# Correlation energy from random phase approximations: A reduced density matrices perspective

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## Abstract

Random phase approximation (RPA) electron correlation methods have gained in popularity in the recent years. A number of RPA correlation energy variants emerged in the Kohn–Sham DFT framework and in the theory of strongly orthogonal geminals. Foundations of most RPA approaches trace back to an exact expression for two-electron reduced density matrix written in terms of one-electron density matrix and dynamic one-electron response functions, originally presented in the seminal paper of McLachlan and Ball (*Rev. Mod. Phys.* 1964, 36, 844). The aim of this article is to give a pedagogical introduction to possible approaches for describing electron correlation energy based on the McLachlan and Ball formula. The focus of the presentation is to formulate electron-interaction energy expressions as functions of reduced density matrices. On one hand, it provides a common umbrella for RPA approximations proposed for uncorrelated (Hartree–Fock or Kohn–Sham) as well as partially correlated (strongly orthogonal geminals) references. On the other hand, such presentation may stimulate new developments in density matrix functional theory.

**KEYWORDS**
adiabatic connection formula, electron correlation energy, random phase approximation, reduced density matrices

## 1 | INTRODUCTION

Predicting ground state energy of electronic systems is a fundamental problem in quantum chemistry. Many computational methods are based on some model picture of independent species. The most widely used one is an independent-electrons model, a single determinant wavefunction being at its root. There are also valence bond models for the wavefunctions that are considered to be more correlated than the Slater determinant ansatz since they typically account for electron-pair correlation and lead to a lower ground state energy than that predicted by the Hartree–Fock method.[1,2] Regardless of the form of the wavefunction, the difference of the corresponding energy with respect to the exact one can be called electron correlation energy. Depending on the shortcomings of the employed model wavefunction, which result in its inability to capture some specific correlation effects, the pertinent correlation energy is called dynamic or static, or in case of electron-pairs models intrapair or interpair electron correlation. There are various approaches of including electron correlation by employing perturbation theory methods or systematically expanding the form of the assumed ansatz. Interestingly, already in the early days of many-electron theory it has been realized that information about the ground state energy can be retrieved from the response of the system to a time-dependent perturbation.[3] In an independent-electron approximation coupling of oscillations of electrons under the influence of periodic electric field gives physical description of electron correlations in the ground state and this has been a base of the Random Phase Approximation.[3–7] In their seminal paper, McLachlan and Ball have shown that the pair-correlation function of electrons in a molecule in its ground state can be obtained exactly from the generalized polarizability, which in turn can be obtained from the time-dependent Hartree–Fock equations.[3] This realization has paved the way to employing RPA in chemistry as a method of obtaining the correlation energy. Establishing the adiabatic connection (AC) formalism in the mid-1970s[8,9] has lead to employing RPA in the framework of the density functional theory. First applications of RPA for predicting electronic structure of molecules appeared only 30 years later.[10]

Recently there has been an outburst in proposing variants of random phase approximations methods and their applications to study electronic structure of molecular systems (for a presentation of variants of RPA see Refs. [11–13]). In DFT a functional composed of an exact exchange and RPA correlation has emerged as a way of including long-range van der Waals interactions,[14,15] or making RPA applicable to small-gap or metallic systems for which perturbation theories break down.[11] More recently the random phase approximation correlation energy has been formulated in the context of independent electron-pairs described by strongly orthogonal geminals[16–18] leading to obtaining excellent results for molecules far from equilibrium geometries.

The goal of this tutorial article is to give a step-by-step derivation of the expression for the two-electron reduced density matrix in terms of one-electron functions: ground state one-particle density matrix and one-particle transition density matrices and to discuss two possible ways of exploiting this relation in formulating expressions for the correlation energy. The aforementioned relation has been realized and utilized in early papers on RPA[4–6] but since it is explicitly presented and discussed in the McLachlan and Ball paper,[3] for brevity it will be called "McLachlan and Ball relation" throughout this work.

One way is more straightforward and it assumes direct employment of the expression for two-electron density matrix for obtaining electron interaction energy. The expected drawback of this approach is that correlation is added only to a two-electron part of the energy. The one-electron part including the kinetic energy and electron-nuclei potential is left uncorrelated and it remains a source of the major inaccuracy of the total energy. The other way of utilizing the McLachlan and Ball relation involves the so-called adiabatic connection, that is, recovering total correlation for a given reference state wavefunction by coupling a fictitious noninteracting or partially interacting system with the real fully interacting one. The adiabatic connection formulation may be seen as a mathematical trick to include correlation in both one- and two-electron contributions to the energy. It has provided a basis for proposing successful RPA methods involving a single determinant reference.[11,12] The McLachlan and Ball relation has been also used to account for the electron-pair correlation, when the reference wavefunction is given as an antisymmetrized product of strongly orthogonal geminals.[16,18] Although the original derivation of the correlation energy formula has been proposed by considering couplings of density fluctuations of pairs of geminals, in fact it can be also derived from the adiabatic connection formula for a perfect-pairing geminal wavefunction.[19]

Both aforementioned approaches toward capturing electron correlation from the McLachlan and Ball relation are discussed in the context of using either a single determinant Hartree–Fock reference or a wavefunction being a product of two-electron functions called geminals.[20] In the latter case a part of electron correlation energy (intrapair correlation) is already accounted for. In section 2, one- and two-particle reduced density functions are introduced and the formula for two-electron reduced density matrix expressed in terms of one-electron properties is derived. In section 3, a direct usage of the formula in reconstructing full two-particle density matrix is discussed. Adiabatic connection formulae for the two considered reference wavefunctions are the subject of section 4. The article is summarized and concluded in section 5.

## 2 | GENERAL CONSIDERATIONS

We begin by introducing one- and two-particle reduced functions. A one-electron reduced density matrix (1-RDM) operator $\hat{\gamma}_{pq}$, a density matrix element $\gamma_{pq}$, and a 1-RDM function $\gamma(\mathbf{x}, \mathbf{x}')$ are defined as

$$\hat{\gamma}_{pq} = \hat{a}_q^\dagger \hat{a}_p, \tag{1}$$

$$\gamma_{pq} = \langle \Psi_0 | \hat{\gamma}_{pq} | \Psi_0 \rangle, \tag{2}$$

$$\gamma(\mathbf{x}, \mathbf{x}') = \sum_{pq} \gamma_{pq} \varphi_p(\mathbf{x}) \varphi_q(\mathbf{x}')^*. \tag{3}$$

Operators $\hat{a}_p^\dagger$, $\hat{a}_p$ are creation and annihilation operators obeying fermionic anticommutator rules, orthonormal spinorbitals $\{\varphi_p(\mathbf{x})\}$ are used as a basis set, $\mathbf{x}$ stands for combined spatial and spin coordinates $\mathbf{x} = (\mathbf{r}, \sigma)$, and $|\Psi_0\rangle$ represents a ground state. A spin-summed diagonal part of $\gamma(\mathbf{x}, \mathbf{x}')$ simply yields an electron density function $\rho$

$$\rho(\mathbf{r}) = \sum_\sigma \gamma(\mathbf{x}, \mathbf{x}), \tag{4}$$

which is normalized to a number of electrons in a system $N$

$$\int \rho(\mathbf{r}) \, d\mathbf{r} = N. \tag{5}$$

Eigenfunctions of one-electron matrix $\{\varphi_p(\mathbf{x})\}$

$$\int \gamma(\mathbf{x}, \mathbf{x}') \varphi_p(\mathbf{x}') \, d\mathbf{x}' = n_p \varphi_p(\mathbf{x}) \tag{6}$$

are called naturals spinorbitals and the eigennumbers $\{n_p\}$—natural occupation numbers. The 1-RDM is diagonal in the representation of the spinor-bitals, that is,

$$\gamma_{pq}=n_p\delta_{pq}. \tag{7}$$

Definitions of two-electron reduced density matrix (2-RDM) operator, $\hat{\Gamma}_{pqrs}$, and the 2-RDM elements read, respectively

$$\hat{\Gamma}_{pqrs}=\hat{a}_r^\dagger\hat{a}_s^\dagger\hat{a}_q\hat{a}_p, \tag{8}$$

$$\Gamma_{pqrs}=\langle\Psi_0|\hat{a}_r^\dagger\hat{a}_s^\dagger\hat{a}_q\hat{a}_p|\Psi_0\rangle. \tag{9}$$

In the position representation 2-RDM takes form

$$\Gamma(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2')=\sum_{pqrs}\Gamma_{pqrs}\varphi_p(\mathbf{x}_1)\varphi_q(\mathbf{x}_2)\varphi_r(\mathbf{x}_1')^*\varphi_s(\mathbf{x}_2')^* \tag{10}$$

and by taking its diagonal part and carrying out summation with respect to spin part one obtains a well-known pair density function

$$\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)=\sum_{\sigma_1,\sigma_2}\Gamma(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1,\mathbf{x}_2) \tag{11}$$

which is normalized to twice the number of pairs of electrons

$$\int\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\,d\mathbf{r}_1d\mathbf{r}_2=N(N-1). \tag{12}$$

Electronic Hamiltonian includes only one- and two-particle operators

$$\hat{H}=\sum_{pq}\hat{a}_q^\dagger\hat{a}_p h_{qp}+\frac{1}{2}\sum_{pqrs}\hat{a}_r^\dagger\hat{a}_s^\dagger\hat{a}_q\hat{a}_p\langle rs|pq\rangle, \tag{13}$$

$$h_{qp}=\int\varphi_q(\mathbf{x})^*\left[\hat{t}+\hat{v}_{\text{ext}}\right]\varphi_p(\mathbf{x})\,d\mathbf{x}, \tag{14}$$

where $\hat{t}$ and $\hat{v}_{\text{ext}}$ are, respectively, the kinetic and the external potential operators, and two-electron integrals are defined as

$$\langle pq|rs\rangle=\int\int\varphi_p(\mathbf{x}_1)^*\varphi_q(\mathbf{x}_2)^*r_{12}^{-1}\varphi_r(\mathbf{x}_1)\varphi_s(\mathbf{x}_2)\,d\mathbf{x}_1d\mathbf{x}_2. \tag{15}$$

