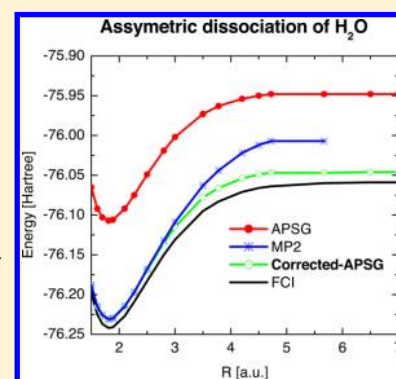


# Intergeminal Correction to the Antisymmetrized Product of Strongly Orthogonal Geminals Derived from the Extended Random Phase Approximation

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**ABSTRACT:** We present a correction to the antisymmetrized product of strongly orthogonalized geminals (APSG) approach accounting for intergeminal correlation energy that APSG lacks. The correction is based on the fluctuation dissipation theorem formulated for geminals with transition density matrices obtained from the recently formulated extended random phase approximation. We show that the proposed intergeminal correlation correction greatly improves upon APSG energies by accounting for short- and long-range dynamical correlation. For covalently bonded molecules the potential energy curves are in good agreement with the exact results in the entire range of bond breaking. Also the description of weakly interacting systems is superior to that of APSG. In particular, we show that the proposed intergeminal correlation energy reduces to the correct form of the dispersion energy and asymptotically yields exact interaction energy of the helium dimer.



## 1. INTRODUCTION

Geminal theories have been proposed as alternatives to the one-electron Hartree–Fock method and, by relying on two-electron functions called geminals, they are potentially capable of accounting for dissociation of bonds, a crucial process in chemistry.<sup>1,2</sup> An ansatz for a wave function is typically given as an antisymmetrized product of geminals, which in general results in a complicated expression for the energy that has to be optimized. The optimization problem is much simplified upon imposing a strong orthogonality condition on geminals leading to the antisymmetrized product of strongly orthogonal geminals (APSG) method.<sup>3,4</sup> Recently, there has been a revival of interest in geminal theories. Algorithms aiming at improving efficiency of optimization of the APSG wave function have been proposed,<sup>5,6</sup> spin unrestricted formulations of strongly orthogonal geminal theory applicable to open shell systems or systems with multiple breaking bonds have been developed,<sup>5,7,8</sup> APSG-based methods for predicting excitation energies have been recently formulated.<sup>9,10</sup> Even though most efforts in turning geminal approaches into a viable tool in quantum chemistry have employed strongly orthogonal geminals, an interesting approach based on the antisymmetrized product of nonorthogonal geminals is also developed.<sup>11,12</sup>

One of the attractive features of the APSG wave function is including correlation between pairs of electrons belonging to the same geminal (intrageminal correlation) and, consequently, accounting for static correlation energy. The major deficiency of the APSG approach is the lack of correlation between electrons described by different geminals (intergeminal correlation), which is responsible for including dynamical electron correlation energy. As a result of this deficiency, total APSG energies are severely overestimated, and molecular

interaction energies are in error due to the lack of dispersion energy component in the APSG interaction energy. One way to add dynamical correlation is to employ perturbation theory. There is, however, no unique way of choosing a zero-order Hamiltonian and a number of different perturbation formulations have been proposed.<sup>13–19</sup> They are often plagued by the quasi-degeneracy problem or suffer from high computational cost. The former problem can be avoided if the correction to the APSG energy is formulated on the basis of the second-order connected moment expansion method.<sup>20</sup>

The aim of the paper is to provide a robust and computationally effective method of including short- and long-range dynamical correlation in the APSG approach. We will employ fluctuation–dissipation theorem and express the intergeminal interaction correction in terms of solutions to the recently formulated extended random phase approximation (ERPA) equations.<sup>9,10</sup> This bears some resemblance to the approach that has recently resulted in developing a new class of density functionals (random phase approximation (RPA) correlation density functionals)<sup>21</sup> although no adiabatic coupling is involved.

In the antisymmetrized product of strongly orthogonal geminal theory, geminals are expanded in mutually disjoint sets of natural spin–orbitals.<sup>22</sup> In other words, if  $\{\varphi_p(x)\}$  is a set of the natural spin–orbitals corresponding to the APSG one-electron reduced density matrix  $\gamma$

$$\gamma(x, x') = \sum_p n_p \varphi_p(x')^* \varphi_p(x) \quad (1)$$

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then the singlet expansion for a geminal  $\psi_I(x_1, x_2)$  reads

$$\begin{aligned} \forall_I \psi_I(x_1, x_2) \\ = 2^{-1/2} \sum_{p \in I} c_p \varphi_p(\mathbf{r}_1) \varphi_p(\mathbf{r}_2) [\alpha(1) \beta(2) - \alpha(2) \beta(1)] \end{aligned} \quad (2)$$

Throughout the paper  $x$  stands for a coordinate that combines spacial and spin components.  $\varphi_p(\mathbf{r})$  is a spatial part of the spin-orbital  $\varphi_p(x)$ . The expansion coefficients  $\{c_p\}$  are directly related to the natural spin-orbital occupation numbers  $\{n_p\}$  via the relation

$$\forall_p c_p^2 = n_p \quad (3)$$

( $n_p$  falls in the range  $[0, 1]$ ). Normalization of each geminal implies

$$\forall_I \sum_{p \in I} c_p^2 = 1 \quad (4)$$

The spin-summed APSG expression for the energy in the representation of the natural orbitals reads<sup>3</sup>

$$\begin{aligned} E^{\text{APSG}}[\{c_p\}, \{\varphi_p\}] = & 2 \sum_p n_p h_{pp} + \sum_I \sum_{p, q \in I} c_p c_q \langle pp|qq \rangle \\ & + \sum_{\substack{I, J \\ I \neq J}} \sum_{\substack{p \in I \\ q \in J}} n_p n_q [2 \langle pq|pq \rangle - \langle pq|qp \rangle] \end{aligned} \quad (5)$$

where  $I, J$  are indices of geminals, the one- and two-electron integrals,  $\{h_{pq} = \int \varphi_p(\mathbf{r})^* [\hat{t} + \hat{v}_{\text{ext}}] \varphi_q(\mathbf{r}) d\mathbf{r}\}$  and  $\{\langle pq|rs \rangle\}$ , respectively, are in the representation of the natural orbitals. The second term in the APSG energy expression involves pairs of orbitals belonging to the same geminal and describes intrageminal electron interaction. This term properly accounts for static correlation in the case of bonds breaking when two orbitals belonging to the same geminal become degenerate in terms of their occupancies. If there are only two electrons in a system (a one-geminal case), the last term in eq 5 vanishes and the APSG energy is exact. For other systems this term accounts for intergeminal (IG) electron interaction. If one introduces geminal one-electron reduced density matrices, i.e.

$$\gamma_I(x, x') = \sum_{p \in I} n_p \varphi_p(x')^* \varphi_p(x) \quad (6)$$

then the IG term in eq 5 can be written as

$$\begin{aligned} E_{\text{IG}}^{\text{APSG}} = & \frac{1}{2} \sum_{\substack{I, J \\ I \neq J}} \iint [\gamma_I(x_1, x_1) \gamma_J(x_2, x_2) \\ & - \gamma_I(x_1, x_2) \gamma_J(x_2, x_1)] |\mathbf{r}_1 - \mathbf{r}_2|^{-1} dx_1 dx_2 \end{aligned} \quad (7)$$

so it is evident that it involves only Coulomb and exchange intergeminal interactions. The goal of the paper is to propose a correction that supplements the intergeminal interaction energy,  $E_{\text{IG}}^{\text{APSG}}$ , with correlation.

