

Orbital Optimization with Spin-unrestricted and Projected Geminals Reference

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ABSTRACT

Variational improvement of the wave-function at the sacrifice of spin-symmetry is exploited within the antisymmetrized product of strongly orthogonal geminals (APSG) Ansatz. The role of orbital optimization is explored for the unrestricted APSG wave-function, with applying half-projection for partial spin purification, prior to variation. Dynamical correlation is incorporated by a symmetry-adapted formulation of perturbation theory, which corrects for spin along with the effect of perturbation. Splitting between the lowest singlet and triplet levels of cyclobutadiene is investigated along the automerization coordinate of the ground state.

KEYWORDS

geminal wave-function; variation after projection; spin-contamination; spin-adapted perturbation theory; singlet-triplet gap; cyclobutadiene

1. Introduction

Two-electron functions, geminals, offer a far more accurate description of the electronic structure of atoms and molecules than the molecular orbital (MO) based mean-field approach does. Accounting for a good amount of static correlation, geminal wave-functions[1–3] are capable of describing single bond fission correctly. They can be thought of as bridging the gap between MO and valence bond (VB) approaches. Unfortunately, general geminal wave-functions are prohibitive to deal with for large electronic systems, similarly to VB methods.

For reasons of tractability, considerable simplifications have been introduced in geminal based models from the early days. Among these, singlet coupling of two-electron units (aka perfect pairing)[4] has become widespread, mostly in combination with the strong orthogonality restriction. The latter entails expanding each geminal with the help of one-electron orbitals, φ which are assigned exclusively to it[5]. Energy optimization of the one-electron orbitals underlying the antisymmetric geminal product is computationally feasible with the above two assumptions. The associated geminal mean-field wave-function has been introduced under the names Generalized Valence

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Bond[6], Antisymmetrized Product of Strongly orthogonal Geminals (APSG)[7, 8] as well as Restricted Strongly orthogonal Singlet-type Geminals[9]. Intergeminal correlation, missing at the geminal mean-field level, may be recovered by Perturbation Theory (PT)[10–17] or coupled-cluster (CC)[18–23] methodology, which usually perform well when the effect is relatively small. There are however important cases, when correlation between singlet geminals becomes substantial. Breaking multiple covalent bonds, rearranging or simultaneously elongating adjacent single bonds is an important example, when perfect pairing breaks down due to spins recoupling in the process[24, 25]. This observation motivated developments allowing for spin-contamination. Singlet-triplet mixture at the geminal level[26–29] directly introduces spin components missed by perfect pairing, while retaining the single geminal product character of the Ansatz. Close relation of APSG with single-reference CC theory[30–32] inspired alternative, cluster considerations based relaxing of the perfect pairing assumption[32–35]. Abandoning strong orthogonality is another avenue of progress, aiming to incorporate the most correlation with geminal based, yet tractable schemes[36–43].

The geminal product Ansatz can be regarded as a theoretical implementation of the Lewis electron pair concept, formulated and employed mostly in relation with the ground state of molecular systems. Accordingly, geminal based modelling of electronically excited states generally adopts a linear response or equation-of-motion (EOM) approach[44–46]. There are however cases where incorporation of triplet geminals in the wave-function affords to target excited states of the system with a genuine geminal product description. Molecules of biradical character provide an example, where one (dominantly) triplet pair and the rest (mostly) singlet pairs can be a realistic first guess for the lowest triplet state[47]. Similarly to the ground state, inclusion of intergeminal correlation has been found imperative for accurate modelling of the triplet state and singlet-triplet gap, when starting from a geminal reference[48–53].

Orbital near-degeneracies are characteristic at the effective one-electron level description of biradicals, which made them popular test systems for electronic structure developments[54–59]. Apart from genuine multireference approaches[60–64], well crafted single reference based descriptions have also been shown to perform well. Examples for the latter include the spin-flip method[65] EOM coupled-cluster (CC) operating with electron-attachment[66–68] or the method of moments in CC[69–71]. Note, that conventional noniterative corrections to CCSD fail for biradicals. The noniterative CC(P;Q) methodology circumvents the problem by stepping beyond singles and doubles in the definition of the cluster operator (denoted as space P) and taking determinants from an orthogonal space Q to construct biorthogonal moments used for noniterative correction[72–75].

When modeling biradicals with unrestricted geminals, the challenge lies not with orbital degeneracy, but with the simultaneous treatment of spin purification and intergeminal correlation. Spin-symmetry violation in the overall wave-function can unfortunately hinder the description of dynamical correlation, as observed both at the single-determinantal[76–80] and at the multi-reference level[13, 50]. Spin restoration of the unrestricted geminals' product function has been investigated previously, either preceding variational optimization or applied a posteriori[81–84]. While the former approach obviously yields more complicated equations, it is free from Coulson-Fischer type discontinuities[85], characteristic of unrestricted schemes and magnified by projection-after-variation. Projected then varied, spin-unrestricted approaches have been extensively studied at the HF level in the 1970's[86] Considering the pair-function character of unrestricted Hartree-Fock (UHF), spin-projected then varied approaches are also to be mentioned here. The field was extensively studied in the 1970's[86]

and has been living a renaissance lately[87–89]. Spin-symmetry breaking has been exploited to account for static correlation not only at the UHF level[90, 91], but also in the spin-projected unrestricted form[92, 93].

Correlation corrections to spin-projected unrestricted wave-functions occurred so far mainly with PT methodology[51, 52, 94–96]. Our own efforts focused on restoration of spin-symmetry by Half-Projection (HP) as advocated by Smeyers[97, 98]. This approach, employing the spin-flip operator, is far more simple than full spin-projection[88, 99–101]. Effect of the HP operator can be incorporated in the equations determining the perturbation corrections. The method, known nowadays as symmetry adapted perturbation theory (SAPT), was elaborated extensively by the Polish school for intermolecular interactions[102–104]. Pilot applications performed on the example of para-benzyne focused on the effect of partitioning and symmetry enforcing in PT and sufficed with partial variational optimization. In particular, optimization of the reference resorted to geminal coefficients, while orbitals were taken as natural orbitals at the unrestricted Hartree-Fock (UHF) level[51].

In the present work we take the simpler diradical test case of cyclobutadiene and examine the effect of full variational optimization, including orbital and geminal coefficients at the level of the reference. Following a brief summary of the essence of the half-projected and perturbed, unrestricted geminal theory in Section 2., results of the computations are presented vis à vis highly accurate benchmark data provided by Refs.[64, 105].

