

Efficient Adiabatic Connection Approach for Strongly Correlated Systems: Application to Singlet–Triplet Gaps of Biradicals

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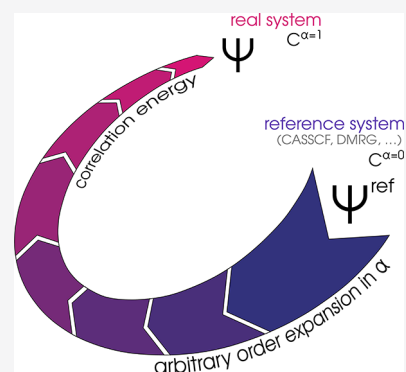


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ABSTRACT: Strong electron correlation can be captured with multireference wave function methods, but an accurate description of the electronic structure requires accounting for the dynamic correlation, which they miss. In this work, a new approach for the correlation energy based on the adiabatic connection (AC) is proposed. The AC_n method accounts for terms up to order n in the coupling constant, and it is size-consistent and free from instabilities. It employs the multireference random phase approximation and the Cholesky decomposition technique, leading to a computational cost growing with the fifth power of the system size. Because of the dependence on only one- and two-electron reduced density matrices, AC_n is more efficient than existing *ab initio* multireference dynamic correlation methods. AC_n affords excellent results for singlet–triplet gaps of challenging organic biradicals. The development presented in this work opens new perspectives for accurate calculations of systems with dozens of strongly correlated electrons.



Electron correlation energy is defined with respect to the energy of a model (a reference) used to describe a given system. In other words, given a Hamiltonian \hat{H} , if Ψ^{ref} is the reference wave function and E^{ref} is the corresponding energy, i.e.,

$$E^{\text{ref}} = \langle \Psi^{\text{ref}} | \hat{H} | \Psi^{\text{ref}} \rangle \quad (1)$$

then electron correlation comprises all electron interaction effects not accounted for by the chosen model, and the correlation energy pertains to the energy error

$$E_{\text{corr}} \equiv E_{\text{exact}} - E^{\text{ref}} \quad (2)$$

computed with respect to the exact energy E_{exact} (an eigenvalue of the Hamiltonian \hat{H}). Strongly correlated molecular systems require model wave functions consisting of multiple configurations to capture static correlation effects. The complete active space (CAS) method assumes the selection of a number of (active) electrons and orbitals crucial to the static correlation followed by exact diagonalization in the active orbital subspace.^{1,2} The CAS model is a base of the CASSCF wave function and is also frequently employed in density matrix renormalization group (DMRG) calculations. The DMRG method is one of the most promising tools for strongly correlated molecules^{3–7} because of its favorable scaling, which enables the handling of much more extensive active spaces than CASSCF allows. The reference energy, E^{ref} in eq 1, for all CAS-based methods does not include a substantial portion of the electron correlation, called dynamic correlation, E_{corr} in eq 2. Even the inclusion of dozens of

orbitals in the active space is not sufficient to achieve a reliable description, and the necessity to recover dynamic correlation remains the major challenge of DMRG.⁶ Although there exist many post-CAS methods aimed at including dynamic correlation (e.g. ref 7), none are satisfactory because of the limitations in both accuracy and efficiency. In particular, perturbation-theory-based approximations may suffer from the lack of size-consistency, intruder states, or the unbalanced treatment of closed- and open-shell systems, which must be cured by level-shifting.⁸ The limitation of PT2 when combined with DMRG is the high scaling with the number of active orbitals resulting from the treatment of three- and four-electron reduced density matrices (RDMs). Efforts to reduce the cost of handling high-order RDMs in NEVPT2 are worth noticing. These include the stochastic strongly contracted scheme,^{9,10} employing the cumulant expansion¹¹ or prescreening techniques.¹² However, the improved efficiency may come at the cost of introducing additional intruder states.¹³ Alternative approaches for molecular systems with strongly correlated electrons, which might also be viewed as CAS-like methods, are represented by embedding schemes. These comprise the self-energy embedding theory,¹⁴ active-space

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embedding,¹⁵ or subsystem embedding subalgebras¹⁶ leading to the active-space coupled-cluster downfolding techniques.¹⁷

The goal of this work is to address the challenge of recovering dynamic correlation and proposing an efficient and reliable computational method applicable to large active spaces. The presented approach builds upon the adiabatic connection formalism first introduced in the framework of Kohn–Sham DFT^{18–21} and recently formulated for CAS models.^{22,23}

Although the following discussion will pertain to a ground-state energy, the presented formalism is general and can be directly applied to higher states. Derivation of the formula for the correlation energy in the adiabatic connection (AC) formalism begins with assuming a model Hamiltonian $\hat{H}^{(0)}$ (typically the electron–electron interaction is either reduced or removed from $\hat{H}^{(0)}$) such that the reference function Ψ^{ref} is its eigenfunction

$$\hat{H}^{(0)}|\Psi^{\text{ref}}\rangle = E^{(0)}|\Psi^{\text{ref}}\rangle \quad (3)$$