## 2. INTERGEMINAL CORRELATION ENERGY FROM RESPONSE FUNCTIONS

Consider the electron–electron interaction given by an electron pair density,  $\rho^{(2)}(x_1, x_2)$ ,

$$E_{\text{ee}} = \frac{1}{2} \iint \rho^{(2)}(x_1, x_2) |\mathbf{r}_1 - \mathbf{r}_2|^{-1} dx_1 dx_2 \quad (8)$$

Let  $|0\rangle$  denote a ground state vector, i.e.,  $\rho^{(2)}(x_1, x_2) = \langle 0 | \hat{\rho}^{(2)}(x_1, x_2) | 0 \rangle$ . A pair density operator  $\hat{\rho}^{(2)}(x_1, x_2)$  can be written in terms of the density  $\rho(x)$  and the density fluctuation operator  $\delta\hat{\rho}(x)$

$$\delta\hat{\rho}(x) = \hat{\rho}(x) - \rho(x) \quad (9)$$

as

$$\begin{aligned} \rho^{(2)}(x_1, x_2) = & \langle 0 | \delta\hat{\rho}(x_1) \delta\hat{\rho}(x_2) | 0 \rangle + \rho(x_1) \rho(x_2) \\ & - \delta(x_1 - x_2) \rho(x_1) \end{aligned} \quad (10)$$

The fluctuation term  $\langle 0 | \delta\hat{\rho}(x_1) \delta\hat{\rho}(x_2) | 0 \rangle$  represents a fluctuation of the density at  $x_1$  tied to a fluctuation at  $x_2$  and it gives rise to electron correlation.<sup>23</sup> A sum of the fluctuation term together with the last term in eq 10 integrated with the electron interaction operator yields the exchange–correlation energy. To find an expression for the intergeminal correlation energy, we will consider only contributions to the fluctuation term originating from pairs of geminals  $I \neq J$ . For that purpose consider a geminal density operator and a corresponding fluctuation density operator

$$\hat{\rho}_I(x) = \sum_{p, q \in I} \hat{a}_q^\dagger \hat{a}_p \varphi_q(x)^* \varphi_p(x) \quad (11)$$

and

$$\delta\hat{\rho}_I(x) = \hat{\rho}_I(x) - \rho_I(x) \quad (12)$$

respectively, where  $\rho_I(x)$  is a diagonal part of the reduced density matrix of the  $I$ th geminal introduced in eq 6, i.e.

$$\rho_I(x) = \sum_{p \in I} n_p \varphi_p(x)^* \varphi_p(x) \quad (13)$$

Define the intergeminal correlation (IGcorr) contribution to the pair density resulting from pairwise interactions of geminals as

$$\begin{aligned} \rho_{\text{IGcorr}}^{(2)}(x_1, x_2) \\ = \frac{1}{2} \sum_{\substack{I, J \\ I > J}} [\langle 0 | \delta\hat{\rho}_I(x_1) \delta\hat{\rho}_J(x_2) | 0 \rangle + \langle 0 | \delta\hat{\rho}_J(x_1) \delta\hat{\rho}_I(x_2) | 0 \rangle] \end{aligned} \quad (14)$$

Notice that the intergeminal correlation pair density has a proper symmetry to interchanging coordinates, namely  $\rho_{\text{IGcorr}}^{(2)}(x_2, x_1)^* = \rho_{\text{IGcorr}}^{(2)}(x_1, x_2)$ . The expression for the intergeminal correlation energy follows immediately from eqs 8 and 14 and reads

$$\begin{aligned} E_{\text{IGcorr}} = & \frac{1}{4} \sum_{\substack{I, J \\ I > J}} \iint [\langle 0 | \delta\hat{\rho}_I(x_1) \delta\hat{\rho}_J(x_2) | 0 \rangle \\ & + \langle 0 | \delta\hat{\rho}_J(x_1) \delta\hat{\rho}_I(x_2) | 0 \rangle] |\mathbf{r}_1 - \mathbf{r}_2|^{-1} dx_1 dx_2 \end{aligned} \quad (15)$$

The fluctuation terms that enter the expression for  $E_{\text{IGcorr}}$  can be obtained from the linear response functions formulated within the APSG theory. Namely, a perturbation of the fluctuation density of the geminal  $I$  at  $x'$  caused by a fluctuation density of geminal  $J$  at  $x$  reads

$$\chi_{IJ}(x', x, \omega) = \sum_{\nu \neq 0} \left\{ \frac{\langle 0 | \delta \hat{\rho}_I(x') | \nu \rangle \langle \nu | \delta \hat{\rho}_J(x) | 0 \rangle}{\omega - E_\nu + E_0 + i\eta} - \frac{\langle 0 | \delta \hat{\rho}_J(x) | \nu \rangle \langle \nu | \delta \hat{\rho}_I(x') | 0 \rangle}{\omega + E_\nu - E_0 + i\eta} \right\} \quad (16)$$

where  $E_\nu$  is the energy of the excited state  $\nu$ . A sum of  $\chi_{IJ}(x', x, i\omega)$  and  $\chi_{JI}(x, x', i\omega)$  will be considered a contribution from geminals  $I$  and  $J$  to the total response giving rise to intergeminal correlation between  $I$  and  $J$ . It reads

$$\begin{aligned} & -\frac{1}{\pi} \int_0^\infty [\chi_{IJ}(x', x, i\omega) + \chi_{JI}(x, x', i\omega)] d\omega \\ &= \frac{2}{\pi} \sum_{\nu \neq 0} \int_0^\infty \frac{E_\nu - E_0}{\omega^2 + (E_\nu - E_0)^2} d\omega \\ & \quad \times [\langle 0 | \delta \hat{\rho}_I(x') | \nu \rangle \langle \nu | \delta \hat{\rho}_J(x) | 0 \rangle + \langle 0 | \delta \hat{\rho}_J(x) | \nu \rangle \langle \nu | \delta \hat{\rho}_I(x') | 0 \rangle] \\ &= \langle 0 | \delta \hat{\rho}_I(x') \delta \hat{\rho}_J(x) | 0 \rangle + \langle 0 | \delta \hat{\rho}_J(x) \delta \hat{\rho}_I(x') | 0 \rangle \end{aligned} \quad (17)$$

where the last line has been obtained by utilizing the integral  $\int_0^\infty (\omega^2 + a^2)^{-1} d\omega = \pi/(2|a|)$  and the fact that the expectation values of the fluctuation density operators vanish, i.e.,  $\langle 0 | \delta \hat{\rho}_I(x) | 0 \rangle = 0$ . The latter allowed us to include in the summation a  $\nu = 0$  term and use a resolution of the identity  $\sum_\nu |\nu\rangle \langle \nu| = 1$  in the last line. Equation 17 can be seen as a fluctuation–dissipation theorem for geminals. The intergeminal correlation energy, eq 15, expressed in terms of the intergeminal density–density response functions reads

$$\begin{aligned} E_{\text{IGcorr}} &= -\frac{1}{4\pi} \sum_{\substack{I,J \\ I>J}} \int dx_1 \int dx_2 \int_0^\infty d\omega [\chi_{IJ}(x_1, x_2, i\omega) \\ & \quad + \chi_{JI}(x_2, x_1, i\omega)] |\mathbf{r}_1 - \mathbf{r}_2|^{-1} \end{aligned} \quad (18)$$

For practical purpose it is more convenient to express  $E_{\text{IGcorr}}$  in terms of elements of transition density matrices  $\mathbf{T}_\nu$  defined as

$$(\mathbf{T}_\nu)_{pq} = \langle 0 | \hat{a}_q^\dagger \hat{a}_p | \nu \rangle \quad (19)$$

Employing eqs 11 and 12 in eq 16 and using definition 19 allows one to turn eq 18 into

$$E_{\text{IGcorr}} = \frac{1}{2} \sum_{\substack{I,J \\ I>J}} \sum_{pq \in I} \sum_{rs \in J} \sum_\nu (\mathbf{T}_\nu)_{qp} (\mathbf{T}_\nu)_{rs}^* \langle pr | qs \rangle \quad (20)$$