2. Theory

2.1. Half-projected geminal reference

The strongly orthogonal geminal wave-function Ansatz pertinent to this study can be written as

$$\Psi = \prod_{\mu}^{N/2} \psi_{\mu}^{+} |\text{vac}\rangle \quad (1)$$

with geminal ψ_{μ} expanded with the help of one-electron orbitals in the form

$$\psi_{\mu}^{+} = \sum_{ij}^{(\mu)} C_{ij}^{(\mu)} \varphi_{i\beta}^{+} \varphi_{j\alpha}^{+} . \quad (2)$$

Number of electrons in the system, denoted by N is assumed to be even. Restriction on the sum in Equation (2) refers to orbitals assigned to subspace μ . Geminal coefficient matrix \mathbf{C} , built with entries $C_{ij}^{(\mu)}$ is accordingly blockdiagonal over orbital subspaces. Normalization of ψ_{μ} implies

$$\sum_{ij}^{(\mu)} |C_{ij}^{(\mu)}|^2 = 1 . \quad (3)$$

Throughout the paper latin letters are used for spatial orbital index, μ, ν refer to geminals and α, β are spin-indices.

Unrestricted nature of geminals manifests in the geminal coefficient matrix \mathbf{C} having a nonzero symmetric and antisymmetric part in general. This induces a spin-symmetry breaking in the product of Equation (1), which is partially remedied by applying the HP operator

$$\hat{\mathcal{P}}_{HP} = \frac{1}{2} (1 + f\hat{\mathcal{P}}) \quad (4)$$

yielding

$$\Psi_{\text{HP-APSG}} = \hat{\mathcal{P}}_{HP} \Psi . \quad (5)$$

In the above $\hat{\mathcal{P}}$ is the spin-flip operator and $f = (-1)^S$ distinguishes between even and odd spin quantum number, targeting a singlet or a triplet state by the spin projection in Equation (5).

Full variational optimization of HP-APSG implies

$$\langle \delta \Psi_{\text{HP-APSG}} | \hat{H} - E_{\text{HP-APSG}} | \Psi_{\text{HP-APSG}} \rangle = 0 \quad (6)$$

with taking into account variation of geminal coefficients $C_{ij}^{(\mu)}$ and one-electron orbitals φ_i when composing $\delta \Psi_{\text{HP-APSG}}$. The HP-APSG energy is obtained as the Rayleigh-quotient

$$E_{\text{HP-APSG}} = \frac{\langle \Psi_{\text{HP-APSG}} | \hat{H} | \Psi_{\text{HP-APSG}} \rangle}{\langle \Psi_{\text{HP-APSG}} | \Psi_{\text{HP-APSG}} \rangle} , \quad (7)$$

as the wave-function in Equation (5) is not normalized to unity.

Variation with respect to geminal coefficients leads to pseudo eigenvalue equations, yielding optimal geminals ψ_μ as

$$\hat{H}_\mu^{\text{eff}} \psi_\mu = E_\mu \psi_\mu , \quad \mu = 1, \dots, N/2 \quad (8)$$

The effective geminal Hamiltonian

$$\hat{H}_\mu^{\text{eff}} = \sum_{kl}^{(\mu)} \left(\mathcal{N}F_{kl}^a + f \eta_\mu \mathcal{M}F_{kl}^a \hat{\mathcal{P}}_\mu \right) \varphi_{k\alpha}^+ \varphi_{l\alpha}^- \quad (9a)$$

$$+ \sum_{kl}^{(\mu)} \left(\mathcal{N}F_{kl}^b + f \eta_\mu \mathcal{M}F_{kl}^b \hat{\mathcal{P}}_\mu \right) \varphi_{k\beta}^+ \varphi_{l\beta}^- \quad (9b)$$

$$+ \frac{1}{2} \sum_{klmn}^{(\mu)} [kl|mn] \sum_{\sigma, \sigma'} \varphi_{k\sigma}^+ \varphi_{l\sigma'}^+ \varphi_{n\sigma'}^- \varphi_{m\sigma}^- \left(1 + f \eta_\mu \hat{\mathcal{P}}_\mu \right) \quad (9c)$$

$$- f \kappa_\mu \hat{\mathcal{P}}_\mu \quad (9d)$$

includes explicit two-body terms, responsible for intrageminal correlation, while terms involving $\mathcal{N}\mathbf{F}^a$ and $\mathcal{N}\mathbf{F}^b$ describe ordinary mean-field interaction. Appearance of the local spin flip-operator, $\hat{\mathcal{P}}_\mu$ in Equation (9) is a consequence of HP. It contributes zero-, one- and two-body terms to \hat{H}_μ^{eff} , all bringing a coupling beyond mean-field. Explicit

expression of the overlap-related constant η_μ , the energy-related quantity κ_μ as well as that of the Fockian-type operators in Equation (9) is not particularly relevant from our present purpose, and is skipped for brevity. We refer to Equation (11) of Ref.[84] on this matter, for completeness.

A methodological novelty of the present work is full variational optimization of the half-projected geminal wave-function, for which the HP-APSG acronym is introduced.¹ It implies solving Equation (8) for geminal coefficients in ψ_μ in a self-consistent manner in optimization micro cycles, while the energy is minimized with respect to orbital rotation by a Newton–Raphson type process in iteration macro cycles. The unitary transformation corresponding to orbital rotation can be expressed as[106, 107] $\hat{U} = \exp(\hat{R})$, where

$$\hat{R} = \sum_{pq} R_{pq} \hat{E}_{pq} , \quad (10)$$

matrix \mathbf{R} is antisymmetric and the spin-summed excitation operator is defined as

$$\hat{E}_{pq} = \sum_{\sigma} \varphi_{p\sigma}^+ \varphi_{q\sigma}^- . \quad (11)$$

Energy is expanded with respect to \hat{R} , its $\mathcal{O}(\hat{R})$ term yielding the orbital gradient[108]

$$g_{pq} = \langle [\hat{H}, \hat{E}_{pq} - \hat{E}_{qp}] \rangle = 2(F_{pq} - F_{qp}) \quad (12)$$

in the real case, for $p < q$. Elements of the generalized Fockian are given by

$$F_{pq} = \sum_j h_{pj} \gamma_{jq} + 2 \sum_{jkl} [pj|kl] \Gamma_{kl,qj} \quad (13)$$

and elements of the one- and two-body reduced density matrices, γ and $\mathbf{\Gamma}$ are evaluated as

$$\begin{aligned} \gamma_{pq} &= \langle \Psi_{\text{HP-APSG},n} | \hat{E}_{qp} | \Psi_{\text{HP-APSG},n} \rangle , \\ \Gamma_{pq,rs} &= \frac{1}{2} \langle \Psi_{\text{HP-APSG},n} | \hat{E}_{rp} \hat{E}_{sq} - \delta_{ps} \hat{E}_{rq} | \Psi_{\text{HP-APSG},n} \rangle , \end{aligned} \quad (14)$$

with $\Psi_{\text{HP-APSG},n}$ denoting the normalized HP-APSG function. Note that \mathbf{F} of Equation (13) is different from the Fockian-type matrices appearing in Equation (9).