The AC Hamiltonian \hat{H}^α is introduced as a combination of $\hat{H}^{(0)}$ and a scaled complementary operator \hat{H}'

$$\forall \alpha \in [0,1] \quad \hat{H}^\alpha = \hat{H}^{(0)} + \alpha \hat{H}' \quad (4)$$

$$\hat{H}' = \hat{H} - \hat{H}^{(0)} \quad (5)$$

The eigenequation for \hat{H}^α reads

$$\hat{H}^\alpha|\Psi_\nu^\alpha\rangle = E_\nu^\alpha|\Psi_\nu^\alpha\rangle \quad (6)$$

where index ν pertains to the ν th electronic state. The role of the coupling parameter α is to adiabatically turn on full electron correlation by varying α from 0 to 1. Namely, at $\alpha = 0$ electron interaction is reduced according to the assumed $\hat{H}^{(0)}$ model and the reference wave function is obtained as Ψ_0^α

$$|\Psi_0^{\alpha=0}\rangle = |\Psi^{\text{ref}}\rangle \quad (7)$$

The $\alpha = 1$ limit corresponds to electrons interacting at their full strength so that both the exact energy and wave function are obtained

$$E_0^{\alpha=1} = E^{\text{exact}} \quad (8)$$

$$|\Psi_0^{\alpha=1}\rangle = |\Psi^{\text{exact}}\rangle \quad (9)$$

Exploiting the Hellmann–Feynman theorem $\frac{\partial E_0^\alpha}{\partial \alpha} = \langle \Psi_0^\alpha | \hat{H}' | \Psi_0^\alpha \rangle$, satisfied for $\alpha \in [0, 1]$, it is straightforward to show that the correlation energy, eq 2, is given exactly as

$$E_{\text{corr}} = \int_0^1 (\langle \Psi_0^\alpha | \hat{H}' | \Psi_0^\alpha \rangle - \langle \Psi^{\text{ref}} | \hat{H}' | \Psi^{\text{ref}} \rangle) d\alpha \quad (10)$$

The choice for the $\hat{H}^{(0)}$ Hamiltonian depends on the reference wave function. Our interest is in multireference CAS-based models which assume partitioning orbitals into sets of inactive (fully occupied), active (fractionally occupied), and virtual (unoccupied) orbitals and constructing Ψ^{ref} as an antisymmetrized product of a single determinant comprising inactive orbitals and a multiconfigurational function utilizing active orbitals. Thus, we represent $\hat{H}^{(0)}$ as a sum of group Hamiltonians \hat{H}_I ^{22,24}

$$\hat{H}^{(0)} = \sum_I \hat{H}_I \quad (11)$$

where I corresponds to an inactive, active, or virtual group and \hat{H}_I consists of one- and two-particle operators

$$\hat{H}_I = \sum_{pq \in I} h_{pq}^{\text{eff}} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{pqrs \in I} \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_q \hat{a}_p \langle rslpq \rangle \quad (12)$$

$$\forall_{pq \in I} h_{pq}^{\text{eff}} = h_{pq} + \sum_{J \neq I} \sum_{r \in J} n_r [\langle prlqr \rangle - \langle prlqr \rangle] \quad (13)$$

Notice that $\langle rslpq \rangle$ denotes a two-electron integral in the $x_1 x_2 x_1 x_2$ convention and the effective one-electron Hamiltonian h^{eff} is a sum of kinetic and electron–nuclei operators and the self-consistent field interaction of orbitals in group I with the other groups (second term in eq 13). Throughout the letter, it is assumed that indices p, q, r , and s denote natural spin orbitals of the reference ($\alpha = 0$) model and $\{n_p\}$ are the corresponding natural occupation numbers. For this choice of $\hat{H}^{(0)}$, the α -dependent integrand in the correlation energy expression, eq 10, includes, among others, one-electron terms depending on the difference between 1-RDM at $\alpha = 1$ and the reference term, $\gamma^\alpha - \gamma^{\alpha=0} = \gamma^\alpha - \gamma^{\text{ref}}$. Such terms are set to 0 under the assumption that for the properly chosen multi-reference wave function for a strongly correlated system, the variation of γ^α with α can be ignored.

As has been shown in refs 22 and 23 and also in the Supporting Information (SI), choosing $\hat{H}^{(0)}$ as a group Hamiltonian and assuming that 1-RDM stays constant with α turn eq 10 into the following AC correlation energy expression

$$E_{\text{corr}}^{\text{AC}} = \frac{1}{2} \sum'_{pqrs} \left(\int_0^1 \sum_{\nu \neq 0} \gamma_{pr}^{\alpha,0\nu} \gamma_{qs}^{\alpha,\nu 0} d\alpha - \sum_{\nu \neq 0} \gamma_{pr}^{\alpha=0,0\nu} \gamma_{qs}^{\alpha=0,\nu 0} \right) \times \langle rslpq \rangle \quad (14)$$

where $\gamma^{0\nu,\alpha}$ are one-electron transition reduced-density matrices (1-TRDM)

$$\gamma_{pq}^{0\nu,\alpha} = \langle \Psi_0^\alpha | \hat{a}_q^\dagger \hat{a}_p | \Psi_\nu^\alpha \rangle \quad (15)$$

It is important to notice a prime in the AC formula in eq 14, which indicates that terms pertaining to $pqrs$ belonging to the same group are excluded. This implies that electron correlation already accounted for by the active-orbitals component of the reference wave function is not counted twice in $E_{\text{corr}}^{\text{AC}}$.

We now briefly recapitulate developments presented in our earlier works^{22,23,25,26} leading to approximate correlation energy methods called AC and AC0. To formulate a working expression for the AC correlation energy, we have used Rowe's equation of motion^{27,28} in the particle-hole RPA approximation, where the excitation operator \hat{O}_ν^\dagger generating a state ν , $\hat{O}_\nu^\dagger |0\rangle = |\nu\rangle$, is approximated by single excitation operators as $\hat{O}_\nu^\dagger = \sum_{p>q} (X_{pq} \hat{a}_p^\dagger \hat{a}_q + Y_{pq} \hat{a}_q^\dagger \hat{a}_p)$. To distinguish this approximation from the conventional RPA,^{27,29–31} which assumes a single determinant as a reference, we used the ph-RPA equations

$$\begin{pmatrix} \mathcal{A}_-^\alpha & 0 \\ 0 & \mathcal{A}_+^\alpha \end{pmatrix} \begin{pmatrix} \tilde{\mathbf{Y}}_\nu^\alpha \\ \tilde{\mathbf{X}}_\nu^\alpha \end{pmatrix} = \omega_\nu^\alpha \begin{pmatrix} \mathbf{0} & \mathbf{1} \\ \mathbf{1} & \mathbf{0} \end{pmatrix} \begin{pmatrix} \tilde{\mathbf{Y}}_\nu^\alpha \\ \tilde{\mathbf{X}}_\nu^\alpha \end{pmatrix} \quad (16)$$

