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ABSTRACT
We present an implementation of time-dependent linear-response equations for strongly orthogonal geminal wave function models: the time-dependent generalized valence bond (TD-GVB) perfect-pairing theory and the antisymmetrized product of strongly orthogonal geminals. The geminal wave functions are optimized using a restricted-step second-order algorithm suitable for handling many geminals, and the linear-response equations are solved in an efficient way using a direct iterative approach. The wave function optimization algorithm features an original scheme to create initial orbitals for the geminal functions in a black-box fashion. The implementation is employed to examine the accuracy of the geminal linear response for singlet excitation energies of small and medium-sized molecules. In systems dominated by dynamic correlation, geminal models constitute only a minor improvement with respect to time-dependent Hartree–Fock. Compared to the linear-response complete active space self-consistent field, TD-GVB either misses or gives large errors for states dominated by double excitations.

I. INTRODUCTION
The description of molecular electronic structures with wave functions that depend explicitly on pairs of electrons localized on bonds and lone pairs dates back to the idea of Lewis diagrams1 and has been explored since the very beginning of quantum chemistry.2 Among different realizations of this concept, pairing functions built of strongly orthogonal geminals continue to draw considerable attention as inexpensive models, which capture the essential static correlation effects and can be variationally optimized. In this work, we focus on geminal wave functions of two types: the generalized valence bond perfect-pairing (GVB-PP) method3,4 and the antisymmetrized product of strongly orthogonal geminals (APSG).3,5 These wave function Ansätze are multiconfigurational by construction, and, in principle, they can accommodate a major part of the static correlation. Comparing to other multiconfigurational wave function models, APSG and GVB-PP hold promise of treating a large number of active orbitals in an efficient manner, i.e., avoiding the factorial scaling of, for example, complete active space self-consistent field (CASSCF) theory and circumventing the problem of selecting active orbitals based on chemical intuition.

We present an implementation of APSG and GVB-PP models based on the restricted-step second-order optimization algorithm as well as their extension to excited states by time-dependent linear-response formalism. Due to the fact that a geminal wave function is nonlinear, the convergence to the best solution is sensitive to the initial guess. We describe an original method for automatic generation of the initial geminals used in our implementation of the GVB-PP and APSG theories. In the proposed scheme, the active virtual orbitals follow from the diagonalization of an MP2-like density matrix constructed independently for every localized occupied Hartree–Fock (HF) orbital. The method is applied either with Fos- ter and Boys6 or Pipek–Mezey7 localization of the initial HF orbitals.
To the best of our knowledge, the proposed algorithm is the only one that employs a criterion based on the correlation degree to find the initial orbitals coupled in a geminal.

After having obtained a good initial guess, another challenge is the efficient optimization of geminal wave functions. We have adapted the robust restricted-step second-order optimization algorithm first developed for MCSCF wave functions. Although our implementation of the GVB-PP method has been used in several previous studies, its details are discussed here for the first time.

The chief motivation for computing excitations with geminal wave functions in the linear-response framework is the possibility to access singly excited states and some classes of doubly excited states of both single- and multireference systems in a cost-efficient manner. Since both GVB-PP and APSG are free from the problem of active space selection and capable of capturing a significant part of the static correlation effects, their time-dependent formulation may be considered as an alternative to the linear-response complete active space self-consistent field (LR-CASSCF) theory. Time-dependent APSG equations were first derived by Pernal et al., soon followed by a time-dependent generalized valence bond (TD-GVB) study. The authors confirmed that both time-dependent antisymmetrized product of strongly orthogonal geminals (TD-APS) and TD-GVB are capable of describing excitations in out-of-equilibrium geometries. However, apart from these pilot works, no attempt has been made since to establish the level of accuracy offered by time-dependent geminal theory for larger systems of different chemical characters.

In this work, we investigate the TD-GVB performance in a systematic manner using benchmark datasets of singlet excitation energies computed for systems from the datasets of Loos et al. and Schreiber et al. Section V summarizes our findings.

The plan of this paper is as follows: in Sec. II, we describe the implementation of strongly orthogonal geminal wave function optimization, including the procedure for the initial guess generation. The linear-response equations for geminal wave functions are given in the same section. In Sec. III, we provide relevant details of our calculations. In Sec. IV, we discuss the quality of TD-GVB singlet excitation energies computed for systems from the datasets of Loos et al. and Schreiber et al. Section V summarizes our findings.

II. THEORY

The formalism presented in this section is common to strongly orthogonal wave functions of the APSG and GVB-PP types. Thus, in the following, we usually refer to the more general APSG Ansatz.

A. Wave function optimization

The APSG wave function for a closed-shell \(N\)-electron system is given as an antisymmetrized product of geminals,

\[
\Psi_{\text{APSG}}(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \mathcal{A} \prod_{p=1}^{N_G} \psi_p(x_{2p-1}, x_{2p}),
\]

where \(\mathbf{x} = (r, \alpha)\) is a combined spatial and spin coordinate and \(N_G\) denotes the number of geminals equal to half the number of electrons, \(N_G = N/2\). Each pair of geminals obeys the strong orthogonality condition

\[
\forall_{p \neq q} \int \psi_p(\mathbf{x}_1, \mathbf{x}_2) \psi_q(\mathbf{x}_1, \mathbf{x}_2) d\mathbf{x}_2 = 0,
\]

which implies that geminals are expanded in mutually orthogonal and disjoints subsets of spin–orbitals referred to as Arai subspaces. The APSG Ansatz is singlet coupled, which means that each \(\psi_p\) geminal is represented as a pure singlet,

\[
\forall_p \psi_p(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \sum_{c_p} [\psi_p(\mathbf{r}_1) \psi_p(\mathbf{r}_2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)]],
\]

where we chose the natural orbital parameterization; \(\{\psi_p\}\) and \(\{c_p\}\) are natural orbitals and expansion coefficients, respectively. For each geminal, the coefficients are normalized as follows:

\[
\forall_p \sum_{c_p} c_p^2 = 1
\]

and they relate to natural spin–orbital occupation numbers, \(n_p = c_p^2\), where \(n_p \in [0, 1]\). The special case of APSG in which expansion in Eq. (2) is restricted to two orbitals is known as the GVB-PP Ansatz,

\[
\forall_p \psi_p(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \left[ c_1 \psi_1(\mathbf{r}_1) \psi_2(\mathbf{r}_2) + c_2 \psi_2(\mathbf{r}_1) \psi_1(\mathbf{r}_2) \right] [\alpha(1)\beta(2) - \beta(1)\alpha(2)].
\]

