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A non-JKL density matrix functional for intergeminal correlation between closed-shell geminals from analysis of natural orbital configuration interaction expansions

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Almost all functionals that are currently used in density matrix functional theory have been created by some *a priori* ansatz that generates approximations to the second-order reduced density matrix (2RDM). In this paper, a more consistent approach is used: we analyze the 2RDMs (in the natural orbital basis) of rather accurate multi-reference configuration interaction expansions for several small molecules (CH_4, NH_3, H_2O, FH, and N_2) and use the knowledge gained to generate new functionals. The analysis shows that a geminal-like structure is present in the 2RDMs, even though no geminal theory has been applied from the onset. It is also shown that the leading non-geminal dynamical correlation contributions are generated by a specific set of double excitations. The corresponding determinants give rise to non-JKL (non Coulomb/Exchange like) multipole-multipole dispersive attractive terms between geminals. Due to the proximity of the geminals, these dispersion terms are large and cannot be omitted, proving pure JKL functionals to be essentially deficient. A second correction emerges from the observation that the "normal" geminal-like exchange between geminals breaks down when one breaks multiple bonds. This problem can be fixed by doubling the exchange between bond broken geminals, effectively restoring the often physically correct high-spin configurations on the bond broken fragments. Both of these corrections have been added to the commonly used antisymmetrized product of strongly orthogonal geminals functional. The resulting non-JKL functional Extended Löwdin-Shull Dynamical-Multibond is capable of reproducing complete active space self-consistent field curves, in which one active orbital is used for each valence electron. *Published by AIP Publishing.* https://doi.org/10.1063/1.5018671

I. INTRODUCTION

A key quantity of many-electron theory is the second-order reduced density matrix (2RDM) $\Gamma(x_1, x_2; x_1', x_2')$,

$$\Gamma(x_1, x_2; x_1', x_2') = N(N-1) \int \Psi(x_1, x_2, x_3, \ldots, x_N)$$
$$\times \Psi^*(x_1', x_2', x_3, \ldots, x_N) dx_3 \ldots dx_N, \quad (1)$$

which determines the electronic energy E_e,

$$E_e = T + V + W = -\frac{1}{2} \int \nabla_{r'}^2 \gamma(x, x')|_{x'=x} dx$$
$$+ \int v_{ext}(r)\rho(x)dx + \frac{1}{2} \int \frac{\Gamma(x_1, x_2)}{r_{12}} dx_1 dx_2. \quad (2)$$

In (1), Ψ is the wave function of an N-electron system; in (2), the electron-electron interaction energy W is expressed through the diagonal part of the 2RDM, the pair density $\Gamma(x_1, x_2)$ (x stands for both spatial r and spin s coordinates). In its turn, the kinetic energy T is expressed through the 1RDM $\gamma(x, x')$, the integral of the 2RDM

$$\gamma(x_1, x_1') = \frac{1}{N-1} \int \Gamma(x_1, x_2; x_1', x_2')|_{x_2'=x_2} dx_2, \quad (3)$$

while the electron-nuclear energy V is calculated with the electron density $\rho(x)$, the diagonal part of $\gamma(x, x')$. Then, the analysis of the 2RDMs and their contributions to E_e obtained

from highly correlated wave functions of prototype systems is of importance for the conceptual description of the electronic structure as well as for the development and assessment of various approximate approaches.

A useful way to analyze and describe electron correlation is based on the expansion of the 2RDM in terms of the natural orbitals (NOs) ϕ_i inserted in the expression for W,

$$W = \frac{1}{2} \sum_{ijkl} \Gamma_{ijkl}(ij|kl). \quad (4)$$

The NOs are the eigenfunctions of the 1RDM with the occupation numbers (ONs) ($0 \le n_i \le 1$) as the eigenvalues

$$\gamma(r, r') = \sum_i 2n_i \phi_i(r) \phi_i^*(r'), \quad (5)$$

and these orbitals are especially suitable for the description of electron correlation (see Sec. III).

The expansion (4) obtained from highly correlated wave functions can serve as an important benchmark for density matrix functional theory (DMFT),[1–17] in which the matrix elements Γ_{ijkl} are approximated as functions F of the ONs

$$W^{DMFT}[\{\phi\}, \{n\}] = \sum_{ijkl} F_{ijkl}(\{n\})(ij|kl). \quad (6)$$

The DMFT development mainly draws its inspiration from W obtained with certain simple types of wave functions, the

most important 2RDM matrix elements Γ_{ijkl} of which can be explicitly expressed through the ONs. Other sources for the functionals include 2RDM inequality restrictions, modeling of the exchange-correlation hole, and simple tensor expansions.[4,6,18] In all cases, one uses some kind of ansatz in order to produce a closed form for the functional. Current DMFT functionals in the literature belong almost exclusively to the *JKL* (non Coulomb/Exchange like)-only type,[15,19]

$$W^{JKL}[\{\phi\}, \{n\}] = 2\sum_{kl} F_J(n_k, n_l)J_{kl} + \sum_{kl} F_K(n_k, n_l)K_{kl} + \sum_{kl} F_L(n_k, n_l)L_{kl}, \tag{7}$$

i.e., only the well-known *J* and *K* types of two-electron integrals,

$$J_{kl} = \int \frac{\phi_k(\boldsymbol{r}_1)\phi_k^*(\boldsymbol{r}_1)\phi_l(\boldsymbol{r}_2)\phi_l^*(\boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}d\boldsymbol{r}_1 d\boldsymbol{r}_2 = (kk|ll), \tag{8}$$

$$K_{kl} = \int \frac{\phi_k(\boldsymbol{r}_1)\phi_l^*(\boldsymbol{r}_1)\phi_l(\boldsymbol{r}_2)\phi_k^*(\boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}d\boldsymbol{r}_1 d\boldsymbol{r}_2 = (kl|lk), \tag{9}$$

and also the so-called *L* integrals,

$$L_{kl} = \int \frac{\phi_k(\boldsymbol{r}_1)\phi_l^*(\boldsymbol{r}_1)\phi_k(\boldsymbol{r}_2)\phi_l^*(\boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}d\boldsymbol{r}_1 d\boldsymbol{r}_2 = (kl|kl), \tag{10}$$

enter the expression (7) for $W^{JKL}[\{\phi\}, \{n\}]$. The most general type of configuration interaction (CI) wave function that only contains these types of two electron integrals in its energy expression is the so-called doubly occupied CI (DOCI) wave function Ψ^{DOCI},[20–24]

$$\Psi^{DOCI} = c_0\Phi_0 + \sum_i\sum_a c_{ii}^{a\bar{a}}\Phi_{ii}^{a\bar{a}} + \sum_{i,j(\neq i)}\sum_{a,b(\neq a)} c_{iijj}^{a\bar{a}b\bar{b}}\Phi_{iijj}^{a\bar{a}b\bar{b}} + \cdots. \tag{11}$$