The orbital Hessian, evaluated for ($p < q, r < s$) is obtained from the $\mathcal{O}(\hat{R}^2)$ term of the energy expansion as

$$H_{pq,rs}^{\text{orb}} = \frac{1}{2} (1 - \hat{P}_{pq})(1 - \hat{P}_{rs}) \left(\langle [[\hat{H}, \hat{E}_{pq}], \hat{E}_{rs}] \rangle + \langle [[\hat{H}, \hat{E}_{rs}], \hat{E}_{pq}] \rangle \right) , \quad (15)$$

where \hat{P}_{ab} is a permutation operator. In our applications, we resorted to a diagonal

¹While APSG often stands for the singlet coupled Ansatz, we use it here to encompass the spin-unrestricted case as well and let prefix HP remind to that. Note that HP has no effect on singlet-coupled APSG.

approximation of the orbital Hessian, with elements given by

$$\begin{aligned}
 H_{pq,pq}^{\text{orb}} = & 2h_{qq}\gamma_{pp} + 2h_{pp}\gamma_{qq} - 4h_{qp}\gamma_{qp} - 2F_{qq} - 2F_{pp} \\
 & + 4 \sum_{ij} ([iq|jq]\Gamma_{pj,pi} + [ip|jp]\Gamma_{qj,qi} + [qi|jq]\Gamma_{pj,ip} + [pi|jp]\Gamma_{qj,iq}) \\
 & - 8 \sum_{ij} ([iq|jp]\Gamma_{qj,pi} + [qi|jp]\Gamma_{qj,ip} + [qp|ji]\Gamma_{ij,qp}) \\
 & + 4 \sum_{ij} ([pp|ij]\Gamma_{ij,qq} + [qq|ij]\Gamma_{ij,pp}) ,
 \end{aligned} \tag{16}$$

assuming all involved quantities are real.

Computational cost of calculating the HP-APSG reference function is determined by transformation of one- and two-electron integrals to the basis of new MOs, performed at each step of the orbital optimization macro cycle. A slight advantage in economy is offered by the fact, that integrals indexed solely by orbitals of the so-called virtual geminal (i.e. featuring zero occupation number in HP-APSG) are not needed. The necessary integrals in a macro cycle can therefore be obtained at the cost of $\mathcal{O}(N_o N_b^4)$, with N_b denoting the number of basis functions and N_o referring to the number of orbitals belonging to any of the $\mu = 1, \dots, N/2$ subsets. Convergence of the macro iteration was enhanced by direct inversion in the iterative subspace method[109], similarly to previous studies[110, 111].

It is possible to avoid the integral transformation by expressing all quantities on the basis on atomic orbitals, as reported by Rassolov[9], formal scaling of the most costly procedure is however unchanged. A final note on HP-APSG is that geminal subspace dimension, i.e. length of the expansion in Equation (2) is kept fixed, at difference with Ref.[9] where it is treated as a variational parameter.

2.2. Symmetry-adapted perturbation correction

A convenient PT correction to Equation (1), exploiting the strongly orthogonal geminal product structure can be devised as

$$|\Psi^{(1)}\rangle = \sum_{K \neq 0} c_K^{(1)} |\Psi_K\rangle , \tag{17}$$

with excited states Ψ_K taking the form

$$|\Psi_K\rangle = \prod_{\mu}^{N/2} \psi_{\mu,K}^+ |\text{vac}\rangle . \tag{18}$$

Functions $\psi_{\mu,K}$ in Equation (18) are expanded over geminal subspace μ , they may however be excited solutions of Equation (8), moreover they are not necessarily two-electron functions. Focusing on the first-order interacting space, one-, three- and four-electron functions occur among $\psi_{\mu,K}$. This construction ensures orthogonality of Ψ_K 's. All $\psi_{\mu,K}$ coming from the lowest root of the geminal eigenvalue equation corresponds to the function of Equation (1), designated as $K = 0$ when needed. Excited functions contributing to Equation (17) accommodate at least two $\psi_{\mu,K}$ different from the ground state solution of Equation (8)[50].

The linear equation of the first order coefficients $c_K^{(1)}$ reads as

$$\sum_{K \neq 0} G_{LK} c_K^{(1)} = -H_{L0} \quad (19)$$

where $G_{LK} = \langle \Psi_L | \hat{H}^{(0)} | \Psi_K \rangle - E^{(0)} \delta_{LK}$ and $H_{L0} = \langle \Psi_L | \hat{H} | \Psi \rangle$. With the zero-order operator taking a sum over geminal operators form

$$\hat{H}^{(0)} = \sum_{\mu=1}^{N/2} \hat{H}_\mu + \hat{H}_V, \quad (20)$$

the zero-order energy is a sum of geminal eigenvalues

$$E^{(0)} = \sum_{\mu=1}^{N/2} E_\mu \quad (21)$$

and matrix \mathbf{G} adopts a block-diagonal structure, allowing a block-by-block solution of Equation (19). Operators on the rhs of Equation (20), \hat{H}_μ and \hat{H}_V , where V refers to the subset of virtual orbitals, are defined further below. Description of excited state blocks, as well as many-body formulae of G_{LK} and H_{L0} contributing to the first order wave-function are given in Ref.[50].

Correction schemes as detailed above serve well for improving geminal product type reference functions[13, 50, 112, 113], the spin-projection element of HP-APSG however calls for additional attention. Seeking a correction to the wave-function of Equation (5), one may apply a general PT framework to HP-APSG[52], adopting a partitioning successful at the HF level, e.g. Møller-Plesset or Epstein-Nesbet. Alternatively, it is possible to rely on the Dyll-type[114] zero-order of Equation (20), involving genuine two-body interaction. With this latter option a step back has to be taken concerning the zero-order wave-function, since a sum-over-geminals operator features product-over-geminals eigenfunctions of the type of Equation (1) but not that of Equation (5). Symmetry-projection can however be incorporated in the PT equations, thereby restoring symmetry at finite orders of the series, in the spirit of SAPT[102–104]. With HP playing the role of the symmetry-operator, SAPT-type corrections to HP-APSG have been worked out in two alternative forms. In both formulations Equation (7) represents the energy up to first order, denoted E_{HP} below, for brevity. The second order energy is expressed as[51]

$$E_w^{(2)} = \frac{\sum_{K \neq 0} c_K^{(1)} (H_{0K} + f \tilde{H}_{0K} - f E_{\text{HP}} M_{0K})}{1 + f \langle \Psi | \hat{\mathcal{P}} | \Psi \rangle} \quad (22)$$

in the weak symmetry forcing scheme, with $\tilde{H}_{0K} = \langle \Psi | \hat{H} \hat{\mathcal{P}} | \Psi_K \rangle$, and $M_{0K} = \langle \Psi | \hat{\mathcal{P}} | \Psi_K \rangle$, many-body formulae of which are given in Ref.[51].