Optimization of the APSG wave function requires a suitable parameterization, which avoids redundancy in the coefficient space. Due to the normalization condition [Eq. (4)], a direct parameterization in terms of the geminal coefficients \(c_p\) would be highly redundant. Instead, we propose a parameterization,

\[
\forall_{p \neq q} c_p = \frac{c_p^0 + x_p}{\sqrt{1 + 2 \sum_{q \neq q} c_q^0 c_p^0 + \sum_q c_q^0 c_q^0}},
\]

where the parameters \(x_p\) are unconstrained and \(\forall_p : \sum_{p \neq q} (c_p^0)^2 = 1\). Note that Eq. (6) resembles the MCSCF parameterization introduced in Ref. 10. With this choice, the proper normalization of each geminal [Eq. (4)] is preserved. The geminal coefficients are unchanged with respect to the redundant transformation \(\forall_{p \neq q} x_p = a c_p^0 \Rightarrow c_p = c_p^0\) (a is a real number). In the implementation, the redundancy in the \(x\)-vectors is easily handled by allowing only \(x\)-vectors orthogonal to their \(c\) coefficients,

\[
\forall_p \sum_{p \neq q} x_p c_p^0 = 0.
\]

Changes in the orbitals are described with the antisymmetric real singlet orbital-rotation operator

\[
\hat{k} = \sum_{pq} \kappa_{pq} \hat{E}_{pq} \equiv \sum_{pq} \kappa_{pq} (\hat{E}_{pq} - \hat{E}_{qp}) \equiv \sum_{pq} \kappa_{pq} \hat{E}_{pq},
\]

where \(\kappa\) is an antisymmetric matrix and \(\hat{E}_{pq}\) is the singlet excitation operator, \(\hat{E}_{pq} = \delta_{pa}^{1\downarrow} \hat{h}_{pq} + \delta_{ps}^{1\uparrow} \hat{h}_{pq}\).
The APSG/GVB wave function optimization with respect to orbitals and geminal coefficients is carried out with the restricted-step second-order optimization algorithm, originally developed by Jensen and Jørgensen for MCSCF wave functions and available in Dalton. The algorithm is based on second-order Taylor expansion of the electronic energy,

$$E(\lambda) = E_0 + \mathbf{g}^T \lambda + \frac{1}{2} \lambda^T \mathbf{H} \lambda,$$  \hfill (9)

where $\lambda = (x, k)$ denotes the wave function parameters, i.e., the geminal coefficients and orbital-rotation variables; $\mathbf{g}$ and $\mathbf{H}$ denote the electronic gradient and electronic Hessian, respectively. Explicit expressions for the gradient and Hessian follow from taking derivatives of the APSG energy expression. In the natural orbital representation, the electronic energy takes the form

$$E_{\text{APSG}} = 2 \sum_p c_p^2 h_{pp} + \sum_{pq} c_p c_q (pp|qq) + \sum_{pq} c_p c_q [2(pq|pq) - (pq|qp)],$$  \hfill (10)

where $h_{pq}$ are the matrix elements of the one-electron Hamiltonian and $I_p$ denotes the index of the geminal, which contains the $p$th orbital. The orbital part of the gradient and the orbital–orbital block of the Hessian are identical to the MCSCF expressions (see, e.g., Ref. 10). The formulas for the energy derivatives with respect to geminal coefficients and mixed derivatives entering the Hessian, which are specific for APSG, are presented in the supplementary material.

The adopted approach to wave function optimization avoids diagonalization of the full Hessian matrix by using direct linear transformations with trial vectors $\mathbf{b}_n$,

$$\sigma_n = \mathbf{PK} \mathbf{b}_n = \mathbf{PK} \mathbf{b}_n = \mathbf{P} \begin{pmatrix} \mathbf{K}^c & \mathbf{K}^o \\ \mathbf{K}^o & \mathbf{K}^c \end{pmatrix} \begin{pmatrix} \mathbf{b}_c \\ \mathbf{b}_v \end{pmatrix},$$  \hfill (11)

where $\mathbf{K}$ is the augmented Hessian for the real-valued APSG wave function and indices $c$ and $o$ refer to derivatives with respect to geminal and orbital coefficients, respectively. Technically, the redundant variables are removed with the projector operator, the matrix representation of which $\mathbf{P}$ takes the form

$$\mathbf{P} = \mathbf{1} - \mathbf{O} = \mathbf{1} - \sum_Q \mathbf{P}^Q (\mathbf{P}^Q)^T,$$  \hfill (12)

with the redundancy vector $\mathbf{p}^Q$ for each geminal $Q$ defined as

$$\forall Q \quad \mathbf{p}^Q = \begin{pmatrix} x^Q \\ 0 \end{pmatrix},$$  \hfill (13)

$$\forall Q \quad x^Q = [c_1 b_{1Q}, c_2 b_{2Q}, \ldots].$$  \hfill (14)

Note that trial vectors are chosen to fulfill $\mathbf{P} \mathbf{b}_n = \mathbf{b}_n$, which makes the handling of the redundancies easy in the code.