For this particular wave function, the diagonal 2RDM elements can be directly expressed in terms of the ONs ($F_J(n_k, n_k)$ $= n_k$).[25] However, there is no closed expression for the other 2RDM elements. This leads us to a wave function based on a geminal approach,[24,26–29] in which all 2RDM elements can be expressed in terms of the ONs. The so-called antisymmetrized product of strongly orthogonal geminals (APSG) wave function is by definition a subset of the DOCI wave function. While DOCI places no restrictions on which orbitals can be doubly occupied in the same determinant, APSG only allows for a single doubly occupied orbital from each geminal set in each determinant when one uses the NO basis. The APSG wave function is expressed as follows:

$$\Psi^{APSG}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N) = \hat{A}\prod_{g=1}^{\frac{N}{2}} \psi_g^{LS}(\boldsymbol{x}_{2g-1}, \boldsymbol{x}_{2g}). \tag{12}$$

It employs the two-electron wave functions ψ_g^{LS} of the Löwdin and Shull (LS)[1] type, the CI coefficients of which are expressed through the ONs

$$\psi_g^{LS}(\boldsymbol{x}_1, \boldsymbol{x}_2) = \sqrt{n_i}|\phi_i(\boldsymbol{x}_1)\bar{\phi}_i(\boldsymbol{x}_2)| - \sum_{a\in S_g} \sqrt{n_a}|\phi_a(\boldsymbol{x}_1)\bar{\phi}_a(\boldsymbol{x}_2)|, \quad i\in S_g, \tag{13}$$

of the NOs assigned to the geminal ψ_g^{LS}. In (13), which is a paradigmatic case in DMFT, ϕ_i is the strongly occupied NO ($i \leq N/2$, $n_i > 0.5$), which specifies the geminal, while the

weakly occupied NOs ϕ_a ($a \geq N/2$, $n_a < 0.5$) belong, together with ϕ_i, to the subset S_g of the NOs assigned to the geminal ψ_g^{LS}. Note that the usual empirical convention of fixing the $+$ and $-$ signs of the coefficients has been used. The ONs within each geminal set sum up to two electrons. The energy W^{APSG} of Ψ^{APSG},

$$W^{APSG}[\{\phi\}, \{n\}] = \sum_g^{\frac{N}{2}} W_g^{LS}[\{\phi\}, \{n\}] + \sum_{g<h}^{\frac{N}{2}} W_{gh}^{HF}[\{\phi\}, \{n\}], \tag{14}$$

is naturally subdivided into the intrageminal LS type

$$W_g^{LS}[\{\phi\}, \{n\}] = \sum_{j\in S_g} n_j J_{jj} - 2\sum_{a\in S_g} \sqrt{n_i n_a}L_{ia} + \sum_{(a,b\neq a)\in S_g} \sqrt{n_a n_b}L_{ab}, \quad i\in S_g \tag{15}$$

and intergeminal Hartree-Fock (HF) type

$$W_{gh}^{HF} = 4\sum_{p\in S_g}\sum_{q\in S_h} n_p n_q[J_{pq} - \frac{1}{2}K_{pq}] \tag{16}$$

contributions. One of the most challenging aspects of this functional in practical calculations is the subdivision of the available space of one-electron functions (NOs in this case) into disjoint sets belonging to the geminals. It is usually easy to pair a single weakly occupied orbital NO ϕ_a to a strongly occupied NO; however, adding more orbitals to the sets is often ambiguous and computationally inefficient.[27,30] So most functionals employed in the field put heavy restrictions on the number of orbitals in the sets. In the aforementioned simplest case of the perfect pairs (PPs), S_g contains just a single weakly occupied NO. Piris' NO functional PNOF5[31] is identical to this simplest PP case of the APSG functional.[32] Unfortunately, even APSG's bigger brother DOCI, which does not have any set restrictions at all, is often only able to describe 20%-35% of the dynamical correlation energy (see Sec. III and Refs. 24, 33, and 34). So the APSG ansatz needs to be augmented. To this effect, different types of perturbative treatment have been proposed in the literature. These include the direct application of the perturbation theory,[35–38] the approach based on the fluctuation-dissipation theorem,[16,39] and the addition of the correction terms developed within the coupled cluster (CC) theory.[40,41] Non-perturbative treatments include the PNOF6 and PNOF7 functionals and the extended Löwdin-Shull (ELS) series of functionals.[15,17,42] Note that all of these functionals are still strictly JKL only. The PNOF6 functional generates small improvements over the PNOF5 functional, while the PNOF7 functional incorporates a multibond correction, like the one that will be described below. The ELS series of functionals were developed for quasi-two-electron systems and will not work for generic many-electron systems without modifications. One could in principle try to modify the functionals using techniques that were used in the generation of the original functionals and optimize them to obtain the desired results.

In this paper, we follow a different route. A definitive assessment of how to further develop intergeminal correlation within a nonperturbative DMFT framework can be based on the analysis of the energy expansion (4) obtained from near full-CI wave functions for prototype molecules. This analysis

will reveal to which extent the leading terms of the expansion (4) resemble those for the simple wave functions, such as (11) and (12). Then, the important terms which are present in the accurate expansion (4), but are missing in the simplified expressions, will show the way for improvement of the approximate approaches.

In this paper, the benchmark 2RDM energy expansion (4) is obtained with a high quality multi-reference CI with single, double, triple, and quadruple excitations (MR-CISDTQ) for the prototype series of the 10-electron molecules CH_4, NH_3, H_2O, and HF with single bonds as well as for the N_2 molecule with a triple bond. Computational details are given in Sec. II. It is shown in Sec. III that the MR-CISDTQ 2RDM energy expansion contains (without it having been imposed) the basic geminal structure with each PP characterized by a bonding/stabilizing NO ϕ_i and an antibonding/destabilizing NO ϕ_a. The leading non-APSG terms of the obtained expansion represent attractive intergeminal interactions of dispersion type, well known from van der Waals interactions: double excitations consisting of single intrageminal excitations $\phi_i \rightarrow \phi_a$ on geminal A and $\phi_j \rightarrow \phi_b$ on geminal B. These terms provide the description of dynamical correlation of electrons of different closed shells (geminals), and they give rise to dispersive multipole-multipole non-*JKL* terms. Due to the proximity of the geminals, these dispersion energies are large and generate roughly half of the PP space dynamical correlation at equilibrium distance. This proves that it is imperative to augment the JKL functionals with these non-JKL terms in order to obtain a correct description of intergeminal dynamical correlation.

A different correction that is essential to obtain proper dissociation of double or triple bonds emerges from the analysis of the 2RDM of N_2 at the dissociation limit. Additional non-JKL elements surface that use 2 orbitals from each of the bond broken geminals. Upon closer inspection, it is clear that these terms effectively double the local exchange at each atom in order to have the physically correct local high spin configuration. This correction has a size of roughly 0.105 hartree, making it mandatory for most multibond dissociation descriptions. In Sec. IV, a new functional that includes both of these corrections is proposed. Calculations show that it is capable of reproducing Complete Active Space Self Consistent Field (CASSCF) calculations, in which the active space contains as many orbitals as there are valence electrons. In Sec. V, the conclusions are drawn.

