512

each Cartesian component. The lowest p-orbital pair has a geminal expansion coefficient of -0.037, and its MO coefficients are [0.487, 0.637]. In contrast, the Hartree–Fock calculation yields lowest virtual p orbital with MO coefficients [-0.061, 1.034]. The $1s$ orbitals in two calculations are nearly identical, as one expects for weakly correlated systems. The big difference in p orbitals is explained by a different optimization procedure. In the Hartree–Fock case, the diagonalization of the Fock matrix implies that each virtual orbital is optimized by minimizing its orbital energy, subject to orthogonality to all other orbitals with lower energy. In the SSG case, each "virtual" orbital pair is effectively optimized to increase its interaction with the "occupied" orbital pair. This yields lower energy virtual orbitals that are localized in the regions of occupied orbitals. As a result, energy gaps between excited- and ground-state configurations are much larger in SSG than in Hartree–Fock. Larger energy gaps should lead to smoother convergence of perturbative expansion. We want to emphasize that relatively large gaps are obtained without artificial energy shifts (such shifts may lead to smoother, but slower convergence). Instead, they are a natural result of the inclusion of most important two-electron interactions in the reference Hamiltonian.

As an illustration of perturbation convergence we look at semidissociated NH_2 radical, studied by Murray and Davidson.[35] The N–H bond distance is 2.026 Å, with HNH angle of 103.2°. We show SSG and CCSD(T) results along with their single reference UMPPT and ENPT results in Table I. Our actual calculation was performed by adding an extra hydrogen supporting a single STO-3G basis function 10 Å away from nitrogen, as described in the next section. While we have computed only the leading term in the EN perturbation expansion as applied to spin-unrestricted SSG reference, it is apparent that this model is free from problems seen in the single reference case. This is so because the leading term recovers 89% of remaining correlation energy, yielding the result in close agreement with CCSD model.

The comparison of ENPT and MPPT applied to SSG reference state for a wide variety of chemical systems has to be studied further. We plan to pursue this study when our capabilities are extended to open-shell systems. In this paper we focus on overall chemical performance of perturbatively corrected geminal model, and on the investigation of the quality of SSG reference wave function. The Epstein–Nesbet

version of perturbation theory is better suited for the latter task, as discussed in Sec. V. Therefore, we choose H_0 given by Eq. (9) as the reference Hamiltonian, with many-electron basis functions Ψ_k taken as eigenfunctions of the Hamiltonian given by Eq. (6). We designate this theory as SS-G(EN). In this paper we use leading corrections of SSG(EN) and designate them as SSG(EN2).

The formal computational bottleneck of SSG(EN2) perturbation expansion is the full $O(N^5)$ integral transformation to the molecular orbital basis.

III. TECHNICAL DETAILS

One of the biggest challenges that we have faced in this work is computer code debugging. A relatively complicated structure of excited states that differs by the number of electrons and numbers of unpaired orbitals in each geminal requires that many separate cases need to be coded. For testing purposes we have implemented SSG(EN2) theory in two different ways. One implementation examines each individual excited state and computes all relevant matrix elements for it. The second implementation precomputes all excited states of each geminal, assembles them into multigeminal excited states, and computes each type of matrix elements for the whole list of these states. In addition, we have used GAMESS-US[38] to assemble MCSCF wave functions that resemble the reference SSG wave function. Then, we add individual excited states to the MCSCF and examine the relevant matrix elements. We are reasonably confident that the data presented in this work are free from errors.

So far, the theory has been implemented only for closed-shell systems. The open-shell case does not present any additional conceptual challenges. Its implementation, however, would require a large amount of additional computer code, and will further complicate debugging. Therefore, we limit current studies to molecules in singlet spin states. In the meantime, atomic energies that are required to investigate size consistency were obtained by performing spin-unrestricted calculations on the dissociated XH_n molecules with hydrogen atoms removed by at least 10 Å from the atom under study. The hydrogen atoms supported a single basis function each, eliminating a possibility of dispersion interaction between the ghost hydrogen(s) and a heavy atom. In the course of wave function optimization each hydrogen would support a single spin-unrestricted uncorrelated geminal, with orbital of one spin type localized on hydrogen, and the other spin orbital localized on heavy atom. In the subspace of a heavy atom such wave function is equivalent to atomic USSG.