**B. Automatic generation of initial geminals**

The problem of wave function optimization requires construction of an initial guess. Two aspects of the initial guess generation specific for APSG are the choice of initial orbitals and having an effective way of pairing them into starting geminals. The strongly occupied (SO) orbitals, i.e., orbitals for which $1.0 > n_\alpha > 0.5$, are often obtained by localization of valence Hartree–Fock molecular orbitals. The so-called pseudo-Hartree–Fock molecular orbitals, introduced by Langlois et al. 29 to avoid diagonalization of the Fock matrix, should also be mentioned in this context. The weakly occupied (WO) orbitals, i.e., orbitals for which $0.5 > n_\alpha > 0$, may also be generated in various ways. For instance, Wang et al. 26 used projection from the original HF virtual space onto the analogous virtual space in the minimal basis set. In the same work, the authors explored employing unrestricted natural orbitals 30 for the construction of the entire active pair space (i.e., both occupied and virtual orbitals). A similar approach had been used in the unrestricted perfect-pairing formulation of Beran et al. 31 The method proposed by Sano 32 is different in that it creates the virtual orbitals by maximizing the exchange integral set up separately for each of the localized strongly occupied orbitals. Since the orbitals forming a geminal in the converged wave function are localized in the same region in space, a reasonable criterion for the pairing is some measure of spatial vicinity, e.g., the distance between the centroids of occupied and virtual orbitals or transition-dipole-like integrals between occupied and virtual orbitals. 26,33 In contrast, weakly occupied orbitals created in the scheme of Sano are paired by construction and properly localized.

The unique aspect of our APSG/GVB-PP implementation is a two-step, black-box scheme for generating initial geminals in which pairing of the orbitals relies on their mutual correlation instead of spatial overlap. First, the SO orbitals entering geminals are obtained by localizing the relevant SCF orbitals. Usually, core orbitals are excluded and all valence orbitals are localized. If required, a different active space can be requested. Second, a set of WO orbitals is constructed separately for each of the localized occupied orbitals by diagonalization of a one-electron reduced density matrix of the MP2 type,

$$P_{ab}^{(Q)} = 2 \sum_i \frac{2(i|i\alpha) - (i|i\beta)}{D_{ii}^{-1} D_{ii}} (\langle i|i\alpha | ii\beta \rangle - \langle i|i\beta | ii\alpha \rangle),$$  \hfill (15)

where $i$ refers to a localized occupied orbital, $a, b$, and $c$ pertain to virtual orbitals, and $D_{ii}^{-1} = \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b$ denotes the orbital energy difference. The correlating orbitals are then selected from the weakly occupied set based on their occupation numbers. The orbital $a$ with the largest occupation is always included in a given geminal. If the remaining correlating orbitals fulfill the $n_a/n_b > \alpha$ condition for $b > a$, they are also added to the Arai space (the natural occupation numbers $n_\alpha$ are arranged in the descending order, and $\alpha > 0$ is set as default to 0.85). In other words, when no degeneracies or near-degeneracies occur in any of the generated weakly occupied spaces, one recovers the GVB-PP wave function. In the following, we refer to the fractionally occupied orbitals as the active orbitals.

One should note that extending the number of orbitals in a geminal according to the proposed near-degeneracy criterion will lead to a different APSG wave function than if a full, variational optimization of the geminal subspaces were performed, e.g., as proposed by Rassolov. 34 An APSG wave function obtained in our approach
should be considered a minimal extension of the GVB–PP model that gives a well-balanced description of the system.

Both the final APSG wave function and energy obtained with the proposed protocol may depend on the shape of the initial localized orbitals. We have tested two localization schemes: the Pipek–Mezey (PM) method, which preserves the concept of \(\sigma–\pi\) separation, and the Foster–Boys (B) approach that leads to localized orbitals of a mixed \(\sigma–\pi\) character.

To improve convergence to the global minimum, the generation of the correlating orbitals is followed by rotation of the strongly occupied orbitals. In the case of Boys localization, all localized orbitals are rotated. The angle of 10° was established as sufficient to distort the symmetry without affecting the orbital localization and good convergence behavior. In the case of orbitals localized with the Pipek–Mezey scheme, a special issue appears. On the one hand, rotation of all orbitals would destroy the desired \(\sigma–\pi\) separation. On the other hand, preservation of the \(\sigma–\pi\) symmetry leads to poor description of the lone-pair geminals, e.g., for H₂O, lone-pair geminals on the oxygen do not possess the \(sp^3\) hybridization and correspond to the \(s\) and \(p\) orbitals instead. To resolve this issue in the PM scheme, the rotation by 10° is applied only to orbitals that enter the initial guess for lone-pair geminals. These geminals are identified as localized on the same atoms based on the Mulliken population analysis. Our numerical experience shows that rotation is sufficient to guarantee the correct shape of lone pairs when initial PM-localized orbitals are employed. In the last step of the guess generation, the weakly occupied orbitals are orthonormalized using symmetric orthonormalization (the Löwdin scheme). Since Gram–Schmidt orthonormalization distorts the symmetry of the orbitals, it can be used as an alternative to the rotation of the strongly occupied orbitals localized with the Boys scheme.

To recap, construction of the initial guess involves (a) localization of selected SCF orbitals to obtain the initial strongly occupied orbital, (b) creating weakly occupied correlating partners by diagonalization of the one-electron, MP2-like reduced density matrix for each of the strongly occupied orbitals, (c) rotation of either all strongly occupied orbitals (used with the Boys localization) or orbitals included in lone-pair geminals (used with PM localization), and (d) symmetric orthonormalization of the weakly occupied orbitals.