The expectation value of the Hamiltonian—the electronic energy—is determined by one- and two-electron reduced density matrices

$$E=\langle\Psi_0|\hat{H}|\Psi_0\rangle=E_{\text{one}}+E_{\text{ee}}, \tag{16}$$

where

$$E_{\text{one}}=\sum_{pq}\gamma_{pq}h_{qp} \tag{17}$$

and

$$E_{\text{ee}}=\frac{1}{2}\sum_{pqrs}\Gamma_{pqrs}\langle rs|pq\rangle. \tag{18}$$

Following McLachlan and Ball[3] one can show that 2-RDM is determined exactly by one-electron reduced quantities such as 1-RDM and one-electron transition reduced density matrices (defined below). To derive the McLachlan and Ball relation one employs anticommutation relations for fermionic creation and annihilation operators

$$\hat{a}_q\hat{a}_p=-\hat{a}_p\hat{a}_q, \tag{19}$$

$$\hat{a}_s^\dagger\hat{a}_p=-\hat{a}_p\hat{a}_s^\dagger+\delta_{ps} \tag{20}$$

in the definition for the 2-RDM operator, Equation 8, to express $\hat{\Gamma}_{pqrs}$ solely in terms of 1-RDM operators defined in Equation 1, namely

$$\hat{\Gamma}_{pqrs}=\hat{a}_r^\dagger\hat{a}_s^\dagger\hat{a}_q\hat{a}_p=-\hat{a}_r^\dagger\hat{a}_s^\dagger\hat{a}_p\hat{a}_q=-\hat{a}_r^\dagger\left(-\hat{a}_p\hat{a}_s^\dagger+\delta_{ps}\right)\hat{a}_q=\hat{a}_r^\dagger\hat{a}_p\hat{a}_s^\dagger\hat{a}_q-\hat{a}_r^\dagger\hat{a}_q\delta_{ps}$$
$$=\hat{\gamma}_{pr}\hat{\gamma}_{qs}-\hat{\gamma}_{qr}\delta_{ps}. \tag{21}$$

Employing Equations 21 and 2 in Equation 9 results in

$$\Gamma_{pqrs}=\langle\Psi_0|\hat{\Gamma}_{pqrs}|\Psi_0\rangle=\langle\Psi_0|\hat{\gamma}_{pr}\hat{\gamma}_{qs}|\Psi_0\rangle-\langle\Psi_0|\hat{\gamma}_{qr}|\Psi_0\rangle\delta_{ps}. \tag{22}$$

By inserting a resolution of identity (valid due to completeness of a set of all electronic states $\{|\Psi_\nu\rangle\}$)

$$\hat{1}=\sum_\nu|\Psi_\nu\rangle\langle\Psi_\nu|=|\Psi_0\rangle\langle\Psi_0|+\sum_{\nu\neq0}|\Psi_\nu\rangle\langle\Psi_\nu| \tag{23}$$

in the first term of Equation 22 one is led to

$$\Gamma_{pqrs} = \langle\Psi_0|\hat{\gamma}_{pr}|\Psi_0\rangle\langle\Psi_0|\hat{\gamma}_{qs}|\Psi_0\rangle + \sum_{v\neq 0}\langle\Psi_0|\hat{\gamma}_{pr}|\Psi_v\rangle\langle\Psi_v|\hat{\gamma}_{qs}|\Psi_0\rangle - \langle\Psi_0|\hat{\gamma}_{qr}|\Psi_0\rangle\delta_{ps}.$$ (24)

The elements $\langle\Psi_0|\hat{\gamma}_{pr}|\Psi_v\rangle$ are one-electron transition density matrix elements for electronic excitation from a ground state $|\Psi_0\rangle$ to an excited state $|\Psi_v\rangle$. By introducing the notation

$$\gamma_{pr}^{0v} = \langle\Psi_0|\hat{\gamma}_{pr}|\Psi_v\rangle = \langle\Psi_v|\hat{\gamma}_{rp}|\Psi_0\rangle^* = \left(\gamma_{rp}^{v0}\right)^*$$ (25)

and employing Equation 2 one arrives at the final form of the expression for the 2-RDM presented by McLachlan and Ball[3] reading

$$\Gamma_{pqrs} = \gamma_{pr}\gamma_{qs} + \sum_{v\neq 0}\gamma_{pr}^{0v}\gamma_{qs}^{v0} - \gamma_{qr}\delta_{ps}.$$ (26)

Employing the relation in Equations 10 and 11 results in expressing pair density in terms of electron density and transition density functions, that is,

$$\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) + \sum_{v\neq 0}\rho^{0v}(\mathbf{r}_1)\rho^{0v}(\mathbf{r}_2) - \rho(\mathbf{r}_1)\delta(\mathbf{r}_1-\mathbf{r}_2),$$ (27)

where transition density function for the excitation $|\Psi_0\rangle \rightarrow |\Psi_v\rangle$ has been defined as

$$\rho^{0v}(\mathbf{r}) = \rho^{v0}(\mathbf{r})^* = \sum_{\sigma}\sum_{pr}\gamma_{pr}^{0v}\varphi_p(\mathbf{x})\varphi_r(\mathbf{x})^*$$ (28)

and the appearance of the Dirac delta function $\delta(\mathbf{r}_1-\mathbf{r}_2)$ in Equation 27 is a consequence of the completeness of a set of orbitals

$$\sum_p \varphi_p(\mathbf{r}_1)\varphi_p(\mathbf{r}_2)^* = \delta(\mathbf{r}_1-\mathbf{r}_2).$$ (29)

The central relation shown in Equation 26 leads immediately to a conclusion that electron interaction energy $E_{ee}$ given in Equation 18 can be expressed in terms of one-electron reduced quantities

$$E_{ee} = E_{ee}[\gamma, \{\gamma^{0v}\}].$$ (30)

Since the one-electron energy, Equation 17, is determined by 1-RDM the total electronic energy becomes a function of one-electron reduced ground state density matrix $\gamma$ and transition density matrices $\{\gamma^{0v}\}$

$$E = E_{one}[\gamma] + E_{ee}[\gamma, \{\gamma^{0v}\}].$$ (31)

The derived expression for 2-RDM could be used in a straightforward manner if combined with a method capable of yielding sufficiently accurate one-electron reduced density matrix $\gamma$ and transition density matrices $\{\gamma^{0v}\}$. Another way of exploiting the relation in Equation 26 to find the total energy proceeds via the so-called adiabatic connection (AC) approach. The advantage of the AC over the direct usage of expression (26) in Equation 31 is that AC provides correlation correction to both one- and two-electron components of the energy. In the following sections both direct and AC approaches will be discussed in details for two reference states: Hartree–Fock determinant and perfect-pairing generalized valence bond (GVB). On examples of two molecules: dissociating hydrogen and water molecules we will show performance of both methods and expose excellent performance of AC formulated for the GVB ground state.

# 3 | RECONSTRUCTION OF THE FULL TWO-ELECTRON REDUCED DENSITY MATRIX FROM REDUCED ONE-ELECTRON FUNCTIONS

Equation 26 shows that a full two-electron ground state reduced density matrix is in principle determined by a ground state 1-RDM and all transition density matrices. This relation is exact. Thus, the electron interaction energy, Equation 18, obtained by employing a fully reconstructed 2-RDM given in Equation 26 is also exact. Electron interaction energy obtained from the reconstructed 2-RDM can be written as

$$E_{ee} = E_{Coul}[\gamma] + \frac{1}{2}\sum_{pqrs}\left(\sum_{v\neq 0}\gamma_{pr}^{0v}\gamma_{qs}^{v0} - \gamma_{qr}\delta_{ps}\right)\langle rs|pq\rangle.$$ (32)

The first term represents a classical Coulomb repulsion component

$$E_{Coul}[\gamma] = \frac{1}{2}\sum_{pqrs}\gamma_{pr}\gamma_{qs}\langle rs|pq\rangle = \frac{1}{2}\int\int\frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d\mathbf{r}_1 d\mathbf{r}_2.$$ (33)

The second-term in Equation 18 shall be called exchange-correlation energy

$$E_{xc} = \frac{1}{2} \sum_{pqrs} \left( \sum_{v \neq 0} \gamma_{pr}^{0v} \gamma_{qs}^{v0} - \gamma_{qr} \delta_{ps} \right) \langle rs | pq \rangle$$

$$= \frac{1}{2} \iint \frac{\sum_{v \neq 0} \rho^{0v}(\mathbf{r}_1) \rho^{0v}(\mathbf{r}_2) - \rho(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2.$$

(34)

The consequence of choosing a particular way of factorization 2-RDM in Equation 21 becomes evident now. Namely, only those transition density matrices (or transition densities), which correspond to spin-preserving excitations are needed to evaluate the exchange-correlation part of the electron interaction energy.

As a proof-of-principle we have computed transition density matrices for hydrogen molecule from exact linear response time-dependent two-electron equations (TD-FCI) presented in Ref. [21] and employed them to find electron interaction energy given in Equation 32 with 2-RDM reconstructed from exact (FCI) one-electron functions according to Equation 26. As it is shown in Figure 1 [cf. curve labeled 2-RDM(TD-FCI)-FCI] the error of electron interaction energy with respect to its exact (FCI) counterpart is equal to zero for all interatomic distances, as it should.