An additional technical issue that must be discussed is the efficiency of the proposed perturbative treatment. The reference Hamiltonian that defines the spectrum Ψ_k is separable into parts associated with individual geminals. Therefore, each Ψ_k can be represented as antisymmetrized product of geminal wave functions. In general, each geminal can contain an arbitrary number of electrons in excited states, up to a total number of orbitals in the geminal. In practice, the leading terms of perturbation expansion do not involve terms beyond four electrons in a geminal. Anything above that does not couple to the ground state, which contains two elec-

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trons in each geminal. It is convenient to classify all excited states by the number of electrons in excited geminals. The overall classification scheme and formal properties of excited states are discussed by Rosta and Surjan in Ref. 19. We label the excited state types by the number of electrons in excited geminals. Thus, $\Psi(1, 3)$ contains two excited geminals, one geminal with one electron and the other geminal with three electrons. All other geminals remain in their ground states. It is easy to see that leading perturbative terms require $\Psi(2, 2)$, $\Psi(1, 3)$, $\Psi(1, 2, 3)$, $\Psi(0, 3, 3)$, $\Psi(1, 1, 3, 3)$, $\Psi(1, 1, 4)$, and $\Psi(0, 4)$ types. The excitations of $\Psi(2)$ types are not coupled to the ground state and need not be considered.

Now, we must classify the excitations within each geminal. Because of the two types of two-electron interactions in $\tilde{H}_0$, all excited states can be separated with respect to these terms. One type of excitation couples occupied orbital pairs. The other type couples unpaired orbitals in configurations that can be obtained by spin permutations among these orbitals. For instance, three-electron geminals can be divided into two types

$$\psi_a(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = \hat{A}\left[\phi_k(\mathbf{r}_1)\sum_{i \neq k} D_i^a \phi_i(\mathbf{r}_2)\bar{\phi}_i(\mathbf{r}_3)\right],$$

$$\psi_b(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = \hat{A}[D_1^b \phi_k(\mathbf{r}_1)\phi_i(\mathbf{r}_2)\bar{\phi}_j(\mathbf{r}_3)$$
$$+ D_2^b \phi_k(\mathbf{r}_1)\bar{\phi}_i(\mathbf{r}_2)\phi_j(\mathbf{r}_3)$$
$$+ D_3^b \bar{\phi}_k(\mathbf{r}_1)\phi_i(\mathbf{r}_2)\phi_j(\mathbf{r}_3)],$$

(11)

with coefficients D^a determined by the first two-electron term in Eq. (6), and coefficients D^b determined by the second two-electron term. For a geminal made up of N_a orbitals, there are $N_a(N_a-1)$ states of the first type for a given spin state, and $3N_a(N_a-1)(N_a-2)$ of the second type. In general, both of these types of excitations will couple to the ground state via two-electron perturbation. However, only the first type contributes to the most numerous four-geminal $\Psi(1, 1, 3, 3)$ excited states. Overall, for all excitations of four given geminals with N_{a1}, N_{b1} orbitals in one-electron geminals, and N_{a3}, N_{b3} orbitals in three-electron geminals, there are $6N_{a1}N_{b1}N_{a3}(N_{a3}-1)N_{b3}(N_{b3}-1)$ excited states coupled to the ground state. The numerical factor 6 comes from all possible spin permutations. Evaluation of matrix elements between all these excitations and the ground state is a computational bottleneck of this perturbative scheme. To alleviate this, we use the approximation in which all states of three-electron geminal ψ_a are further divided into two groups. One group consists of states formed by creation operators $a_k^\dagger$ acting on the ground-state geminals, and the second group is formed by states that are eigenfunctions of $\tilde{H}_0$ *subject to orthogonality to the first group*. Only the first of these contributes nonzero matrix elements to $\Psi(1, 1, 3, 3)$ excited states. This reduces the total number of excited states in the example above to $6N_{a1}N_{b1}N_{a3}N_{b3}$, leading to significant computational savings. This approximation is not expected to affect the computed properties of chemical systems, including those with strong multireference character. For the systems that were studied in the present work, this

TABLE II. SSG(EN2) optimized geometries (in Å) with 6-31G* and G3MP2Large basis sets.