C. Time-dependent linear-response APSG

The time-dependent linear-response APSG (TD-APSG) equations were first formulated by Pernál et al. based on the stationary condition of the action integral principle. 5, 7 To arrive at TD-APSG equations in a form suitable for direct iterative techniques developed for large scale MCSCF wave functions, 33, 34 we have repeated the derivation of Ref. 19. For completeness, we briefly reiterate the crucial steps leading to linear-response formalism based on the APSG Ansatz.

The action integral for the APSG wave function takes the form

\[
\mathcal{A} = \int_0^T \langle \Psi^\text{APSG}(t) | \hat{H}(t) - i \frac{\partial}{\partial t} | \Psi^\text{APSG}(t) \rangle
\]

\[= -i \sum_P \langle \phi_P(t)^* \phi_P(t) - 2 \sum_P \langle \phi_P(t)^* \phi_P(t) \phi_P(t) | \hat{H}(t) | \phi_P(t) \rangle + \hat{E}(t) \]. \quad (16)

where

\[
\hat{E}(t) = 2 \sum_P \langle \phi_P(t)^* \phi_P(t) | h_{pp}(t) | \phi_P(t) \rangle + \sum_{PQ} \langle \phi_P(t)^* \phi_Q(t) | \langle \phi_P(t) | p(t)| \phi_Q(t) \rangle \rangle \]

\[= \sum_{PQ} \langle \phi_P(t) | n_P(t) | \phi_Q(t) \rangle \langle \phi_Q(t) | n_P(t) | \phi_P(t) \rangle \]

\[= \langle \phi_P(t) | n_P(t) | \phi_Q(t) \rangle \langle \phi_Q(t) | n_P(t) | \phi_P(t) \rangle \]

\[= \langle \phi_P(t) | p(t) | \phi_Q(t) \rangle \langle \phi_Q(t) | q(t) | \phi_P(t) \rangle \]. \quad (17)

In Eqs. (16) and (17), natural orbitals and geminal coefficients are time-dependent and a dot above a pertinent symbol indicates a time-derivative. The Hamiltonian in Eq. (16) includes a time-dependent perturbation, \( \hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{ex} + \delta \hat{V}(t) \). The response equations follow from the principle of action, \( \delta \mathcal{A} = 0 \), applied to variations of the geminal coefficients and orbitals,

\[\left( E^{[2]} - \omega S^{[2]} \right) A = -i V^{[1]} \], \quad (18)

where \( V^{[1]} \) is a gradient type property vector. Excitation energies correspond to poles of the response functions, i.e., they follow by setting the external perturbation to zero. The non-perturbed problem can be cast in a matrix form as follows:

\[\left( E^{[2]} - \omega S^{[2]} \right) \Lambda_n = 0 \], \quad (19)

where \( \Lambda_n \) denotes the eigenvector and the \( \omega \) eigenvalues are approximations to excitation energies. Both the Hessian and the metric, \( E^{[2]} \) and \( S^{[2]} \), respectively, have a block structure,

\[
E^{[2]} = \begin{pmatrix}
A^{cc} & A^{co} & B^{cc} & B^{co} \\
A^{oc} & A^{oo} & B^{oc} & B^{oo} \\
B^{cc} & B^{oc} & A^{cc} & A^{co} \\
B^{oc} & B^{oo} & A^{oc} & A^{oo}
\end{pmatrix}
\]

\[
S^{[2]} = \begin{pmatrix}
\Sigma^{cc} & 0 & 0 & 0 \\
0 & \Sigma^{oo} & 0 & 0 \\
0 & 0 & -\Sigma^{cc} & 0 \\
0 & 0 & 0 & -\Sigma^{oo}
\end{pmatrix}
\]

\[\Lambda_n = \begin{pmatrix}
[\Lambda_n]^{cc} \\
[\Lambda_n]^{oc} \\
[\Lambda_n]^{oc} \\
[\Lambda_n]^{oo}
\end{pmatrix}
\]

where

\[\forall_{pq} \left[ \Sigma^{cc} \right]_{pq} = \delta_{pq}, \quad (21)

\[\forall_{pq>st} \left[ \Sigma^{oo} \right]_{pq,st} = 2 \delta_{ps} \delta_{qt} (n_p - n_q). \quad (22)

Note that the \( E^{[4]} \) matrix follows from both real and imaginary variations of a real-valued wave function, while the Hessian in Eq. (9) is derived from real variations of a real-valued function. The elements of the A and B blocks have the form


\[
\forall pq \left[ A^\alpha \right]_{pq} = E_{pq}^{cc} - \mu_p \delta_{pq}, \tag{23}
\]

\[
\forall pq \left[ B^\alpha \right]_{pq} = E_{pq}^{cc} \tag{24}
\]

\[
\forall p,r,s \left[ A^\alpha \right]_{pr,s} = \left[ A^\alpha \right]_{rs,p} = E_{pr,s}^{cc} - E_{rs,p}^{cc}, \tag{25}
\]

\[
\forall p,q,r,s \left[ B^\alpha \right]_{pq,r,s} = E_{pq,r,s}^{cc} + E_{qs,p,r}^{cc} - E_{qs,r,p}^{cc} - E_{qs,s,p}^{cc}, \tag{26}
\]

\[
\forall p,q,r,s \left[ A^\alpha \right]_{pq,r,s} = E_{pq,r,s}^{cc} + E_{qs,p,r}^{cc} - E_{qs,r,p}^{cc} - E_{qs,s,p}^{cc}, \tag{28}
\]

where we have introduced the following notation:

\[
E_{pq}^{cc} = \frac{\partial^2 E}{\partial \rho_p \partial \rho_q}, \tag{29}
\]

\[
\tilde{E}_{pq}^{cc} = \frac{\partial^2 \tilde{E}}{\partial \rho_p \partial \rho_q}, \tag{30}
\]

\[
E_{pq,r,s}^{cc} = \frac{\partial^2 E}{\partial \rho_p \partial \rho_{r,s}}, \tag{31}
\]

\[
\tilde{E}_{pq,r,s}^{cc} = \frac{\partial^2 \tilde{E}}{\partial \rho_p \partial \rho_{r,s}}, \tag{32}
\]

and analogously for the \( E_{pq,r,s}^{cc} \) and \( \tilde{E}_{pq,r,s}^{cc} \) terms. While Eqs. (23)–(26) are unique for APSG, Eqs. (27) and (28) are the same as for MCSCF, as they depend solely on one- and two-electron reduced density matrices.