which are introduced for a general, multiconfigurational reference: the extended RPA (ERPA).^{28,32} The ERPA equations have been written for the AC Hamiltonian (eq 4) leading to \mathcal{A}_\pm^α defined as

$$\forall_{p>q} \quad \mathcal{A}_{\pm}^{\alpha}{}_{pq,rs} = \frac{\langle \Psi^{\text{ref}} | [\hat{a}_p^\dagger \hat{a}_q, [\hat{H}^\alpha, \hat{a}_s^\dagger \hat{a}_r]] \pm [\hat{a}_p^\dagger \hat{a}_q, [\hat{H}^\alpha, \hat{a}_s^\dagger \hat{a}_r]] | \Psi^{\text{ref}} \rangle}{(n_p - n_q)(n_r - n_s)} \quad (17)$$

Explicit expressions of \mathcal{A}_\pm^α in terms of 1- and 2-RDMs are presented in the SI. Both \mathcal{A}_+^α and \mathcal{A}_-^α are symmetric and positive-definite at $\alpha = 0$ and 1 for the Hellmann–Feynman reference wave function Ψ^{ref} . Because the coupling constant dependence is passed to ERPA equations only via AC Hamiltonian \hat{H}^α , the matrices \mathcal{A}_\pm^α are linear in α , i.e.,

$$\mathcal{A}_\pm^\alpha = \mathcal{A}_\pm^{(0)} + \alpha \mathcal{A}_\pm^{(1)} \quad (18)$$

In the ERPA model,³³ the α -dependent 1-TRDMs (eq 15) are given by the eigenvectors $\tilde{\mathbf{Y}}_\nu^\alpha$ as $\forall_{p>q} (n_p^{1/2} + n_q^{1/2})[\tilde{\mathbf{Y}}_\nu^\alpha]_{pq} = \gamma_{qp}^{\alpha,0\nu} + \gamma_{pq}^{\alpha,0\nu}$, which allows one to turn eq 14 into a spin-free formula²⁵

$$E_{\text{corr}}^{\text{AC}} = 2 \sum_{\substack{p>q \\ r>s}} (n_p^{1/2} + n_q^{1/2})(n_r^{1/2} + n_s^{1/2}) \times \left(\int_0^1 \sum_\nu [\tilde{\mathbf{Y}}_\nu^\alpha]_{pq} [\tilde{\mathbf{Y}}_\nu^\alpha]_{rs} d\alpha - [\tilde{\mathbf{Y}}_\nu^{(0)}]_{pq} [\tilde{\mathbf{Y}}_\nu^{(0)}]_{rs} \right) \times \langle prlqs \rangle \quad (19)$$

where $\tilde{\mathbf{Y}}_\nu^{(0)} = \tilde{\mathbf{Y}}_\nu^{\alpha=0}$. Equations 16 and 19 form the basis for practical correlation energy calculations. This, however, requires solving the ERPA problem which formally scales with the sixth power of the system size. In addition, using the reference wave function in which the choice of the active orbitals is not optimal could lead to developing instability in the ERPA problem for $\alpha \gg 0$.²⁵ To lower the computational cost and avoid potential instabilities, we introduced an AC0 variant, assuming linearization of the integrand in eq 19, namely, using $\tilde{\mathbf{Y}}_\nu^\alpha = \tilde{\mathbf{Y}}_\nu^{(0)} + \tilde{\mathbf{Y}}_\nu^{(1)} \alpha$, by keeping the linear terms in α and carrying out the α integration,²⁵

$$E_{\text{corr}}^{\text{AC0}} = 2 \sum_{\substack{p>q \\ r>s}} (n_p^{1/2} + n_q^{1/2})(n_r^{1/2} + n_s^{1/2}) \times \sum_\nu [\tilde{\mathbf{Y}}_\nu^{(0)}]_{pq} [\tilde{\mathbf{Y}}_\nu^{(1)}]_{rs} \langle prlqs \rangle \quad (20)$$

The low computational cost of AC0 stems from the fact that ERPA equations must be solved only at $\alpha = 0$, and for this value of the coupling constant, the \mathcal{A}_\pm matrices are block diagonal. The largest block has dimensions of $N_{\text{act}}^2 \times N_{\text{act}}^2$ (N_{act} denotes the number of active orbitals), so the cost of its diagonalization is marginal even for dozens of active orbitals.

Despite the fact that encouraging results have been obtained with AC0 when combined with CASSCF^{25,26,34} or DMRG,³⁵ α integration should in principle account for correlation more

accurately than AC0. It is thus desirable to develop an AC method which on the one hand is exact at all orders of α and on the other avoids solving the expensive ERPA problem. Ideally, such a method would be free of potential instabilities that might occur when α approaches 1. A novel AC method satisfying all of the requirements is presented in this work.