Recently it has been shown that approximate transition density matrix elements can be obtained from extended random phase approximation (ERPA) equations.[16] Within ERPA singlet electron excitation energies, $\omega_v$, follow from solving the generalized eigenequation of the form[21,23]

$$\begin{pmatrix} \mathcal{A} & \mathcal{B} \\ \mathcal{B} & \mathcal{A} \end{pmatrix} \begin{pmatrix} \mathbf{X}^v \\ \mathbf{Y}^v \end{pmatrix} = \omega_v \begin{pmatrix} -\mathcal{N} & \mathbf{0} \\ \mathbf{0} & \mathcal{N} \end{pmatrix} \begin{pmatrix} \mathbf{X}^v \\ \mathbf{Y}^v \end{pmatrix}.$$

(35)

Notice that in the original derivation of the ERPA equations presented in Ref. [23] ERPA eigenvectors involve additional components $\mathbf{Z}^v$. Since their contributions to excitation energies are negligible they (and the corresponding block in the ERPA main matrix) can be neglected.[16] The matrices $\mathcal{A}$, $\mathcal{B}$, $\mathcal{N}$ (real-valued) are determined solely by ground state one- and two-electron reduced density matrices, that is,

$$\forall_{r>s, p>q} \quad \mathcal{A}_{pqrs} = \mathcal{A}_{pqrs}(\gamma, \Gamma),$$

(36)

$$\forall_{r>s, p>q} \quad \mathcal{B}_{pqrs} = \mathcal{A}_{pqsr}(\gamma, \Gamma),$$

(37)

$$\forall_{r>s, p>q} \quad \mathcal{N}_{pqrs} = \mathcal{N}_{pqrs}(\gamma).$$

(38)

In the representation of the natural spinorbitals they read[23]

$$\forall_{pqrs} \quad \mathcal{A}_{rspq}(\gamma, \Gamma) = h_{sq} \delta_{pr}(n_p - n_s) + h_{pr} \delta_{sq}(n_q - n_r)$$

$$+ \sum_{tu} \langle st || qu \rangle \Gamma_{purt} + \sum_{tu} \langle up || tr \rangle \Gamma_{stqu} + \frac{1}{2} \sum_{tu} \langle ps || tu \rangle \Gamma_{turq} + \frac{1}{2} \sum_{tu} \langle tu || qr \rangle \Gamma_{sptu}$$

$$+ \frac{1}{2} \delta_{sq} \sum_{twu} \langle tp || wu \rangle \Gamma_{wurt} + \frac{1}{2} \delta_{pr} \sum_{tuw} \langle tu || wq \rangle \Gamma_{swtu},$$

(39)

where

$$\langle pq || rs \rangle = \langle pq | rs \rangle - \langle pq | sr \rangle$$

(40)

and

$$\mathcal{N}_{pqrs} = (n_p - n_q) \delta_{pr} \delta_{qs}.$$

(41)

It should be noted that if 1- and 2-RDM's obtained from a Hartree–Fock (HF) single-determinantal wavefunction are employed in Equations 35–39 the ERPA equations become equivalent to the time-dependent Hartree–Fock (TD-HF) approach.[23] In any case the eigenvectors satisfy the normalization constraint

$$2 \begin{pmatrix} \mathbf{X}^v \\ \mathbf{Y}^v \end{pmatrix}^T \begin{pmatrix} -\mathcal{N} & \mathbf{0} \\ \mathbf{0} & \mathcal{N} \end{pmatrix} \begin{pmatrix} \mathbf{X}^v \\ \mathbf{Y}^v \end{pmatrix} = 1$$

(42)

and they are directly related to transition density matrix elements in ERPA approximation, namely

$$\gamma^{0v} = \mathbf{T}^v,$$

(43)

where

$$\forall_{p>q} \quad T_{qp}^v = (n_q - n_p) Y_{pq}^v,$$

(44)

$$\forall_{p<q} \quad T_{qp}^v = (n_p - n_q) X_{qp}^v,$$

(45)

$$\forall_p \quad T_{pp}^v = 0.$$

(46)

Thus, transition density matrix elements resulting from solving ERPA equations allow one, in principle, to reconstruct full 2-RDM via Equation 26. In the representation of the natural spinorbitals of $\gamma$, such reconstructed 2-RDM takes form
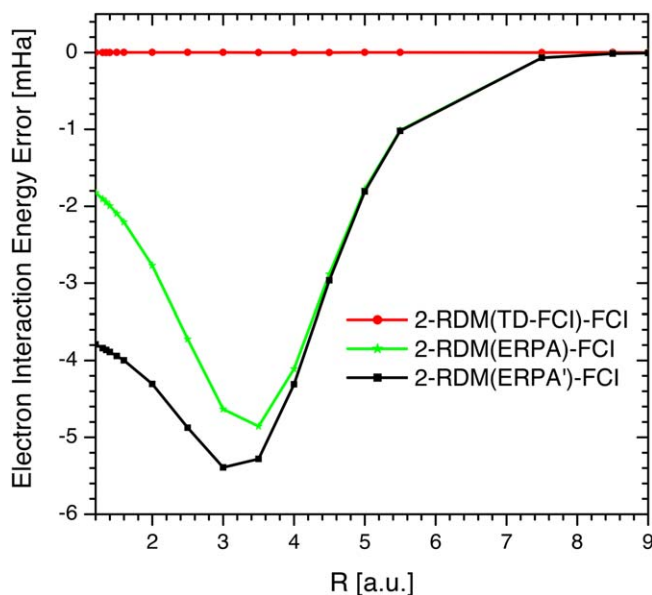
**FIGURE 1** Dissociation of the $H_2$ molecule in cc-pVTZ[22] basis set. Electron interaction energy errors computed with respect to the FCI values

$$\Gamma^{ERPA}_{pqrs}(\gamma,\Gamma)=n_p n_q \delta_{pr}\delta_{qs}+\sum_{\nu\neq 0} T^\nu_{pr}\left(T^\nu_{sq}\right)-n_q\delta_{qr}\delta_{ps}. \tag{47}$$

Let us notice that the reconstructed two-electron density matrix is consistent with the input 1-RDM $\gamma$ in the following sense

$$\sum_q \Gamma^{ERPA}_{pqrq}(\gamma,\Gamma)=(N-1)n_p\delta_{pr}, \tag{48}$$

(a normalization property of $\gamma$, namely $\sum_p n_p = N$ has been used), that is, a partial summation of $\Gamma^{ERPA}$ yields the input 1-RDM $\gamma$. In other words, $\Gamma^{ERPA}$ does not provide any refinement to one-electron density matrix. One should also note that even though $\Gamma^{ERPA}$ is properly normalized, $\sum_{pq}\Gamma^{ERPA}_{pqpq}(\gamma,\Gamma)=N(N-1)$, in general it does not satisfy symmetry conditions and, therefore, it is not $N$-representable.

Electron interaction energy following from the reconstructed $\Gamma^{ERPA}$ reads

$$E^{ERPA}_{ee}[\gamma,\Gamma]=\frac{1}{2}\sum_{pqrs}\Gamma^{ERPA}_{pqrs}(\gamma,\Gamma)\langle rs|pq\rangle. \tag{49}$$

Naturally, since ERPA equations are not exact, the resulting transition density matrices are only approximate. Consequently, the equality $\Gamma^{ERPA}(\Gamma,\gamma)=\Gamma$ does not hold and the electron interaction energy given in Equation 49 is not exact even when exact (obtained from full configuration interaction, FCI, wavefunction) reduced density matrices are used used in ERPA equations. This fact is illustrated in Figure 1. The energy $E^{ERPA}_{ee}[\gamma,\Gamma]$ has been obtained by employing FCI one- and two-electron reduced density matrix in ERPA equations, Equations 35–39, reconstructing two-electron density matrix 2-RDM(ERPA) from transition density matrices according to Equation 47 and employing it in Equation 49. The error of such computed electron interaction energy with respect to the exact values is shown in Figure 1, where the corresponding curve is labeled 2-RDM(ERPA)-FCI. One can see that for the hydrogen molecule the error is negative for all interatomic distances and it does not exceed 5 [mHa].

The important feature of ERPA equations is that contributions of excitations among all possible pairs of orbitals $p$, $q$ are taken into account so the number of elements of $\mathbf{Y}^\nu$ (and $\mathbf{X}^\nu$) vector is $M(M-1)/2$, where $M$ is a number of all orbitals (equal to a number of basis set functions). Excitations between orbitals with occupancies close to 0 are expected to be of minor importance. To confirm this prediction for $H_2$ molecule the ERPA matrices, Equation 35, have been truncated to keep only elements corresponding to excitations from the two most strongly occupied orbitals $\sigma$ and $\sigma^*$, that is,

$$\forall_\nu \forall_{p>q}\ Y^\nu_{pq}, X^\nu_{pq}:\ q=\sigma\ \text{or}\ q=\sigma^* \tag{50}$$

resulting in reducing the number of elements of $\mathbf{Y}^\nu$ (and $\mathbf{X}^\nu$) vectors to only $2(M-1)-1$. Solving the truncated ERPA equations with the exact (FCI) 1- and 2-RDM's, and computing electron energy from the reconstructed two-particle density matrix given in Equation 47 leads to a conclusion that truncation does not introduce substantial error into electron interaction energy. Namely, as shown in Figure 1, cf. curve labeled 2-RDM(ERPA')-FCI, the maximal absolute error only slightly rises above 5 [mHa].