The transition density matrix elements needed for evaluation of intergeminal correlation energy can be obtained from the APSG ground state properties by employing either the recently introduced extended random phase approximation (ERPA) or the time-dependent APSG linear response formalism (TD-APSG).<sup>9,10</sup> The ERPA approach is derived from the equation of motion of Rowe.<sup>24</sup> The initial assumption in Rowe's theory is that an excited state  $|\nu\rangle$  arises upon acting with an excitation operator  $\hat{O}^\dagger$  on a ground state vector  $|0\rangle$ . In ERPA such an operator includes only single-type excitations and the singlet excitation operator reads<sup>9</sup>

$$\begin{aligned} \hat{O}_{\text{ERPA}}^\dagger &= \sum_{p>q} (X_\nu)_{pq} (\hat{a}_{p_\alpha}^\dagger \hat{a}_{q_\alpha} + \hat{a}_{p_\beta}^\dagger \hat{a}_{q_\beta}) \\ & \quad + \sum_{p>q} (Y_\nu)_{pq} (\hat{a}_{q_\alpha}^\dagger \hat{a}_{p_\alpha} + \hat{a}_{q_\beta}^\dagger \hat{a}_{p_\beta}) \end{aligned} \quad (21)$$

where the creation and annihilation operators,  $\hat{a}_{p_\sigma}^\dagger$  and  $\hat{a}_{p_\sigma}$ , respectively, act in the space of the natural spin–orbitals [in ref 9 the excitation operator  $\hat{O}_{\text{ERPA}}^\dagger$  includes also a diagonal term  $\sum_p (Z_\nu)_p \hat{a}_{p_\sigma}^\dagger \hat{a}_{p_\sigma}$ , but because its contribution to excitation energies is negligible, it is skipped in this paper]. In Rowe's theory the transition matrix elements of a given operator  $\hat{F}$  follow as expectation values of a commutator of  $\hat{F}$  and the excitation operator  $\hat{O}^\dagger$ , i.e.,  $\langle 0 | \hat{F} | \nu \rangle = \langle 0 | [\hat{F}, \hat{O}^\dagger] | 0 \rangle$ . Notice that this relation is exact if the deexcitation operator  $\hat{O}$  satisfies the so-called killer condition reading  $\hat{O} | 0 \rangle = 0$ . The ERPA deexcitation operator acting on the APSG ground state vector in general violates the killer condition;<sup>9</sup> nevertheless, Rowe's relation for the transition matrix of  $\hat{F}$  can be used as an approximation. Setting  $\hat{F} = \hat{a}_p^\dagger \hat{a}_q$  and employing eq 21, it is straightforward to show that in ERPA approximation a sum of the transition density matrix defined in eq 19 and its transpose,  $\mathbf{T}_\nu + (\mathbf{T}_\nu)^T$ , reads

$$\forall_{p>q} (n_p - n_q) [(Y_\nu)_{pq} - (X_\nu)_{pq}] = (\mathbf{T}_\nu)_{pq} + (\mathbf{T}_\nu)_{qp} \quad (22)$$

Therefore, the ERPA equations<sup>9</sup>

$$\begin{pmatrix} \mathbf{0} & \mathbf{A}^+ \\ \mathbf{A}^- & \mathbf{0} \end{pmatrix} \begin{pmatrix} \tilde{\mathbf{Y}}_\nu \\ \tilde{\mathbf{X}}_\nu \end{pmatrix} = \omega_\nu \begin{pmatrix} \tilde{\mathbf{Y}}_\nu \\ \tilde{\mathbf{X}}_\nu \end{pmatrix} \quad (23)$$

where

$$\forall_{p>q} (\tilde{\mathbf{Y}}_\nu)_{pq} = (c_p - c_q) [(Y_\nu)_{pq} - (X_\nu)_{pq}] \quad (24)$$

$$\forall_{p>q} (\tilde{\mathbf{X}}_\nu)_{pq} = (c_p + c_q) [(Y_\nu)_{pq} + (X_\nu)_{pq}] \quad (25)$$

solved with the ground state reduced density matrices obtained from the APSG approximation yield the ERPA-APSG approximation to the transition density matrix elements through eq 22.

In ref 10 we have formulated the linear-response equations for the APSG functional, which for a real frequency-dependent perturbation  $\tilde{w}(\mathbf{r}, \omega)$  read

$$\begin{pmatrix} \omega \mathbf{1} & \mathbf{0} & -\mathbf{A}^+ & -\mathbf{D}^+ \\ \mathbf{0} & \omega \mathbf{1} & -2(\mathbf{D}^+)^T & -\mathbf{E}^+ \\ -\mathbf{A}^- & -\mathbf{D}^- & \omega \mathbf{1} & \mathbf{0} \\ -2(\mathbf{D}^-)^T & -\mathbf{E}^- & \mathbf{0} & \omega \mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{P}^{\text{Re}} \\ \mathbf{P}_D^{\text{Re}} \\ \mathbf{P}^{\text{Im}} \\ \mathbf{P}_D^{\text{Im}} \end{pmatrix} = \begin{pmatrix} \mathbf{0} \\ \mathbf{0} \\ \tilde{\mathbf{w}} \\ \tilde{\mathbf{w}}_D \end{pmatrix} \quad (26)$$

where

$$\forall_{p \geq q} \tilde{w}_{pq} = (c_p + c_q) w_{qp}(\omega) \quad (27)$$

$$\forall_p (\tilde{w}_D)_p = 2c_p w_{pp}(\omega) \quad (28)$$

$$\forall_p (\mathbf{P}_D^{\text{Im}})_p = (\mathbf{P}^{\text{Im}})_{pp} \quad (29)$$

and the components of the vector  $\mathbf{P}$  are directly related to the frequency-dependent response of the one-electron reduced density matrix  $\gamma(\omega)$ , namely

$$\forall_{p>q} (\mathbf{P}^{\text{Re}})_{pq} = (c_p + c_q)^{-1} \gamma_{pq}^{\text{Re}}(\omega) \quad (30)$$

$$\forall_p (\mathbf{P}_D^{\text{Re}})_p = (2c_p)^{-1} \gamma_{pp}^{\text{Re}}(\omega) \quad (31)$$

$$\forall_{p>q} (\mathbf{P}^{\text{Im}})_{pq} = (c_q - c_p)^{-1} \gamma_{pq}^{\text{Im}}(\omega) \quad (32)$$

Notice that the indices  $p, q$  pertain to the APSG natural orbitals and we employ a notation  $f^{\text{Re}}(\omega)$  and  $f^{\text{Im}}(\omega)$  for the Fourier transforms of the real and imaginary parts of  $\delta f(t)$  (the first-order perturbation to the quantity  $f$ ), i.e.  $f^{\text{Re}}(\omega) = \mathcal{F}[\text{Re} \delta f(t)](\omega)$  and  $f^{\text{Im}}(\omega) = i\mathcal{F}[\text{Im} \delta f(t)](\omega)$ . The real part of  $\gamma(\omega)$  following from eqs 26–32 takes the form

$$\gamma_{pq}^{\text{Re}}(\omega) = 2 \sum_{\nu} \sum_{r>s} \frac{\omega_{\nu}(c_p + c_q)(\tilde{Y}_{\nu})_{pq}(\tilde{Y}_{\nu})_{rs}(c_r + c_s)}{\omega^2 - \omega_{\nu}^2} w_{rs}(\omega) + 2 \sum_{\nu} \sum_r \frac{\omega_{\nu}(c_p + c_q)(\tilde{Y}_{\nu})_{pq}(\tilde{W}_{\nu})_r c_r}{\omega^2 - \omega_{\nu}^2} w_{rr}(\omega) \quad (33)$$

where vectors  $\tilde{Y}_{\nu}$  and  $\tilde{W}_{\nu}$  are components of eigenvectors solving the TD-APSG equations [cf. eq 26]

$$\begin{pmatrix} \mathbf{0} & \mathbf{0} & \mathbf{A}^+ & \mathbf{D}^+ \\ \mathbf{0} & \mathbf{0} & 2(\mathbf{D}^+)^T & \mathbf{E}^+ \\ \mathbf{A}^- & \mathbf{D}^- & \mathbf{0} & \mathbf{0} \\ 2(\mathbf{D}^-)^T & \mathbf{E}^- & \mathbf{0} & \mathbf{0} \end{pmatrix} \begin{pmatrix} \tilde{Y}_{\nu} \\ \tilde{W}_{\nu} \\ \tilde{X}_{\nu} \\ \tilde{V}_{\nu} \end{pmatrix} = \omega_{\nu} \begin{pmatrix} \tilde{Y}_{\nu} \\ \tilde{W}_{\nu} \\ \tilde{X}_{\nu} \\ \tilde{V}_{\nu} \end{pmatrix} \quad (34)$$

and corresponding to pertinent positive eigenvalues (excitation energies)  $\omega_{\nu}$ . They satisfy the following normalization condition

$$2(\tilde{Y}_{\nu})^T \tilde{X}_{\nu} + (\tilde{W}_{\nu})^T \tilde{V}_{\nu} = 1 \quad (35)$$

A comparison of eq 33 with a spin-summed expression for  $\gamma_{pq}^{\text{Re}}(\omega)$  resulting from the standard linear response theory (see for example eq 66 in ref 25) provides the following relation between the elements of the transition density matrices and the  $\tilde{Y}_{\nu}$  and  $\tilde{W}_{\nu}$  vectors

$$\forall_{p>q} (c_p + c_q)(\tilde{Y}_{\nu})_{pq} = (T_{\nu})_{pq} + (T_{\nu})_{qp} \quad (36)$$

$$\forall_p c_p(\tilde{W}_{\nu})_p = (T_{\nu})_{pp} \quad (37)$$

Notice that eq 36 also holds for  $\tilde{Y}_{\nu}$  vectors solving the ERPA-APSG equations, cf. eqs 22 and 24.