Molecule	Expt.	6-31G*	G3MP2L
LiH	1.596	1.653	1.603
FH	0.917	0.944	0.922
HCl	1.275	1.300	1.276
Li$_2$	2.673	2.723	2.683
LiF	1.564	1.573	1.582
CO	1.128	1.148	1.129
N$_2$	1.098	1.119	1.096
F$_2$	1.412	1.437	1.410
Na$_2$	3.079	3.153	3.110
P$_2$	1.893	1.910	1.878
Cl$_2$	1.988	2.111	1.994
NaCl	2.361	2.372	2.397
SiO	1.510	1.531	1.518
SC	1.535	1.544	1.529
FCl	1.628	1.702	1.661
H$_2$	0.741	0.746	0.742

approximation changes absolute energies by fractions of millihartrees, while changes in relative energies are below microhartree.

All reported calculations are performed with a modified version of the Q-CHEM program.[39] Efficiency of computer code was sacrificed in favor of code simplicity in order to simplify the debugging process. For instance, the two-electron integrals are retrieved from scratch space on hard drive one by one as needed in the evaluation of matrix elements. This has a major impact on timing of calculations. Nevertheless, the computation of perturbative corrections for FOX-7 molecule with 158 basis functions took 45 wall clock hours on a modern Linux workstation, compared to 321 hours for CCSD calculation. We are confident that better I/O management will reduce the reported computational time of SSG(EN2) by factor of 5 or more.

IV. DESCRIPTION OF CHEMICAL BONDS

The original investigation of the SSG model was based on a study of all diatomic molecules from the G2/97 test set.[40] This set includes molecules with diverse types of chemical bonds. Currently we have implemented perturbative corrections only for singlet states. This reduces the test set to 16 molecules, and includes single and multiple covalent bonds, ionic bonds, and bonds with strong dispersion contributions. We believe this to be a sufficiently diverse set for studying the general quality of SSG(EN2) model.

First, we optimized bond distances using SSG(EN2) theory. The results are summarized in Table II. The root-mean-square deviations from experimental geometries are summarized in Table III. Overall, the agreement with experimental values[41] is very good when sufficiently large G3MP2Large basis set[42] is used. It is somewhat disappointing that for a popular 6-31G* basis set the calculated bond distances are inferior to MP2. With G3MP2Large basis [which is very close to $6\text{-}311+G(2df,2p)$], the SSG(EN2) geometries dramatically improve single reference MP2 values.

TABLE III. Root-mean-square deviations of theoretical bond distances, relative to experiment, for various correlated models. The data are evaluated on the set of molecules shown in Table II. All values are in angstroms.

Basis set	HF	MP2	CCSD	SSG	SSG(EN2)
6-31G*	0.093	0.032	0.034	0.047	0.047
G3MP2L	0.144	0.038	0.011	0.044	0.016

Next, we analyze bond energies. The atomization energies are taken from Ref. 43. They are essentially deduced from experimental enthalpies of formation (0 K) in the JANAF thermochemical tables.[44] In order to compare these data to the computed bond energies, we use atomic spin–orbit interaction corrections[45] and zero-point vibration energy, as computed in G3 theory.[46] The molecular and atomic energies are summarized in Table IV. These values are then used to compute atomization energies, shown in Tables V and VI. For smaller 6-31G* basis, the SSG(EN2) atomization energies are very good, better than with other correlated methods. The larger basis improves the agreement with experiment for all methods. Overall, relative energies of MP2, CCSD, and SSG(EN2) correlated methods are comparable with each other, reflecting the fact that test molecules are well described by single reference wave functions.