Employing exact reduced density matrices in the ERPA equations and using such obtained transition density matrices to reconstruct full 2-RDM as shown in Equation 47 has only served to illustrate capabilities of ERPA reconstruction scheme. The interesting question is if the presented reconstruction scheme improves the electronic energy obtained with an approximate reference wavefunction. Let us, therefore, investigate whether employing an approximate two-electron density matrix $\Gamma$ obtained from uncorrelated or partially correlated reference wavefunctions in ERPA Equations 35–39 leads to obtaining electron interaction energy $E_{ee}^{ERPA}$, Equation 49, which is more accurate than uncorrected $E_{ee}[\Gamma]$. First consider a Hartree–Fock reference being a Slater determinant $\Psi^{HF}$. HF spinorbitals are at the same time natural spinorbitals whose occupation numbers are 1 or 0. A two-particle density matrix in the representation of the HF spinorbitals reads

$$\Gamma_{pqrs}^{HF} = \langle \Psi^{HF} | \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_q \hat{a}_p | \Psi^{HF} \rangle = n_p n_q (\delta_{pr}\delta_{qs} - \delta_{ps}\delta_{qr}), \tag{51}$$

where

$$n_p = \begin{cases} 1 \\ 0 \end{cases} \tag{52}$$

and the electron interaction energy consists of the Coulomb and exchange parts

$$E_{ee}^{HF} = \frac{1}{2}\sum_{pq} n_p n_q (\langle pq|pq \rangle - \langle pq|qp \rangle). \tag{53}$$

The other reference to be considered is the perfect-pairing generalized valence bond (GVB) wavefunction defined as an antisymmetrized product of $N/2$ two-electron functions $\Psi^I$ (geminals)[2,20,24–30]

$$\Psi^{GVB} = \hat{A}\prod_{I=1}^{N/2}\Psi^I, \tag{54}$$

where $\hat{A}$ is an antisymmetrizing operator including a normalization factor. GVB wavefunction is defined for an even-number-electron system, $N$ is a number of electrons. Each function $\Psi^I$ is of a singlet type and its spatial part is expanded in the subset of only two orbitals $G_I = \{\varphi_p(\mathbf{r}_1), \varphi_q(\mathbf{r}_2)\}$, that is,

$$\Psi^I(\mathbf{x}_1, \mathbf{x}_2) = 2^{-1/2}\sum_{p\in I} c_p \varphi_p(\mathbf{r}_1)\varphi_p(\mathbf{r}_2)(\alpha\beta - \beta\alpha), \tag{55}$$

where the symbol $p \in I$ indicates that a natural orbital $\varphi_p(\mathbf{r}_1)$ belongs to the two-dimensional set $G_I$. Notice that in Equation 55 the squares of expansion coefficients $c_p$ are simply the occupation numbers of GVB spinorbitals

$$\forall_p \quad c_p^2 = n_p \in [0, 1]. \tag{56}$$

The subsets $G_I$ are disjoint, which assures that geminals are strongly orthogonal,[31] that is, they satisfy the condition

$$\forall_{I\neq J} \int \Psi^I(\mathbf{x}_1, \ldots, \mathbf{x}_{N_I})^* \Psi^J(\mathbf{x}_1, \ldots, \mathbf{x}_{N_J}) d\mathbf{x}_1 = 0. \tag{57}$$

Strong orthogonality leads to a simple expression for a GVB two-electron reduced density matrix reading

$$\Gamma_{pqrs}^{GVB} = \langle \Psi^{GVB} | \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_q \hat{a}_p | \Psi^{GVB} \rangle = \sum_I^{N/2} \Gamma_{pqrs}^I \delta_{I_p I}\delta_{I_q I}\delta_{I_r I}\delta_{I_s I} + n_p n_q (1 - \delta_{I_p I_q})(\delta_{pr}\delta_{qs} - \delta_{ps}\delta_{qr}). \tag{58}$$

where

$$\Gamma_{pqrs}^I = \langle \Psi^I | \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_q \hat{a}_p | \Psi^I \rangle \tag{59}$$

and a symbol $I_p$ in Equation 58 indicates a subspace which a spinorbital $\varphi_p$ belongs to. The expectation value of the Hamiltonian for the ansatz given in Equation 54 after integrating out spin variables is of the form

$$E^{GVB} = 2\sum_p c_p^2 h_{pp} + E_{ee}^{GVB}, \tag{60}$$

where the one-electron Hamiltonian matrix is defined in Equation 14 and the electron interaction energy reading

$$E_{ee}^{GVB} = \sum_I^{N/2}\sum_{pq} c_p c_q \delta_{I_p I}\delta_{I_q I}\langle pp|qq \rangle + \sum_{I\neq J}^{N/2}\sum_{pq}\delta_{I_p I}\delta_{I_q J} n_p n_q (2\langle pq|pq \rangle - \langle pq|qp \rangle), \tag{61}$$

is composed of the sum of intrageminal and intergeminal electron interaction terms. The latter includes only Coulomb and exchange interaction terms. Due to the restriction that each geminal is expanded in two-dimensional set of orbitals the GVB reference is not exact even for two-electron systems. Only in the dissociation limit $R_{H_2} \to \infty$ of the hydrogen molecule when out of all exact natural spinorbitals only two remain occupied,
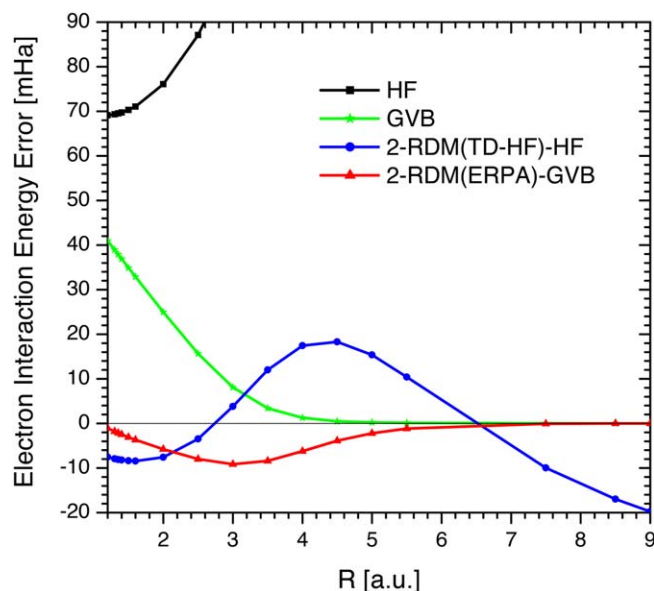
**FIGURE 2** Dissociation of the $H_2$ molecule in cc-pVTZ[22] basis set. Electron interaction energy errors computed with respect to the FCI values

$n_\sigma = n_{\sigma^*} = 1/2$, GVB wavefunction and the corresponding energy become exact. GVB ansatz evidently lacks intergeminal electron correlation, which leads to inaccuracies in prediction of total energies, dissociation energies and energy barriers.[18] On the other hand, since two-electron correlation effects are accounted for by geminals, static correlation effects responsible for correct bond dissociation are already accounted for in the GVB ansatz. To find a ground state energy in the GVB approximation the energy given in Equation 60 is optimized with respect to orbitals (subject to orthogonality constraint) and coefficients $\{c_p\}$. The latter must obey the inequality conditions given in Equation 56 and the normalization constraint, namely $\sum_p c_p^2 = 1$. Prior to beginning the optimization of the energy the orbitals should be assigned initial coefficients. In addition, orbitals must be coupled in pairs (geminals). In principle, a perfect optimizer would find a global minimum for any initial occupation and coupling pattern. In practice, a reasonable choice of the coefficients and a pairing scheme is essential for efficiently converging calculations. We have found out that it is helpful to start with $N/2$ localized occupied Hartree–Fock or correlated MP2 natural orbitals together with $N/2$ localized virtual orbitals (or nearly virtual if MP2 orbitals are used). Initial values of the coefficients $c_p$ are set to values 1 or 0. For a given localized occupied orbital a localized virtual orbital is found based on the similarity criteria and such a pair of orbitals form a geminal.

In Figure 2 errors of electron interaction energy obtained from the HF (Equation 53) and GVB (Equation 61) two-electron reduced density matrices are shown (cf. curves HF and GVB). At the equilibrium bond distance, $R_{eq} = 1.41$ [a.u.], the errors amount to as much as 70 and 37 [mHa] for the two methods. For HF the error exceeds 200 [mHa] in the dissociation limit, whereas for GVB it drops to 0 as it should. Employing 1- and 2-RDM from the two approaches in the ERPA equations, constructing new 2-RDM's, called 2-RDM(TD-HF)-HF and 2-RDM(ERPA)-GVB, according to Equation 47, and using them to compute electron interaction energy (Equation 49) is expected to lead to reduction of the HF and GVB errors. Reconstructed ERPA 2-RDM's should account for dynamic electron correlation effects missing in the pertinent (HF or GVB) approximations. Indeed, already for the hydrogen molecule one observes a striking reduction of the error in the energy interaction at equilibrium geometry if the reconstructed 2-RDM's is used, for both HF and GVB references, as shown in Figure 2 (cf. curves labeled 2-RDM(TD-HF)-HF and 2-RDM(ERPA)-GVB for errors in interaction energy obtained from 2-RDM reconstructed from initial HF and GVB density matrices, respectively). For HF the absolute error drops to 8 [mHa] and for the GVB reference to only 1 [mHa]. This is quite pleasing, but one should remember that the reconstructed ERPA 2-RDM does not bring any changes to the 1-RDM so the one-electron component of the energy is not corrected at all. In Figure 3 errors of the total energy are shown. One notices immediately that even though at equilibrium bond distance of $H_2$ a huge error of the HF electronic interaction energy has been substantially reduced by using a reconstructed 2-RDM the total energy error (curve labeled 2-RDM(TD-HF)-HF in Figure 3) remains as large as the HF energy error (HF curve). For large interatomic distance the error is smaller than that of HF, it decreases to $-10$ [mHa] for $R_{H_2} = 20$ [a.u.], but this is due to a fortuitous cancelation of errors of the one- and two-electron components of the energy. Similar observations hold for the GVB reference. Namely, at equilibrium bond distance the total energy error obtained with the GVB 1-RDM and the reconstructed ERPA 2-RDM based on the GVB density matrices (curve 2-RDM(ERPA)-GVB in Figure 3) is as large as the error resulting from simply using uncorrected GVB RDM's (curve GVB). Thus, one concludes so far that reconstructing 2-RDM from approximate ERPA transition density matrices via Equation 47 allows one to account for correlation effects not included in the original reference and to reduce the error of the electron interaction energy. One-electron part of the energy stays uncorrected and, since the error cancelation between one- and two-electron parts is lost, at least for the HF and GVB references, the error of the total energy is not substantially reduced. The reconstruction scheme for 2-RDM presented in this section would be valuable only if used with sufficiently accurate (leading to small errors in the one-electron part of the energy) 1-RDM.
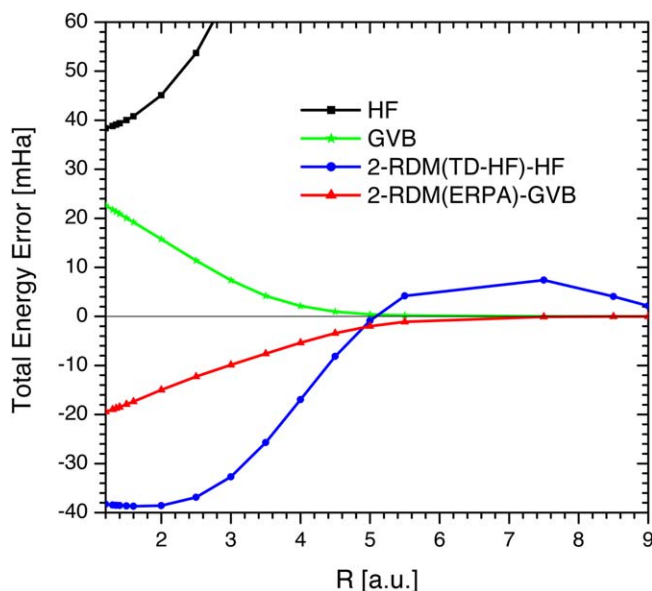
**FIGURE 3**  Dissociation of the $H_2$ molecule in cc-pVTZ[22] basis set. Total energy errors computed with respect to the FCI values

