Electron Correlation from the Adiabatic Connection for Multireference Wave Functions

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(Received 26 June 2017; published 5 January 2018)

An adiabatic connection (AC) formula for the electron correlation energy is derived for a broad class of multireference wave functions. The AC expression recovers dynamic correlation energy and assures a balanced treatment of the correlation energy. Coupling the AC formalism with the extended random phase approximation allows one to find the correlation energy only from reference one- and two-electron reduced density matrices. If the generalized valence bond perfect pairing model is employed a simple closed-form expression for the approximate AC formula is obtained. This results in the overall M^5 scaling of the computation cost making the method one of the most efficient multireference approaches accounting for dynamic electron correlation also for the strongly correlated systems.

DOI: 10.1103/PhysRevLett.120.013001

A long-standing challenge in quantum chemistry is development of methods that are capable of describing many-electron systems whose electronic structure is determined by different types of electron correlation. Dynamic short-range electron correlation effects are responsible for binding atoms in molecules; those acting on long ranges contribute to molecular interactions dominating in van der Waals complexes. It is known that single reference methods are likely to fail if strong correlation effects are significant, and a successful theoretical method must be based on a multideterminantal (being a linear combination of at least two Slater determinants) wave function. Nowadays, one of the most widely used multireference approaches in chemistry are CASSCF (complete active space self-consistent field) and its variants [1]. Recently, a DMRG (density matrix renormalization group) method has gained a lot of interest as an computationally attractive alternative [2]. In general, multireference methods suffer from ambiguities in choosing a set of active orbitals and high computational scaling. Including dynamic correlation in an efficient and a size-consistent manner remains another problem. Truncated configuration interaction (CI) expansions break size consistency and may lead to factorial scaling. Perturbation methods are problematic too due to ambiguities in choosing a zeroth-order Hamiltonian, difficulties with preserving size-extensivity, and a possible erratic behavior resulting from an intruder state problem.

We propose to account for dynamic electron correlation by deriving a pertinent expression within the adiabatic connection (AC) formalism. The AC formalism has first appeared in the literature in the context of DFT (density functional theory) [3] and, together with the random phase approximation, has recently led to emergence of a new family of orbital-dependent correlation functionals [4]. So far, the AC formalism has not been considered for multireference wave functions. In this Letter, we present a general framework how the AC theory, together with the extended random phase approximation, can be used to obtain correlation energy for a broad family of multireference models. The excellent performance of this novel AC approach is illustrated on examples of molecules entering a strong correlation regime.

Consider the following ansatz for a many-electron wave function

$$|\Psi\rangle = \prod_I \hat{\psi}_I^\dagger |\mathrm{vac}\rangle. \tag{1}$$

An operator $\hat{\psi}_I^\dagger$ creates an N_I-electronic multideterminantal state and it is defined as

$$\hat{\psi}_I^\dagger = \sum_{\mathcal{Q}\in I} D_{\mathcal{Q}}^I \hat{a}_{q_1}^\dagger \hat{a}_{q_2}^\dagger \ldots \hat{a}_{q_{N_I}}^\dagger, \tag{2}$$

where $\mathcal{Q}$ is a string of N_I indices corresponding to one-electron basis functions, i.e. $\mathcal{Q} = q_1 q_2 \ldots q_{N_I}$. The states $\{\psi_I\}$, called group functions, are assumed to be strongly orthogonal. Consequently, a set of orthogonal spin orbitals is partitioned into disjoint subspaces $I, J, \ldots$, and a given group function $\psi_I = \hat{\psi}_I^\dagger|\mathrm{vac}\rangle$, is expanded in a subspace I. Originally, such a form of a wave function was considered by McWeeny to describe weakly interacting groups of electrons [5], forming, for example, shells in atoms, different functional groups in the same molecule, or groups belonging to different interacting molecules [6]. Rosta *et al.* recognized that the ansatz given by Eqs. (1)–(2) includes, as special cases, not only a single determinantal (Hartree-Fock) wave function (each group would be of a single-electron type) and an antisymmetrized product of strongly orthogonal geminals (APSG) but also CASSCF multireference wave functions [7]. In fact, in this work we consider the proposed form of a wave function in an even broader sense; namely, it would stand for any wave function defined in a restricted space of spin orbitals, so the formalism presented below would be applicable in addition to the aforementioned models, also to DMRG and MCSCF wave functions, or to variational wave function-free models that involve only a two-electron reduced density matrix, e.g., Ref. [8].