The chemical potential \( \mu_p \) in Eq. (23) is identical for all orbitals in a given geminal. It can be obtained as

\[
c_p \mu_p = \frac{\partial E}{\partial c_p} = 2 c_p h_{pp} + \sum_{l_i \neq l_i} c_i (pp|ss) + 2 c_p \sum_{l_i \neq l_i} c_i \{2 (ps|ps) - (ps|sp)\}. \tag{33}
\]

Similar to the wave function optimization problem, the linear-response equations are solved using direct iterative techniques, which avoids explicit construction of \( E^{(2)} \) by relying on linear transformations with the trial vectors. Explicit formulas for the \( E^{(2)} \) elements in the \( \chi \)-parameterization as well as details of the TD-APSG implementation are given in the supplementary material.

The question of identifying doubly excited states in TD-APSG warrants a comment. In the geminal response theory, double excitations can be recognized by inspection of the response vector elements. Compared to time-dependent Hartree–Fock (TD-HF) or time-dependent density functional theory (TD-DFT), the response vector \( \Lambda \) contains additional elements, and analogously for \( \tilde{\Lambda} \), where \( \Lambda^{cc} \) corresponds to the response of geminal coefficients, and the extra part of the orbital response \( \Lambda^{oo} \) are excitations between two strongly or weakly occupied orbitals. Thus, double excitations recovered in TD-GVB should manifest either as large \( \Lambda^{cc} \) elements or large orbital-response contributions \( \Lambda^{oo} \) of the “SO–SO” or “WO–WO” types. This is in line with the interpretation of one-electron transition reduced density matrices (1-TRDMs) proposed by Giesbertz et al.\textsuperscript{36,37} and the relation between 1-TRDMs and the TD-APSG eigenvectors established by Pernal et al.\textsuperscript{19,20} Two classes of double excitations that can be distinguished are the off-diagonal and diagonal excitations. Off-diagonal double excitations, i.e., excitations to two different virtual orbitals or from two different occupied orbitals, can be traced to \( \Lambda^{oo} \) components in which both orbital indices correspond to SO orbitals (active–active rotations) or two WO orbitals (virtual–virtual rotations), cf. Eq. (34). Since these states do not couple to the configuration part of the eigenvectors, they are recovered in TD-APSG solely due to the multiconfigurational character of the APSG Ansatz.\textsuperscript{26} Diagonal double excitations are linked to the \( \Lambda^{cc} \) elements of the eigenvectors, and they involve a promotion of two electrons from a strongly occupied orbital to a weakly occupied orbital in the same geminal. Note that this includes transitions of the \( (\text{HOMO})^2 \rightarrow (\text{LUMO})^2 \) type, and for small HOMO–LUMO gaps, this double excitation is important for proper description of the lowest excited totally symmetric singlet state.

### III. Computational Details

Both the second-order APSG/GVB-PP wave function optimization and TD-APSG/TD-GVB linear-response equations were implemented in a development version of the Dalton\textsuperscript{24} program. To avoid numerical instabilities when solving the TD-GVB equations, rotations among active orbitals, which do not fulfill the \( |p_q - q_p| > 1 \times 10^{-4} \) criterion, are discarded. Note that this includes discarding rotations between inactive and active orbitals conforming to \( (2 - n_q) < 1 \times 10^{-4} \) as well as active-secondary rotations for which \( n_p < 1 \times 10^{-4} \) is satisfied.

The implementation of linear-response equations was verified against an independent, locally developed code with input reduced density matrices and one- and two-electron integrals taken from Dalton. We have observed a perfect agreement for systems studied in Ref. 19: the low-lying excited states of Li\textsubscript{2}, BH\textsubscript{2}, and H\textsubscript{2}O, including out-of-equilibrium geometries. Additionally, we have verified that, for two-electron systems, TD-GVB recovers the same excitation energies as LR-CASSCF with a CAS(2,2) active space.

Singlet excitation energy calculations were performed for subsets of two benchmark datasets: the dataset of Loos et al.,\textsuperscript{21} which we refer to as set A, and the dataset of Schreiber et al.,\textsuperscript{22} which we refer to as set B. Set A is composed of 18 small molecules: diatomics (dinitrogen and carbon monooxide), inorganic molecules (ammonia, water, and hydrogen sulfide), and non-aromatic organic compounds including hydrocarbons, aldehydes, amines, and amides. The set
analyzed in this work comprises 53 excitations. Set B includes theoretical best estimates for 28 small and medium organic molecules, which can be grouped into four subsets: (a) unsaturated aliphatic hydrocarbons, (b) aromatic hydrocarbons and heterocycles, (c) aldehydes, ketones, and amides, and (d) nucleobases. For set B, we selected 117 excitation energies from the original set of Ref. 22. As reference, we use coupled cluster (CC) results at the CC3 level of theory reported in Refs. 21 and 22.