Finally, notice that the energy following from reconstruction of the full 2-RDM for the GVB reference is not equivalent to the recently introduced ERPA-GVB method.[18] In the latter only partial reconstruction of 2-RDM takes place, that is, only those blocks of the 2-RDM which accounts for the intergeminal correlation and partial intrageminal correlation are recovered from the relation given in Equation 47. In fact, it has been recently shown that performance of the ERPA-GVB method parallels that of the adiabatic connection approximation discussed below.[19]

# 4 | ADIABATIC-CONNECTION FORMULAE FOR THE CORRELATION ENERGY

In the previous section, it has been shown that the formula (26) expressing two-electron density matrix in terms of one-electron quantities could offer a way of accounting for correlation in electron interaction energy by reconstructing an improved 2-RDM as shown in Equations 47 and 49. Reconstructing 2-RDM adds correlation only to a two-electron part of the energy without affecting a one-electron energy component. As a result, as we have shown using the example of the hydrogen molecule, the error of the total energy stays large if HF or GVB reduced density matrices follow from the reconstruction approach. A question arises if the formula (26) can be used in a different framework so that both one- and two-electron energy parts are corrected. For the Hartree–Fock reference a positive answer has been provided by McLachlan and Ball who have shown a formalism leading to the so-called adiabatic connection (AC) formula.[3] More recently, an insightful and complete presentation of the AC approximations for the correlation energy corresponding to the HF reference and a comparison with similar approaches toward correlation energy in the KS-DFT framework has been shown in Ref. [12]. Adiabatic connection formula can be also established for the GVB wavefunction.[19] Adiabatic connection formulae for the HF and GVB references will be presented and compared with the reconstruction approach introduced in the previous section.

Let us first derive the correlation energy expression for the HF reference state $\Psi^{HF}$. The correlation energy $E_{c,HF}$ is measured with respect to the exact energy $E_0$, that is

$$E_{c,HF} = E_0 - \langle \Psi^{HF} | \hat{H} | \Psi^{HF} \rangle. \tag{62}$$

Derivation of the AC expression for the correlation energy begins with introducing a so-called adiabatic connection Hamiltonian $\hat{H}^\alpha$

$$\hat{H}^\alpha = \hat{F} + \alpha \hat{H}', \tag{63}$$

where $\hat{F}$ is the usual Fock operator

$$\hat{F} = \hat{T} + \hat{V}_{ne} + \hat{J} + \hat{K},$$

($\hat{T}$, $\hat{V}_{ne}$, $\hat{J}$, $\hat{K}$ are kinetic energy, nuclei-electron interaction, Coulomb, and exchange operators, respectively). $\hat{H}'$, on the other hand, is a perturbation operator being a difference between full electron interaction ($\hat{V}_{ee}$) and Coulomb $\hat{J}$ and exchange ($\hat{K}$) operators

$$\hat{H}' = \hat{V}_{ee} - \hat{J} - \hat{K}. \tag{64}$$

A real number $\alpha$ takes values between 0 and 1. Consider an eigenequation for the adiabatic connection Hamiltonian

$$\hat{H}^{\alpha}\Psi_{\nu}^{\alpha}=E_{\nu}^{\alpha}\Psi_{\nu}^{\alpha}. \tag{65}$$

Clearly for $\alpha = 0$ the adiabatic connection Hamiltonian corresponds to a noninteracting system and its eigenfunctions are simply Slater determinantal wavefunctions, that is,

$$\alpha=0 \; : \; \Psi_0^{\alpha=0}=\Psi^{HF} \; ; \; E_0^{\alpha=0}=\langle\Psi^{HF}|\hat{F}|\Psi^{HF}\rangle=\sum_i^{occ}\varepsilon_i, \tag{66}$$

$\{\varepsilon_i\}$ being HF occupied-orbital energies. At adiabatic constant $\alpha = 1$ the Hamiltonian $\hat{H}^{\alpha=1}$ (63) is equal to the Hamiltonian $\hat{H}$ of a fully interacting system. Consequently,

$$\alpha=1 \; : \; \Psi_0^{\alpha=1}=\Psi_0 \; ; \; E_0^{\alpha=1}=E_0. \tag{67}$$

By employing the Hellman–Feynman theorem one obtains (cf. Equation 63)

$$\frac{\partial E_0^{\alpha}}{\partial\alpha}=\left\langle\Psi_0^{\alpha}\left|\frac{\partial\hat{H}^{\alpha}}{\partial\alpha}\right|\Psi_0^{\alpha}\right\rangle=\langle\Psi_0^{\alpha}|\hat{H}'|\Psi_0^{\alpha}\rangle. \tag{68}$$

On one hand integration of the derivative $\frac{\partial E_0^{\alpha}}{\partial\alpha}$ with respect to $\alpha$ simply yields

$$\int_0^1\frac{\partial E_0^{\alpha}}{\partial\alpha}d\alpha=\int_0^1\langle\Psi_0^{\alpha}|\hat{H}'|\Psi_0^{\alpha}\rangle\,d\alpha\,, \tag{69}$$

on the other hand by employing Equations 66 and 67, taking into account that $\hat{F}=\hat{H}-\hat{H}'$, and using the definition of the correlation energy (62) one is led to

$$\int_0^1\frac{\partial E_0^{\alpha}}{\partial\alpha}d\alpha=E_0-\langle\Psi^{HF}|\hat{F}|\Psi^{HF}\rangle=E_{c,HF}+\langle\Psi^{HF}|\hat{H}'|\Psi^{HF}\rangle. \tag{70}$$

By comparing Equations 69 and 70 the adiabatic connection (AC) formula for the HF correlation energy follows immediately and it reads

$$E_{c,HF}=\int_0^1\langle\Psi_0^{\alpha}|\hat{H}'|\Psi_0^{\alpha}\rangle d\alpha-\langle\Psi^{HF}|\hat{H}'|\Psi^{HF}\rangle. \tag{71}$$

Such obtained AC formula is exact but not very useful in its current form. It requires solving eigenequation (65) for $\Psi_0^{\alpha}$ for $\alpha$ ranging from 0 up to 1, which would be even more difficult than solving the original problem for the fully interacting Hamiltonian. To introduce approximations to the AC formula one uses definition of the perturbation operator, Equation 64, and writes

$$E_{c,HF}=\int_0^1\left(\langle\Psi_0^{\alpha}|\hat{V}_{ee}|\Psi_0^{\alpha}\rangle-\langle\Psi^{HF}|\hat{V}_{ee}|\Psi^{HF}\rangle\right)d\alpha$$
$$-\int_0^1\left(\langle\Psi_0^{\alpha}|\hat{J}+\hat{K}|\Psi_0^{\alpha}\rangle-\langle\Psi^{HF}|\hat{J}+\hat{K}|\Psi^{HF}\rangle\right)d\alpha. \tag{72}$$

To set the second integral to 0 requires a crude assumption that for each $\alpha$ density matrices of a partially interacting and a noninteracting system are equal

$$\forall_{\alpha\in[0,1]}\;\;\gamma^{\alpha}=\gamma^{\alpha=0}=\gamma^{HF}, \tag{73}$$

which leads to

$$E_{c,HF}=\int_0^1\left(\langle\Psi_0^{\alpha}|\hat{V}_{ee}|\Psi_0^{\alpha}\rangle-\langle\Psi^{HF}|\hat{V}_{ee}|\Psi^{HF}\rangle\right)d\alpha. \tag{74}$$