Throughout the Letter, operators and integrals are represented in the natural spin orbitals corresponding to the ansatz (1). Natural spin orbitals, denoted as $\{\varphi_p(\mathbf{x})\}$, form a basis for diagonalizing a one-electron reduced density matrix $\gamma_{pq} = \langle\Psi|\hat{a}_q^\dagger\hat{a}_p|\Psi\rangle$. The expectation value of an electronic Hamiltonian for the assumed wave function given in Eq. (1) can be written as

$$E = \sum_I \langle\psi_I|\left[\sum_{i=1}^{N_I}\hat{h}(\mathbf{x}_i) + \sum_{i<j}^{N_I} r_{ij}^{-1}\right]|\psi_I\rangle + \sum_{I>J} E_{HX}^{IJ}. \qquad (3)$$

The second term in Eq. (3) collects group-pairwise Coulomb (H) and exchange (X) electron interaction contributions and, apparently, electron correlation among different groups is missing. Correlation energy is introduced as a difference between an exact ground state energy, E_0, of a given system and E given in Eq. (3), i.e.,

$$E_{\mathrm{corr}} \equiv E_0 - E. \qquad (4)$$

The optimal wave function (1), minimizing the energy expression given in Eq. (3), is composed of group-wave functions ψ_I satisfying group eigenequations, namely,

$$\hat{H}_I\psi_I = E_I\psi_I. \qquad (5)$$

A group Hamiltonian $\hat{H}_I$ is given as

$$\hat{H}_I = \sum_{pq\in I} h_{pq}^{\mathrm{eff}}\hat{a}_p^\dagger\hat{a}_q + \frac{1}{2}\sum_{pqrs\in I}\hat{a}_r^\dagger\hat{a}_s^\dagger\hat{a}_q\hat{a}_p\langle rs|pq\rangle, \qquad (6)$$

where an effective one-electron Hamiltonian element, h_{pq}^{eff}, for a group I includes a contribution from the Coulomb and exchange interaction with all other groups, namely, $\forall_{pq\in I} h_{pq}^{\mathrm{eff}} = h_{pq} + \langle p|\hat{v}_{HX}^I|q\rangle$, where $\langle p|\hat{v}_{HX}^I|q\rangle = \sum_{J\neq I}\sum_{r\in J} n_r[\langle pr|qr\rangle - \langle pr|rq\rangle]$. As it has been already noted in Ref. [7], an optimal group function (1) is an eigenfunction of the zeroth-order Hamiltonian

$$\hat{H}^{(0)} = \sum_I \hat{H}_I. \qquad (7)$$

To find the expression for the correlation energy in the adiabatic connection framework, define an adiabatic connection Hamiltonian as

$$\hat{H}^\alpha = \hat{H}^{(0)} + \alpha\hat{H}', \qquad (8)$$

where $\hat{H}' = \hat{H} - \hat{H}^{(0)}$. By varying the coupling strength parameter α between 0 and 1, one smoothly switches between a group-noncorrelated system ($\alpha = 0$) and a fully interacting case ($\alpha = 1$). Let $\{\Psi_\nu^\alpha\}$ be a complete set of eigenfunctions of the adiabatic connection Hamiltonian