The SSG(EN2) theory describes covalent and noncovalent bonds equally well. This is in contrast to the SSG model, where vibration frequencies and equilibrium bond lengths of covalent bonds are superior to noncovalent ones.[15] We do not

expect that open-shell molecules will be a challenge for the SSG(EN2) model, because their description in SSG model was comparable to closed-shell cases.

Additional information about the SSG(EN2) model can be learned from the potential energy surface of CO molecule, computed with 6-31G* basis set and shown in Fig. 1. All calculations are performed with spin-unrestricted formalism, and total energy is given relative to the energy of atomic fragments within each model. Near equilibrium geometry, where wave function can be accurately described by a single reference, the SSG(EN2) potential mimics that of MP2. Note that MP2 energy is closer to experimental value, when zero-point vibration and spin–orbit interactions are taken into account (Table V). When the bond is stretched, the single reference is no longer adequate. This is reflected in a significant deterioration of MP2 energy. Interestingly, when this happens the SSG(EN2) model no longer follows MP2, and yields results in close agreement with CCSD calculation.

V. QUALITY OF SSG REFERENCE WAVE FUNCTION

One of the principal goals of the present work is the assessment of suitability of strongly orthogonal geminals to model chemical phenomena. It has been argued that strong orthogonality is too severe of an approximation.[4,13,47] We think that some deficiencies associated with strongly orthogonal geminals were due to the incomplete optimization of the geminal wave function in earlier studies.[15]

The best way to evaluate the quality of approximations used in the SSG model is, in our view, to examine all perturbative corrections. The EN2 perturbation expansion is the best choice for such a study, because the EN perturbation coefficients of wave function expansion are equal to those in configuration interaction in the limit of weak correlation. Essentially, each EN2 coefficient is a result of a perturbative diagonalization of a 2×2 matrix in a subspace formed by the ground- and a single excited configurations.

We subdivide all perturbative corrections to the SSG reference wave function into three types. A dispersion-type correction (D) involves simultaneous excitation of two electrons, each within its geminal. We have denoted such excitations as $\Psi(2, 2)$. These corrections give rise to dispersion interactions missing in the mean-field description. If such interactions had significant contributions to the perturbed wave function, this would indicate that mean-field description of intergeminal interactions is too restrictive for a given system. Mathematically, the mean-field approximation is manifested in the description of a wave function as an antisymmetrized product of geminals. It is independent of the strong orthogonality approximation.

TABLE IV. SSG(EN2) energies with 6-31G* and G3MP2Large basis sets. All energies are computed at equilibrium bond distances shown in Table II, and given in hartrees.

Molecule	6-31G*	G3MP2L
LiH	−8.003 476	−8.036 691
FH	−100.204 404	−100.367 544
HCl	−460.229 344	−460.459 312
Li$_2$	−14.897 964	−14.932 652
LiF	−107.158 588	−107.323 291
CO	−113.056 760	−113.202 477
N$_2$	−109.290 878	−109.417 644
F$_2$	−199.072 726	−199.330 282
Na$_2$	−323.712 565	−324.062 193
P$_2$	−681.707 810	−682.087 812
Cl$_2$	−919.256 658	−919.666 717
NaCl	−621.576 177	−621.974 685
SiO	−364.080 747	−364.359 389
SC	−435.595 965	−435.847 814
FCl	−559.181 685	−559.524 110
H$_2$	−1.151 698	−1.170 865
H	−0.498 233	−0.499 818
Li	−7.431 965	−7.447 266
C	−37.751 108	−37.785 550
N	−54.485 633	−54.529 475
O	−74.893 555	−74.983 300
F	−99.505 676	−99.636 933
Na	−161.843 447	−162.018 006
Si	−288.895 155	−289.060 209
P	−340.766 279	−340.949 136
S	−397.582 413	−397.774 137
Cl	−459.585 083	−459.795 841

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TABLE V. Atomization energies of diatomic molecules with 6-31G* basis set. Zero-point energies and spin–orbit corrections are the same as in G3 theory. All energies are in kcal/mol. ''rms'' stands for root-mean-square deviations from experimental atomization energies, corrected for zero-point vibrations and spin–orbit interactions.