Finally, since $\langle\Psi_0^{\alpha}|\hat{V}_{ee}|\Psi_0^{\alpha}\rangle=\frac{1}{2}\sum_{pqrs}\Gamma_{pqrs}^{\alpha}\langle rs|pq\rangle$, where $\Gamma_{pqrs}^{\alpha}$ is a two-electron density matrix for the $\alpha$-interacting system, one exploits the previously obtained relation (26) to write (cf. Equation 32)

$$\langle\Psi_0^{\alpha}|\hat{V}_{ee}|\Psi_0^{\alpha}\rangle=E_{Coul}[\gamma^{\alpha}]+\frac{1}{2}\sum_{pqrs}\left(\sum_{\nu\neq0}\gamma_{pr}^{\alpha,0\nu}\gamma_{qs}^{\alpha,\nu0}-\gamma_{qr}^{\alpha}\delta_{ps}\right)\langle rs|pq\rangle, \tag{75}$$

where $E_{Coul}[\gamma^{\alpha}]$ is the Coulomb energy defined in Equation 33. The energy $\langle\Psi_0^{HF}|\hat{V}_{ee}|\Psi_0^{HF}\rangle$ comprises only Coulomb and exchange terms

$$\langle\Psi_0^{HF}|\hat{V}_{ee}|\Psi_0^{HF}\rangle=E_{Coul}[\gamma^{HF}]-\frac{1}{2}\sum_{pqrs}\gamma_{ps}^{HF}\gamma_{qr}^{HF}\langle pq|rs\rangle. \tag{76}$$

After employing Equations 75 and 76 in Equation 74 and using the assumed equality of 1-RDM's given in Equation 73 leading to cancelation of Coulomb terms, one is left with the final approximate AC formula written in the representation of the HF spinorbitals

$$E_{c,\text{HF}} = \frac{1}{2} \int_0^1 d\alpha \sum_{pqrs} \left( \sum_{v \neq 0} \gamma_{pr}^{\alpha,0v} \gamma_{qs}^{\alpha,v0} - n_q(1-n_p)\delta_{qr}\delta_{ps} \right) \langle rs|pq \rangle. \tag{77}$$

The HF occupation numbers $\{n_p\}$ take values 0 or 1 for virtual and occupied orbitals, respectively. Elements $\{\gamma^{\alpha,0v}\}$ are transition density matrices for $\alpha$-interacting system

$$\gamma_{pr}^{\alpha,0v} = \langle \Psi_0^\alpha | \hat{\gamma}_{pr} | \Psi_v^\alpha \rangle. \tag{78}$$

As it has been already mentioned general ERPA equations given by Equations 35–41 provides approximate transition density matrices for a given reference ground state. If the HF ground state is used, ERPA becomes equivalent to TD-HF equations and the elements of eigenvectors $\mathbf{X}, \mathbf{Y}$ correspond to excitations from virtual to occupied spinorbitals. The latter will be indexed with the letters $i, j, \ldots$ the former with $a, b, \ldots$. It can be shown that ERPA equations corresponding to the adiabatic connection Hamiltonian, Equation 63, and the HF reference state involves $\mathcal{A}^\alpha$, $\mathcal{B}^\alpha$, and $\mathcal{N}$ matrices of the following forms[32]

$$\mathcal{N}_{aibj} = -\delta_{ab}\delta_{ij}, \tag{79}$$

$$\mathcal{A}_{aibj}^\alpha = \delta_{ba}\delta_{ij}(\varepsilon_a - \varepsilon_i) + \alpha[2\langle ij|ab \rangle - \langle ib|ja \rangle], \tag{80}$$

$$\mathcal{B}_{aibj}^\alpha = -\alpha[2\langle ij|ab \rangle - \langle ji|ab \rangle]. \tag{81}$$

After employing Equations 44 and 45 the correlation energy, Equation 77, turns into the following spin-summed expression

$$E_{c,\text{HF}} = 2 \int_0^1 d\alpha \sum_{ijab} \left( \sum_v (Y_{v,ia}^\alpha - X_{v,ia}^\alpha)(Y_{v,jb}^\alpha - X_{v,jb}^\alpha) - \frac{1}{2}\delta_{ij}\delta_{ab} \right) \langle ij|ab \rangle \tag{82}$$

and the total HF-reference-energy corrected for the electron correlation follows from

$$E^{\text{AC(HF)}} = \langle \Psi^{\text{HF}} | \hat{H} | \Psi^{\text{HF}} \rangle + E_{c,\text{HF}}. \tag{83}$$

What has been obtained for the HF reference, that is, Equations 79–82, pertains to one of the variants of the RPA's correlation energy known as RPAx or RPAx-I, cf. Ref. [13]. Notice that derivation of the AC correlation energy for the Kohn–Sham reference proceeds by assuming that electron density is constant for all values of adiabatic parameter $\alpha$ but the final expression for the RPAx formula is the same as Equation 82.

Interestingly, the adiabatic connection formula can be also derived for the GVB reference, Equations 54 and 55. The AC formula for a more general reference wavefunction—a group product function—has been presented in Ref. [19]. Begin by defining the GVB correlation energy as

$$E_{c,\text{GVB}} = E_0 - \langle \Psi^{\text{GVB}} | \hat{H} | \Psi^{\text{GVB}} \rangle, \tag{84}$$

where $\hat{H}$ is the full Hamiltonian given in Equation 13. To derive an adiabatic connection formula for $E_{c,\text{GVB}}$ one should notice that a geminal $I$ given in Equation 55, which in the second quantization formalism can be written as

$$\Psi^I = \hat{\Psi}^I |\text{vac}\rangle, \tag{85}$$

$$\hat{\Psi}^I = \sum_{p \in I} c_p \hat{a}_{p_\alpha}^\dagger \hat{a}_{p_\beta}^\dagger \tag{86}$$

(operators $\hat{a}_{p_\alpha}^\dagger \hat{a}_{p_\beta}^\dagger$ create electrons in the natural spinorbitals of spatial part $p$ and spin parts $\alpha$ and $\beta$) is an eigenstate of an electron-pair Hamiltonian reading[33]

$$\hat{H}_I = \sum_{pq \in I} h_{pq}^{\text{eff}} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{pqrs \in I} \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_q \hat{a}_p \langle rs|pq \rangle, \tag{87}$$

An effective one-body Hamiltonian $\mathbf{h}^{\text{eff}}$ for a geminal $I$ includes, apart from the kinetic and electron-nuclei interaction terms, cf. Equation 14, contributions from the Coulomb and exchange interaction with all other geminals

$$h_{pq}^{\text{eff}} = h_{pq} + \sum_{J \neq I} \sum_{r \in J} n_r \langle pr||qr \rangle. \tag{88}$$

Consequently, a GVB state

$$\Psi^{\text{GVB}} = \prod_{I=1}^{N/2} \hat{\Psi}^I |\text{vac}\rangle, \tag{89}$$

is an eigenstate of a noninteracting-pair Hamiltonian reading

$$\hat{H}^{(0)} = \sum_{I=1}^{N/2} \hat{H}_I. \tag{90}$$

The adiabatic connection Hamiltonian can be easily defined as

$$\hat{H}^{\alpha} = \hat{H}^{(0)} + \alpha \hat{H}', \tag{91}$$

where

$$\hat{H}' = \hat{H} - \hat{H}^{(0)}. \tag{92}$$

It connects a system of noninteracting pairs ($\alpha = 0$) with the fully interacting system ($\alpha = 1$). Derivation of the adiabatic connection formula for the GVB correlation energy given in Equation 84 proceeds alongside steps already employed in derivation of the AC for the HF reference. By repeating steps leading to Equation 71 one obtains that for the GVB reference Equation 84 turns into

$$E_{c,\text{GVB}} = \int_0^1 \langle \Psi_0^{\alpha} | \hat{H}' | \Psi_0^{\alpha} \rangle d\alpha - \langle \Psi^{\text{GVB}} | \hat{H}' | \Psi^{\text{GVB}} \rangle. \tag{93}$$

Since expectation value of the primed Hamiltonian, Equation 92, computed with the GVB reference reads

$$\langle \Psi^{\text{GVB}} | \hat{H}' | \Psi^{\text{GVB}} \rangle = -\frac{1}{2} \sum_{I \neq J}^{N/2} \sum_{pq} \delta_{I_p I} \delta_{I_q J} n_p n_q [\langle pq|pq \rangle - \langle pq|qp \rangle] \tag{94}$$

then Equation 93 can be written as

$$\begin{aligned}
E_{c,\text{GVB}} =\ & \frac{1}{2} \sum_{pqrs} (1 - \delta_{I_p I_q} \delta_{I_q I_r} \delta_{I_r I_s}) \int_0^1 \Gamma_{pqrs}^{\alpha} d\alpha \, \langle rs|pq \rangle \\
& - \sum_I^{N/2} \sum_{pq} \delta_{I_p I} \delta_{I_q I} \sum_{J \neq I}^{N/2} \delta_{I_r J} \, n_r [\langle pr|qr \rangle - \langle pr|rq \rangle] \int_0^1 \gamma_{qp}^{\alpha} d\alpha \\
& + \sum_{pq} (1 - \delta_{I_p I_q}) h_{pq} \int_0^1 \gamma_{qp}^{\alpha} d\alpha \\
& + \frac{1}{2} \sum_{I \neq J}^{N/2} \sum_{pq} \delta_{I_p I} \delta_{I_q J} n_p n_q [\langle pq|pq \rangle - \langle pq|qp \rangle],
\end{aligned} \tag{95}$$

where $\gamma^{\alpha}$ and $\Gamma^{\alpha}$ are, respectively, the one- and two-electron reduced density matrices corresponding to a ground state $\Psi_0^{\alpha}$ pertaining to the AC Hamiltonian $\hat{H}^{\alpha}$. The relation (95) is exact. It can be simplified by assuming that one-electron reduced density matrix along the adiabatic path is constant and equal to the GVB 1-RDM $\gamma^{\text{GVB}}$, which in turn is equal to 1-RDM corresponding to a geminal-noninteracting ($\alpha = 0$) system $\gamma^{\alpha=0}$. In the representation of the GVB natural spinorbitals the assumption takes form

$$\forall_{\alpha \in [0,1]} \quad \gamma_{pq}^{\alpha} = \gamma_{pq}^{\alpha=0} = \gamma_{pq}^{\text{GVB}} = \delta_{pq} n_p. \tag{96}$$