Let us use the integral identity $\forall_{\text{Re}a>0} 2a/\pi \int_0^\infty (\omega^2 + a^2)^{-1} d\omega = 1$ to express the AC correlation energy by means of the α -dependent dynamic density–density response matrix.³⁶ This can be attained by employing the relations

$$\begin{aligned} \sum_\nu [\tilde{\mathbf{Y}}_\nu^\alpha]_{pq} [\tilde{\mathbf{Y}}_\nu^\alpha]_{rs} &= \frac{2}{\pi} \int_0^\infty d\omega \sum_\nu [\tilde{\mathbf{Y}}_\nu^\alpha]_{pq} [\tilde{\mathbf{Y}}_\nu^\alpha]_{rs} \frac{\omega_\nu^\alpha}{\omega^2 + (\omega_\nu^\alpha)^2} \\ &\equiv \frac{1}{\pi} \int_0^\infty d\omega [\mathbf{C}^\alpha(\omega)]_{pq,rs} \end{aligned} \quad (21)$$

in eq 19, resulting in the formula

$$E_{\text{corr}}^{\text{AC}} = \frac{2}{\pi} \int_0^1 d\alpha \int_0^\infty d\omega \text{Tr}\{[\mathbf{C}^\alpha(\omega) - \mathbf{C}^{\alpha=0}(\omega)] \mathbf{g}\} \quad (22)$$

where

$$\forall_{r>s} \quad \mathbf{g}_{pq,rs} = (n_p^{1/2} + n_q^{1/2})(n_r^{1/2} + n_s^{1/2}) \langle prlqs \rangle \quad (23)$$

and the prime in eq 22 indicates that when taking a product of matrices \mathbf{C} and \mathbf{g} , terms $pqrs \in \text{active}$ are excluded. By using spectral representations of the matrices \mathcal{A}_+^α and \mathcal{A}_-^α in terms of the ERPA eigenvectors,³⁷ it is straightforward to show that the dynamic linear response matrix $\mathbf{C}^\alpha(\omega)$ follows from the linear equation given as (see the SI for details)

$$[\mathcal{A}_+^\alpha \mathcal{A}_-^\alpha + \omega^2 \mathbf{1}] \mathbf{C}^\alpha(\omega) = \mathcal{A}_+^\alpha \quad (24)$$

To reduce the computational cost of solving eq 24, we introduce a decomposition of the modified two-electron integrals \mathbf{g}

$$\mathbf{g}_{pq,rs} = \sum_{L=1}^{N_{\text{Chol}}} D_{pq,L} D_{rs,L} \quad (25)$$

where $D_{pq,L}$ are the natural-orbital-transformed Cholesky vectors of the Coulomb matrix multiplied by factors $n_p^{1/2} + n_q^{1/2}$, cf. eq 23. We expand $\mathbf{C}^\alpha(\omega)$ at $\alpha = 0$

$$\mathbf{C}^\alpha(\omega) = \sum_{n=0} \frac{1}{n!} \mathbf{C}(\omega)^{(n)} \alpha^n \quad (26)$$

$$\mathbf{C}(\omega)^{(n)} = \left. \frac{\partial^n \mathbf{C}^\alpha(\omega)}{\partial \alpha^n} \right|_{\alpha=0} \quad (27)$$

and solve eq 24 iteratively in the reduced space by retrieving, in the n th iteration, the n th-order correction $\mathbf{C}^{(n)}$ projected onto the space spanned by N_{Chol} transformed Cholesky vectors $\{\mathbf{D}_L\}$. To account for the prime (exclusion of terms for all-active indices $pqrs$) in the AC correlation energy, eq 22, we define the auxiliary matrices of the transformed Cholesky vectors as

$$\forall_{p>q} \quad D_{pq,L}^1 = \begin{cases} 2D_{pq,L} & \text{if } pq \in \text{active} \\ D_{pq,L} & \text{otherwise} \end{cases} \quad (28)$$

Table 1. ST Gaps ($E_T - E_S$), Mean Errors (ME), Mean Unsigned Errors (MUE), and Standard Deviations (std dev) Computed with Respect to CC3 Reference Data^a

molecule	T state	CASSCF ^b	AC1 _n	AC _n	AC0	NEVPT2 ^c	CASPT2 ^d	CC3 ^d
ethene	1 ³ B _{1u}	3.78	4.53	4.56	4.69	4.60	4.60	4.48
E-butadiene	1 ³ B _u	2.77	3.44	3.43	3.46	3.38	3.34	3.32
all-E-hexatriene	1 ³ A _g	2.66	2.83	2.81	2.80	2.73	2.71	2.69
all-E-octatetraene	1 ³ B _u	2.25	2.46	2.43	2.39	2.32	2.33	2.30
cyclopropene	1 ³ B ₂	3.78	4.42	4.44	4.56	4.56	4.35	4.34
cyclopentadiene	1 ³ B ₂	2.75	3.34	3.34	3.37	3.32	3.28	3.25
norbornadiene	1 ³ A ₂	3.07	3.92	3.89	3.86	3.79	3.75	3.72
benzene	1 ³ B _{1u}	3.74	4.17	4.21	4.37	4.32	4.17	4.12
naphthalene	1 ³ B _{2u}	2.93	3.19	3.21	3.29	3.26	3.20	3.11
furan	1 ³ B ₂	3.54	4.09	4.16	4.30	4.33	4.17	4.48
pyrrole	1 ³ B ₂	3.95	4.47	4.52	4.67	4.73	4.52	4.48
imidazole	1 ³ A'	4.42	4.70	4.74	4.85	4.77	4.65	4.69
pyridine	1 ³ A ₁	3.81	4.28	4.34	4.53	4.47	4.27	4.25
s-tetrazine	1 ³ B _{3u}	2.43	2.27	2.05	1.51	1.64	1.56	1.89
formaldehyde	1 ³ A ₂	3.32	3.80	3.74	3.77	3.75	3.58	3.55
acetone	1 ³ A ₂	4.17	4.27	4.29	4.90	4.10	4.08	4.05
formamide	1 ³ A''	4.72	5.31	5.47	5.60	5.64	5.40	5.36
acetamide	1 ³ A''	4.77	5.46	5.57	5.73	5.52	5.53	5.42
propanamide	1 ³ A''	4.79	5.51	5.61	5.80	5.54	5.44	5.45
ME		- 0.38	0.08	0.10	0.18	0.10	0.00	-
MUE		0.45	0.13	0.13	0.24	0.14	0.07	-
std dev		0.35	0.15	0.11	0.23	0.13	0.12	-