Molecule	$D0$(expt)	ZPE+SO	MP2	CCSD	SSG	SSG(EN2)
LiH	56	1.81	39.9	44.2	44.1	44.2
FH	135.2	5.94	117.6	113.8	95.7	119.9
HCl	102.2	4.91	84.1	84.3	73.2	86.7
Li_2	24	0.43	11.4	21.0	20.6	20.9
LiF	137.6	1.70	129.2	122.4	97.4	136.9
CO	256.2	3.43	253.7	235.6	188.8	255.2
N_2	225.1	3.52	211.5	191.5	146.3	197.0
F_2	36.9	2.35	35.8	26.9	2.1	36.2
Na_2	16.6	0.20	7.3	15.5	14.8	15.9
P_2	116.1	1.16	93.1	82.9	52.6	108.8
Cl_2	57.2	2.45	39.7	35.7	9.9	51.8
NaCl	97.5	1.30	87.0	84.2	69.8	91.4
SiO	190.5	2.45	182.9	164.9	123.6	180.8
SC	169.5	2.47	159.3	146.8	100.8	162.2
FCl	60.3	2.39	53.0	45.7	15.6	54.7
H_2	103.3	5.93	86.7	91.5	91.5	91.5
rms			13.3	19.5	46.4	10.8

A strong orthogonality correction (S) involves simultaneous transfer of two electrons between geminals. They include $\Psi(0, 3, 3)$, $\Psi(1, 1, 3, 3)$, $\Psi(1, 1, 4)$, $\Psi(0, 4)$, and part of $\Psi(1, 3)$ type that keeps three-electron geminal in its ground state. All these excitations break strong orthogonality approximation, and their large role would indicate that strong orthogonality approximation is too restrictive for a given system. The third type of correction (DS) is the mixture of these two types. It includes the remaining part of $\Psi(1, 3)$ and $\Psi(1, 2, 3)$ types. They describe simultaneous breaking of strong orthogonality and mean-field approximations.

The significance of perturbative contributions does, naturally, depend on the target accuracy of the method. In the case of single reference states it is sometimes assumed that the configurations with the expansion coefficients higher than 0.1 in magnitude in the CI calculations indicate that single reference may be deficient. A similar criterion is often used to examine doubles amplitude in the CC expansion. We will use the value of 0.1 in the magnitude of the perturbative correction by individual configuration as a guide to the quality of approximations.

First, let us examine our set of diatomic molecules. Table VII shows the magnitudes of largest perturbative corrections of each type, computed with the 6-31G* basis set at the SSG(EN2) equilibrium bond distances. The ground state of all SSG wave functions is spin restricted. These are com-

TABLE VI. Atomization energies of diatomic molecules with G3MP2Large basis set. Zero-point energies and spin–orbit corrections are the same as in G3 theory. All energies are in kcal/mol. ''rms'' stands for root-mean-square deviations from experimental atomization energies, corrected for zero-point vibrations and spin–orbit interactions.