Employing Equation 96 in Equation 95 results in obtaining the following expression for the correlation energy

$$\begin{aligned}
E_{c,\text{GVB}} =\ & \frac{1}{2} \int_0^1 \sum_{pqrs} (1 - \delta_{I_p I_q} \delta_{I_q I_r} \delta_{I_r I_s}) \Gamma_{pqrs}^{\alpha} \langle rs|pq \rangle d\alpha \\
& - \frac{1}{2} \sum_I \sum_{p \in I} \sum_{J \neq I} \sum_{r \in J} n_p n_q [\langle pq|pq \rangle - \langle pq|qp \rangle].
\end{aligned} \tag{97}$$

The McLachlan and Ball relation given in Equation 26 used in Equation 97 together with the assumption from Equation 96 yields finally

$$E_{c,\text{GVB}} = \frac{1}{2} \int_0^1 d\alpha \sum_{pqrs} (1 - \delta_{I_p I_q} \delta_{I_q I_r} \delta_{I_r I_s}) \left( \sum_{v \neq 0} \gamma_{pr}^{\alpha,0v} \gamma_{qs}^{\alpha,v0} - n_q (1 - n_p) \delta_{qr} \delta_{ps} \right) \langle rs|pq \rangle. \tag{98}$$

In the above expression the orbitals $p, q, \ldots$ are the GVB natural spinorbitals, and $n_p, n_q, \ldots$ are the corresponding natural occupation numbers. Notice that apart from a set of fractionally occupied orbitals for which $0 < n_p < 1$ (for each geminal there are two fractionally occupied orbitals) there is also a set of virtual orbitals for which $n_p = 0$. The Kronecker delta $\delta_{I_p I_q}$ takes value 1 only if two spinorbitals $p$ and $q$ belong to the same geminal so the symbol $(1 - \delta_{I_p I_q} \delta_{I_q I_r} \delta_{I_r I_s})$ present in the formula (98) is equal to 0 only if all spinorbitals $p, q, r, s$ belong to the same set $G_I$, that is, if they span the same geminal.

The AC formula corrects the GVB energy for the intrageminal and intergeminal dynamic correlation missing in the GVB ansatz. The transition density matrix elements follow from the equation of motion ERPA equations[23,34] rederived for the adiabatic connection Hamiltonian $\hat{H}^{\alpha}$ and the reference state $|\Psi_0^{\alpha}\rangle$. The $\alpha$-ERPA linear equations involve, therefore, $\mathcal{A}_{\alpha}$ and $\mathcal{B}_{\alpha}$ matrices obtained from the nested commutator[23] defined as

$$\mathcal{A}_{pqrs}^{\alpha} = \mathcal{B}_{pqsr}^{\alpha} = \langle \Psi_0^{\alpha} | \left[ \hat{a}_p^{\dagger} \hat{a}_q, \left[ \hat{H}^{\alpha}, \hat{a}_s^{\dagger} \hat{a}_r \right] \right] | \Psi_0^{\alpha} \rangle. \tag{99}$$

After employing anticommutation rules for the fermionic creation and annihilation operators, and definitions of the reduced density matrices one arrives at expressions for the main matrices, which involve one- and two-electron reduced density matrices, $\gamma^{\alpha}$ and $\Gamma^{\alpha}$, of the $\alpha$-interacting system

$$\mathcal{A}^{\alpha} = \mathcal{A}^{\alpha}[\gamma^{\alpha}, \Gamma^{\alpha}], \tag{100}$$

$$\mathcal{B}^{\alpha} = \mathcal{B}^{\alpha}[\gamma^{\alpha}, \Gamma^{\alpha}]. \tag{101}$$

Transition density matrices that are needed to find the AC correlation energy from Equation 98 would follow from the eigenvectors $\left[\mathbf{X}_{\nu}^{\alpha}, \mathbf{Y}_{\nu}^{\alpha}\right]$ of the $\alpha$-ERPA eigenproblem if Equation 43–45 are employed. Evidently, the difficulty is for a given coupling strength $\alpha$ reduced density matrices are not known and finding them exactly would involve solving $\alpha$-interacting Schrödinger equation, which is exactly what we want to avoid. Approximate eigenvectors can be obtained perturbatively in the first-order in $\alpha$ (the correlation energy is vanishing if eigenvectors obtained in the zero-order approximation are employed). We adopt approximation consisting in employing in Equations 100 and 101 the zero-order (GVB) density matrices, which, after employing Equation 96 results in the following expression

$$
\begin{aligned}
\forall_{pqrs} \quad \mathcal{A}_{rspq}^{\alpha} = \mathcal{B}_{rsqp}^{\alpha} = {}& h_{sq}^{\alpha} \delta_{pr}(n_p - n_s) + h_{pr}^{\alpha} \delta_{sq}(n_q - n_r) \\
& + \sum_{tu} \tilde{g}_{stqu}^{\alpha} \Gamma_{purt}^{GVB} + \sum_{tu} \tilde{g}_{uptr}^{\alpha} \Gamma_{stqu}^{GVB} + \frac{1}{2} \sum_{tu} \tilde{g}_{pstu}^{\alpha} \Gamma_{turq}^{GVB} + \frac{1}{2} \sum_{tu} \tilde{g}_{tuqr}^{\alpha} \Gamma_{sptu}^{GVB} \\
& + \frac{1}{2} \delta_{sq} \sum_{twu} \tilde{g}_{tpwu}^{\alpha} \Gamma_{wurt}^{GVB} + \frac{1}{2} \delta_{pr} \sum_{tuw} \tilde{g}_{tuwq}^{\alpha} \Gamma_{swtu}^{GVB},
\end{aligned}
\tag{102}
$$

where $\Gamma^{GVB}$ is given in Equation 58 and

$$h_{pq}^{\alpha} = \alpha h_{pq} + \delta_{I_p I_q}(1 - \alpha) h_{pq}^{eff}, \tag{103}$$

$$\tilde{g}_{pqrs}^{\alpha} = g_{pqrs}^{\alpha} - g_{pqsr}^{\alpha}, \tag{104}$$

$$g_{pqrs}^{\alpha} = \left[\alpha + \delta_{I_p I_q} \delta_{I_q I_r} \delta_{I_r I_s}(1 - \alpha)\right] \langle pq|rs \rangle. \tag{105}$$

It is expected that such linearized in $\alpha$ ERPA equations should provide accurate transition density elements not only for small values of the coupling strength parameter but also for large, that is, approaching 1, values. The reason is that the reference zero-order GVB wavefunction already accounts for electron correlation, which is mainly of the static type. So it captures the correct structure of the 1- and 2-RDM's. Even for strongly correlated systems the zero-order one-electron reduced density matrix provides a good approximation to the exact 1-RDM (corresponding to $\alpha = 1$) since it correctly predicts some natural spinorbitals to become degenerate (their occupancies approach the value 1/2). Thus, the assumption of equality of 1-RDM's for all values $\alpha$, Equation 96, for the GVB reference is much more justified than a similar assumption made for the HF reference in Equation 73. A convincing illustration of such conclusions is provided in Figure 5, where excellent performance of the AC correlation correction obtained for the GVB reference is confronted with a failure of the AC formula corresponding to HF reference, when two bonds in the water molecule dissociate simultaneously.

Solution of such $\alpha$-ERPA equations (Equation 35) with the matrices defined by Equations 102–105 yields eigenvectors related to transition density matrices via relation (44)-(45). The working form of the spin-summed AC correlation energy expression reads, therefore,

$$
\begin{aligned}
E_{c,GVB} = {}& 2 \int_0^1 d\alpha \sum_{p>q} \sum_{r>s} (1 - \delta_{I_p I_q} \delta_{I_q I_r} \delta_{I_r I_s}) \\
& \times \Big\{ (n_p - n_q)(n_r - n_s) \sum_{\nu} (Y_{\nu,pq}^{\alpha} - X_{\nu,pq}^{\alpha})(Y_{\nu,rs}^{\alpha} - X_{\nu,rs}^{\alpha}) \\
& - \frac{1}{2}[n_p(1 - n_q) + n_q(1 - n_p)]\delta_{pr}\delta_{qs} \Big\} \langle pr|qs \rangle
\end{aligned}
\tag{106}
$$

and the electron correlation-corrected total energy for the GVB reference is obtained from

$$E^{AC(GVB)} = \langle \Psi^{GVB} | \hat{H} | \Psi^{GVB} \rangle + E_{c,GVB}. \tag{107}$$

It should be emphasized that although the GVB wavefunction has been defined for even numbers of electrons, the AC correlation energy expression does not hinge on this assumption. In other words, if the GVB wavefunction is extended to odd-number-electron systems, and such extensions have been already proposed by Rassolov et al.,[35–37] the AC expression given in Equation 98 would be still valid. It is also worth mentioning that the AC(GVB) approach is based on the multireference wavefunction but the method is far superior in efficiency to other multireference methods like multiconfiguration SCF (e.g., CASSCF) or DMRG (density matrix renormalization group) approaches. Optimization of the GVB energy expression amounts to finding $N$ optimal orthogonal orbitals and only $N$ coefficients $c_p$. Optimization algorithm offering a scaling of only $O(M^4 N)$, where $M$ is a number of basis set functions, has been proposed.[35] On the other hand, a formal scaling of the computation cost of solving the ERPA equations is $O(M^6)$.