II. COMPUTATIONAL DETAILS

All wave function calculations have been performed using the 2012 version of the GAMESS-US program,[43] while all DMFT calculations have been performed with our homebrew DMFT program using the GAMESS-US data files as input. The (Cartesian) aug-cc-pVDZ basis has been used for all calculations (9 functions for H and 25 functions for the 2nd row elements), unless specified otherwise. This basis is far from being complete, but it is good enough considering the fact that the main calculations of interest in this paper only use a very small active space. The visualizations were generated with the wxmacmolplt program.[44] All calculations presented

use natural orbitals (generated by other accurate calculations) as starting orbitals, and the core orbitals are kept at full occupancy in all calculations. The APSG-PP calculations are APSG calculations, in which each geminal consists of a perfect pair (PP) of 2 orbitals. All CASSCF, DOCI, and APSG calculations are used in conjunction with orbital optimization (full orbital Hessian). We have performed calculations on the CH_4, NH_3, H_2O, HF, and N_2 molecules. The results of the MR-CI calculations for the 10-electron molecules CH_4, NH_3, H_2O, and HF with single bonds display the same qualitative trends; as a result, we will only present the analysis data for the H_2O and N_2 molecules in Sec. III. The dissociation curves are displayed for all of these molecules in Sec. IV.

III. ANALYSIS OF THE 2RDM ELEMENTS

In this section, the analysis results for the H_2O and N_2 molecules will be presented for both the equilibrium distance and the dissociation limit (defined as the geometry in which the broken bond has 3 times the equilibrium bond distance). We will look at the 2RDM elements in the NO basis (generated by MR-CI calculations) and at the effect on the total energy of restricting the expansion space of determinants. We will begin with the latter since this gives us a lot of insight into the limitations of the APSG and DOCI methods.

A. Analysis of the (correlation) energies obtained with various CI expansions

The energies and natural occupation numbers of the selected systems are shown in Tables I–IV. The correlation energy of the MR-CI calculations using all orbitals in the basis set (it still uses a frozen core occupation, as for all calculations in this paper) is defined as 100% of the correlation. This is of course not completely correct since it is not a full-CI calculation. However, it should contain (95+%) of the full-CI correlation energy,[45] which is adequate for our intents and purposes. The equilibrium H_2O results show that one can apply a heavy truncation of the active space and still obtain high percentage of correlation. One can even obtain 50+% of the correlation by using a perfect pair like active space for the CASSCF calculations [CASSCF(8,8) for H_2O and CASSCF(10,10) for N_2]. At the same time it is quite clear that the DOCI wave function is only capable of producing 28% when using the same PP active space, only being able to gain an additional 11% when 19 additional orbitals are added to the active space, with the first 5 added generating the majority of the extra correlation. In both cases, the amount of charge flowing to the "virtual" orbitals for the APSG and PP expansions is just half of the charge that flows in case of the properly correlated CI expansions. The APSG-PP result is very similar to the DOCI-PP result, indicating that the additional non-geminal like terms in DOCI are not important for this system. The equilibrium results for the N_2 molecule paint a similar picture: DOCI, and by extension APSG, is not able to describe the majority of the dynamical correlation. The results for the (single) bond broken H_2O geometry show that a CASSCF(2,2) calculation can obtain 50% of the total correlation. This correlation can be considered as being fully non-dynamical, so the other 50% represents dynamical correlation. According to this principle, the

TABLE I. Energies (hartree) of H_2O at equilibrium distance and natural occupations for various active spaces. Hartree-Fock energy: −76.041 95. Occupation numbers are for orbitals (summed over spin orbitals). Only the largest occupations are shown. The last 3 rows show the summed occupations of subsets of weakly occupied NOs, i.e., the charge that is transferred from the highly occupied orbitals due to correlation.

Method	MR-CISDTQ	MR-CISDTQ	MR-CISDTQ	MR-CISDTQ	CASSCF(8,8)	DOCI	DOCI	APSG-PP
Active orbs	2-43	2-28	2-14	2-9	2-9	2-28	2-9	2-9
Energy	−76.2775	−76.2756	−76.2397	−76.1656	−76.1699	−76.1343	−76.1085	−76.1072
Correlation (%)	100.0	99.2	84.0	52.5	54.3	39.2	28.3	27.7
1	2	2	2	2	2	2	2	2
2	1.9816	1.9817	1.9845	1.9886	1.9877	1.9897	1.9909	1.9912
3	1.9621	1.9624	1.9664	1.9768	1.9777	1.9882	1.9909	1.9912
4	1.9585	1.9589	1.9641	1.9734	1.9757	1.9803	1.9823	1.9824
5	1.9584	1.9585	1.9639	1.9733	1.9750	1.9800	1.9823	1.9824
6	0.0300	0.0300	0.0284	0.0268	0.0249	0.0169	0.0181	0.0176
7	0.0280	0.0280	0.0267	0.0259	0.0244	0.0168	0.0181	0.0176
8	0.0228	0.0227	0.0220	0.0222	0.0216	0.0090	0.0087	0.0088
9	0.0143	0.0142	0.0131	0.0130	0.0130	0.0080	0.0087	0.0088
10	0.0074	0.0074	0.0066			0.0017		
11	0.0070	0.0070	0.0064			0.0017		
12	0.0069	0.0069	0.0063			0.0016		
13	0.0061	0.0061	0.0058			0.0016		
14	0.0061	0.0060	0.0057			0.0016		
15	0.0014	0.0013				0.0013		
Δ6-9	0.0950	0.0949	0.0902	0.0879	0.0839	0.0507	0.0536	0.0528
Δ10-14	0.0335	0.0334	0.0309			0.0082		
Δ15+	0.0109	0.0102				0.0029		

CASSCF(8,8) wave function generates 40% of the dynamical correlation (70% of the total correlation), the APSG-PP generates 24%, and the DOCI is only able to increase this up to 34% when it uses a larger active space. So the same picture is still correct in the dissociation limit as well. The bond broken N_2 structure shows a very unexpected result. The CASSCF(6,6)

TABLE II. Energies (hartree) for H_2O with a single bond broken ($R = 3R_e$) and natural occupations for various active spaces. Hartree-Fock energy: −75.707 51. Occupation numbers are for orbitals (summed over spin orbitals). Only the largest occupations are shown. The last 3 rows show the summed occupations of subsets of weakly occupied NOs, i.e., the charge that is transferred from the highly occupied orbitals due to correlation.