| Molecule	$D0$(expt)	MP2	CCSD	SSG	SSG(EN2)
LiH	56	48.8	54.4	53.6	54.4
FH	135.2	136.3	130.2	104.4	138.9
HCl	102.2	99.2	97.1	80.0	97.8
Li_2	24	15.2	23.4	21.7	23.5
LiF	137.6	139.8	130.7	99.2	148.3
CO	256.2	264.0	243.0	189.1	268.7
N_2	225.1	227.8	206.3	154.7	221.6
F_2	36.9	37.5	25.4	−4.5	33.1
Na_2	16.6	10.2	16.7	13.8	16.2
P_2	116.1	109.7	97.2	62.3	117.8
Cl_2	57.2	56.1	47.0	16.2	44.6
NaCl	97.5	97.9	91.7	69.9	99.6
SiO	190.5	197.0	176.3	134.1	195.8
SC	169.5	171.8	154.1	104.9	178.3
FCl	60.3	60.8	49.9	14.4	54.9
H_2	103.3	96.5	101.5	101.5	101.5
rms		4.9	10.6	42.5	6.3
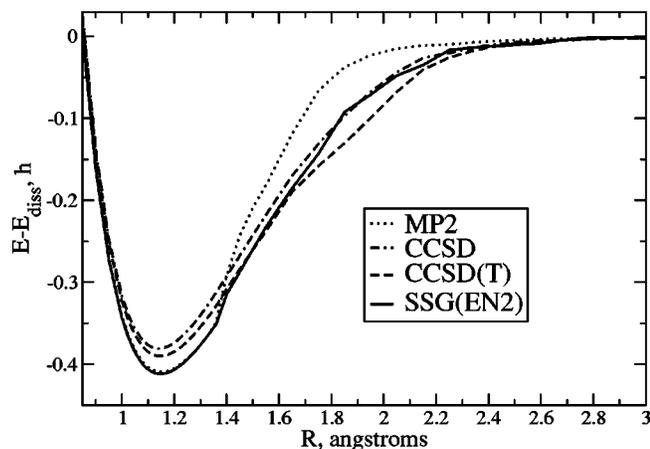
FIG. 1. Potential energy surface of CO molecule with 6-31G* basis set. Calculations with SSG(EN2) model are compared with Møller–Plesset to the second order, coupled-cluster singles and doubles, and couple cluster singles doubles with perturbative triples correction. All methods use spin-unrestricted formalism. All energies are given relative to energies of separated fragments, computed with the same methods.

pared with leading amplitudes of CCSD single reference wave functions, which are spin unrestricted in the Li_2 case, and spin restricted in all other cases.

It is obvious that the approximation of antisymmetric product is more restrictive than that of strong orthogonality. In all cases the perturbations that break strong orthogonality approximation have amplitudes less than or around 0.05. The important corrections come from dispersion, with the largest amplitude of 0.1318 in the case of interactions between π bonds in N_2 molecule. Somewhat smaller amplitudes in the cases of CO, P_2, and SC molecules all arise from π-bond dispersion interactions.

The use of a larger basis set does not alter this conclusion. For instance, the leading perturbative amplitudes for CO molecule wave function with G3MP2Large basis are 0.1191 for "D" type, 0.0282 for "S" type, and 0.0275 for "DS" type. With exception of the mixed DS type of excita-

TABLE VII. Amplitudes of the leading perturbative corrections for diatomic molecules with 6-31G* basis set. "D" labels dispersion corrections, "S" labels corrections that break strong orthogonality approximation, "DS" labels mixed corrections, and "CC" labels leading amplitudes in coupled-cluster CCSD wave functions.

Molecule	D	S	DS	CC
LiH	0.0032	0.0028	0.0013	0.0565
FH	0.0582	0.0120	0.0135	0.0463
HCl	0.0295	0.0251	0.0219	0.0708
Li_2	0.0042	0.0024	0.0011	0.2421
LiF	0.0660	0.0126	0.0143	0.0364
CO	0.1211	0.0297	0.0193	0.0788
N_2	0.1318	0.0341	0.0206	0.1067
F_2	0.0466	0.0193	0.0120	0.1881
Na_2	0.0058	0.0043	0.0029	0.1356
P_2	0.1287	0.0366	0.0302	0.1361
Cl_2	0.0320	0.0242	0.0257	0.1163
NaCl	0.0325	0.0255	0.0263	0.0364
SiO	0.0837	0.0330	0.0193	0.0716
SC	0.1278	0.0525	0.0367	0.0993
FCl	0.0584	0.0263	0.0208	0.1126

tions, these numbers are in close agreement with the 6-31G* case. In fact, the shortcomings of strong orthogonality approximation are, in general, alleviated by larger basis sets, due to increased flexibility of geminal localization procedure.