We used the same basis sets as in the reference calculations, the aug-cc-pVTZ of Dunning \cite{ccpvtz,ccpvtz2} for set A\cite{dunning} and the TZVPP\cite{augccpvtz} basis set for set B.\cite{augccpvtz} The LR-CASSCF excitation energies for set B were taken from Ref. 42. For set A, we performed LR-CASSCF calculations in Dalton with the active space selection adapted from Ref. 43. The TD-HF calculations for both sets were performed in Dalton. All GVB-PP and APSG calculations employed the \( \alpha = 0.85 \) parameter for initial geminal guess generation (see Sec. II B). Since APSG/GVB-PP calculations do not make use of the point group symmetry, assignment of excitation energies followed from visualization of active natural orbitals, the analysis of the dominant orbital contributions to the excitation vectors and the oscillator strengths. The calculated singlet excitation energies for all systems, together with absolute APSG and GVB-PP electronic energies, are provided in the supplementary material (Tables S1 and S2).

IV. RESULTS AND DISCUSSION

A. The effect of the localization method: APSG and GVB-PP

In this section, we briefly comment on how the initial geminal guess impacts both the final APSG/GVB-PP geminals and energy. We compare the results obtained with either Boys or Pipek–Mezey localization of the occupied SCF orbitals. We use the method/B and method/PM abbreviations to refer to the results obtained with Boys and Pipek–Mezey localization methods, respectively.

All organic molecules included in the selected excitation energy benchmark datasets could be adequately described with the GVB-PP Ansatz. Only in the case of CO and N\(_2\), the extension from GVPB to APSG was required—lone-pair geminals were described with three correlating orbitals to account for near-degeneracy in the WO space, as described in Sec. II B (see also Table S3 and Figs. S1–S4 in the supplementary material).

In general, geminals obtained with Boys-localized and PM-localized orbitals in the initial guess may differ for molecules involving multiple bonds. Calculations for systems from the A and B datasets reveal that GVB/B is lower in energy compared to GVPB/PM at the cost of spatial symmetry breaking (see Tables S4 and S5 in the supplementary material). The differences between GVB/PM and GVB/B energies fall in the 0.2–28.0 m\( E_h \), range with the median of 2.0 m\( E_h \). The same effect for GVPB/PM functions obtained either with Boys- or PM-localized orbitals in the initial guess was observed by Wang et al.\cite{wang} Although the PM-based guess keeps the \( \sigma-\pi \) symmetry, the final GVB/PM wave function may include unphysical geminals delocalized over three atomic centers. These GVB/PM solutions correspond to local minima lying markedly higher in energy compared to GVB/B ones, e.g., by 28 m\( E_h \) for ethylene and by 20 m\( E_h \) for diazomethane.

The convergence of the GVB/B and GVB/PM wave function optimization is somewhat different. The GVB-PP functions based on PM-localized orbitals show a convergence behavior similar to that of CASSCF in terms of the number of macroiterations, while typically requiring more microiterations (see Tables S6 and S7 in the supplementary material). In the case of GVB/B, we distort the symmetry of the initial geminals to facilitate convergence to the global minimum (see Sec. II B). In consequence, the symmetry-broken GVB/B solutions usually take several more macroiterations compared to GVB/PM.

To summarize, when GVB/B and GVB/PM solutions differ, the former is the preferred one according to the variational principle, as being lower in energy.\cite{cc3} Yet, the choice of a symmetry-broken wave function entails erroneous description of molecular properties, including response to external perturbations. In Sec. IV B, we analyze this problem from the perspective of linear response of the geminal functions.

B. Singlet excitation energies with TD-GVB

In this section, we examine the accuracy of the geminal-based linear response. We present singlet excitation energies for two benchmark datasets of small and medium-sized molecules. Compared to the dataset of Loos et al.\cite{loos} (set A), excited states chosen from the set introduced by Schreiber et al.\cite{schreiber} (set B) pose a more significant challenge to TD-GVB: while set A includes states dominated by single excitations, set B also contains reference data for states of a doubly excited character.

As discussed in Sec. IV A, a geminal wave function may converge to different solutions depending on whether Boys- or PM-localized orbitals are selected in the initial guess. The corresponding discrepancies between TD-GVB/B and TD-GVB/PM excitation energies observed for systems from the two benchmark datasets fall in the 0.1–1.1 eV range. These deviations mirror the differences in the geminal structure of the underlying wave functions. A good example are excitations involving geminals that break the spatial symmetry in the GVB/B reference, such as the 2\( ^1A' \) state of adenine where Boys- and PM-based results differ by 1.1 eV. For this excitation, the symmetry-broken TD-GVB/B result is less accurate—compared to the CC3 reference, TD-GVB/B overestimates by 0.9 eV, while the TD-GVB/PM result agrees to within 0.1 eV with the benchmark (see Table S1 in the supplementary material). In several cases, the breaking of spatial symmetry in TD-GVB/B lifts the degeneracy of an excited state, e.g., the 1\( ^1II \) state of CO splits into two components located at 8.2 and 8.6 eV. Nonoptimal geminals delocalized over three atoms, which may appear in the Pipek–Mezey scheme, can also affect the accuracy. An illustrative example is the 1\( ^1B_1 \) state of diazomethane, for which excitation energies from the GVB/B and GVB/PM geminal functions differ by more than 0.5 eV. The TD-GVB/PM prediction deviates by 0.6 eV from the CC3 value, in contrast to Boys-based excitation energy overestimated only by 0.1 eV with respect to CC3 results (see Table S2 in the supplementary material).

When solving linear-response equations for GVB functions, which correspond to a local minimum, i.e., when there exists a lower-energy solution, one typically encounters imaginary frequencies (see Tables S1 and S2 in the supplementary material). These occurred only for GVB/PM functions and were never
TABLE I. Summary of error statistics (in eV) for singlet excitation energies for molecules from the work of Loos et al.21 (set A) and Schreiber et al.22 (set B). Calculations for set A employed the aug-cc-pVTZ basis, and for set B, the TZVP basis. LR-CASSCF values for set B were taken from Ref. 42. Errors are given with respect to CC3 results.