We have shown, therefore, that both ERPA-APSG and TD-APSG equations provide approximations to transition density matrices  $T_{\nu}$  defined in eq 19. Because the matrices  $\mathbf{A}^{\pm}$  entering ERPA and TD-APSG equations are identical,<sup>10</sup> the solutions of both eigenproblems are also equal if the vectors  $\tilde{W}_{\nu}$  and  $\tilde{V}_{\nu}$  do not contribute. Consequently, as will be discussed in section 4, solutions of ERPA and TD-APSG equations lead to practically the same results if used to obtain the intergeminal correlation energy given in eq 20. The spin-summed expression for the latter for real transition density matrix elements and orbitals reads

$$E_{\text{IGcorr}} = 2 \sum_{\substack{I,J \\ I>J}} \sum_{\substack{p \geq q \\ p,q \in I}} \sum_{\substack{r \geq s \\ r,s \in J}} (c_p + c_q)(c_r + c_s) \sum_{\nu} (F_{\nu})_{pq} (F_{\nu})_{rs} \langle prlqs \rangle \quad (38)$$

Vectors  $\mathbf{F}_{\nu}$  are two-component in the case of TD-APSG approximation, eq 34, i.e.

$$\mathbf{F}_{\nu} = \begin{pmatrix} \tilde{Y}_{\nu} \\ \frac{1}{2} \tilde{W}_{\nu} \end{pmatrix} \quad (39)$$

and there is no  $\tilde{W}_{\nu}$  component if ERPA equations, eq 23, are employed.

The intergeminal correlation correction introduced in this section accounts for mainly two-body dispersion interactions of geminals. Accounting for this type of interaction is crucial in describing noncovalently bonded systems. It turns out, however (see section 4), that the amount of the dynamical correlation that  $E_{\text{IGcorr}}$  adds to the APSG energy is insufficient to yield potential energy curves of covalently bonded species with satisfactory accuracy. A straightforward extension of the formula 38 that goes beyond dispersion-only geminal interactions is feasible. In eq 20 only pairs of spin-orbitals belonging to different geminals  $I$  and  $J$ , i.e.,  $p, q \in I$  and  $r, s \in J$  and  $I \neq J$ , are allowed. This restriction is now lifted and all quarters of spin-orbital  $pqr$ s are included unless they belong to the same geminal (this amounts to excluding intrageminal correlation that is already properly accounted for in the APSG functional). The resulting intergeminal correlation energy written in terms of spin-orbitals reads

$$E'_{\text{IGcorr}} = \frac{1}{4} \sum_{pqrs} (1 - \delta_{I_p I_q} \delta_{I_r I_s}) \left[ \sum_{\nu \neq 0} (T_{\nu})_{qp} (T_{\nu})_{rs}^* - n_p (1 - n_r) \delta_{ps} \delta_{rq} \right] \langle prlqs \rangle \quad (40)$$

In the expression above  $I_p$  stands for index of a geminal which a spin-orbital  $p$  belongs to. The correlation energy introduced in eq 40 would be divergent without including the second term in the square bracket. Its form has been obtained by using the matrix representation of the pair density given in eq 10 and inserting the resolution of identity,  $1 = \sum_{\nu} |\nu\rangle \langle \nu|$ , in the fluctuation term,  $\langle 0 | \delta \hat{\rho}(x_1) \delta \hat{\rho}(x_2) | 0 \rangle = \sum_{\nu \neq 0} \langle 0 | \hat{\rho}(x_1) | \nu \rangle \langle \nu | \hat{\rho}(x_2) | 0 \rangle$ , which leads to

$$\begin{aligned} \langle 0 | a_p^{\dagger} a_r^{\dagger} a_s a_q | 0 \rangle &= n_p n_r (\delta_{pq} \delta_{rs} - \delta_{ps} \delta_{rq}) \\ &+ \sum_{\nu \neq 0} \langle 0 | a_p^{\dagger} a_q | \nu \rangle \langle \nu | a_r^{\dagger} a_s | 0 \rangle - n_p (1 - n_r) \delta_{ps} \delta_{rq} \end{aligned} \quad (41)$$

Only intergeminal correlation contributions (arising from the last two terms) are included in eq 40. The first two terms give rise to intergeminal Coulomb and exchange interaction already accounted for in the APSG energy. Notice that the term  $n_p n_r \delta_{ps} \delta_{rq}$  in the square bracket in eq 40 is responsible for removing some portion of the intergeminal exchange energy present in the APSG energy. Finally, the spin-summed, working form of the ERPA-APSG total energy expression being a sum of the APSG energy, eq 5, and the intergeminal correlation energy defined in (40) with the transition density matrix elements obtained via eqs 36, 37, and 39 reads

$$\begin{aligned} E^{\text{ERPA-APSG}} &= E^{\text{APSG}} + \sum_{p \geq q} \sum_{r \geq s} (1 - \delta_{I_p I_q} \delta_{I_r I_s} \delta_{I_p I_r}) \\ &\times \left[ (c_p + c_q)(c_r + c_s) \sum_{\nu} (F_{\nu})_{pq} (F_{\nu})_{rs} \right. \\ &\left. - \frac{1}{2} [n_p (1 - n_q) + n_q (1 - n_p)] \delta_{pr} \delta_{qs} \right] \langle prlqs \rangle \end{aligned} \quad (42)$$

where the summation with respect to  $\nu$  runs through solutions of the ERPA or TD-APSG equations corresponding to positive eigenvalues.



### 3. EMERGENCE OF DISPERSION ENERGY FOR WEAKLY INTERACTING SUBSYSTEMS

As already mentioned in section 2, intergeminal correlation energy present in the energy functional (42) describes a dispersive part of the interaction when applied to a supermolecule comprising two closed-shell weakly interacting subsystems. In particular, in the limit of the separation  $R$  between subsystems becoming large the intergeminal correction should reduce to the second-order dispersion energy expression involving properties of isolated monomers. To show this asymptotic behavior, first consider the TD-APSG eq 34 rewritten in a symmetric and compact fashion:

$$\begin{pmatrix} \mathbf{M}^- & \mathbf{0} \\ \mathbf{0} & \mathbf{M}^+ \end{pmatrix} \begin{pmatrix} \mathbf{Y}'_n \\ \mathbf{X}'_n \end{pmatrix} = \omega_n \Omega \begin{pmatrix} \mathbf{Y}'_n \\ \mathbf{X}'_n \end{pmatrix} \quad (43)$$

where

$$\mathbf{M}^\pm = \begin{pmatrix} \mathbf{A}^\pm & 2^{1/2} \mathbf{D}^\pm \\ 2^{1/2} (\mathbf{D}^\pm)^T & \mathbf{E}^\pm \end{pmatrix} \quad (44)$$

$$\Omega = \begin{pmatrix} \mathbf{0} & \mathbf{1} \\ \mathbf{1} & \mathbf{0} \end{pmatrix}$$

and

$$\begin{pmatrix} \mathbf{Y}'_n \\ \mathbf{X}'_n \end{pmatrix} = \begin{pmatrix} \tilde{\mathbf{Y}}_n \\ 2^{-1/2} \tilde{\mathbf{W}}_n \\ \tilde{\mathbf{X}}_n \\ 2^{-1/2} \tilde{\mathbf{V}}_n \end{pmatrix} \quad (45)$$