The second order pertinent to the strong symmetry forcing variant reads

$$E_s^{(2)} = E_w^{(2)} + \frac{\sum_{K,L \neq 0} H_{0K} G_{KL}^{-1} H_{L0} - \sum_{K,L \neq 0} (\tilde{H}_{0K} - E_{\text{HP}} M_{0K}) G_{KL}^{-1} (\tilde{H}_{L0} - E_{\text{HP}} M_{L0})}{2(1 + f \langle \Psi | \hat{\mathcal{P}} | \Psi \rangle)} \quad (23)$$

Note, that $E_s^{(2)}$ is considerably more demanding computationally than $E_w^{(2)}$ due to the second term in the numerator on the rhs of Equation (23). It involves excited states $|\Psi_K\rangle$ for which \tilde{H}_{0K} is nonzero, which may involve excitations conserving M_S quantum number and electron number of geminals, on top of the elements of the first order interacting space of $|\Psi_K\rangle$, as discussed in relation to Equation (18).

It remains to specify geminal Hamiltonians, contributing to Equation (20). Operator \hat{H}_V belonging to the virtual geminal subspace is the simplest to derive from Equation (9), by omitting $\hat{\mathcal{P}}_\mu$ containing terms altogether. Operator \hat{H}_μ for $\mu = 1, \dots, N/2$ requires more consideration due to the fact, that Equation (9) was deduced from the variational equations focusing on the ground state of geminal subspace μ [84]. Its application as zero-order regarding other states of subspace μ may have adverse effect, e.g. intruder states. For this reason \hat{H}_μ is defined with the help of projectors in subspace μ , ensuring that its effect is identical to that of \hat{H}_μ^{eff} only on the ground state of geminal μ . Interaction between ground and excited states in subspace μ are omitted in \hat{H}_μ . Regarding the block of excited geminal states, various possibilities were tested. We here apply option 3 of Ref.[51], defining \hat{H}_μ as

$$\frac{\mathcal{N}\hat{H}_\mu + \langle\psi_\mu|\hat{\mathcal{P}}_\mu|\psi_\mu\rangle\mathcal{M}\hat{H}_\mu^s}{1 + f\langle\Psi|\mathcal{P}\Psi\rangle} \quad (24)$$

when acting on excited functions in subspace μ . In the above $\mathcal{N}\hat{H}_\mu$ arises from the first terms in the round braces in terms (9a)-(9c) of \hat{H}_μ^{eff} . Second term in the round braces of terms (9a)-(9c) of \hat{H}_μ^{eff} give rise to $\mathcal{M}\hat{H}_\mu^s$ by omitting $\hat{\mathcal{P}}_\mu$ and symmetrizing.

3. Cyclobutadiene automerization process

Gradual transformation of cyclobutadiene from one rectangular Kekulé-structure to the other through the square arrangement is an example highlighting the shortcoming of perfect pairing. The characteristic cusp at the square geometry on the ground state potential energy curve obtained by the singlet-coupled model is mitigated when letting geminals become singlet-triplet mixed[25, 81]. Orbitals underlying the two wavefunction models are also markedly different. While natural orbitals of singlet geminals tend to localize on bonds, lone pairs, etc., spin-contamination at the geminal level delocalizes the orbitals. This is already present with natural orbitals of the UHF wavefunction, which adheres to Equation (1), with spin-unrestricted geminals and a constrained parametrization of the geminal coefficient matrix. Here we examine the effect of stepping from UHF Natural Orbitals (UNO) to those optimized with the full-blown parametrization of matrix \mathbf{C} entering the energy expression of the half-projected geminal product. Acronym HP-APSG refers to the fully optimized reference function, HP-APSG(U) stands for results obtained on the basis of UNOs. Geminal subspace dimensions are kept at two, as inherited from UHF and six geminals are correlated in the APSG model. Core orbitals are frozen at the level of UHF or HP-APSG.

Focusing on the lowest singlet and triplet states of the system, energies by the weak symmetry forcing PT scheme on top of HP-APSG are displayed in Fig.1, labeled PT2w. Performance of the strong symmetry forcing variant, PT2s is shown in Fig.2. A blow-up in the computational effort generated by the second term in the numerator on the right hand side of Equation (23) is avoided by starting with those excited states K, L which enter the first term and allowing at most one extra gemi-

nal becoming excited in these. Benchmark data taken from Ref.[105] are provided by CCSDT and the perturbatively corrected selected configuration interaction methodology of Malrieu, termed CIPSI[115]. Both benchmarks rest on the orbitals optimized at the single determinantal level, restricted HF (RHF) in the case of the singlet and restricted open-shell HF for the triplet state. This represents a particular challenge for the ground state. To alleviate the cusp feature produced with RHF orbitals, the high-level methodology of full triples is needed in the case of CC. Regarding the selected CI procedure, a variational space dimension on the order of 100,000 must be reached, and the same quality is needed for the CIPSI-driven CC(P;Q) ground state curve to become of correct shape. Sampling of the determinantal space is significantly more modest in the case of HP-APSG based PT. The six geminals correlated at the level of HP-APSG generate an incomplete model space of dimension 4096. It is the number of excited functions of the form of Equation (18), contributing to PT2w, that is on the order of 500,000, comparable to the dimension of the variational space of CIPSI, mentioned above.

While curve shape by geminal based PT methods is satisfactory in the vicinity of $\lambda = 1$, barrier height of the ground state and singlet-triplet gap are less favorable. The ground state curve by PT2w is too flat, producing a roughly 50% deficit in the barrier height as compared to the benchmark value. This results in an overestimation of the singlet-triplet gap at $\lambda = 1$ even if the excited state curve nicely overlaps with those by the benchmarks, as reflected by Fig.1. The ground state curve by PT2s displayed in Fig.2 overcompensates the defect of PT2w, resulting in more than 50% overestimation of the barrier height. Deviation of the singlet-triplet gap at $\lambda = 1$ from the benchmark value is also affected by the excited state curve of PT2s, as it is shifted up by some 15-20 mE_h from CCSDT or CIPSI+PT2. By a compensation of errors, the 7.5 mE_h HP-APSG-PT2s singlet-triplet gap at $\lambda = 1$ is in good agreement with the benchmark 7.6 mE_h by CCSDT. The 9.5 mE_h CIPSI-PT2 gap is slightly larger than CCSDT but even that is overcome by the HP-APSG-PT2w value of 12.7 mE_h , which is clearly too large. Singlet-triplet gap at $\lambda = 1$ by alternative multireference PT methodologies in similar quality basis (631+G(d)) vary in the 6.5 – 8.5 mE_h range[64], in good agreement with the 7.5 mE_h HP-APSG-PT2s value in cc-pVDZ basis.