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>GVB/B</th>
<th>GVB/PM</th>
<th>CASSCF</th>
<th>HF</th>
<th>GVB/B</th>
<th>GVB/PM</th>
<th>CASSCF</th>
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<tr>
<td>( \bar{\Delta} )</td>
<td>0.35</td>
<td>0.44</td>
<td>0.47</td>
<td>0.38</td>
<td>0.73</td>
<td>0.87</td>
<td>0.84</td>
<td>0.54</td>
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<tr>
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<td>0.53</td>
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<td>( \sigma )</td>
<td>0.80</td>
<td>0.45</td>
<td>0.46</td>
<td>0.29</td>
<td>0.87</td>
<td>0.70</td>
<td>0.70</td>
<td>0.67</td>
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<tr>
<td>( \Delta_{\text{max}} )</td>
<td>2.04</td>
<td>1.45</td>
<td>1.45</td>
<td>1.38</td>
<td>3.25</td>
<td>2.64</td>
<td>2.64</td>
<td>2.69</td>
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<tr>
<td>Set B</td>
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</table>

observed for GVB optimized with Boys-localized orbitals. This problem resembles the triplet instability well-known from the Hartree–Fock theory.44 Although restriction of TD-GVB equations to the Tamm–Dancoff approximation (TDA) by setting \( B = 0 \) in \( E^2 \) eliminates the imaginary frequencies, it invariably results in larger errors. Importantly, the occurrence of imaginary frequencies does not necessarily correspond to large deviations between TD-GVB/PM and TD-GVB/B results nor to larger TD-GVB/PM errors compared to TD-GVB/B.

Despite appreciable discrepancies between TD-GVB/B and TD-GVB/PM excitation energies for a number of molecules, errors in both schemes average to nearly identical values, as evidenced by the error statistics presented in Table I. In terms of mean absolute errors (\( \Delta_{\text{abs}} \)), the difference between the TD-GVB/B and TD-GVB/PM amounts only to 0.03 eV for both A and B sets. This is also reflected in the boxplot representation of errors presented in Fig. 1. Nevertheless, due to the lack of symmetry breaking, the interpretation of electronic spectra obtained with the TD-GVB/PM variant is more straightforward. Thus, we recommend the use of Pipek–Mezey localization in TD-GVB and TD-APSF linear-response calculations. In the following discussion, we refer to TD-GVB/PM results and, for convenience, drop the PM notation.

Table I contains the error statistics for both A and B datasets given in terms of mean error (\( \bar{\Delta} \)), mean absolute error (\( \Delta_{\text{abs}} \)), standard deviation (\( \sigma \)), and maximum error (\( \Delta_{\text{max}} \)) computed with respect to the CC3 reference. The errors are also presented in the form of a boxplot in Fig. 1. Next to TD-GVB, we report the results of TD-HF and linear-response CASSCF (LR-MCSCF)35 calculations, also referred to as multiconfigurational random-phase approximation (MC-RPA)45 in the literature.

The lack of dynamic correlation in the GVB wave function results in TD-GVB mean errors exceeding 0.5 eV in both datasets (Table I). The mean absolute error in set A amounts to 0.5 eV and is accompanied by the standard deviation of roughly the same magnitude. TD-GVB is significantly less accurate for systems of the B set with the \( \Delta_{\text{abs}} \) and \( \sigma \) values of 0.9 and 0.7 eV, respectively. The same difference in accuracy between sets A and B is observed for linear response employing Hartree–Fock and CASSCF wave functions. Comparison of these three approaches reveals a clear trend in both sets. LR-CASSCF performs best in this group, followed by TD-GVB and TD-HF. The improvement in going from TD-HF to TD-GVB is small and reflected in a reduced spread of errors afforded by the latter method (cf. Fig. 1). This is expected since most of the analyzed systems can be correctly described with a single Slater determinant.

Accordingly, relatively large errors persist at the LR-CASSCF level of theory (0.4 and 0.3 eV in terms of \( \Delta_{\text{abs}} \) and \( \sigma \) for set A, while, for set B, the corresponding values amount to 0.7 eV).

Let us analyze the difference in the performance of TD-GVB and LR-CASSCF more closely. As a starting point, we focus on doubly excited states of the B set. In practice, the assignment of doubly excited states in TD-GVB is not straightforward. In particular, it may be difficult to establish whether a given fully symmetric doubly excited state is truly missing in the TD-GVB spectrum or if it is shifted to high energies, since non-negligible \( \Lambda_{cc} \) elements occur not only for doubly, but also for certain singly excited states (see the discussion in Sec. II C). Because of that, in set B, we were not able

FIG. 1. Boxplots of errors (\( \bar{\Delta} \), in eV) in the singlet excitation energies for molecules from the work of Loos et al.21 (set A) and Schreiber et al.22 (set B). The box and outer fences encompass 50% and 95% of the distribution, respectively. The outliers are marked as single points.
to assign excitations to the $2^1A_g$ states of butadiene, hexatriene, and octatetraene, the $2^1A_1$ state of cyclopentadiene as well as the $2^1A_g$ state of pyrazine.