It is worthwhile comparing adiabatic connection formulae proposed with RPA or ERPA approximations for the GVB, Hartree–Fock, and Kohn–Sham reference wavefunctions. For the latter a number of excellent reviews is available,[11,12,38,39] where formalisms involved in derivations of different variants of RPA-KS-DFT approximations are presented together with illustrative examples of their performance. The AC correlation
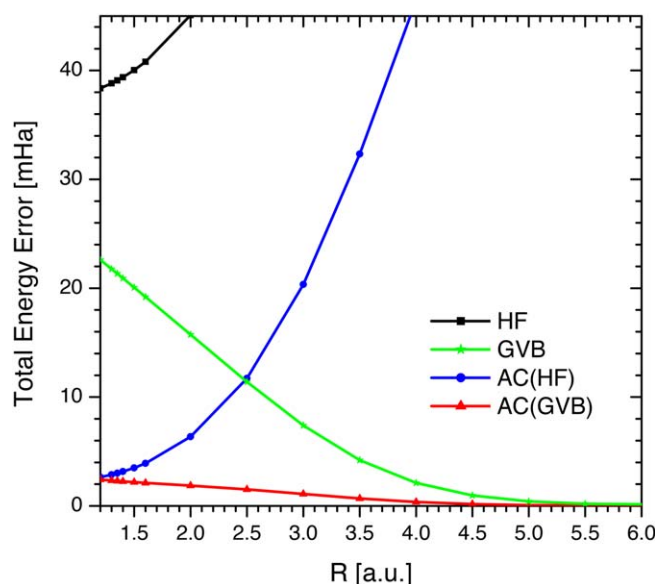
**FIGURE 4** Dissociation of the $H_2$ molecule in cc-pVTZ[22] basis set. Total energy errors computed with respect to the FCI values

expressions given in Equations 77 and 98 obtained for the HF and GVB references, respectively, are not exact since they assume invariance of the 1-RDM to changes in the coupling strength parameter. An analogous expression formulated for the KS reference is exact, since a definition of the adiabatic connection Hamiltonian in DFT assures that electron density is constant along the AC path. Employment of the fluctuation-dissipation theorem makes it possible to express the coupling strength integrand in terms of the frequency-dependent linear density-density response function of the noninteracting and interacting systems. Since the interacting response function is in principle exactly provided by the time-dependent DFT (TD-DFT) equations the AC correlation expression together with the TD-DFT equations would provide a way to obtain exact correlation energy in DFT. However, since the exact exchange-correlation kernel present in TD-DFT equations is not known, in the most widely used approximations it is either set to zero or only its exchange part is retained. In the end, therefore, the usable RPA approximations formulated in the DFT framework depend on the quality of the KS orbitals and orbital energies, and approximations involved in the TD-DFT equations. The final form for the adiabatic connection formula presented in Equation 106 obtained for the GVB reference is based on two approximations: that a one-electron reduced density matrix is fixed along the AC path and that transition density matrix elements can be accurately obtained from the ERPA equations. GVB is by construction a multireference approach and by adding the AC electron correlation energy the method is expected to stay stable and accurate not only for weakly correlated systems but also for those that are dominated by strong correlation. On the other hand, even though RPA approximations
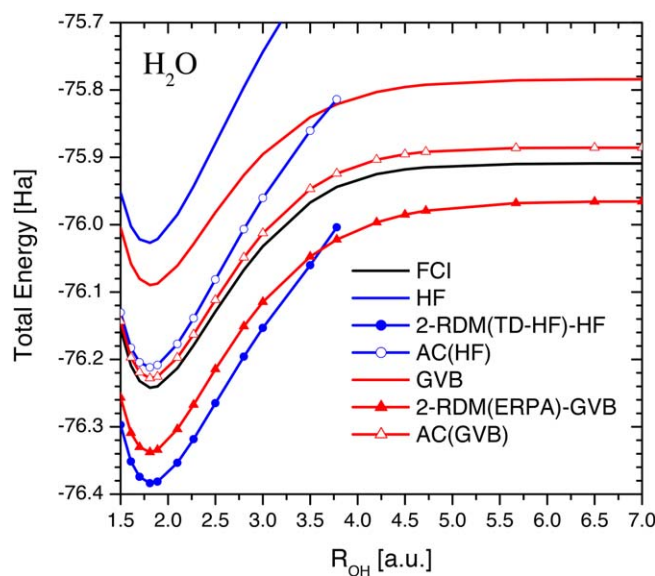


**FIGURE 5** Symmetric dissociation of the OH bonds in $H_2O$ molecule in cc-pVDZ[22] basis set

proposed in the KS-DFT framework are capable of partially accounting for static correlation[38] they will fail if strong correlation effects are of importance.

Computing AC-corrected HF and GVB energies, Equations 83 and 107, for the dissociating hydrogen molecule leads to total energies only in error of 1 [mHa] at equilibrium geometry for both methods as shown in Figure 4 [cf. curves labeled AC(HF) and AC(GVB)]. The errors are, therefore, much smaller than those obtained from the energies resulting from employing the ERPA-reconstructed 2-RDM as discussed in the previous section. Apparently the AC formulae do introduce correlation to the one- and two-electron part of the energy unlike the reconstructed 2-RDM which corrects only the two-electron energy component. When the bond is stretched the accuracy of the AC(HF) energy quickly deteriorates and the error amounts to 100 [mHa] for $R_{H_2} = 11$ [a.u.]. AC correlation energy for GVB reference correctly vanishes in the dissociation limit and and the error of the AC(GVB) energy tends to 0 as can be seen from Figure 4.

The hydrogen molecule may seem as a the particularly simple case for the AC correlation since there is only one geminal for this system and AC must only correct for the intrageminal correlation. To show that conclusions drawn for $H_2$ are in fact more general and the AC(GVB) approximation retains good accuracy for more challenging systems a symmetric dissociation of water molecule (both OH bonds are stretched simultaneously) has been investigated. The 2-RDM reconstruction scheme and the AC correlation correction for both HF and GVB references have been applied. The results are presented in Figure 5. For the HF reference the reconstruction approach (2-RDM(TD-HF)-HF curve) hugely overestimates the correlation energy at equilibrium geometry, $R_{OH} = 1.81$ [a.u], while its AC(HF) counterpart is in error by 30 [mHa] with respect to the FCI value. When OH bonds are stretched, this error rapidly increases. For the GVB the situation is different. Even though the absolute error of the energy is the lowest along the dissociation path for the AC(GVB) method all three curves presenting GVB, 2-RDM(ERPA)-GVB and AC(GVB) energies seem to be of the correct shape. However, examination of the dissociation energy calculated as difference in energy corresponding to $R_{OH} = 7.0$ and $R_{OH} = 1.81$ [a.u] reveals that AC(GVB) dissociation energy is the most accurate, the error with respect to the FCI value amounting to only 9 [mHa]. GVB and 2-RDM(ERPA)-GVB dissociation energies are in much larger errors, namely $-28$ [mHa] for the former and 39 [mHa] for the latter method. Thus, similarly to the hydrogen molecule, one concludes that adiabatic connection formula for the GVB reference leads to obtaining accurate dissociation curve for the challenging system of $H_2O$ with two dissociating bonds.

## 5 | SUMMARY AND CONCLUSIONS

It has been shown that the exact expression for a two-particle reduced density matrix in terms of reduced one-particle density functions presented in Equation 26 can be used as a basis for developing approximations to electron correlation energy for the assumed model Hamiltonian. At least two possible routes are possible. One, called here a 2-RDM reconstruction approach, employs directly factorization of 2-RDM in finding full electron interaction energy as presented in Equation 32. Although the relation given in Equation 26 is formally exact, in practice the final accuracy of the total energy hinges on the quality of the one-electron reduced density matrix needed in the one-electron part of the energy and the transition reduced density matrices entering the reconstruction scheme for 2-RDM. Approximate transition reduced density matrix follows from solving equations of motion in the RPA (for the Hartree–Fock reference) or ERPA (for the geminal wavefunction) approximation, cf. Equations 44–49. Using examples of dissociating hydrogen and water molecules we have shown that the reconstruction of 2-RDM does indeed compensate for the lack of correlation in the two-electron part of the energy. Since the one-electron energy component is computed with the uncorrected 1-RDM the total energy error is large, no matter if HF or GVB references are used. The reconstruction scheme could still be worth exploring in the context of the reduced density matrix functional theory.[40] Currently available functionals lead to obtaining correlated 1-RDM but they are deficient in the two-electron energy part. For example, they are incapable of describing van der Waals complexes since the dispersion component of the molecular interaction energy is missing.[41]

The other, much more exploited, way of employing factorization of the 2-RDM shown in Equation 26 involves the adiabatic connection formula. The AC correlation energy expression has been for long known for the single determinantal reference. Recently it has been also formulated for the geminal wavefunction GVB.[19] The AC correlation energy expressions for both references are formally exact but they require knowledge of one-electron reduced density properties along the whole adiabatic connection. To turn AC into a viable approach one assumes that the 1-RDM is constant along the adiabatic connection path and the transition density matrix elements follow from ERPA equations solved separately for each value of the adiabatic constant. Since the AC formula accounts for correlation in the one- and two-electron parts of the energy, it is expected to work better than the reconstruction scheme (limited by the inaccuracies in the 1-RDM part) even if approximate ERPA transition density matrices are employed. It is indeed the case for the HF and GVB references as illustrated on the examples of hydrogen and water dissociation curves. In particular, the AC(GVB) energy is very accurate for hydrogen molecule and for a much more demanding case of water molecule with two OH bonds simultaneously dissociating.

So far the adiabatic connection has turned out to be more accurate than 2-RDM reconstruction in correcting HF an GVB energies for the missing correlation energy. For an arbitrary electronic wavefunction approximation the feasibility of formulating the adiabatic connection formula for the correlation energy is determined by the existence of the zero-order Hamiltonian (i.e., a Hamiltonian for which the reference wavefunction is an

eigenstate). The reconstruction scheme is more universal since it only requires one- and two-electron reduced density matrices. The underlying wavefunction is never explicitly used. For methods based on reduced density matrix functionals the reconstruction approach may be an interesting way of accounting for the full or partial electron correlation. This path still awaits exploration.

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