Considering the effect of orbital optimization at the level of HP-APSG, it improves energies in the correct direction for both the ground and excited state in Fig.1, the order of magnitude of the effect is however small. Orbital optimization appears especially marginal when compared to the effect of symmetry forcing, i.e. the difference between HP-APSG-PT2 data between Figs.1 and 2. With this in mind, and regarding that the PT2s formula is implemented with a rather crude approximation, it appears premature to draw conclusion on the seemingly negative impact of orbital optimization in Fig.2. At the same time, the need for more refined approximations in evaluating Equation (23) is underlined.

An insight into active orbitals is provided by the contour plots in Figures 3 and 4, giving occupation numbers (i.e. diagonal elements of the spin-summed density matrix γ) and total spin-squared expectation value as well. Point-group symmetry conforming feature of orbitals plots is in line with the delocalization effect of geminal spin-contamination. A conservation of locality also applies in that σ pairs extend mainly over carbon atoms and less for hydrogens. One can say to a good approximation that C – H σ bonds remain at the RHF level. Occupation numbers in Figs. 3 and 4 are in agreement with the expectation that correlation mainly affects π geminals. In fact, with Pulay's standard UNO thresholds[116] of 1.98, 0.02 only the π geminals would be correlated. We applied a less stringent threshold with the purpose of giving more

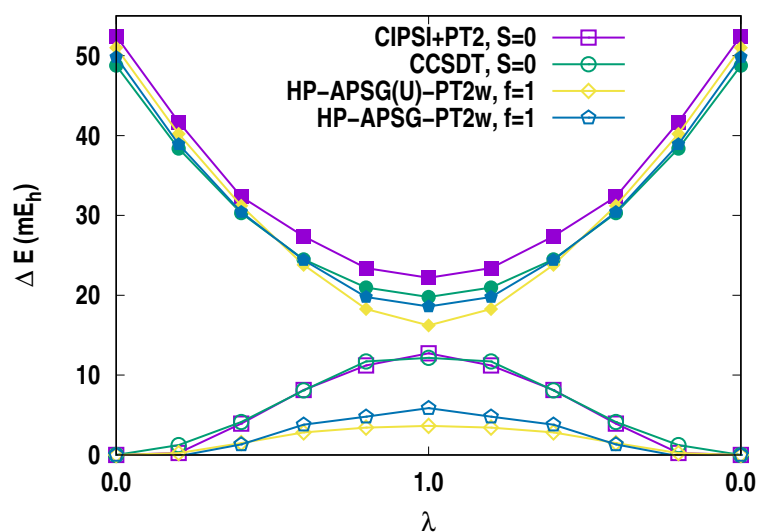


Figure 1. Potential energy curve of the lowest two states of cyclobutadiene in cc-pVDZ basis, along a rectangle to square ($\lambda = 1$) transformation. Reaction coordinate, λ is defined in [64]. Energy difference, ΔE is measured from the ground state value at $\lambda = 0.0$ for each method. Hollow symbols are used for the ground state, filled symbols indicate the first excited state. Note, that HP-APSG based results are not spin-pure, $f = -1$ is applied in Equation (4) for the excited state. Perturbation correction in the weak symmetry forcing variant, labeled PT2w is evaluated according to Equation (22). Results labeled CIPSI+PT2 and CCSDT are taken from [105]. The former corresponds to the perturbatively corrected CIPSI energies, extrapolated at each geometry based on the six largest variational space data.

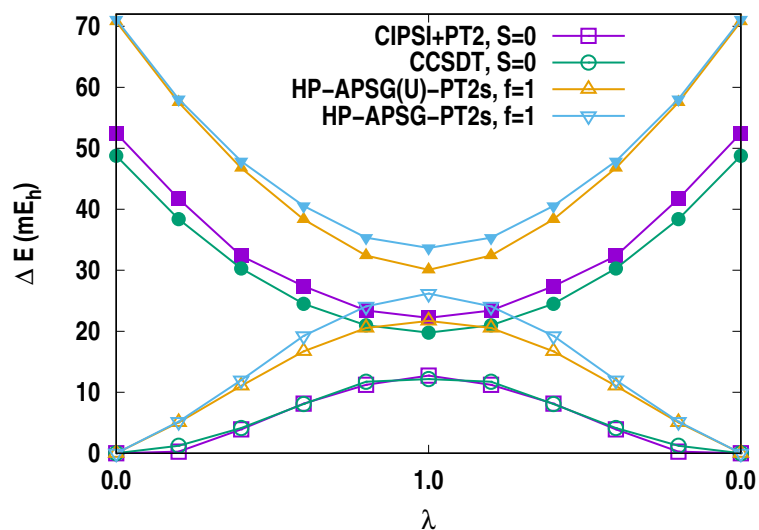


Figure 2. Potential energy curve of the lowest two states of cyclobutadiene in cc-pVDZ basis, along the reaction coordinate, λ defined in [64]. Perturbation correction in the strong symmetry forcing variant, labeled PT2s is evaluated according to Equation (23) in an approximate form. See text and legend of Fig.1 for more.

variational flexibility to the HP-APSG(U) and HP-APSG reference.

Focusing on occupation numbers and total spin in comparison of UHF and HP-APSG(U), it is apparent in Figs. 3 and 4, that geminal coefficient optimization with orbitals kept as UHF has a significant effect. (This obviously does not apply to the 1.000 occupation numbers of the most correlated geminal at $\lambda = 1.0$, being a mark of the perfect biradical structure.) When stepping from HP-APSG(U) to orbitals optimized at the level of HP-APSG, changes are significantly smaller in occupation numbers as well as in the expectation value of total spin-squared. Orbital plots of π -geminals, dominated by carbon p_z orbitals, remain unaffected by variational improvement. Tiny changes can be observed on the orbital plots of HP-APSG σ -geminals as compared to UHF, e.g. hydrogen contributions slightly diminish. Similarity in HP-APSG geminals of the ground and excited state in both Figures lends support to spin-flip approaches.

4. Conclusion

The HP-APSG reference represents an economical wavefunction model, providing a geminal-based interpretation of the electronic structure and serving as reliable starting point for correlation correction. Geminal-unrestriction accompanied by spin-projection at the many-electron level extends the applicability of the strongly orthogonal geminal product reference to the lowest singlet and triplet states of biradicals. Starting from natural orbitals of the UHF wavefunction a HP-APSG optimized orbital set can be easily reached. Alternative, local minima may deserve further exploration, e.g. in the vicinity of the perfect-pairing optimized orbital set. Symmetry restoration of the unrestricted geminal Ansatz is an essential element of the methodology. Symmetry forcing at finite orders of the PT series appears more promising in the strong variant than its weak counterpart.