$$\hat{H}^\alpha\Psi_\nu^\alpha = E_\nu^\alpha\Psi_\nu^\alpha. \qquad (9)$$

For $\alpha = 0$ the intergroup correlation effects are absent and a ground state eigenfunction Ψ_0^α turns into a group function Ψ given in Eq. (1), whereas the energy is given by a sum of the group energies, i.e., $E_0^{\alpha=0} = \sum_I E_I$. A derivation of the adiabatic connection formula for the correlation energy employs an exact relation between a two-electron reduced density matrix $\Gamma^\alpha = \langle\Psi_0^\alpha|\hat{\Gamma}|\Psi_0^\alpha\rangle$, a one-electron reduced density matrix $\gamma^\alpha = \langle\Psi_0^\alpha|\hat{\gamma}|\Psi_0^\alpha\rangle$, and transition one-electron density matrices $\gamma^{\alpha,0\nu} = \langle\Psi_0^\alpha|\hat{\gamma}|\Psi_\nu^\alpha\rangle$ reading [9]

$$\Gamma_{pqrs}^\alpha = \gamma_{pr}^\alpha\gamma_{qs}^\alpha + \sum_{\nu\neq 0}\gamma_{pr}^{\alpha,0\nu}\gamma_{qs}^{\alpha,\nu 0} - \gamma_{qr}^\alpha\delta_{ps}. \qquad (10)$$

The final adiabatic connection expression for the correlation energy reads (cf. the Supplemental Material [10])

$$E_{\mathrm{corr}}^{\mathrm{AC}} = \int_0^1 W^\alpha d\alpha, \qquad (11)$$

where

$$W^\alpha = \frac{1}{2}{\sum_{pqrs}}'\left(\sum_{\nu\neq 0}\gamma_{pr}^{\alpha,0\nu}\gamma_{qs}^{\alpha,\nu 0} + (n_p - 1)n_q\delta_{rq}\delta_{ps}\right)\langle rs|pq\rangle \qquad (12)$$

and a prime indicates that terms corresponding to spin orbitals p, q, r, s, belonging to the same group, are excluded from the summation. The expression for the adiabatic connection integrand given in Eq. (12) has been obtained by assuming that for each value of α, a one-electron reduced density matrix γ^α is equal to γ, i.e.,

$$\forall_{\alpha\in[0,1]} \qquad \gamma_{pq}^\alpha = \delta_{pq}n_p. \qquad (13)$$

A similar assumption has been exploited in the derivation of the AC correlation energy expression for a reference wave function in a form of just a single determinant [4,9]. Notice, however, that (contrary to a single determinantal case) the approximation assumed in Eq. (13) is well justified if a multireference wave function is employed in the zeroth order, as it is the case here. Namely, already at $\alpha = 0$, a one-electron density matrix possesses a correct structure of an occupation numbers vector, which should not change upon varying α from 0 to 1. The reason for the latter is that the adiabatic connection is mainly responsible for accounting for the dynamic correlation, if a multireference wave function is employed, which does not lead to significant changes in the one-electron reduced density matrix [11].

The usefulness of the AC expression presented in Eq. (12) relies upon the availability of a viable and general formalism, providing dynamic properties, in particular, the transition density matrices $\gamma^{\alpha,0\nu}$ within the assumed reference model. The recently proposed extended random phase approximation (ERPA) [12], based on Rowe's equation of motion [13], allows one to find the approximate transition density matrix elements for the adiabatic connection Hamiltonian $\hat{H}^\alpha$ given in Eq. (8). By following a derivation of the ERPA equations shown in Ref. [12] with the fully interacting Hamiltonian $\hat{H}$ replaced by its adiabatic connection counterpart $\hat{H}^\alpha$, one is led to the following set of α-ERPA equations

$$\begin{pmatrix} \mathcal{A}^\alpha & \mathcal{B}^\alpha \\ \mathcal{B}^\alpha & \mathcal{A}^\alpha \end{pmatrix} \begin{pmatrix} \mathbf{X}_\nu^\alpha \\ \mathbf{Y}_\nu^\alpha \end{pmatrix} = \omega_\nu \begin{pmatrix} -\mathcal{N} & \mathbf{0} \\ \mathbf{0} & \mathcal{N} \end{pmatrix} \begin{pmatrix} \mathbf{X}_\nu^\alpha \\ \mathbf{Y}_\nu^\alpha \end{pmatrix}. \tag{14}$$