The matrices  $\mathbf{M}^+$  and  $\mathbf{M}^-$  are symmetric and positive definite and the eigenvalues  $\omega_n$  come in pairs of values of opposite signs

$$\mathbf{M} = \begin{pmatrix} (M^-)_{pqrs} & (M^-)_{pqab} & 0 & 0 & 0 & 0 & 0 & 0 \\ (M^-)_{abpq} & (M^-)_{abcd} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & (M^-)_{paqb} & (M^-)_{pabq} & 0 & 0 & 0 & 0 \\ 0 & 0 & (M^-)_{apqb} & (M^-)_{apbq} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & (M^+)_{pqrs} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & (M^+)_{abcd} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & (M^+)_{paqb} & (M^+)_{pabq} \\ 0 & 0 & 0 & 0 & 0 & 0 & (M^+)_{apqb} & (M^+)_{apbq} \end{pmatrix} \quad (48)$$

The ERPA-APSG energy expression, eq 42, takes a form of a sum of the ERPA-APSG energies of the isolated systems,  $E_1^{\text{ERPA-APSG}} + E_2^{\text{ERPA-APSG}}$  and the interaction energy. The intergeminal-correlation part of the latter component reads

$$E_{\text{IGcorr}} = 2 \sum_{p \geq q} \sum_{a \geq b} \sum_n (c_p + c_q)(c_a + c_b)(F_n)_{pq}(F_n)_{ab} \langle palqb \rangle \quad (49)$$

Notice that the same expression follows from both eq 38 and its extension given in eq 40 because the only nonvanishing terms

and equal moduli, i.e.  $\omega_{n-} = -\omega_{n+}$ . The eigenvectors satisfy the following orthonormality relation [which is consistent with the normalization in eq 35]

$$\mathbf{V}_{m,n} \begin{pmatrix} \mathbf{Y}'_m \\ \mathbf{X}'_m \end{pmatrix}^T \Omega \begin{pmatrix} \mathbf{Y}'_n \\ \mathbf{X}'_n \end{pmatrix} = \text{sgn}(\omega_n) \delta_{mn} \quad (46)$$

If the main matrix of the generalized eigenproblem 43 is perturbed with  $\mathbf{M}^{(1)}$ , then the perturbation theory leads to obtaining first-order corrections to the eigenvectors corresponding to positive eigenvalues  $\mathbf{V}_{n+}^{(1)}$  (analogous expressions hold for  $\mathbf{V}_{n-}^{(1)}$ ) reading

$$\mathbf{V}_{n+}^{(1)} = \sum_{m_+ \neq n_+} \frac{[\mathbf{V}_{m_+}^{(0)}]^T \mathbf{M}^{(1)} \mathbf{V}_{n_+}^{(0)}}{\omega_{n_+}^{(0)} - \omega_{m_+}^{(0)}} \mathbf{V}_{m_+}^{(0)} - \sum_{m_- \neq n_+} \frac{[\mathbf{V}_{m_-}^{(0)}]^T \mathbf{M}^{(1)} \mathbf{V}_{n_+}^{(0)}}{\omega_{n_+}^{(0)} - \omega_{m_-}^{(0)}} \mathbf{V}_{m_-}^{(0)} \quad (47)$$

where vectors  $\mathbf{V}_n^{(i)}$  are composed of the pertinent  $(\mathbf{Y}'_n)^{(i)}$  and  $(\mathbf{X}'_n)^{(i)}$  components, i.e.,  $\mathbf{V}_n^{(i)} = [(\mathbf{Y}'_n)^{(i)}, (\mathbf{X}'_n)^{(i)}]$ .

To analyze the energy expression 42 in the case of two closed-shell interacting subsystems I and II when the separation  $R$  becomes large, consider the matrices in eq 44 in the basis of the APSG orbitals of the supermolecule at  $R \rightarrow \infty$ . In this case the basis set is the union of orbitals  $p, q, r, s, \dots$  of the isolated system I and  $a, b, c, d, \dots$  orbitals of the subsystem II. Because the orbitals are completely localized in one of the subsystems, only the matrix elements  $\{h_{pq}\}$  and  $\{h_{ab}\}$ , and the two-electron integrals  $\{\langle pqrs \rangle\}$ ,  $\{\langle abcd \rangle\}$ , and  $\{\langle palqb \rangle\}$  do not vanish. Under such assumptions and taking into account eq 44 together with definitions of the  $\mathbf{A}^\pm$ ,  $\mathbf{D}^\pm$ , and  $\mathbf{E}^\pm$  matrices provided in ref 10, it is straightforward to show that the main matrix  $\mathbf{M} = \begin{pmatrix} \mathbf{M}^- & \mathbf{0} \\ \mathbf{0} & \mathbf{M}^+ \end{pmatrix}$  in the TD-APSG equation (43) acquires the following block structure:

are those contributing to the two-body dispersion intergeminal interaction. The vectors  $\mathbf{F}_n$  can be decomposed into the zero-order part  $(\mathbf{F}_n)^{(0)}$  corresponding to the limit  $R \rightarrow \infty$  and the small remainder  $(\mathbf{F}_n)^{(1)}$ , namely

$$\mathbf{F}_n = (\mathbf{F}_n)^{(0)} + (\mathbf{F}_n)^{(1)} \quad (50)$$

Assume that at the  $R \rightarrow \infty$  limit excitations localized in the subsystem I are indexed with  $\nu_+$  and those localized in II with  $\mu_+$ , i.e.

$$(F_{\mu_+})_{pq}^{(0)} = 0 \quad (51)$$

$$(F_{\nu_+})_{ab}^{(0)} = 0 \quad (52)$$

Together with eq 50 this allows one to write the main contribution to the correlation interaction energy as

$$E_{\text{IGcorr}} = 2 \sum_{p \geq q} \sum_{a \geq b} (c_p + c_q)(c_a + c_b) \left[ \sum_{\nu_+} (F_{\nu_+})_{pq}^{(0)} (F_{\nu_+})_{ab}^{(1)} + \sum_{\mu_+} (F_{\mu_+})_{pq}^{(1)} (F_{\mu_+})_{ab}^{(0)} \right] \langle palqb \rangle \quad (53)$$

By comparing definitions (39) and (45), we immediately find a relation between elements of the  $\mathbf{Y}'_n$  and  $\mathbf{F}_n$  vectors, namely

$$\forall_{k>l} (Y'_n)_{kl} = (F_n)_{kl} \quad (54)$$

$$\forall_k (Y'_n)_{kk} = \sqrt{2} (F_n)_{kk} \quad (55)$$

$$\mathbf{M}' = \begin{pmatrix} (M^-)_{pqrs}^{(0)} + (M^-)_{pqrs}^{(1)} & (M^-)_{pqab}^{(1)} & 0 & 0 \\ (M^-)_{abpq}^{(1)} & (M^-)_{abcd}^{(0)} + (M^-)_{abcd}^{(1)} & 0 & 0 \\ 0 & 0 & (M^+)_{pqrs}^{(0)} + (M^+)_{pqrs}^{(1)} & 0 \\ 0 & 0 & 0 & (M^+)_{abcd}^{(0)} + (M^+)_{abcd}^{(1)} \end{pmatrix} \quad (57)$$

$(\mathbf{M}^\pm)^{(0)}$  are the matrices corresponding to the limit  $R \rightarrow \infty$  with vectors  $(\mathbf{Y}')^{(0)}$  and  $(\mathbf{X}')^{(0)}$  being the pertinent eigenvectors.  $(\mathbf{M}^\pm)^{(1)}$  are vanishing perturbing terms whose elements are provided by definitions given in eq 44. The off-diagonal elements read

$$\forall_{p>q} \forall_{a>b} (M^-)_{pqab}^{(1)} = (M^-)_{abpq}^{(1)} = 4(c_p + c_q)(c_a + c_b) \langle palqb \rangle \quad (58)$$

$$\forall_{p>q} (M^-)_{pqaa}^{(1)} = (M^-)_{aapq}^{(1)} = 2^{5/2} c_a (c_p + c_q) \langle palqa \rangle \quad (59)$$

$$\forall_{p>q} (M^-)_{abpp}^{(1)} = (M^-)_{ppab}^{(1)} = 2^{5/2} c_p (c_a + c_b) \langle aplbp \rangle \quad (60)$$

$$\forall_{pa} (M^-)_{ppaa}^{(1)} = (M^-)_{aapp}^{(1)} = 8c_p c_a \langle palpa \rangle \quad (61)$$