Method	MR-CISDTQ	MR-CISDTQ	MR-CISDTQ	CASSCF(2,2)	CASSCF(8,8)	CASSCF(8,9)	DOCI	DOCI	APSG-PP
Active orbs	2-43	2-15	2-9	5-6	2-9	2-10	2-28	2-9	2-9
Energy	−76.0887	−76.0659	−75.9771	−75.9007	−75.9788	−76.0000	−75.9646	−75.9448	−75.9441
Correlation (%)	100.0	94.0	70.7	50.7	71.2	76.7	67.4	62.2	62.1
1	2	2	2	2	2	2	2	2	2
2	1.9781	1.9800	1.9899	2.0000	1.9899	1.9876	1.9908	1.9925	1.9926
3	1.9646	1.9684	1.9801	2.0000	1.9807	1.9794	1.9901	1.9925	1.9926
4	1.9588	1.9638	1.9734	2.0000	1.9747	1.9740	1.9791	1.9817	1.9818
5	1.1814	1.1733	1.1812	1.1538	1.1795	1.1721	1.1581	1.1558	1.1535
6	0.8109	0.8200	0.8189	0.8462	0.8206	0.8218	0.8419	0.8443	0.8465
7	0.0301	0.0288	0.0271		0.0258	0.0261	0.0176	0.0187	0.0182
8	0.0212	0.0205	0.0193		0.0188	0.0199	0.0073	0.0073	0.0074
9	0.0117	0.0108	0.0101		0.0101	0.0110	0.0068	0.0073	0.0074
10	0.0088	0.0084				0.0081	0.0018		
11	0.0060	0.0055					0.0017		
12	0.0059	0.0055					0.0013		
13	0.0053	0.0052					0.0010		
14	0.0052	0.0052					0.0009		
15	0.0048	0.0046					0.0007		
16	0.0012						0.0002		
Δ6-9	0.8739	0.8801	0.8754	0.8462	0.8753	0.8788	0.8736	0.8776	0.8795
Δ10-15	0.0360	0.0344				0.0081	0.0074		
Δ16+	0.0072						0.0002		

TABLE III. Energies (hartree) of N_2 at equilibrium distance and natural occupations for various active spaces. Hartree-Fock energy: −108.961 10. Only the largest occupations are shown. The last 3 rows show the summed occupations of subsets of weakly occupied NOs, i.e., the charge that is transferred from the highly occupied orbitals due to correlation.

Method	MR-CISD	MR-CISD	MR-CISD	MR-CISD	CASSCF(10,10)	DOCI	DOCI	APSG-PP
Active orbs	3-50	3-24	3-19	3-12	3-12	3-24	3-12	3-12
Energy	−109.2980	−109.2776	−109.2398	−109.1430	−109.1447	−109.0819	−109.0599	−109.0511
Correlation (%)	100.0	93.9	82.7	54.0	54.5	35.8	29.3	26.7
1	2	2	2	2	2	2	2	2
2	2	2	2	2	2	2	2	2
3	1.9809	1.9819	1.9860	1.9900	1.9900	1.9953	1.9956	1.9957
4	1.9602	1.9622	1.9671	1.9786	1.9790	1.9864	1.9880	1.9933
5	1.9562	1.9581	1.9628	1.9771	1.9788	1.9864	1.9880	1.9933
6	1.9185	1.9222	1.9259	1.9401	1.9420	1.9405	1.9401	1.9373
7	1.9183	1.9220	1.9258	1.9400	1.9420	1.9405	1.9401	1.9373
8	0.0776	0.0757	0.0722	0.0668	0.0638	0.0612	0.0652	0.0627
9	0.0776	0.0757	0.0722	0.0668	0.0638	0.0612	0.0652	0.0627
10	0.0229	0.0225	0.0212	0.0204	0.0202	0.0065	0.0065	0.0067
11	0.0153	0.0145	0.0148	0.0128	0.0127	0.0065	0.0065	0.0067
12	0.0098	0.0093	0.0092	0.0074	0.0076	0.0038	0.0046	0.0043
13	0.0076	0.0074	0.0071			0.0019		
14	0.0072	0.0070	0.0068			0.0019		
15	0.0071	0.0069	0.0064			0.0014		
16	0.0067	0.0067	0.0063			0.0014		
17	0.0067	0.0067	0.0063			0.0012		
18	0.0054	0.0052	0.0049			0.0012		
19	0.0054	0.0052	0.0049			0.0006		
20	0.0023	0.0022				0.0006		
21	0.0023	0.0022				0.0006		
22	0.0022	0.0022				0.0006		
23	0.0022	0.0022				0.0002		
24	0.0019	0.0018				0.0002		
25	0.0012							
Δ8-12	0.2030	0.1977	0.1897	0.1741	0.1681	0.1392	0.1480	0.1431
Δ13-24	0.0569	0.0558	0.0427			0.0118		
Δ25+	0.0060							

calculation, which should account for all non-dynamical correlation, covers 81% of the total correlation energy, while the DOCI and APSG calculations are only able to obtain 71% of the correlation energy. So in addition to not being able to generate the majority of the dynamical correlation, they are also not able to generate all of the non-dynamical correlation for this system. As we will show in the N_2 2RDM analysis below, this discrepancy is caused by the incorrect description of exchange between the unpaired electrons on the (atomic) fragments.

B. Analysis of the 2RDM elements and the type of correlation they embody

We now proceed with the 2RDM analysis in order to gain some more understanding of the failures of DOCI/APSG. The total number of 2RDM elements scales quartically with the basis set size, so only a small selection can be shown here. Our initial analysis shows that a perfect pairing like geminal structure is present in the PP space of all of our selected molecules. In order to demonstrate this, and to show the most important deviation from pure geminals that is present in all of our systems, we show all 2RDM elements between 3 of

these perfect pairs in the H_2O equilibrium structure (Table V). In order to understand the physical relevance of some of the 2RDM elements, it is best to visualize the natural orbitals used in these geminals. The strongly occupied NOs ϕ_3, ϕ_4, and ϕ_5 (the NOs are ordered according to their decreasing occupations) and their associated lowly occupied orbitals are shown in Fig. 1. The ϕ_5 NO is the out of phase combination of bonding character in the regions of the individual O–H bonds, the ϕ_4 NO is the related axial combination, and NO ϕ_3 represents the lone pair of the π type. The corresponding lowly occupied orbitals located in the same spatial region as their highly occupied counterpart, only having more nodes, as is required in order to stay orthogonal and to have maximal intrageminal correlation (large L integrals). As already mentioned before, the geminal structure is easily visible. The intrageminal blocks basically just contain diagonal repulsion terms and the (attractive) dynamical correlation. The Coulomb interaction between orbitals in the same geminal set is nearly absent. This is one of the biggest indicators of geminal behavior since these terms can only be generated by determinants that contain both orbitals. Such determinants are completely absent in a proper APSG wave function. The intergeminal

TABLE IV. Energies (hartree) of N_2 after bond breaking ($R = 3R_e$) and natural occupations for various active spaces. Hartree-Fock energy: $-107.976\,88$. The occupation numbers are for orbitals (summed over spin orbitals). Only the largest occupations are shown. The last 3 rows show the summed occupations of subsets of weakly occupied NOs, i.e., the charge that is transferred from the highly occupied orbitals due to correlation.