The matrices $\mathcal{A}^\alpha$, $\mathcal{B}^\alpha$, $\mathcal{N}$ are given solely by the α-dependent elements of the adiabatic connection Hamiltonian and one- and two-electron reduced density matrices (cf. the Supplemental Material for the explicit forms of the matrices $\mathcal{A}^\alpha$ and $\mathcal{B}^\alpha$). Solutions of the α-ERPA equations come in pairs of positive and negative eigenvalues corresponding, respectively, to excitation and deexcitation energies [14]. The elements of the matrices $\mathcal{A}^\alpha$, $\mathcal{B}^\alpha$ are linear in terms of the coupling strength parameter α, which can be written explicitly as $\mathcal{A}^\alpha = \mathcal{A}^{(0)} + \alpha\mathcal{A}^{(1)}$ and $\mathcal{B}^\alpha = \mathcal{B}^{(0)} + \alpha\mathcal{B}^{(1)}$, with the $\mathcal{A}^{(0)}$, $\mathcal{B}^{(0)}$, $\mathcal{A}^{(1)}$, and $\mathcal{B}^{(1)}$ matrices being α independent. The eigenvectors $(\mathbf{X}_\nu^\alpha, \mathbf{Y}_\nu^\alpha)$ are directly related to transition density matrix elements in the ERPA approximation, namely [15],

$$\forall_{p>q} \qquad [\boldsymbol{\gamma}^{\alpha,0\nu}]_{qp} = (n_q - n_p)[\mathbf{Y}_\nu^\alpha]_{pq}, \tag{15}$$

$$\forall_{q>p} \qquad [\boldsymbol{\gamma}^{\alpha,0\nu}]_{qp} = (n_p - n_q)[\mathbf{X}_\nu^\alpha]_{qp}. \tag{16}$$

Using Eqs. (15)–(16), the spin-summed AC integrand shown in Eq. (12) takes the form

$$\begin{aligned} W^\alpha = 2 \sum_{p>q,r>s}{}' \{ & (n_p - n_q)(n_r - n_s) \\ & \times \sum_\nu ([\mathbf{Y}_\nu^\alpha]_{pq} - [\mathbf{X}_\nu^\alpha]_{pq})([\mathbf{Y}_\nu^\alpha]_{rs} - [\mathbf{X}_\nu^\alpha]_{rs}) \\ & - \frac{1}{2}[n_p(1-n_q) + n_q(1-n_p)]\delta_{pr}\delta_{qs}\} \langle pr|qs \rangle. \end{aligned} \tag{17}$$

Notice that only eigenvectors corresponding to positive eigenvalues (excitation energies) enter the expression. Equations (11) and (17) constitute a central achievement of the paper. They provide a way to obtain electron correlation for a broad class of multireference models, including CASSCF, DMRG, or geminals-product [16] approaches. The adiabatic connection correlation energy in Eq. (11), which employs the formula given in Eq. (17), is not exact, and it relies upon two approximations. One is the invariance of the one-electron density matrix along the AC path, cf. Eq. (13), and another one concerns transition density matrices obtained from the α-ERPA equations, Eqs. (14), (15), and (16).

Since the static electron correlation is assumed to be taken into account by the multireference character of the wave function, one expects the near-linear behavior of the AC integrand. Consequently, W^α could be approximated with the two lowest-order terms in the α expansion, i.e.,

$$W^\alpha = W^{(0)} + \alpha W^{(1)}, \tag{18}$$

which results in the following expression for the correlation energy

$$E_{\mathrm{corr}}^{\mathrm{AC0}} = W^{(0)} + \frac{1}{2}W^{(1)}. \tag{19}$$

Notice that in a special case of a single reference wave function, the correlation expression (19) reduces to the well known MP2 form. For a general multireference wave function, the zeroth- and first-order terms $W^{(0)}, W^{(1)}$ can be found by applying perturbation theory to the ERPA eigenproblem. Another possible approximation for the AC integrand proposed in this Letter, consists in the linear interpolation between the full-correlation limit and the correct no-intergroup-correlation limit for which $W^{(0)}$ is set to 0 that, i.e.,