Taking elements of the matrices  $(\mathbf{M}^\pm)^{(1)}$  as perturbations and employing the linear response equations, eq 47, results in the following expressions for the elements of the first-order perturbation to  $\mathbf{Y}'_n$  vectors:

$$\forall_{a \geq b} (Y'_{\nu_+})_{ab}^{(1)} = \sum_{\mu_+} (Y'_{\mu_+})_{ab}^{(0)} \sum_{\substack{c \geq d \\ r \geq s}} (Y'_{\mu_+})_{cd}^{(0)} (M^-)_{cdrs}^{(1)} (Y'_{\nu_+})_{rs}^{(0)} \times \left[ \frac{1}{\omega_{\nu_+} - \omega_{\mu_+}} - \frac{1}{\omega_{\nu_+} + \omega_{\mu_+}} \right] \quad (62)$$

and

Equation 53 implies that only  $(Y'_n)_{pq}$  and  $(Y'_n)_{ab}$  elements are needed [as expected, charge transfer elements  $(Y'_n)_{pa}$  do not contribute]. To find them, notice that the eigenproblem 48 splits into two separate eigenproblems. One of them involves the  $pq$  and  $ab$  components whereas the other only the  $ap$  and  $pa$  elements. The former problem is of interest and it reads

$$\mathbf{M}' \begin{pmatrix} (Y'_n)_{pq} \\ (Y'_n)_{ab} \\ (X'_n)_{pq} \\ (X'_n)_{ab} \end{pmatrix} = \omega_n \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} (Y'_n)_{pq} \\ (Y'_n)_{ab} \\ (X'_n)_{pq} \\ (X'_n)_{ab} \end{pmatrix} \quad (56)$$

where

$$\forall_{p \geq q} (Y'_{\mu_+})_{pq}^{(1)} = \sum_{\nu_+} (Y'_{\nu_+})_{pq}^{(0)} \sum_{\substack{r \geq s \\ c \geq d}} (Y'_{\nu_+})_{rs}^{(0)} (M^-)_{rscd}^{(1)} (Y'_{\mu_+})_{cd}^{(0)} \times \left[ \frac{1}{\omega_{\mu_+} - \omega_{\nu_+}} - \frac{1}{\omega_{\mu_+} + \omega_{\nu_+}} \right] \quad (63)$$

It has been exploited that  $\nu_+$  corresponds to excitations that in the limit  $R \rightarrow \infty$  are localized on the subsystem I; thus,  $(Y'_{\nu_+})_{cd}^{(0)} = 0$  [analogously  $\mu_+$  excitations are localized on II; therefore,  $(Y'_{\mu_+})_{rs}^{(0)} = 0$ ]. Multiplying eq 62 by  $(Y'_{\nu_+})_{pq}^{(0)}$  and taking a sum with respect to  $\nu_+$ , similarly eq 63 is multiplied by  $(Y'_{\mu_+})_{ab}^{(0)}$  and summed up with respect to  $\mu_+$ , and exploiting the symmetry  $\forall_{r \geq s} (M^-)_{rscd}^{(1)} = (M^-)_{cdsr}^{(1)}$  lead to

$$\forall_{p \geq q} \sum_{\nu_+} (Y'_{\nu_+})_{pq}^{(0)} (Y'_{\nu_+})_{ab}^{(1)} + \sum_{\mu_+} (Y'_{\mu_+})_{pq}^{(1)} (Y'_{\mu_+})_{ab}^{(0)} = -2 \sum_{\nu_+, \mu_+} \frac{\sum_{\substack{c \geq d \\ r \geq s}} (Y'_{\mu_+})_{cd}^{(0)} (M^-)_{rscd}^{(1)} (Y'_{\nu_+})_{rs}^{(0)}}{\omega_{\nu_+} + \omega_{\mu_+}} (Y'_{\nu_+})_{pq}^{(0)} (Y'_{\mu_+})_{ab}^{(0)} \quad (64)$$

Taking into account eqs 58–61 and the relations

$$\forall_{p>q} (Y'_{\nu_+})_{pq}^{(0)} (c_p + c_q) = (T_{\nu_+})_{pq} + (T_{\nu_+})_{qp} \quad (65)$$

$$\forall_p 2^{1/2} (Y'_{\nu_+})_{pp}^{(0)} c_p = (T_{\nu_+})_{pp} \quad (66)$$

[analogously for  $(Y'_{\mu_+})_{ab}^{(0)}$ ] that result from eqs 36, 37, and 45, one obtains

$$\begin{aligned} \forall_{p \geq q} \sum_{a \geq b} (Y'_{\nu_a})_{pq}^{(0)} (Y'_{\nu_a})_{ab}^{(1)} + \sum_{\mu_a} (Y'_{\mu_a})_{pq}^{(1)} (Y'_{\mu_a})_{ab}^{(0)} \\ = -2 \sum_{\nu_a, \mu_a} \frac{4 \sum_{rs} \sum_{cd} (T_{\nu_a})_{rs} (T_{\mu_a})_{cd} \langle rclsd \rangle}{\omega_{\nu_a} + \omega_{\mu_a}} (Y'_{\nu_a})_{pq}^{(0)} (Y'_{\mu_a})_{ab}^{(0)} \end{aligned} \quad (67)$$

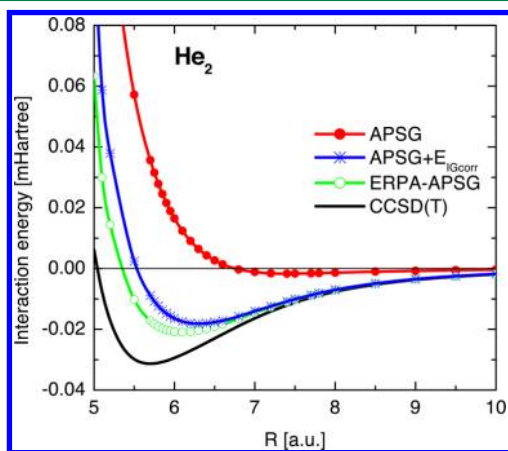
Equation 67 together with eqs 54 and 55 finally leads to expressing the correlation interaction energy in terms of the transition density matrix elements of the isolated subsystems as

$$E_{\text{IGcorr}} = - \sum_{\nu_a, \mu_a} \frac{[4 \sum_{pq} \sum_{ab} (T_{\nu_a})_{pq} (T_{\mu_a})_{ab} \langle palqb \rangle]^2}{\omega_{\nu_a} + \omega_{\mu_a}} \quad (68)$$

One can see immediately that the obtained asymptotic expression for  $E_{\text{IGcorr}}$  coincides with the second-order dispersion interaction energy<sup>26</sup>

$$E_{\text{disp}}^{(2)} = - \sum_{\nu_a, \mu_a} \frac{|\langle \Psi_0^I \Psi_0^II | \hat{V}_{\text{int}} | \Psi_{\nu_a}^I \Psi_{\mu_a}^II \rangle|^2}{(E_{\nu_a}^I - E_0^I) + (E_{\mu_a}^II - E_0^II)} \quad (69)$$

[ $\hat{V}_{\text{int}}$  is the interaction potential between the subsystems] if the latter is written in terms of the elements of  $\mathbf{T}$  for isolated systems in a basis set of orbitals localized on monomers. The multipole expansion for  $E_{\text{IGcorr}}$  would therefore show correct powers of  $R$  and the accuracy of the  $C_n$  coefficients would be determined by the quality of the transition density matrix elements and excitation energies obtained from TD-APSG equations for isolated subsystems. Let us consider a helium dimer consisting of two geminals (localized on He atoms). Because the APSG functional lacks intergeminal correlation, it is unable to capture dispersion interaction energy and the interaction energy curve, Figure 1, is not binding. The



**Figure 1.** Interaction energy curves for the helium dimer in the aug-cc-pVTZ basis set. Unmarked line: CCSD(T). Closed circles: APSG. Asterisks: APSG+ $E_{\text{IGcorr}}$  [cf. eq 38]. Open circles: ERPA-APSG [cf. eq 42].

intergeminal correlation functional defined in eq 42 includes dispersion and for large separation  $R$  reduces to the correct interaction energy expression given in 68. Moreover, because APSG and TD-APSG approaches yield exact ground state properties and excitation energies for the helium atom, the ERPA-APSG energy shows exact asymptotic behavior visible in Figure 1.