Method	MR-CISD	MR-CISD	CASSCF(10,10)	CASSCF(6,6)	DOCI	APSG-PP
Active orbs	3-50	3-28	3-12	5-10	3-12	3-12
Energy	−108.9737	−108.9656	−108.8019	−108.7805	−108.6832	−108.6831
Correlation (%)	100.0	99.2	82.8	80.6	70.9	70.8
1	2	2	2	2	2	2
2	2	2	2	2	2	2
3	1.9658	1.9673	1.9943	2.0000	1.9982	1.9982
4	1.9640	1.9658	1.9941	2.0000	1.9982	1.9982
5	1.0835	1.0820	1.0780	1.0762	1.1413	1.1369
6	1.0114	1.0111	1.0146	1.0143	1.0268	1.0260
7	1.0114	1.0111	1.0146	1.0143	1.0268	1.0260
8	0.9768	0.9771	0.9854	0.9857	0.9732	0.9740
9	0.9768	0.9771	0.9854	0.9857	0.9732	0.9740
10	0.9049	0.9064	0.9222	0.9238	0.8588	0.8631
11	0.0125	0.0121	0.0060		0.0018	0.0018
12	0.0105	0.0102	0.0055		0.0018	0.0018
13	0.0062	0.0062				
Δ8-12	2.8815	2.8829	2.9045	2.8952	2.8088	2.8147
Δ13+	0.0824	0.0797				

blocks show both true geminal terms and a correlation correction. The normal APSG terms consist of the Coulomb repulsion and exchange interaction between the different geminals. The Coulomb/exchange ratio of the interactions between the highly occupied orbitals is very close to the closed shell APSG/HF value of 2. The interactions between lowly occupied orbitals only deviate a little bit from this ratio. The ratio has a much larger deviation in favor of the exchange interaction for highly occupied/lowly occupied combinations, indicating that some amount of intergeminal correlation is expressed through exchange integrals. Even though these exchange 2RDMs have an appreciable value, their integrals are very small, resulting in a diminutive contribution to the intergeminal correlation energy. The majority of the intergeminal correlation within the PP space is provided by a non-JKL 2RDM element (bold in Table V) whose integral is given by

$$D_{ia,jb} = \int \frac{\phi_i(\boldsymbol{r}_1)\phi_a^*(\boldsymbol{r}_1)\phi_j(\boldsymbol{r}_2)\phi_b^*(\boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} d\boldsymbol{r}_1 d\boldsymbol{r}_2, \ i,a \in S_g; \ j,b \in S_h.$$

(17)

So the orbitals within the same geminal are multiplied, effectively creating a multipolar charge distribution [a product of an orbital with itself only gives the density, multiplying different orbitals with a different nodal structure in the same spatial region (forced by orthogonality) generates areas of positive and negative charge]. These multipolar charge distributions interact with each other and generally lower the electron-electron interaction energy. This is very similar to how intrageminal correlation works when one uses the LS (NO basis) expansion of the geminal. In that case, the correlation is governed by exchange (like) L integrals between the different orbitals in the geminal. The energy lowering terms generally involve integrals between the highly occupied orbital (these orbitals generally have the lowest possible number of nodes

for their given symmetry at their spatial location) and the lowly occupied orbitals. The products involving the orbitals also generate multipolar charge distributions; the only difference is the fact that the energy is lowered by allowing the charge distribution to interact with a copy of itself that uses the other spatial coordinate. Exchange integrals that use orbitals on different and spatially distant geminals are not very capable of generating an adequate amount of correlation. As we have seen earlier, this is caused by the fact that there is little to no overlap between these geminals, resulting in a vanishing exchange integral. This explains why DOCI and APSG are incapable of describing the majority of dynamical correlation. It is very clear that this new non-JKL dispersive interaction (whose integral has $1/R^3$ long range scaling for localized geminals due to the orthogonality of the orbitals) has to be introduced to DMFT functionals in order to generate the missing dynamical correlation in a more physical way. In principle, the knowledge of this 2RDM element is enough for our purposes. However, in the interest of showing how this arises in wave functions, we will look at the largest CI coefficients of the wave function (see Table VI). The highest CI coefficient is used for the single reference HF like determinant. The next 3 determinants describe the intrageminal correlation of the 3 geminals we have covered in the previous paragraph. The final 10 determinants are all generating the multipole-multipole terms (only a short list is used in order to save space); this can be observed if one expands the sandwiching of the Hamiltonian between the reference determinant and these determinants using the Slater-Condon rules. It is interesting to note that all of these off-diagonal doubly excited determinants are generated by simultaneous single excitations within two different geminals. The importance of these terms was also stressed in perturbative approaches.[35,40] The value of the present findings stems from the fact that the importance of the elements has been determined by

TABLE V. Integrals (hartree) and their associated 2RDM elements and products for the 3 major geminals in equilibrium H_2O. The first 3 blocks refer to intergeminal interactions, and the last 3 blocks are intrageminal terms.

Classification	A(1)	B(1)	C(2)	D(2)	Integral	2RDM	Product
Non-JKL	5	4	7	6	0.057	−0.065	−0.004
Non-JKL	6	4	7	5	0.042	−0.006	0.000
Non-JKL	**6**	**5**	**7**	**4**	**0.123**	**−0.206**	**−0.025**
J	4	4	5	5	0.613	3.848	2.360
J	4	4	6	6	0.616	0.045	0.028
J	5	5	7	7	0.611	0.043	0.026
J	6	6	7	7	0.620	0.008	0.005
K/L	5	4	5	4	0.052	−1.908	−0.099
K/L	6	4	6	4	0.053	−0.076	−0.004
K/L	7	5	7	5	0.049	−0.070	−0.003
K/L	7	6	7	6	0.087	0.010	0.001
Non-JKL	5	3	8	6	0.021	−0.044	−0.001
Non-JKL	6	3	8	5	0.014	0.073	0.001
Non-JKL	**6**	**5**	**8**	**3**	**0.116**	**−0.208**	**−0.024**
J	3	3	5	5	0.614	3.852	2.366
J	3	3	6	6	0.611	0.052	0.032
J	5	5	8	8	0.527	0.039	0.020
J	6	6	8	8	0.537	0.006	0.003
K/L	5	3	5	3	0.029	−1.918	−0.057
K/L	6	3	6	3	0.019	−0.046	−0.001
K/L	8	5	8	5	0.014	−0.029	0.000
K/L	8	6	8	6	0.021	0.002	0.000
Non-JKL	4	3	8	7	0.018	−0.041	−0.001
Non-JKL	7	3	8	4	0.009	0.087	0.001
Non-JKL	**7**	**4**	**8**	**3**	**0.111**	**−0.208**	**−0.023**
J	3	3	4	4	0.631	3.853	2.431
J	3	3	7	7	0.606	0.047	0.028
J	4	4	8	8	0.541	0.038	0.021
J	7	7	8	8	0.532	0.006	0.003
K/L	4	3	4	3	0.032	−1.918	−0.062
K/L	7	3	7	3	0.030	−0.057	−0.002
K/L	8	4	8	4	0.018	−0.033	−0.001
K/L	8	7	8	7	0.027	0.002	0.000
$J_{diagonal}$	3	3	3	3	0.726	0.969	0.704
$J_{diagonal}$	8	8	8	8	0.541	0.004	0.002
J	3	3	8	8	0.607	0.016	0.010
K/L	8	3	8	3	0.157	−0.107	−0.017
One electron	3	3			−6.951		
One electron	8	8			−5.206		
$J_{diagonal}$	4	4	4	4	0.676	0.966	0.654
$J_{diagonal}$	7	7	7	7	0.670	0.005	0.004
J	4	4	7	7	0.631	0.026	0.016
K/L	7	4	7	4	0.143	−0.113	−0.016
One electron	4	4			−6.803		
One electron	7	7			−5.913		
$J_{diagonal}$	5	5	5	5	0.670	0.966	0.648
$J_{diagonal}$	6	6	6	6	0.672	0.006	0.004
J	5	5	6	6	0.650	0.025	0.016
K/L	6	5	6	5	0.166	−0.126	−0.021
One electron	5	5			−6.736		
One electron	6	6			−6.025		