Physically, our finding implies that approximating individual electron pairs in molecules as occupants of their distinct orbital subspaces is less restrictive than the assumption that interactions between electron pairs are of mean-field type. This finding corresponds to a standard chemical picture that views molecules as a collection of distinct electron pairs (chemical bonds, lone pairs, fully occupied core shells), with interactions between pairs that may include dispersion.

In order to investigate the generality of these conclusions, we have applied the SSG(EN2) model to other chemical systems. One of the simplest systems for which MP2 theory is known to fail dramatically is O_2^{2+} dication.[48] This metastable molecule has probably the shortest known bond between two heavy atoms. We have used the bond length of 1.057 Å taken from multireference calculation.[49] Another small system with known multireference character is ozone. The third system is the benzene molecule, which we chose to observe the effect of electron delocalization on the quality of the SSG wave function. The SSG model may prove to be especially suitable for transition metal compounds, because of strong multireference character in many such wave functions.[50] For this reason we included VH molecule in singlet state (the ground state of this molecule is quintet). The last three molecules are studied in RMP2/6-31G* equilibrium geometry. Finally, we chose a somewhat larger system with multireference ground-state wave function 1,1-diamino-2,2-dinitroethylene (also known as FOX-7). It is speculated that multireference character of this system is delocalized among nitrogen groups,[51] and we were curious to see the geminal description of this molecule. We have used B3LYP/6-31G* equilibrium geometry of FOX-7 in our study.

The multireference character of these wave functions can be deduced by looking at the degree of intrageminal correlation in the reference wave functions. The π-bond geminals of oxygen molecule dication have geminal expansion coefficients of second orbital pair of -0.235. The multireference character of O_3 is even more pronounced: The geminal that corresponds to HOMO is localized on peripheral oxygen nuclei, with its second orbital pair coefficient of -0.477. We find that it is a common feature of molecular fragments that contain two oxygen atoms bound to the same nuclei. Such fragments usually have a geminal that is localized on both oxygens, with a high degree of correlation in it. The FOX-7 compound is an exception: Its most correlated geminals describe N–O bonds, with second orbital pair expansion coefficient of -0.199. The SSG wave function of singlet VH is strongly correlated. The d-electron geminal on vanadium has a second coefficient of -0.424. In benzene the most correlated geminal has its second coefficient equal to -0.150. This geminal is located on a pair of adjacent carbon atoms. It reflects the general feature that geminal wave functions often break spatial symmetry. Geminals tend to favor orbital localization at the expense of overall wave function

TABLE VIII. Amplitudes of the leading perturbative corrections for molecules with various types of chemical bonding, using 6-31G* basis set. All calculations are spin restricted. "D" labels dispersion corrections, "S" labels corrections that break strong orthogonality approximation, "DS" labels mixed corrections, and "CC" labels leading amplitudes in coupled-cluster CCSD wave functions.

Molecule	D	S	DS	CC
O_2^{2+}	0.1343	0.0343	0.0195	0.1425
O_3	0.0438	0.0218	0.0488	0.2133
C_6H_6	0.0710	0.0195	0.0246	0.0934
VH	0.0428	0.0461	0.0336	0.1672
$(NH_2)_2C_2(NO_2)_2$	0.0886	0.0200	0.0457	0.0595

symmetry. This feature actually helps to stabilize the ENPT by increasing the energy gaps of charge-transfer excitations.