$$W^\alpha = \alpha W^{\alpha=1} \tag{20}$$

leading to

$$E_{\mathrm{corr}}^{\mathrm{AC1}} = \frac{1}{2}W^{\alpha=1}. \tag{21}$$

Consider now a particular form of the multireference wave function, Eq. (1), when each group function describes two electrons, $\forall_I \; N_I = 2$. In addition, spins are singlet coupled in each group, and each subset of orbitals I is of dimension two (unoccupied orbitals will form a separate group). This model has been known in the literature as a generalized valence bond perfect pairing (GVB-PP) or simply a GVB ansatz [17,18]. It accounts for intra-electron-pair static correlation and qualitatively describes a chemical bond dissociation well [19]. Interestingly, for the GVB wave function, the interpolated AC formula $E_{\mathrm{corr}}^{\mathrm{AC1}}$ is identical to the recently developed ERPA-GVB correlation

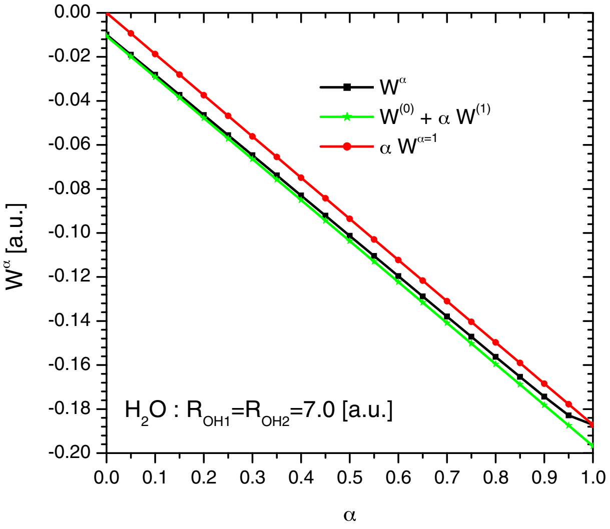

FIG. 1. Adiabatic connection integrand W^α [Eq. (12)], its first-order approximation [Eq. (18)], and the $\alpha = 1$ interpolation formula [Eq. (20)] for the H_2O molecule with both OH bonds dissociating. Results for the GVB reference wave function.

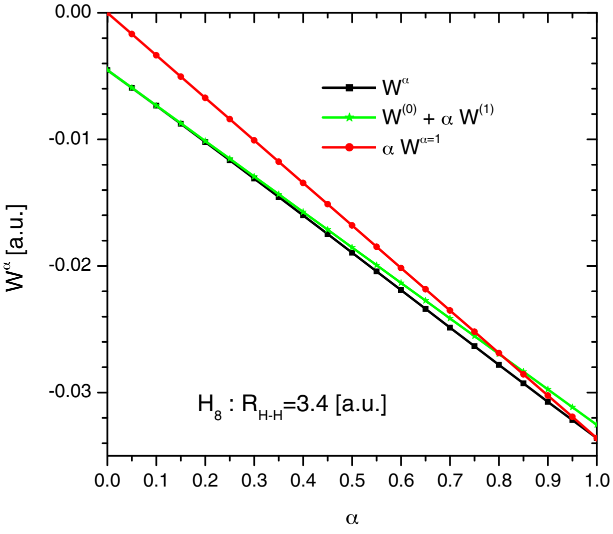

FIG. 2. Linear H_8 chain with equidistant hydrogen nuclei. The same notation as in Fig. 1 has been used.

TABLE I. Energy values obtained in the cc-pVDZ basis set [22] by exploiting formulas given in Eqs. (11), (19), and (21) for the GVB reference wave function (AC-GVB, AC0-GVB, and AC1-GVB methods, respectively). For F_2, H_2O, and H_8 molecules, the reference energy values have been obtained with the CCSDTQ (data from Ref. [23]), FCI, and DMRG methods, respectively. Atomic units are used. $\Delta E = E_{\mathrm{diss}} - E_{\mathrm{eq}}$.