observing a nearly exact and fully variational approach. One of the benefits of using these elements in a DMFT functional over using them in a perturbative fashion is the fact that they are a part of the system that is optimized. The pure geminal excitations only generate roughly half of the natural occupancy, so including the additional interactions could potentially lead to natural orbital shapes that show a closer resemblance to the exact ones.

C. Single bond dissociation in H_2O

We move on to the 2RDM analysis of the H_2O molecule, in which one bond has been dissociated. Instead of showing all the interactions, only the significant non-JKL elements are shown (Table VII). The intergeminal interaction between orbital pairs belonging to the same geminal 2/9, 3/8 and 4/7 are present, just as was the case at equilibrium distance (the 2/9 interaction at equilibrium distance was not shown for brevity's sake). However, the interaction between the bond broken orbital pair 5/6 and the other pairs is not present. Instead, the orbital pairs 5/10 and 6/10 are used to generate dynamical intergeminal correlation between the bond broken geminal and the remaining ones. The newly introduced orbital (10) is a p type orbital at each of the fragments directed along the broken bond. This additional orbital is required due to the fact that the contributions of a regular off-diagonal doubly excited determinant (containing a single occupied orbital 5 and 6 and two singly occupied orbitals from another geminal) would be quenched in the dissociation limit because of the opposing signs of the coefficients of the two reference determinants with which it would interact. The use of an additional orbital has also been observed in selected equilibrium cases. However, in most cases, the assignment of these additional orbitals to the geminal sets is only clear when one has (partially) dissociated bonds. In order to avoid ambiguous assignment problems, these additional orbitals will not be considered here any further.

D. Multiple bond dissociation in N_2

Proceeding with the analysis of the N_2 molecule, we note that the geminal structure is somewhat less clear for the N_2 molecule. At equilibrium distance, the π-bonding frontier NOs ϕ_6 and ϕ_7 have geminal-like behavior, as can be seen in Tables VIII and IX. But the pairing is not perfect for the other 3 geminals, as is evidenced by the Coulomb to exchange ratio between elements of these geminals. Nonetheless, the importance of the non-JKL multipole-multipole terms for this system is very prominent and similar to the H_2O molecule.

The dissociated N_2 system, however, has deviant behavior. Several new types of non-JKL elements appear, as is seen in Table X. These additional elements are the coordinate swapped companions of the dispersive interactions. The integral value of these elements is equal to the corresponding intergeminal exchange integrals. In order to understand this, we are going to look at a model system that consists of two geminals, a σ bond (2× S) and a π bond (2× p_y, P in the equations), between equivalent atoms A and B. The APSG intergeminal energy is given by the following expression:

$$\begin{aligned} E_{\sigma\pi} = {} & 4n_{\sigma_g}n_{\pi_u}J_{\sigma_g\pi_u} - 2n_{\sigma_g}n_{\pi_u}K_{\sigma_g\pi_u} \\ & + 4n_{\sigma_u}n_{\pi_u}J_{\sigma_u\pi_u} - 2n_{\sigma_u}n_{\pi_u}K_{\sigma_u\pi_u} \\ & + 4n_{\sigma_g}n_{\pi_g}J_{\sigma_g\pi_g} - 2n_{\sigma_g}n_{\pi_g}K_{\sigma_g\pi_g} \\ & + 4n_{\sigma_u}n_{\pi_g}J_{\sigma_u\pi_g} - 2n_{\sigma_u}n_{\pi_g}K_{\sigma_u\pi_g}, \end{aligned} \tag{18}$$
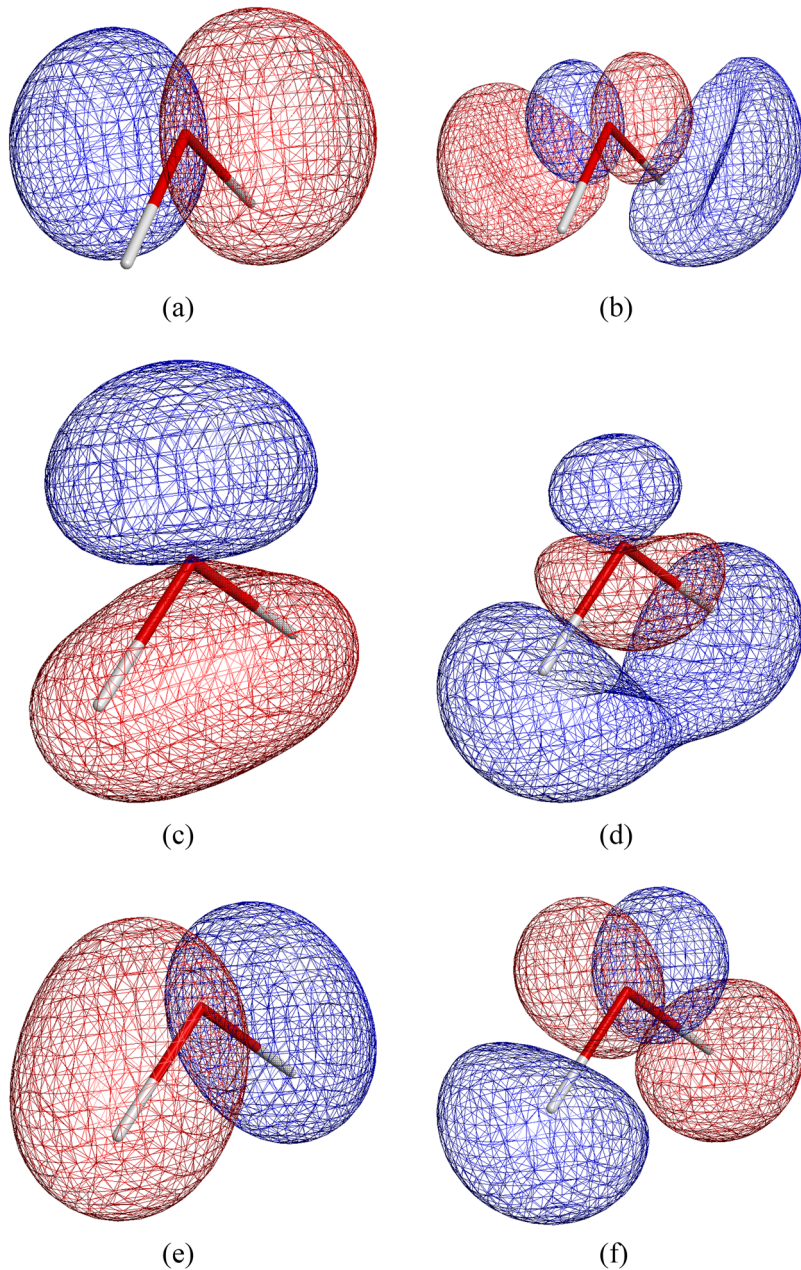
FIG. 1. Visualizations of important NOs for equilibrium H_2O; the occupation numbers are in parentheses. (a) NO 3 (1.9621). (b) NO 8 (0.0228). (c) NO 4 (1.9585). (d) NO 7 (0.0280). (e) NO 5 (1.9584). (f) NO 6 (0.0300).