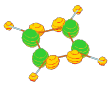
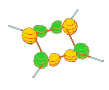
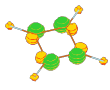
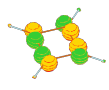
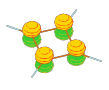
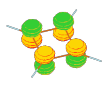
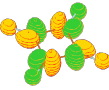

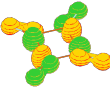
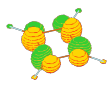
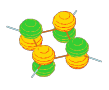

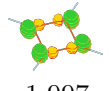
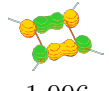
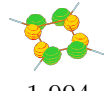
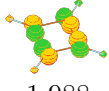
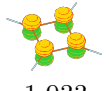







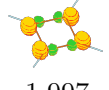
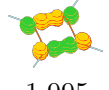
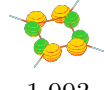
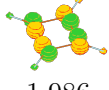
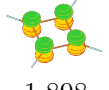
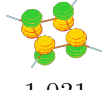






	C-C σ pairs				C-C π pairs	
UHF $\langle S^2 \rangle = 1.014$	 1.998	 1.997	 1.997	 1.992	 1.910	 1.443
	 0.002	 0.003	 0.003	 0.008	 0.090	 0.557
HPAPSG(U) $\langle S^2 \rangle = 0.273$	1.998	1.997	1.996	1.989	1.928	1.732
	0.002	0.003	0.004	0.011	0.072	0.267
HPAPSG(U) $\langle S^2 \rangle = 2.018$	1.997	1.996	1.995	1.988	1.892	1.036
	0.003	0.004	0.005	0.012	0.108	0.964
HPAPSG $\langle S^2 \rangle = 0.255$	 1.997	 1.996	 1.994	 1.988	 1.933	 1.763
	 0.003	 0.004	 0.006	 0.012	 0.067	 0.237
HPAPSG $\langle S^2 \rangle = 2.019$	 1.997	 1.995	 1.993	 1.986	 1.898	 1.031
	 0.003	 0.005	 0.007	 0.014	 0.102	 0.969

Figure 3. Optimized orbitals and occupation numbers at the UHF and HP-APSG level, at the end point of the automerization process, $\lambda = 0.0$. Occupation numbers of HP-APSG(U) correspond to γ of the HP-APSG wavefunction, evaluated on the basis of UNOs. Contour plots are drawn at the $|0.1|$ value of the orbitals in all cases.





































	C-C σ pairs				C-C π pairs	
UHF $\langle S^2 \rangle = 1.244$	 1.998	 1.997	 1.995	 1.995	 1.891	 1.000
	 0.002	 0.003	 0.005	 0.005	 0.109	 1.000
HPAPSG(U) $\langle S^2 \rangle = 0.397$	1.995	1.997	1.994	1.994	1.895	1.000
	0.005	0.003	0.006	0.006	0.105	1.000
HPAPSG(U) $\langle S^2 \rangle = 2.015$	1.995	1.997	1.994	1.994	1.901	1.000
	0.005	0.003	0.006	0.006	0.099	1.000
HPAPSG $\langle S^2 \rangle = 0.391$	 1.994	 1.997	 1.993	 1.993	 1.897	 1.000
	 0.006	 0.003	 0.007	 0.007	 0.103	 1.000
HPAPSG $\langle S^2 \rangle = 2.016$	 1.995	 1.997	 1.993	 1.993	 1.905	 1.000
	 0.005	 0.003	 0.007	 0.007	 0.095	 1.000

Figure 4. The same as Fig.3 at the square geometry, $\lambda = 1.0$.

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References

- [1] R. McWeeny and B.T. Sutcliffe, Proc. R. Soc. Lond. A **273**, 103 (1963).
- [2] W. Kutzelnigg, J. Chem. Phys. **40**, 3640 (1964).
- [3] E. Kapuy, Acta Phys. Hung. **10**, 125 (1959).
- [4] A.C. Hurley, J. Lennard-Jones and J.A. Pople, Proc. R. Soc. Lond. A **220**, 446 (1953).
- [5] T. Arai, J. Chem. Phys. **33**, 95 (1960).
- [6] F.W. Bobrowicz and W.A. Goddard-III, in *Methods of Electronic Structure Theory*, edited by H. F. Schaefer-III (Plenum, New York, 1977), p. 79.
- [7] P.R. Surján, Topics in current chemistry **203**, 63–88 (1999).
- [8] P. Surján, Reference Module in Chemistry, Molecular Sciences and Chemical Engineering, Theoretical and Computational Chemistry **137** (2016).
- [9] V.A. Rassolov, J. Chem. Phys. **117**, 5978 (2002).
- [10] R.B. Murphy and R.P. Messmer, J. Chem. Phys. **97**, 4170 (1992).
- [11] R.B. Murphy, T. Pollard and R.A. Friesner, J. Chem. Phys. **106**, 5073 (1997).
- [12] E. Rosta and P.R. Surján, Int. J. Quantum Chem. **80**, 96 (2000).
- [13] V.A. Rassolov, F. Xu and S. Garashchuk, J. Chem. Phys. **120**, 10385–10394 (2004).
- [14] M. Kobayashi, Á. Szabados, H. Nakai and P.R. Surján, J. Chem. Theory Comput. **6**, 2024–2033 (2010).
- [15] G.J.O. Beran, M. Head-Gordon and S.R. Gwaltney, The Journal of Chemical Physics **124** (11), 114107 (2006).
- [16] M. Tarumi, M. Kobayashi and H. Nakai, Journal of Chemical Theory and Computation **8**, 4330–4335 (2012).
- [17] P.A. Limacher, P.W. Ayers, P.A. Johnson, S. De Baerdemacker, D.V. Neck and P. Bultinck, Phys. Chem. Chem. Phys. **16**, 5061–5065 (2014).
- [18] S. Li, J. Ma and Y. Jiang, The Journal of Chemical Physics **118** (13), 5736–5745 (2003).
- [19] J.A. Parkhill and M. Head-Gordon, The Journal of Chemical Physics **133** (12), 124102 (2010).
- [20] T. Zoboki, Á. Szabados and P.R. Surján, J. Chem. Theory Comput. **9**, 2602–2608 (2013).
- [21] Q. Wang, M. Duan, E. Xu, J. Zou and S. Li, The Journal of Physical Chemistry Letters **11**, 7536–7543 (2020).
- [22] Á. Margócsy and Á. Szabados, The Journal of Chemical Physics **152**, 204114 (2020).
- [23] Á. Margócsy and Á. Szabados, Journal of Chemical Theory and Computation **17**, 6947–6964 (2021).
- [24] P.A. Schultz and R.P. Messmer, Journal of the American Chemical Society **115** (23), 10938–10942 (1993).
- [25] P. Jeszenszki, V. Rassolov, P.R. Surján and Á. Szabados, Mol. Phys. **113**, 249–251 (2015).