Molecule	Method	E_{eq}	E_{diss}	ΔE
F_2	Reference	−199.104	−199.059	0.045
$R_{\mathrm{eq}} = 2.80$	GVB	−198.825	−198.808	0.017
$R_{\mathrm{diss}} = 8.00$	AC-GVB	−199.071	−199.032	0.040
	AC0-GVB	−199.080	−199.036	0.044
	AC1-GVB	−199.072	−199.025	0.047
H_2O	Reference	−76.242	−75.909	0.333
$R_{\mathrm{eq}} = 1.81$	GVB	−76.090	−75.784	0.305
$R_{\mathrm{diss}} = 7.00$	AC-GVB	−76.227	−75.886	0.341
	AC0-GVB	−76.234	−75.888	0.346
	AC1-GVB	−76.227	−75.878	0.349
H_8	Reference	−4.495	−4.130	0.365
$R_{\mathrm{eq}} = 1.83$	GVB	−4.380	−4.085	0.296
$R_{\mathrm{diss}} = 3.40$	AC-GVB	−4.462	−4.104	0.358
	AC0-GVB	−4.454	−4.103	0.351
	AC1-GVB	−4.467	−4.101	0.365

energy expression [15,20,21]. The latter has been originally proposed based on the reconstruction of the missing intergeminal correlation part of the GVB two-electron reduced density matrix. The GVB ansatz leads to obtaining an explicit and surprisingly simple expression for the correlation energy $E_{\mathrm{corr}}^{\mathrm{AC0}}$ in the interpolated formula (19). Namely, a block-diagonal structure of the ERPA matrices for $\alpha = 0$ results in the following expression for the zeroth-order integrand

$$W^{(0)} = 2\sum_{p>q}{}' n_p(n_q - 1)\langle pp|qq\rangle, \tag{22}$$

(where, as before, a prime indicates that terms corresponding to indices p, q belonging to the same group are excluded and it has been assumed that the orbitals are in a descending order with respect to the occupation numbers, i.e., $n_p < n_q$ if $p > q$) and the first-order term follows from a perturbation theory applied to the ERPA problem (for details cf. the Supplemental Material). We have investigated the AC integrand given in Eq. (17) corresponding to the GVB reference wave function for a number of systems of diversified electronic structures and found that its dependence on α does not deviate significantly from a linear behavior even when strongly correlated orbitals are present. Figures 1–2 show the plots of the AC integrand for two representative examples when two or seven orbital pairs become degenerate. The results of the absolute and relative values of energies collected in Table I (cf. also Fig. 3) support the conclusion that the total energy values obtained by employing the full AC formula (AC-GVB), its first-order approximation (AC0-GVB), and the $\alpha = 1$ interpolating formula (AC1-GVB) perform equally well at equilibrium geometries and when bonds are breaking.

Clearly, employing the formulas $E_{\mathrm{corr}}^{\mathrm{AC0}}$ or $E_{\mathrm{corr}}^{\mathrm{AC1}}$ allows one to avoid performing numerical α integration. Usage of the expression $E_{\mathrm{corr}}^{\mathrm{AC0}}$ provides further advantage in reducing the computation cost, since there is no need to solve full ERPA problem and only solutions of the separate ERPA problems for each group function are required. For the GVB model, the formal scaling of the computation cost of the AC0 correction amounts to only M^5 (M is the number of basis set functions). To show generality and prove the validity of the proposed adiabatic connection approach, we have employed its AC1 variant, based on Eqs. (21), (17), and (14), to obtain a correlation energy for a widely used CASSCF model. Results, denoted as AC1-CASSCF and presented in Fig. 3 and Table II for the symmetrically dissociating water molecule and triple bond breaking in the

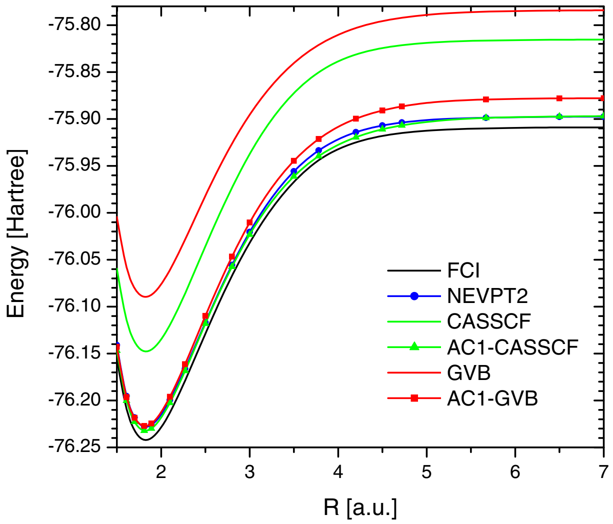

FIG. 3. Symmetric dissociation (both OH bonds are equally stretched) of the H_2O molecule.