To establish the doubly excited character, we used the $T_1$ diagnostic from the CC3 model. States from the B dataset for which $T_1$(CC3) values fell in the 62%–88% range were classified as doubly excited (33 datapoints, see Table S1 in the supplementary material). In this subgroup, we observe largest deviations between TD-GVB and LR-CASSCF results, the latter remaining in closer agreement with the CC3 benchmark (the $\Delta_{\text{abs}}$ values of 1.2 and 0.7 eV for TD-GVB and LR-CASSCF, respectively). These results corroborate the findings of Ref. 19, which revealed that geminal-based representation of doubly excited states is often inadequate. The authors reported errors exceeding 2.5 eV for excitations to the $1^1\Delta$ state of the BH molecule. For the same molecule, TD-APSG altogether missed the doubly excited $3^3\Sigma^+$ state. The poor performance of TD-GVB relative to LR-CASSCF, demonstrated here on the subset of systems from the set of Schreiber et al., shows that the geminal-based response is, in general, not capable of correctly representing states of a doubly excited character.

Comparison of TD-HF, TD-GVB, and LR-CASSCF for single excitations reveals a better agreement than in the case of doubly excited states. Largest differences between TD-GVB and LR-CASSCF are observed for nucleobases (in set B), where mean absolute errors of TD-GVB excitations are ~0.4 eV larger than the LR-CASSCF ones. Still, TD-GVB improves upon the TD-HF results for these systems ($\Delta_{\text{abs}}$ values of 1.0 and 1.3 eV, respectively; see Fig. S5 in the supplementary material). Interestingly, for other aromatic systems of set B, both methods show a similar performance. Apparently, a single resonance structure recovered at the GVB-PP level of theory is sufficient for the correct linear response. This is in contrast with the well-known problems of describing the ground-state energy of conjugated aromatic molecules using geminal wave functions.\textsuperscript{156,46,47} For the remaining subsets of set B (unsaturated aliphatic hydrocarbons, aldehydes, ketones, and amides) and for the entire set A, mean errors from geminal- and CASSCF-based response with respect to the CC3 benchmark do not deviate by more than 0.2 eV.

V. CONCLUSIONS

We presented an implementation of the ground-state strongly orthogonal geminal wave function theory and its time-dependent linear-response formulation. The geminal wave functions, either of the GVB-PP or the APSG type, are optimized with a robust restricted-step second-order algorithm,\textsuperscript{12} which is capable of handling many geminals. The implementation employs an original scheme for the initial geminal guess generation, described here in detail for the first time. The scheme involves two steps: (i) localization of the initial occupied orbitals selected to enter geminals and (ii) creation of correlating weakly occupied orbitals via diagonalization of the MP2 density matrix, which is set up separately for each of the localized orbitals, see Eq. (15). Linear-response TD-GVB and TD-APSG equations were cast in a form suitable for solution with the direct iterative scheme of Ref. 33 available in Dalton.\textsuperscript{21}

Since a geminal wave function is nonlinear in geminal expansion coefficients, its optimization is more sensitive to the choice of the initial guess than, e.g., CASSCF. In the Dalton implementation, we employed either Boys or Pipek–Mezey orbital localization in the geminal guess. Usually, Boys- and PM-based solutions differ for molecules with multiple bonds. The symmetry-broken geminal wave functions based on Boys-localized orbitals are lower in energy and thus preferable from the standpoint of the variational principle, but not in terms of calculated molecular properties. Irrespective of the orbital localization, we found the proposed automatic approach to geminal generation combined with the restricted-step second-order optimization algorithm to be efficient and robust for all tested systems, including conjugated aromatic molecules.

We have used our implementation to investigate how well TD-APSG and TD-GVB describe singlet excitation energies of small and medium-sized molecules. The pilot studies of linear response for geminal wave functions by Pernal et al., focused on model multireference systems restricted to several geminals. This work complements these previous findings by establishing the accuracy of the method for a diverse group of molecules included in benchmark datasets of Loos et al.\textsuperscript{19} and Schreiber et al.,\textsuperscript{17} which together comprise 42 molecules and 170 datapoints.

For singly excited states, TD-GVB gives mean absolute errors of 0.5 eV (set A $\Sigma^+$) and 0.9 eV (set B $\Sigma^+$), which is ~0.1–0.2 eV less accurate compared to LR-CASSCF results. At the same time, TD-GVB systematically improves upon TD-HF, in particular by reducing the error spread. This is not surprising since both GVB-PP and CASSCF miss dynamical correlation effects and GVB-PP spans a subspace of CASSCF. Although we were able to identify most of the doubly excited states in the TD-GVB spectrum, their quality is generally poor and does not match the LR-CASSCF description.

Regarding the role of the orbital localization scheme in linear response, the lack of spatial symmetry in Boys-based geminal wave functions may result in erroneous oscillator strengths and lifting the excited state degeneracy in the TD-GVB spectrum. Thus, we recommend to perform the TD-GVB calculations with GVB-PP employing PM-localized orbitals in the initial guess.

While, in this work, we put focus on TD-GVB and TD-APSG, development of geminal-based theories remains attractive also for ground state applications. First, the ability of geminal wave functions to capture static correlation gives them a clear advantage over the Hartree–Fock method, e.g., in describing single-bond breaking, equilibrium geometries, vibrational frequencies, or dipole moments.\textsuperscript{8,26} Second, and more important, both GVB-PP and APSG may serve as reference for models that capture dynamic correlation effects.\textsuperscript{13–15,48–61} Our Dalton implementation provides a convenient platform for exploring such approaches. An interesting perspective of accounting for the missing dynamic correlation effects in GVB/APSG, which can also be employed in linear response, lies in combining geminal wave functions with DFT in the framework of range-separated multiconfigurational DFT.\textsuperscript{19a,26} Work along this direction is in progress in our groups.

SUPPLEMENTARY MATERIAL

See the supplementary material for details on the implementation, total GVB-PP energies, and TD-GVB vertical excitation energies for both A and B datasets, wave function convergence analysis, and CPU timings.
ACKNOWLEDGMENTS

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

REFERENCES