- [26] K.V. Lawler, D.W. Small and M. Head-Gordon, *The Journal of Physical Chemistry A* **114**, 2930–2938 (2010).
- [27] G.J.O. Beran, B. Austin, A. Sodt and M. Head-Gordon, *The Journal of Physical Chemistry A* **109**, 9183–9192 (2005).
- [28] V.A. Rassolov and F. Xu, *J. Chem. Phys.* **126**, 234112 (2007).
- [29] K. Nakatani and H. Sato, *The Journal of Chemical Physics* **158**, 211104 (2023).
- [30] I.I. Ukrainskii, *Theor.Math.Phys.* **32**, 816 (1978).
- [31] J. Cullen, *Chem. Phys.* **202**, 217–229 (1996).
- [32] T.V. Voorhis and M. Head-Gordon, *Chem. Phys. Lett.* **317**, 575–580 (2000).
- [33] T.V. Voorhis and M. Head-Gordon, *J. Chem. Phys.* **117**, 9190–9201 (2002).
- [34] D.W. Small and M. Head-Gordon, *J. Chem. Phys.* **137**, 114103 (2012).
- [35] P.B. Gaikwad, T.D. Kim, M. Richer, R.A. Lokhande, G. Sánchez-Díaz, P.A. Limacher, P.W. Ayers and R.A. Miranda-Quintana, *The Journal of Chemical Physics* **160**, 144108 (2024).
- [36] T.V. Voorhis and M. Head-Gordon, *The Journal of Chemical Physics* **112**, 5633–5638 (2000).
- [37] P. Cassam-Chenai, *Phys. Rev. A* **77**, 032103 (2008).
- [38] P. Cassam-Chenai and V. Rassolov, *Chem. Phys. Letters* **487**, 147 – 152 (2010).
- [39] B.A. Cagg and V.A. Rassolov, *The Journal of Chemical Physics* **141** (16), 164112 (2014).
- [40] P. Cassam-Chenai, T. Perez and D. Accomasso, *The Journal of Chemical Physics* **158**, 074106 (2023).
- [41] P. Cassam-Chenai, *J. Math. Chem.* **62**, 222–227 (2024).
- [42] P.A. Johnson, C.É. Fecteau, F. Berthiaume, S. Cloutier, L. Carrier, M. Gratton, P. Bultinck, S.D. Baerdemacker, D.V. Neck, P.A. Limacher and P.W. Ayers, *The Journal of Chemical Physics* **153**, 104110 (2020).
- [43] M. Richer, T.D. Kim and P.W. Ayers, *International Journal of Quantum Chemistry* **125**, e70000 (2025).
- [44] K. Chatterjee and K. Pernal, *The Journal of Chemical Physics* **137**, 204109 (2012).
- [45] K. Chatterjee and K. Pernal, *Theoretical Chemistry Accounts* **134**, 1–9 (2015).
- [46] H. Zhang, J. Zou, X. Ren and S. Li, *The Journal of Physical Chemistry Letters* **14**, 6792–6799 (2023).
- [47] P. Rivero, C.A. Jiménez-Hoyos and G.E. Scuseria, *The Journal of Physical Chemistry A* **117**, 8073–8080 (2013).
- [48] S.C. Wright, D.L. Cooper, J. Gerratt and M. Raimondi, *The Journal of Physical Chemistry* **96**, 7943–7952 (1992).
- [49] P.M. Zimmerman, *The Journal of Physical Chemistry A* **121**, 4712–4720 (2017).
- [50] D. Földvári, Z. Tóth, P.R. Surján and Á. Szabados, *J. Chem. Phys.* **150**, 034103 (2019).
- [51] Z.É. Mihálka, P.R. Surján and Á. Szabados, *J. Chem. Theory Comput.* **17**, 4122–4143 (2021).
- [52] Z.É. Mihálka, Á. Szabados and P.R. Surján, *J. Chem. Phys.* **154**, 234110 (2021).
- [53] X. Ren, J. Zou, W. Li and S. Li, *The Journal of Physical Chemistry Letters* **15**, 11342–11352 (2024).
- [54] L. Salem and C. Rowland, *Angewandte Chemie International Edition in English* **11**, 92–111 (1972).
- [55] W.T. Borden and E.R. Davidson, *Journal of the American Chemical Society* **99**, 4587–4594 (1977).
- [56] G. Trinquier and J.P. Malrieu, *Chemistry – A European Journal* **21**, 814–828 (2015).
- [57] G. Trinquier and J.P. Malrieu, *Chemistry – A European Journal* **21**, 17540–17540 (2015).
- [58] T. Stuyver, B. Chen, T. Zeng, P. Geerlings, F. De Proft and R. Hoffmann, *Chemical Reviews* **119**, 11291–11351 (2019).
- [59] A. Dreuw and M. Hoffmann, *Frontiers in Chemistry* **11**, 1239604 (2023).
- [60] H. Kollmar and V. Staemmler, *Journal of the American Chemical Society* **99**, 3583–3587 (1977).
- [61] W.T. Borden, E.R. Davidson and P. Hart, *Journal of the American Chemical Society*