#### 4. PERFORMANCE OF THE INTERGEMINAL CORRELATION CORRECTION

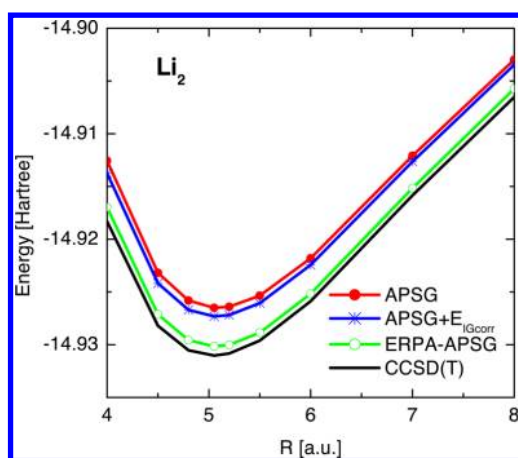
In this section we show that adding the intergeminal correlation energy to the APSG functional as proposed in eq 42 accounts for short- and long-range dynamical correlation energy that greatly improves the APSG performance in describing molecules around equilibrium geometry and when bonds are significantly elongated. The proposed method is also superior in reproducing the interaction energy of weakly interacting systems. Computing the correction follows minimization of the APSG functional, eq 5, which yields optimal APSG orbitals  $\{\varphi_p(\mathbf{r})\}$ , expansion coefficients  $\{c_p\}$ , and optimal partitioning of the set of the APSG orbitals into disjoint subsets forming geminals [cf. eq 2]. In the next step the TD-APSG or ERPA equations are solved [eq 34 or 23, respectively] and the eigenvectors corresponding to positive eigenvalues are employed to calculate the intergeminal correlation energy that is added to the APSG energy. As discussed in ref 10, TD-APSG or ERPA equations may yield spurious excitations that can be avoided by removing rows and columns of the main matrix corresponding to elements  $\tilde{X}_{pq}$  and  $\tilde{Y}_{pq}$  with the  $p, q$  indices such that  $n_p + n_q < 1 \times 10^{-3}$  or  $n_p + n_q > 1.50$ .

All results presented in this section have been obtained by solving the TD-APSG equations. However, we have also investigated how much the values of intergeminal correlation energy change if the ERPA eigenvectors are used. It turns out that in all cases differences do not exceed 1 [mHa]. The results are compared either with the coupled cluster results obtained with the dalton suite of programs<sup>27</sup> or with full configuration data (FCI) computed with the molpro package.<sup>28</sup>

First we compare the performance of the intergeminal correlation that takes into account only dispersion-like two-body geminal interactions introduced in eq 38 with the extended formula given in eq 42. The total energies resulting from the former approach are denoted as APSG+ $E_{\text{IGcorr}}$  and those obtained by means of the expression 42 as ERPA-APSG. As shown in section 3, both approximations reduce to the exact form of the dispersion energy if applied to weakly interacting subsystems at large separation  $R$ . Therefore, in the case of the helium dimer in the range of  $R$  where the interaction energy is mainly of dispersion type, the ERPA-APSG and APSG+ $E_{\text{IGcorr}}$  interaction energy curves should overlap and coincide with the exact result. Figure 1 presenting the curves for He<sub>2</sub> in the aug-cc-pVTZ basis set<sup>29</sup> confirms the predictions. It is apparent that, although ERPA-APSG includes other terms than dispersion-like, it brings only a small improvement over APSG+ $E_{\text{IGcorr}}$ , reducing the error of the binding energy with respect to the CCSD(T) value from 0.013 to 0.010 [mHa]. Nevertheless, the improvement over the APSG curve that completely lacks dispersion is striking.

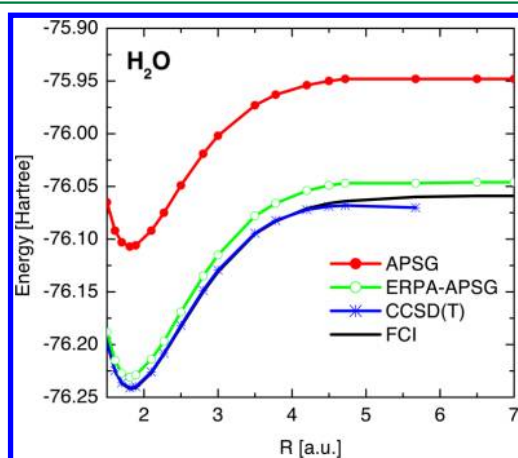
The picture obtained for the covalently bonded Li<sub>2</sub> molecule is quite different. The APSG+ $E_{\text{IGcorr}}$  potential energy curve for this molecule presented in the cc-pVDZ basis set<sup>29</sup> in Figure 2 is only slightly lower than the APSG counterpart, so it is evident that other than dispersion-like intergeminal interaction terms should be included. Such terms are included in the ERPA-APSG functional and the corresponding energy curve is now in an excellent agreement (within 1 [mHa] for the shown range of  $R$ ) with the CCSD(T) results.

Performance of the ERPA-APSG functional in describing 10-electron molecules, H<sub>2</sub>O and FH, around equilibrium geometries and when bonds are stretched is presented in Figures

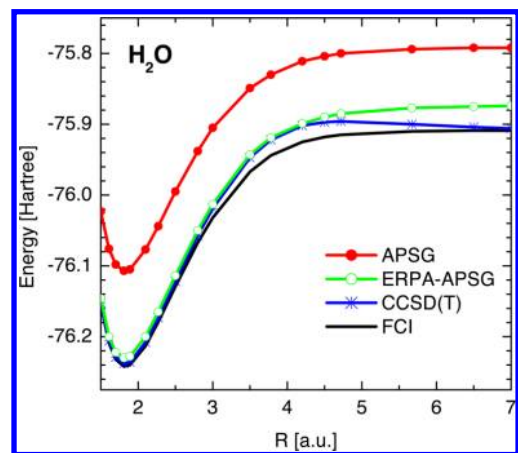


**Figure 2.** Potential energy curves for the  $\text{Li}_2$  molecule in the cc-pVTZ basis set. Unmarked line: CCSD(T). Closed circles: APSG. Asterisks: APSG+E<sub>1Gcorr</sub> [cf. eq 38]. Open circles: ERPA-APSG [cf. eq 42].

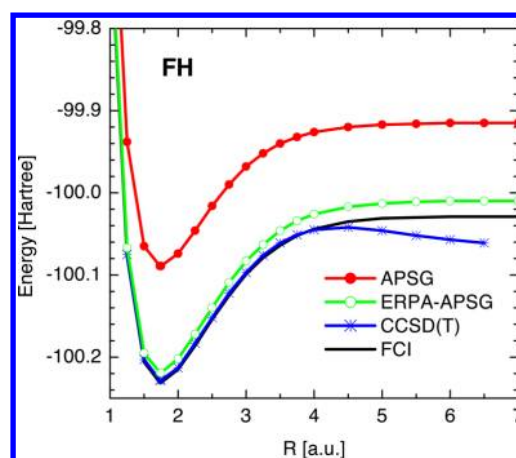
3–5. In the case of water both asymmetric and symmetric dissociation curves have been computed. Calculations have



**Figure 3.** Water asymmetric dissociation in the cc-pVDZ basis set. Unmarked line: FCI. Closed circles: APSG. Open circles: ERPA-APSG [cf. eq 42]. Asterisks: CCSD(T).



**Figure 4.** Water symmetric dissociation in the cc-pVDZ basis set. Unmarked line: FCI. Closed circles: APSG. Open circles: ERPA-APSG [cf. eq 42]. Asterisks: CCSD(T).