^aAll values are in eV. ^bActive spaces from ref 42. ^cResults from ref 47. ^dResults from ref 42.

$$\forall_{p>q} D_{pq,L}^2 = \begin{cases} 0 & \text{if } pq \in \text{active} \\ D_{pq,L} & \text{otherwise} \end{cases} \quad (29)$$

Assuming an expansion of the response matrix $\mathbf{C}^\alpha(\omega)$, cf. eq 26, up to n th order in α and employing the Cholesky decomposition of integrals, eq 25, together with matrices \mathbf{D}^1 and \mathbf{D}^2 in eq 22 leads to a new AC formula for the correlation energy reading

$$E_{\text{corr}}^{\text{AC}_n} = \frac{2}{\pi} \text{Tr} \left[\left(\int_0^\infty d\omega \sum_{k=1}^n \frac{\bar{\mathbf{C}}(\omega)^{(k)}}{k!(k+1)} \right) \mathbf{D}^2 \right] \quad (30)$$

The matrices $\bar{\mathbf{C}}(\omega)^{(n)}$ defined as

$$\bar{\mathbf{C}}(\omega)^{(n)} = \mathbf{C}(\omega)^{(n)} \mathbf{D}^1 \quad (31)$$

have dimensions of $M^2 \times N_{\text{Chol}}$ which are reduced comparing to the $M^2 \times M^2$ dimensions of $\mathbf{C}(\omega)^{(n)}$ because by construction the number of Cholesky vectors is 1 order of magnitude smaller than M^2 , i.e., $N_{\text{Chol}} \approx M$. Employing the linearity in α of the matrices \mathcal{A}_\pm^α , cf. eq 18, in eq 24 one finds the following recursive formulas for the n th-order term $\bar{\mathbf{C}}(\omega)^{(n)}$

$$\bar{\mathbf{C}}(\omega)^{(0)} = \bar{\mathbf{A}}_+^{(0)} \mathbf{D}^1 \quad (32)$$

$$\bar{\mathbf{C}}(\omega)^{(1)} = \bar{\mathbf{A}}_+^{(1)} \mathbf{D}^1 - \bar{\mathbf{A}}^{(1)} \bar{\mathbf{C}}(\omega)^{(0)} \quad (33)$$

$$\forall_{n \geq 2} \bar{\mathbf{C}}(\omega)^{(n)} = -n \bar{\mathbf{A}}^{(1)} \bar{\mathbf{C}}(\omega)^{(n-1)} - n(n-1) \times \bar{\mathbf{A}}^{(2)} \bar{\mathbf{C}}(\omega)^{(n-2)} \quad (34)$$

where the required matrices are given by the ERPA matrices $\mathcal{A}_\pm^{(0)}$ and $\mathcal{A}_\pm^{(1)}$ (see the SI for their explicit forms in terms of 1- and 2-RDMs)

$$\bar{\mathbf{A}}_+^{(0)} = \Lambda(\omega) \mathcal{A}_+^{(0)} \quad (35)$$

$$\bar{\mathbf{A}}_+^{(1)} = \Lambda(\omega) \mathcal{A}_+^{(1)} \quad (36)$$

$$\bar{\mathbf{A}}^{(1)} = \Lambda(\omega) (\mathcal{A}_+^{(0)} \mathcal{A}_-^{(1)} + \mathcal{A}_+^{(1)} \mathcal{A}_-^{(0)}) \quad (37)$$

$$\bar{\mathbf{A}}^{(2)} = \Lambda(\omega) \mathcal{A}_+^{(1)} \mathcal{A}_-^{(1)} \quad (38)$$

$$\Lambda(\omega) = (\mathcal{A}_+^{(0)} \mathcal{A}_-^{(0)} + \omega^2 \mathbf{1})^{-1} \quad (39)$$

The correlation energy expression in eq 30 together with the recursive relation in eqs 32–34 is the central achievement of this work. It allows one to compute the correlation energy for strongly correlated systems at the cost of scaling with only the fifth power of the system size. All matrix operations scale as $M^4 N_{\text{Chol}}$ down from M^6 scaling of the original ERPA problem in eq 16. Notice that the cost of computing the $\Lambda(\omega)$ matrix is marginal because the inverted matrix is block diagonal with the largest block having dimensions of $N_{\text{act}}^2 \times N_{\text{act}}^2$.

By setting the maximum order of expansion of the response matrix $\mathbf{C}(\omega)$ in eq 30 to 1, the correlation energy AC_n becomes equivalent to the AC0 approximation, cf. eq 20. In the limit of $n \rightarrow \infty$, the $E_{\text{corr}}^{\text{AC}_n}$ value approaches the AC energy given according to the formula in eq 19 if the Taylor series is convergent. Numerically, this equality requires sufficient accuracy both in the frequency integration and in the Cholesky decomposition of two-electron integrals.

Going beyond the first-order terms in the coupling constant is potentially beneficial because higher orders gain importance as α approaches 1. Higher-order contributions are effectively maximized if the AC integrand W^α in eq 22, $W^\alpha = \int_0^\infty d\omega \text{Tr} \{ [\mathbf{C}^\alpha(\omega) - \mathbf{C}^{\alpha=0}(\omega)] \mathbf{g} \}$, is linearly extrapolated from $W^{\alpha=1}$ to the exact limit $W^{\alpha=0} = 0$. Such an extrapolation method leading to the approximation

$E_{\text{corr}}^{\text{AC}} = \frac{2}{\pi} \int_0^1 \alpha W^{\alpha=1} d\alpha$ has already been proposed in ref 22. If it is used together with the formula in eq 22, the expansion shown in eq 26, and the Cholesky decomposition of two-electron integrals, then one obtains the formula

$$E_{\text{corr}}^{\text{AC}1_n} = \frac{1}{\pi} \text{Tr} \left[\left(\int_0^{\infty} d\omega \sum_{k=1}^n \frac{\bar{\mathbf{C}}(\omega)^{(k)}}{k!} \right) \mathbf{D}^2 \right] \quad (40)$$

which will be denoted as $\text{AC}1_n$. Notice that the frequency-integrated k th-order term in eq 40 contributes to the correlation energy by a factor of $(k+1)/2$ greater than its counterpart in the expression given in eq 30.