TABLE II. Energy values in [a.u.] obtained in the cc-pVDZ basis set [22] for the CAS (8,8) and CAS (6,6) reference wave functions, for H_2O and N_2 molecules, respectively.

Molecule	Method	E_1	E_2	E_3
H_2O	Reference[a]	−76.242	−75.944	−75.909
$R_1 = 1.81$	CASSCF[b]	−76.147	−75.850	−75.816
$R_2 = 3.78$	NEVPT2[b]	−76.228	−75.934	−75.898
$R_3 = 7.00$	AC1-CASSCF	−76.232	−75.961	−75.897
N_2	Reference[c]	−109.278	−109.086	−108.967
$R_1 = 2.12$	CASSCF[b]	−109.091	−108.889	−108.780
$R_2 = 3.00$	NEVPT2[b]	−109.248	−109.056	−108.936
$R_3 = 4.20$	AC1-CASSCF	−109.261	−109.074	−108.966

[a] FCI data from Ref. [26].
[b] DALTON package [27] calculation.
[c] FCI results obtained using DALTON package [27].

nitrogen molecule, have been obtained by solving the ERPA equations with the $\mathcal{A}$ and $\mathcal{B}$ matrices constructed by employing CASSCF occupation numbers and orbitals and an approximate two-electron reduced density matrix. For testing purposes, the latter has been represented using the Müller approximation [24] reading $\Gamma_{pqrs}=n_p n_q \delta_{pq}\delta_{rs}-\sqrt{n_p n_q}\delta_{ps}\delta_{qr}$. Notice that if the CASSCF wave function is employed, natural orbitals are partitioned into disjoint groups of inactive, active, and secondary orbitals, and the prime in the expression for $W^{\alpha=1}$, given in Eq. (17), indicates that intragroup terms are excluded. The accuracy of the AC1-CASSCF approach for the presented molecules rivals or exceeds that of the perturbation-theory-based NEVPT2 [25] method.

In summary, a new approach towards including dynamic correlation in a broad class of multireference models has been established. It is based on the adiabatic connection formalism, where the assumption was made that a one-electron density matrix stays constant along the AC path, Eq. (13), coupled with the extended random phase approximation equations, Eq. (14). The latter has been used to obtain transition density matrices. Two extrapolation schemes for the AC integrand have been considered: AC0 and AC1, cf. Eqs. (19) and (21), respectively. Computation of the proposed AC correlation energy involves only one- and two-electron reduced density matrices of the reference model. It is worthwhile emphasizing a general nature and simplicity of the proposed AC scheme and its AC1 (or AC0) variants. Having defined a model wave function, one finds the missing electron correlation energy defined in Eq. (4) by: (i) constructing the ERPA matrices from the pertinent one- and two-electron reduced density matrices, (ii) solving the ERPA equations given in Eq. (14), (iii) computing the integrand from Eq. (17), and (iv) finding the correlation energy either from the full adiabatic-connection formula [cf. Eq. (11)] or from the AC1 extrapolation approach according to Eq. (21). For the former approach, the steps (i)–(iii) have to be conducted for a number of values of the coupling constant α, whereas the AC1 requires calculations only at $\alpha = 1$. Application of the proposed adiabatic-connection-based AC1 approach within the generalized valence bond or CASSCF models confirms that it stays stable and reliable in both weak and strong correlation regimes, even when multiple electron pairs dissociate.

This work has been supported by the National Science Centre of Poland under Grant No. DEC-2012/07/E/ST4/03023.

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