Comparison of magnitudes of the largest perturbative correction for these systems is shown in Table VIII. It confirms our main conclusion that strongly orthogonal geminals describe diverse chemical systems very well: all perturbative corrections that break strong orthogonality have amplitudes less than 0.05. It is remarkable that all multireference character of these wave functions is accounted for in the reference state. The perturbative SSG(EN2) corrections for these systems are similar to those of single reference diatomics, with most remaining correlation concentrated in dispersion interactions. This is a very encouraging result, since dispersion interactions are the easiest to treat. We plan to investigate a performance of mixed-order perturbation theory, where dispersion interactions are treated at a higher (possibly fourth) order, with remaining terms at second or third order of perturbation. With the exception of VH molecule, the main deficiency of geminal wave function is the lack of dispersion interactions between geminals.

In general, perturbative corrections of SSG wave functions are smaller than leading CC doubles amplitudes. Notable exceptions are molecules with double π bonds. The main reason for this is the difference in excited states between two models. In both cases the relevant excited states are described by a single excitation in one π bond coupled with the single excitation in another π bond. In the SSG(EN2) model each excitation within a geminal consists of two configuration, coupled by the last term of Eq. (6) to form either singlet or triplet pair. Because an unperturbed geminal has mainly singlet character (it is an exact singlet in the spin-restricted case), only singlet excitation in one geminal coupled with the singlet excitation in another geminal has significant contribution to the perturbed wave function. In contrast, CC excitations consists of single determinants, with each single excitation that can be represented as a mixture of singlet and triplet spin state. Therefore, all four spin combinations contribute to the perturbed wave function for a given double excitation. The expansion coefficient of each contribution is twice smaller than that of SSG(EN2) in the limiting case of weak electron–electron interactions.

VI. CONCLUSIONS

The first paper on geminal model chemistry[15] has introduced a computationally inexpensive model which is applicable to multireference systems, variational, and size consistent. The model is based on a single antisymmetrized product of strongly orthogonal geminals, or SSG. Application of the SSG to studies of various diatomics revealed that the model describes covalent bonds well, and is deficient for bond between atoms with extreme electronegativities. We have attributed the deficiency to dispersion interactions between geminals that is omitted in the SSG. In the present paper we correct this by the inclusion of perturbative corrections to the SSG reference state. Our analysis and computation of test systems revealed that the Epstein–Nesbet form of perturbation theory[33,34] is well suited for geminal models.

Application of a new model to equilibrium bond distances and bond energies of various diatomics demonstrated the accuracy of this model. Overall, the accuracy is comparable to the CCSD model for systems that are well described by single reference wave functions. The study of multireference cases is in progress. The computation of potential energy surface of CO molecule confirms size consistency and accuracy of the SSG model.

A detailed analysis of various perturbative corrections provides an important insight into the nature and quality of the SSG model. There are two independent approximations that are used in the SSG theory. The strong orthogonality approximation describes each correlated electron pair (or geminal) in its own orbital subspace. The antisymmetrized product approximation assumes only mean-field interactions between geminals. It is often assumed that for chemical systems the strong orthogonality is a more restrictive approximation of the two.

We compare relative importance of these approximations by investigating leading perturbative corrections to the SSG wave function in a diverse set of chemical systems. In all cases we find that the dominant correction comes from dispersion interactions. The strong orthogonality approximation is less restrictive and can be improved perturbatively, judging by small values of expansion coefficients of perturbed wave functions.

There are three main practical conclusions that we draw from the present study. First, it may not be advantageous to seek the improvement of geminal reference wave functions by introducing an explicit r_{12} dependence[52] in the framework of the antisymmetrized product approximation. This would significantly complicate the wave function without addressing the main deficiency of a reference model. Second, the most important perturbative correction terms are of the dispersion type. This is true even for the systems with strong multireference character. Formally, they are the easiest to treat, because they do not involve charge transfer between the geminals. Third, the Epstein–Nesbet form of perturbation theory taken to the leading order performs well when applied to the SSG reference wave function. The SSG(EN2) model appears to be a promising candidate for the description of single- and multireference wavefunctions with comparable levels of accuracy. The SSG(EN2) model may be effective for studying chemistry of transition metal elements.

ACKNOWLEDGMENT

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