The Cholesky decomposition of the Coulomb integrals matrix in the AO basis was carried out using a modified program originally used in refs 38 and 39. The implementation was carried out according to ref 40. The Cholesky vectors in the AO basis, $R_{pq,L}$ were generated until the satisfaction of the trace condition $\sum_{p \geq q} \left(\langle pp|qq \rangle - \sum_L R_{pq,L} R_{pq,L} \right) < 10^{-2}$. The convergence threshold was previously tested as a part of the default set of numerical thresholds in Table 1 of ref 38.

For the ω integration in the AC_n correlation energy, we have used a modified Gauss–Legendre quadrature as described in ref 41. With the 18-point grid, the accuracy of the absolute value of energy achieves 10^{-2} mHa, which results in 10^{-2} eV accuracy in the singlet–triplet (ST) gaps.

To assess the accuracy of the AC_n approaches, we have applied them to two benchmark data sets of singlet–triplet energy gaps: the single-reference system set of Schreiber et al.⁴² and the multireference organic biradicals studied by Stoneburner et al.⁴³ In the single-reference data set, we employed the TZVP⁴⁴ basis set and compared our data against the CC3⁴² results. The aug-cc-pVTZ basis and the doubly electron-attached (DEA) equation-of-motion (EOM) coupled-cluster (CC) 4-particle–2-hole (4p–2h) reference⁴³ were used for the biradicals. All CASSCF calculations were performed in the Molpro⁴⁵ program. All AC methods were implemented in the GammCor program.⁴⁶

Computing the correlation energy with the AC_n method requires either fixing the maximum order of expansion with respect to the coupling constant, n in eq 30, or continuing the expansion until a prescribed convergence threshold is met. The advantage of the former strategy is that size consistency is strictly preserved. For each system, we found that the AC_n correlation energy converges with n for the chosen active space. Typical convergence behavior for the singlet, triplet, and ST energies is presented in Figure 1. It can be seen that for $n = 3$ the AC_n ST gap deviates by only 0.01 eV from the AC value, computed using eq 19. For all other biradicals and single-reference systems, we found that setting $n = 10$ in eq 30 is sufficient to converge ST gaps within 10^{-2} eV, thus $n = 10$ has been set for all systems.

In Table 1, we present ST gaps for the subset of the ref 42 data set. The CASSCF method predicts ST gaps that are too narrow, with the mean error approaching -0.4 eV, which results from the unbalanced treatment of closed-shell singlet and open-shell triplet states. The addition of correlation energy using the adiabatic connection greatly reduces the errors. The mean unsigned error (MUE) of $\text{AC}0$ amounts to 0.24 eV. The performance is further improved by AC_n which affords MUE of 0.13 eV. Maximizing the contribution from higher-order terms in α , attained in $\text{AC}1_n$, leads to ST gaps of the same

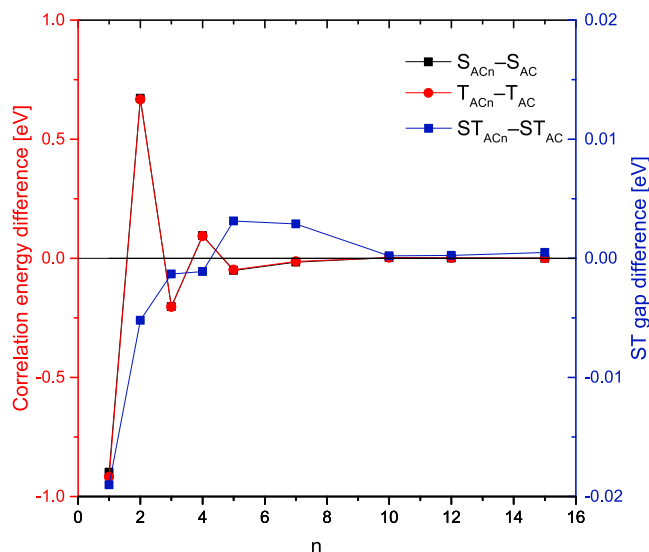


Figure 1. Differences in AC_n and AC correlation energies for singlet (S) and triplet (T) states (left axis) and ST gaps (right axis) as a function of n for the $\text{C}_4\text{H}_2\text{-1,3-(CH}_2\text{)}_2$ biradical. Notice that black markers overlap with the red ones.

unsigned error as that of AC_n . Noticeable, the signed error is reduced, which indicates that higher-order terms play a more important role in the open-shell states than in the closed-shell states. The accuracy of AC_n is on a par with NEVPT2 and only slightly worse than the best CASPT2 estimations from ref 42. The standard deviation of $\text{AC}0$, amounting to 0.23 eV, is reduced to 0.11 eV by AC_n , which parallels the standard deviation of the perturbation methods.