TABLE VI. Highest CI coefficients and their associated determinants for H_2O; the core has been excluded since it is always occupied.

α occ				β occ				Coefficient
2	3	4	5	2	3	4	5	0.9657
2	3	4	6	2	3	4	6	−0.0636
2	4	5	8	2	4	5	8	−0.0573
2	3	5	7	2	3	5	7	−0.0567
2	3	4	6	2	3	5	7	0.0445
2	3	5	7	2	3	4	6	0.0445
2	3	4	6	2	4	5	8	−0.0379
2	4	5	8	2	3	4	6	−0.0379
2	3	5	7	2	4	5	8	0.0363
2	4	5	8	2	3	5	7	0.0363
2	3	4	5	2	5	7	8	0.0289
2	5	7	8	2	3	4	5	0.0289
2	3	4	5	2	4	6	8	−0.0277
2	4	6	8	2	3	4	5	−0.0277

where

$$\sigma_g = \frac{1}{\sqrt{2}}(S_A + S_B),$$

$$\sigma_u = \frac{1}{\sqrt{2}}(S_A - S_B),$$

$$\pi_u = \frac{1}{\sqrt{2}}(P_A + P_B),$$

$$\pi_g = \frac{1}{\sqrt{2}}(P_A - P_B).$$

At infinite distance, we get the following expressions for the integrals (note that all of the J integrals have one common value, and all of the K integrals have one common value at infinite distance):

$$J_{\sigma_g \pi_u} \approx \frac{1}{4}(J_{S_A P_A} + J_{S_B P_B}), \tag{19}$$

TABLE VII. Largest absolute non-JKL contributions to the energy (hartree) for H_2O with a single bond broken.

A(1)	B(1)	C(2)	D(2)	Integral	2RDM	Product
8	3	7	4	0.1141	−0.2239	−0.0256
9	2	8	3	0.1066	−0.1410	−0.0150
9	2	7	4	0.0920	−0.1245	−0.0115
10	5	8	3	0.0790	−0.0925	−0.0073
10	5	7	4	0.0774	−0.0923	−0.0071
10	6	8	3	0.0849	−0.0702	−0.0060
10	6	7	4	0.0827	−0.0688	−0.0057

$$K_{\sigma_g \pi_u} \approx \frac{1}{4}(K_{S_A P_A} + K_{S_B P_B}). \quad (20)$$

So the total interaction at infinite distance (all occupations are 0.5) can be written as

$$E_{\sigma\pi} = J_{S_A P_A} - \frac{1}{2}K_{S_A P_A} \quad (21)$$

$$+ J_{S_B P_B} - \frac{1}{2}K_{S_B P_B}. \quad (22)$$

So on each of the atoms, the electrons have a Coulomb repulsion with the other electron on the atom and half an exchange interaction with the other electron. The exchange part is not physical and is simply created by the fact that one describes the average spinless interaction between two breaking singlet systems and one does not take the spin coupling of the electrons on the fragments into account. The actual exchange contribution should either be −K (fragment triplet states) or +K (fragment singlet open shell states). The triplet state is the most favorable state, so the best course of action is to correct the standard APSG intergeminal in such a way that it doubles the amount of exchange interaction between geminals that represent broken bonds.

It should be noted that the additional exchange interaction is not a minor addition to the total energy, especially when one ends up having multiple unpaired electrons on multiple fragments. For example, in case of the N_2 molecule, where the lone N atoms have 3 electrons with the same spin (quartet), the molecular exchange integral (almost equivalent for all of the interactions between the 6 active orbitals) has a value of 0.0175 hartree. This represents the value of just $\frac{1}{2}K$ (atomic). Each geminal pair has a mismatch of K (atomic), and there are 3 pairings ($\sigma\pi_x/\sigma\pi_y/\pi_x\pi_y$). So that means that one is missing $2*3*0.0175 = 0.105$ hartree of "static" correlation energy when one uses the APSG functional. This indicates that it is mandatory to augment the APSG functional with a multibond dissociation exchange correction.

IV. IMPROVED GEMINAL FUNCTIONALS

We will now generate new DMFT functionals using the knowledge we have just gained. In principle, it would be best to fully reproduce all 2RDM elements faithfully since this would surely generate a correct description of the ground state, and it is generally better for TDDMFT (Time Dependent Density Matrix Functional Theory) excitation calculations as well. However, the microscopic details are just too numerous to handle individually, and it is very unlikely that we will be

TABLE VIII. Integrals (hartree) and 2RDM elements for the intergeminal interactions between the 4 major geminals in equilibrium N_2. Note that the interactions between orbitals 7 and 9 and all non-π orbitals are not shown due to the fact that they are symmetrically equivalent to the respective interactions between the other π orbitals (6 and 8) and the non-π orbitals.