- 100**, 388–392 (1978).
- [62] M. Ecker-Maksić, M. Vazdar, M. Barbatti, H. Lischka and Z.B. Maksić, *J. Chem. Phys.* **125**, 064310 (2006).
- [63] S.J. Stoneburner, J. Shen, A.O. Ajala, P. Piecuch, D.G. Truhlar and L. Gagliardi, *The Journal of Chemical Physics* **147**, 164120 (2017).
- [64] E. Monino, M. Boggio-Pasqua, A. Scemama, D. Jacquemin and P.F. Loos, *The Journal of Physical Chemistry A* **126**, 4664–4679 (2022).
- [65] L.V. Slipchenko and A.I. Krylov, *The Journal of Chemical Physics* **117**, 4694–4708 (2002).
- [66] A.O. Ajala, J. Shen and P. Piecuch, *The Journal of Physical Chemistry A* **121**, 3469–3485 (2017).
- [67] S. Gulania, E.F. Kjørnstad, J.F. Stanton, H. Koch and A.I. Krylov, *The Journal of Chemical Physics* **154**, 114115 (2020).
- [68] M. Musiał, S.A. Kucharski and R.J. Bartlett, *Journal of Chemical Theory and Computation* **7**, 3088–3096 (2011).
- [69] P. Piecuch, K. Kowalski, I.S.O. Pimienta and M.J. McGuire, *Int. Reviews in Physical Chemistry* **21**, 527–655 (2002).
- [70] P. Piecuch, K. Kowalski, I.S.O. Pimienta, P.D. Fan, M. Lodriguito, M.J. McGuire, S.A. Kucharski, T. Kuś and M. Musiał, *Theor. Chem. Acc.* **112**, 349–393 (2004).
- [71] J. Shen and P. Piecuch, *Chemical Physics* **401**, 180–202 (2012).
- [72] J. Shen and P. Piecuch, *Journal of Chemical Theory and Computation* **8**, 4968–88 (2012).
- [73] J.E. Deustua, J. Shen and P. Piecuch, *Physical Review Letters* **119**, 223003 (2017).
- [74] K. Gururangan, J.E. Deustua, J. Shen and P. Piecuch, *The Journal of Chemical Physics* **155**, 174114 (2021).
- [75] K. Gururangan and P. Piecuch, *The Journal of Chemical Physics* **159**, 084108 (2023).
- [76] J. Baker, *Chemical Physics Letters* **152**, 227 – 232 (1988).
- [77] M.R. Nyden and G.A. Petersson, *The Journal of Chemical Physics* **74**, 6312–6318 (1981).
- [78] N.C. Handy, P.J. Knowles and K. Somasundram, *Theor. Chim. Acta* **68**, 87 (1985).
- [79] P.M. Gill and L. Radom, *Chemical Physics Letters* **132**, 16 – 22 (1986).
- [80] A.A. Jarzęcki and E.R. Davidson, *The Journal of Physical Chemistry A* **102**, 4742–4746 (1998).
- [81] V.A. Rassolov and F. Xu, *J. Chem. Phys.* **127**, 044104 (2007).
- [82] A.M. Mak, K.V. Lawler and M. Head-Gordon, *Chemical Physics Letters* **515**, 173 – 178 (2011).
- [83] P. Jeszenszki, P.R. Surján and Á. Szabados, *Journal of Chemical Theory and Computation* **11**, 3096–3103 (2015).
- [84] Z.É. Mihálka, P.R. Surján and Á. Szabados, *J. Chem. Theory Comput.* **16**, 892 (2020).
- [85] P.C. Coulson and M.I. Fischer, *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **40**, 386–393 (1949).
- [86] I. Mayer, in *Advances in Quantum Chemistry*, edited by Per-Olov Löwdin, Vol. 12 (, , 1980), pp. 189 – 262.
- [87] C.A. Jiménez-Hoyos, T.M. Henderson, T. Tsuchimochi and G.E. Scuseria, *J. Chem. Phys.* **136** (16), 164109 (2012).
- [88] Y. Qiu, T.M. Henderson and G.E. Scuseria, *The Journal of Chemical Physics* **145**, 111102 (2016).
- [89] H.Z. Ye and T. Van Voorhis, *Journal of Chemical Theory and Computation* **15** (5), 2954–2965 (2019).
- [90] K. Yamaguchi, K. Ohta, S. Yabushita and T. Fueno, *Chem. Phys. Lett.* **49** (3), 555 – 559 (1977).
- [91] P. Pulay and T.P. Hamilton, *J. Chem. Phys.* **88** (8), 4926–4933 (1988).
- [92] J. Paldus, J. Čížek and M. Takahashi, *Phys. Rev. A* **30**, 2193–2209 (1984).
- [93] P. Piecuch, R. Toboła and J. Paldus, *Phys. Rev. A* **54**, 1210–1241 (1996).
- [94] P.J. Knowles and N.C. Handy, *J. Chem. Phys.* **88**, 6991 (1988).
- [95] T. Tsuchimochi and S.L. Ten-no, *J. Chem. Theory Comput.* **15**, 6688–6702 (2019).

- [96] T. Tsuchimochi and T. Van Voorhis, *J. Chem. Phys.* **141**, 164117 (2014).
- [97] Y.G. Smeyers, *An. Fis.* **67**, 17 (1971).
- [98] Y.G. Smeyers, in , edited by P.-O. Löwdin, J. R. Sabin Sabin, M. C. Zerner, E. Brändas, A. Lami and V. Barone, *Adv. Quantum. Chem.*, Vol. 36 (, , 2000), pp. 253–270.
- [99] P.O. Löwdin, *Phys. Rev.* **97**, 1509–1520 (1955).
- [100] P.O. Löwdin, *Rev. Mod. Phys.* **36**, 966–976 (1964).
- [101] M.P. Viver, *International Journal of Quantum Chemistry* **119** (4) (2019).
- [102] G. Chałasiński, B. Jeziorski and K. Szalewicz, *Int. J. Quantum. Chem.* **11**, 247 (1977).
- [103] B. Jeziorski, K. Szalewicz and G. Chałasiński, *Int. J. Quantum. Chem.* **14**, 271–287 (1978).
- [104] B. Jeziorski, R. Moszynski and K. Szalewicz, *Chem. Rev.* **94**, 1887–1930 (1994).
- [105] S.S. Priyadarsini, K. Gururangan, J. Shen and P. Piecuch, The Singlet-Triplet Gap of Cyclobutadiene: The CIPSI-Driven CC(P;Q) Study. arXiv, physics.chem-ph, <https://arxiv.org/abs/2405.15864> 2024.
- [106] R. Shepard, I. Shavitt and J. Simons, *The Journal of Chemical Physics* **76**, 543–557 (1982).
- [107] B.O. Roos, in (Springer, Berlin–Heidelberg, 1992), Vol. The Multiconfigurational (MC) Self-Consistent Field (SCF) Theory, p. 177.
- [108] R. McWeeny, *Methods of Molecular Quantum Mechanics* (Academic, London, 1989).
- [109] P. Pulay, *J. Comput. Chem.* **3**, 556 (1982).
- [110] M. Tarumi, M. Kobayashi and H. Nakai, *International Journal of Quantum Chemistry* **113**, 239–244 (2013).
- [111] K. Chatterjee, *Theoretical Chemistry Accounts* **135**, 246 (2016).
- [112] E. Rosta and P.R. Surján, *J. Chem. Phys.* **116**, 878–890 (2002).
- [113] E. Xu and S. Li, *The Journal of Chemical Physics* **139** (17), 174111 (2013).
- [114] K. Dyall, *J. Chem. Phys.* **102**, 4909 (1995).
- [115] B. Huron, J.P. Malrieu and R. Rancurel, *J. Chem. Phys.* **58**, 5745–5759 (1973).
- [116] S. Keller, K. Boguslawski, T. Janowski, M. Reiher and P. Pulay, *The Journal of Chemical Physics* **142**, 244104 (2015).