In ref 43, the systematic design of active spaces for biradicals based on the correlated participating orbital (CPO) scheme⁴⁸ is presented. Here, we take a different approach and identify the most appropriate CASs by means of single-orbital entropies and two-orbital mutual information.^{49–51}

Figure 2 shows the correlation measures for singlet and triplet states of prototypical biradicals, C_4H_4 and C_5H_5^+ , obtained with, respectively, CAS(20,22) and CAS(14,16) active spaces (cf., the description in the SI). We observe that the π orbitals of C_4H_4 and C_5H_5^+ are well separated from the others in terms of their single-orbital entropies ($s_i > 0.19$; see the SI) and represent a natural choice of the active space selection. The largest values of s_i correspond to the singly occupied frontier orbitals in the singlet states. These orbital pairs also possess the largest values of mutual information, which stems from the strong correlation of the frontier orbitals due to the singlet-type coupling of these open shells. Notice that both single-orbital entropies and mutual information from the singly occupied orbitals are much lower in the case of the triplet states. This is due to the fact that the triplet states were calculated as high-spin projections and thus can be qualitatively described with a single determinant. However, when analyzing the triplet states, one can see that all of the π orbitals have similar values of their single-orbital entropies and that CAS(2,4) (the $n\text{CPO}$ active space in ref 43) is not a reasonable choice. In fact, for this imbalanced active space, we have experienced divergence of the AC_n series (last entry in Table 1 in the SI).

The analysis of mutual information and single-orbital entropies of prototypical biradicals has allowed us to define

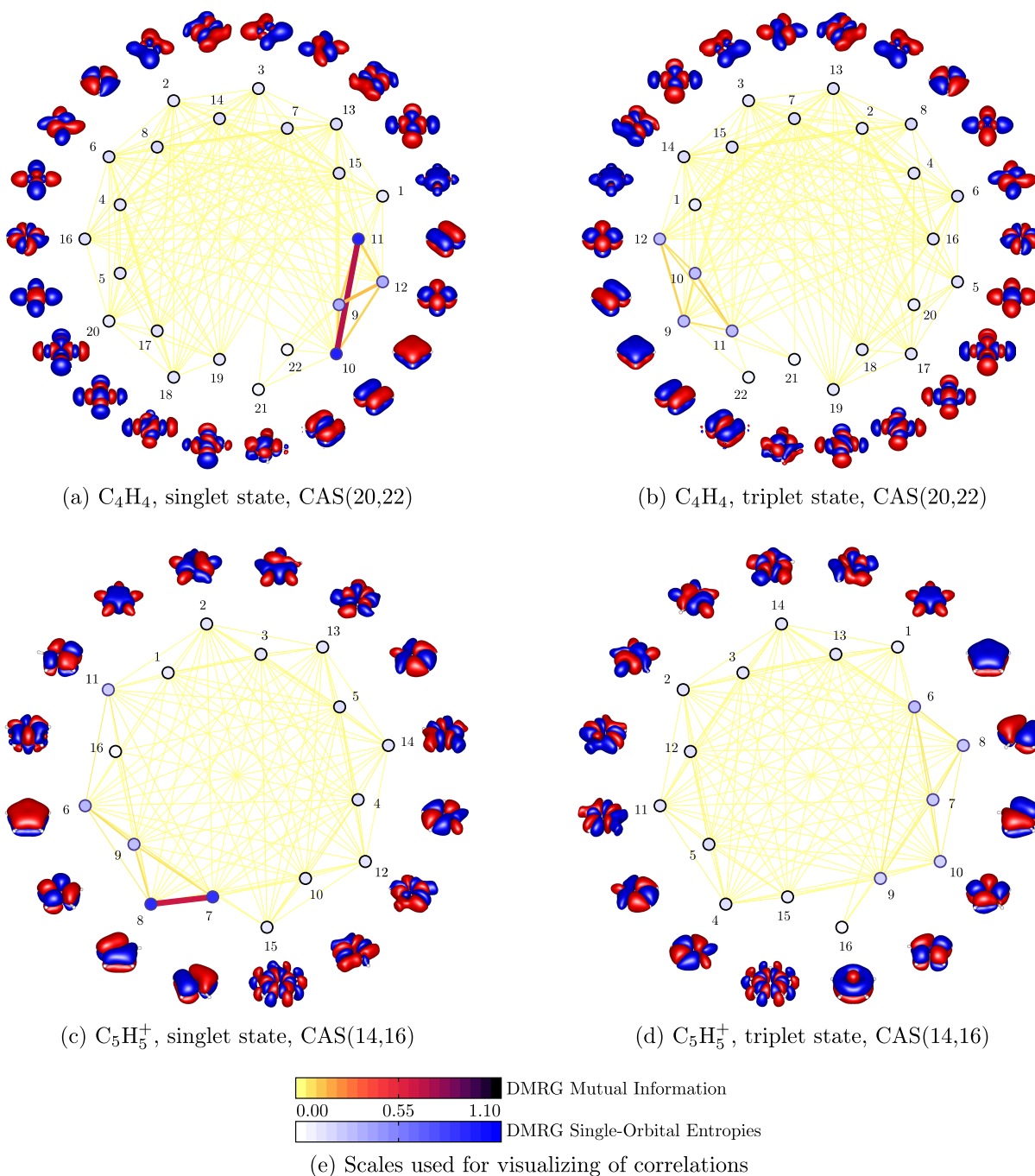


Figure 2. DMRG mutual information (colored edges) and single-orbital entropies (colored vertices) of C_4H_4 and $C_5H_5^+$ for the lowest singlet and triplet states. Numbers in the graphs correspond to indices of the DMRG-SCF (C_4H_4) and CASSCF ($C_5H_5^+$) natural orbitals presented together with their occupation numbers in the SI. Blue circles represent the π orbitals with $s_i > 0.19$.

optimal active spaces: CAS(4,4) for C_4H_4 , $C_4H_3NH_2$, C_4H_3CHO , and $C_4H_2NH_2(CHO)$, CAS(4,5) for $C_5H_5^+$, and CAS(6,6) for $C_4H_2-1,2-(CH_2)_2$, and $C_4H_2-1,3-(CH_2)_2$. The choice of the orbitals in CAS is therefore such that all valence π orbitals on, or adjacent to, the carbon the carbon ring are included and only the mostly correlated orbitals, with occupancies in the range of (0.05, 1.95), enter the active space. The chosen active spaces are close to the π CPO scheme considered in ref 43, with the difference that nearly unoccupied orbitals in π CPO, shown to be uncorrelated according to their mutual information analysis, are excluded.