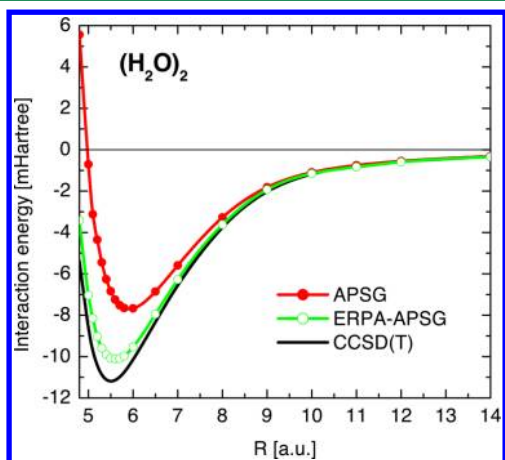
**Figure 5.** Hydrogen fluoride dissociation in the cc-pVDZ basis set. Unmarked line: FCI. Closed circles: APSG. Open circles: ERPA-APSG [cf. eq 42]. Asterisks: CCSD(T).

been performed in the cc-pVDZ basis set<sup>29</sup> and FCI energies are employed as a reference. For comparison we have also included CCSD(T) results in the figures. In all investigated cases, ERPA-APSG provides excellent improvement to APSG energies in the whole range of interatomic distances yielding curves that preserve qualitatively correct shapes of the APSG but are lowered and close to the FCI reference. For  $\text{H}_2\text{O}$  at equilibrium geometry ( $R_{\text{OH}} = 1.808$  a.u.,  $\angle_{\text{HOH}} = 104.5^\circ$ ) the percentage of the correlation energy recovered with APSG and ERPA-APSG increases from 37% to 95%, respectively, and for FH at  $R_{\text{eq}} = 1.733$  a.u. from 35% to 95%. For the water molecule, the errors of the total ERPA-APSG energies with respect to their FCI counterparts range from 0.010 [Ha] at a.u. geometry to 0.012 and 0.034 [Ha] obtained for  $R_{\text{OH}} = 7.000$  a.u. in the case of asymmetric and symmetric dissociation, respectively. For hydrogen fluoride the error increases from 0.009 [Ha] at  $R_{\text{eq}}$  to 0.019 [Ha] at  $R = 7.000$  a.u. Taking differences of energy values corresponding to equilibrium geometries and to geometries when pertinent bonds are stretched to  $R = 7.000$  a.u. provides estimates for dissociation energies  $D_e$ . Interestingly, in the case of asymmetric dissociation of water and dissociation of FH the values of  $D_e$  resulting from ERPA-APSG calculations are in a significantly better agreement with FCI than those of APSG. Namely,  $D_e$  resulting from employing FCI, ERPA-APSG, and APSG methods for asymmetric water dissociation read 0.183 [Ha], 0.184 [Ha], and 0.154 [Ha], respectively. In the case of the FH molecule the obtained dissociation energy values are 0.202 [Ha], 0.209 [Ha], and 0.174 [Ha] for, respectively, FCI, ERPA-APSG, and APSG approaches. Symmetric dissociation of water with the APSG or ERPA-APSG functional result in dissociation energies of similar accuracy. The respective values of  $D_e$  are 0.315 and 0.356 [Ha] to be compared with the FCI value amounting to 0.333 [Ha]. Taking into account the results obtained for  $\text{Li}_2$ ,  $\text{H}_2\text{O}$ , and FH molecules, one concludes that including intergeminal correction given in eq 42 results in adding short-range dynamical electron correlation in all geometries of molecules.

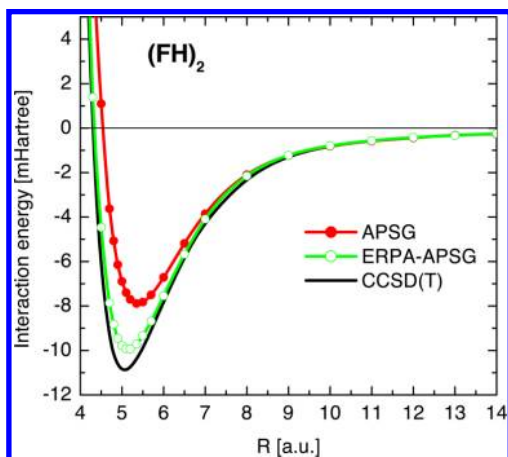
As has been discussed, the APSG approximation is incapable of accounting for dispersion interactions in weakly interacting systems that results in unbounded helium dimer. If the interaction energy includes contributions other than just dispersion, electrostatic interaction, for example, the APSG



interaction energy curve shows a minimum but it is usually too shallow. That is the case for water and hydrogen fluoride dimers whose interaction energy curves obtained in the cc-pVDZ basis are presented in Figures 6 and 7, respectively.



**Figure 6.** Interaction energy curves for water dimer in cc-pVDZ basis set. Unmarked line: CCSD(T). Closed circles: APSG. Open circles: ERPA-APSG [cf. eq 42].



**Figure 7.** Interaction energy curves for hydrogen fluoride dimer in cc-pVDZ basis set. Unmarked line: CCSD(T). Closed circles: APSG. Open circles: ERPA-APSG [cf. eq 42].

Geometries of monomers and their mutual orientations are taken from ref 30, and  $R$  denotes a distance between centers of mass of monomers. The APSG binding energies compared to their CCSD(T) counterparts suffer from rather large errors amounting to 4.4 and 3.0 [mHa] for, respectively,  $\text{H}_2\text{O}$  and  $\text{FH}$  dimers. Adding the intergeminal correlation energy, i.e., employing eq 42, reduces the errors to 1.1 and 1.0 [mHa]. The improvement is attributed mainly to adding a dispersion component to the interaction energy by the intergeminal correction.

## 5. SUMMARY

In this paper we have proposed the intergeminal correlation correction that supplements the APSG energy with the missing dynamical correlation. The correction is based on the fluctuation–dissipation theorem derived for geminals, and it is expressed in terms of the transition density matrix elements that are provided by solving either the ERPA or TD-APSG

equations, eqs 23 and 58, respectively. The method proposed in the manuscript is named ERPA-APSG without distinguishing if the response properties needed to compute the correction originate from ERPA or TD-APSG equations, because pertinent values of corrected energies are the same within 1 [mHa]. The final total energy expression presented in eq 42 being a sum of the APSG energy and the intergeminal correlation energy possesses a number of highly desirable features: (1) it remains exact for singlet two-electron systems (the intergeminal interaction term simply vanishes in this case), (2) for weakly interacting systems the resulting interaction energy reduces asymptotically to the second-order dispersion energy expression, (3) it provides asymptotically exact interaction energy for the helium dimer, and (4) it preserves size consistency of the APSG approach. Consequently, ERPA-APSG yields correct dissociation curves closely matching those of the FCI and it significantly improves the APSG description of noncovalently bonded systems providing binding curves for van der Waals complexes and deepening interaction energy minima of hydrogen-bonded dimers.

The computational scheme leading to obtaining the intergeminal correlation energy is simple and robust amounting to solving either the TD-APSG or the ERPA equations. This step determines the overall computation cost of the proposed method. As has been discussed, both approaches lead to practically the same values of the correlation energy. A direct implementation of the ERPA equations leads to an eigenproblem for a matrix the dimension of which is  $[M(M-1)/2] \times [M(M-1)/2]$ , where  $M$  is the number of basis set functions. The dimensionality of the problem can be safely scaled down, bringing it close to that of a straightforward implementation of RPA methods by retaining in the main matrix only rows and columns corresponding to elements  $\tilde{X}_{pq}$  and  $\tilde{Y}_{pq}$  with the  $p, q$  indices orbitals such that  $q = 1, \dots, N/2 + 1$  and  $p > N/2 \wedge p > q$  (assuming that orbitals are in a descending order with respect to their occupancies and  $N$  stands for a number of electrons). Thus,  $q$  would run through indices of the strongly occupied orbitals plus a bonding orbital (if  $n$  bonds are simultaneously broken than  $q_{\max} = N/2 + n$ ), whereas  $p$  are indices of weakly occupied orbitals. We have checked that the resulting truncation of the EPRA matrix affects the values of total energy by no more than 1 [mHa]. Work on further improvement of efficiency of the proposed method is in progress.

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### Notes

The authors declare no competing financial interest.

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