Similar to the single-reference case, the performance of the CASSCF method for the ST gaps in biradicals is seriously affected by the lack of dynamic correlation (Table 2). Even though the CASSCF gaps of three systems ($C_5H_5^+$, 1,2- and 1,3-isomers) are in error by only 0.1 eV, the overall MUE is as large as 0.20 eV and the mean average unsigned percentage error (MU%E) exceeds 100%. The AC0 method overcompensates for the errors in CASSCF. For biradicals 1, 3, and 4, the excessive reduction of the ST gaps by AC0 results in a wrong ordering of states. Both AC_n and $AC1_n$ approaches capture correlation at high orders of α and greatly improve on

Table 2. ST Gaps ($E_T - E_G$) in eV and Errors with Respect to DEA-EOMCC[4p-2h]⁴³ (ref) Predictions^a

system	CASSCF	AC _{1n}	AC _n	AC0	ftPBE ^b	RASPT2 ^c	ref
1	0.44	0.18	0.13	0.00	0.11	0.19	0.18
2	-0.70	-0.71	-0.77	-0.86	-0.64	-0.65	-0.60
3	0.39	0.12	0.07	-0.08	0.03	0.11	0.12
4	0.41	0.17	0.12	-0.02	0.09	0.16	0.16
5	0.60	0.39	0.37	0.14	0.45	0.32	0.25
6	3.33	3.44	3.44	3.46	3.34	3.27	3.37
7	-0.92	-0.89	-0.90	-0.92	-0.66	-0.80	-0.80
ME	0.13	0.00	-0.03	-0.14	0.01	-0.01	
MUE	0.20	0.06	0.08	0.16	0.09	0.04	
MU%E	102.3	13.7	26.1	69.6	37.6	7.2	
Std. Dev.	0.20	0.09	0.10	0.11	0.12	0.05	

^aLabels: (1) C₄H₄, (2) C₅H₅⁺, (3) C₄H₃NH₂, (4) C₄H₃CHO, (5) C₄H₂NH₂(CHO), (6) C₄H₂-1,2-(CH₂)₂, and (7) C₄H₂-1,3-(CH₂)₂.
^bftPBE results taken from ref 52. ^cRASPT2 (valence- π , π CPO active space) results taken from ref 43.

AC0. The ordering of states is correct and the average error falls below 0.10 eV as compared to the 0.16 eV error in AC0. AC_{1n} performs slightly better than AC_n in terms of MUEs, with the errors being 0.06 and 0.08 eV, respectively, and significantly better in terms of percentage errors. The improved MU%E of AC_{1n} (14 vs 26%) is due to the good performance of this method for small gaps (systems 1, 3, and 4). These excellent results imply a crucial role of the higher-order terms in AC which should enter the correlation energy with high weights.

Table 2 includes the ftPBE results from ref 52. The latter method performs better than other MC-PDFT⁵³ approaches for ST gaps of biradicals. Similarly to AC approximations, MC-PDFT is a post-CASSCF method relying on only 1- and 2-RDMs obtained from CAS. It employs density functional exchange-correlation functionals with modified arguments to describe electron correlation. As shown in Table 2, the accuracy of ST gap predictions by ftPBE does not match that of the AC_{1n} method, with the percentage error nearly tripled and amounting to 38%. When comparing the computational efficiency of the adiabatic connection and MC-PDFT approximations, AC_n (or AC_{1n}) formally scale with the fifth power of the system size, which is one order more than scaling the MC-PDFT. (The timings of both methods are presented in the SI.) It should be noticed, however, that in the cases of both AC_n and MC-PDFT the major share of the total computational time is spent on the CASSCF calculation.

The accuracy achieved by AC_{1n} comes close to that of the RASPT2 method. A comparison of RASPT2 (or CASPT2⁴³) results with those of AC_n requires some care. These perturbation methods involve parameters to remove intruder states and to compensate for their tendency to underestimate gap energies between closed- and open-shell states.⁵⁴ The default value of the ionization potential-electron affinity shift⁸ used in ref 43 improves ST gaps of biradicals predicted by CASPT2 and RASPT2 methods. In general, however, the shift may be problematic for strongly correlated systems, e.g., complexes with transition metals, and their tuning may be required.^{55,56}

In summary, we have proposed a computational approach to the correlation energy in complete active space models. The novel AC_n formula for the correlation energy is based on a

systematic expansion with respect to the adiabatic connection coupling constant α . Application to singlet–triplet gaps of single- and multireference systems revealed the need to account for higher-order terms in the α expansion. The AC_n/AC_{1n} approaches showed a systematic improvement over the first-order AC0 method. The AC_{1n} variant, which maximizes contributions from the higher-order terms, was identified as the best-performing AC approximation. Owing to the Cholesky decomposition technique, the AC_n methods achieve $O(N^5)$ scaling of the computational time with the system size. Because they involve only 1- and 2-RDMs, they are well-suited to treat large active spaces. Importantly, the formalism used to derive AC_n is not limited to a particular form of the model Hamiltonian $\hat{H}^{(0)}$, thus further improvements in accuracy could be achieved with models other than that assumed in this work.

Compared to other correlation energy methods for strong correlation, AC_n emerges as having the most favorable accuracy to cost ratio. Advantages of AC_n over perturbation methods, such as CASPT2 or RASPT2, include not only the ability to treat dozens of active orbitals but also the lack of parameters and strict size consistency.⁵⁷ We believe that the presented development opens new perspectives for meeting the challenge of strong correlation, e.g., by DMRG⁶ methods.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.2c00993>.

Details of the derivation of the AC_n expression; additional results showing convergence of the AC_n energies with n ; timings of AC calculations; single-orbital entropies, mutual information, natural orbitals for selected biradicals (PDF)

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Notes

The authors declare no competing financial interest.

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