Classification	A(1)	B(1)	C(2)	D(2)	Integral	2RDM	Product
Non-JKL	9	6	8	7	0.0173	0.0828	0.0014
Non-JKL	**9**	**7**	**8**	**6**	**0.1454**	**−0.3536**	**−0.0514**
Non-JKL	9	8	7	6	0.0215	−0.1326	−0.0028
J	7	7	6	6	0.5329	3.7072	1.9757
J	8	8	7	7	0.5496	0.1246	0.0685
J	9	9	8	8	0.5908	0.0270	0.0159
K/L	7	6	7	6	0.0232	−1.8315	−0.0426
K/L	8	7	8	7	0.0173	−0.0992	−0.0017
K/L	9	8	9	8	0.0256	0.0137	0.0004
Non-JKL	**11**	**5**	**8**	**6**	**−0.0746**	**0.1289**	**−0.0096**
Non-JKL	11	6	8	5	−0.0102	−0.0317	0.0003
Non-JKL	11	8	6	5	−0.0197	0.0518	−0.0010
J	6	6	5	5	0.4954	3.7626	1.8638
J	8	8	5	5	0.5451	0.1320	0.0719
J	11	11	6	6	0.4122	0.0245	0.0101
J	11	11	8	8	0.4442	0.0040	0.0018
K/L	6	5	6	5	0.0429	−1.8603	−0.0797
K/L	8	5	8	5	0.0797	−0.1626	−0.0130
K/L	11	6	11	6	0.0160	−0.0269	−0.0004
K/L	11	8	11	8	0.0205	0.0058	0.0001
Non-JKL	**10**	**4**	**8**	**6**	**−0.1095**	**0.1764**	**−0.0193**
Non-JKL	10	6	8	4	−0.0009	−0.1159	0.0001
Non-JKL	10	8	6	4	−0.0092	0.0464	−0.0004
J	6	6	4	4	0.5212	3.7713	1.9655
J	8	8	4	4	0.5595	0.1403	0.0785
J	10	10	6	6	0.6232	0.0352	0.0219
J	10	10	8	8	0.6562	0.0086	0.0056
K/L	6	4	6	4	0.0221	−1.8745	−0.0414
K/L	8	4	8	4	0.0300	−0.1225	−0.0037
K/L	10	6	10	6	0.0337	−0.0413	−0.0014
K/L	10	8	10	8	0.0454	0.0047	0.0002
Non-JKL	11	4	10	5	0.0234	0.0016	0.0000
Non-JKL	**11**	**5**	**10**	**4**	**0.0694**	**−0.0890**	**−0.0062**
Non-JKL	11	10	5	4	0.0531	−0.0271	−0.0014
J	5	5	4	4	0.5329	3.8445	2.0489
J	10	10	5	5	0.5657	0.0408	0.0231
J	11	11	4	4	0.4362	0.0214	0.0093
J	11	11	10	10	0.4638	0.0018	0.0008
K/L	5	4	5	4	0.1712	−1.9018	−0.3256
K/L	10	5	10	5	0.0448	−0.0477	−0.0021
K/L	11	4	11	4	0.0563	−0.0601	−0.0034
K/L	11	10	11	10	0.0259	0.0027	0.0001

able to reproduce these elements for all situations. So only the most important and easy to implement terms will be considered. In Sec. III, we have seen that the geminal structure was clearly present in all systems. So it makes sense to use the standard APSG functional as the basis for our new functional, as has been the case for almost all new DMFT functionals that have been developed in the last couple of years. With the APSG functional comes the dilemma of the choice of the set of one-electron orbitals for each geminal. In the analysis, we have shown that one could easily pair a strongly occupied

TABLE IX. Integrals (hartree) and 2RDM elements for the intrageminal interactions of the 4 major geminals in equilibrium N_2.

Classification	A(1)	B(1)	C(2)	D(2)	Integral	2RDM	Product
Diagonal	6	6	6	6	0.5794	0.9379	0.5434
Diagonal	8	8	8	8	0.6421	0.0203	0.0131
J	8	8	6	6	0.5925	0.0583	0.0346
K/L	8	6	8	6	0.1800	−0.2346	−0.0422
One electron	6	6			−8.0705		
One electron	8	8			−8.2086		
Diagonal	5	5	5	5	0.5328	0.9647	0.5140
Diagonal	11	11	11	11	0.3760	0.0016	0.0006
J	11	11	5	5	0.4330	0.0189	0.0082
K/L	11	5	11	5	0.0674	−0.0465	−0.0031
One electron	5	5			−7.6594		
One electron	11	11			−5.5017		
Diagonal	4	4	4	4	0.5731	0.9665	0.5539
Diagonal	10	10	10	10	0.7909	0.0027	0.0021
J	10	10	4	4	0.6344	0.0277	0.0176
K/L	10	4	10	4	0.1197	−0.0685	−0.0082
One electron	4	4			−8.0619		
One electron	10	10			−8.5733		

TABLE X. Largest absolute non-JKL contributions to the energy (hartree) for dissociated N_2.

A(1)	B(1)	C(2)	D(2)	Integral	2RDM	Product
9	8	7	6	0.0176	−1.2886	−0.0227
10	8	7	5	−0.0177	1.2782	−0.0227
10	9	6	5	−0.0177	1.2782	−0.0227
9	7	8	6	0.0175	−1.2883	−0.0226
10	7	8	5	−0.0174	1.2767	−0.0222
10	6	9	5	−0.0174	1.2767	−0.0222

orbital with a single weakly occupied orbital and that an additional orbital could be added in case a geminal describes a broken bond. One could in principle use a different number of orbitals per set for different distances. However, the most simple PP space (2 orbitals per geminal) is used since this makes it less ambiguous to compare the functionals with CASSCF calculations along the entire dissociation coordinate.

The analysis of Sec. III has shown us that one should add two major corrections to the APSG functionals, both of which describe intergeminal correlation. The first correction adds the missing intergeminal dynamical correlation in a physical dispersive non-JKL multipole-multipole like way. The second correction fixes the incorrect exchange interaction on the fragments that occurs between unpaired electrons when multiple bonds are broken.

A. Intergeminal dynamical correlation

We will begin by generating a functional that contains the first correction. This functional will be called ELS-D(ynamical) since it extends the Löwdin Shull/Hartree-Fock description of the APSG functional by adding dynamical intergeminal correlation. The electron-electron interaction energy of this functional is given by

$$W^{ELS-D} = W^{APSG-NO} + \frac{1}{2} \sum_{S_g} \sum_{S_h \neq S_g} F_D(n_i, n_a, n_j n_b) D_{ia,jb},$$

$$i, a \in S_g; \; j, b \in S_h, \quad (23)$$

where $D_{ia,jb}$ is given by Eq. (17) and F_D is the functional prefactor. We have not been able to elucidate the occupation number dependence of the 2RDM elements in our analysis, and it is very unlikely that we will be able find it by using some model wave function. So we will base the occupation dependence on physical constraints and our empirical knowledge of how DMFT functionals work. One of the first constraints that can be applied from a 2RDM symmetry point of view is that F_D should be symmetrical with respect to geminal set interchanges (coordinate swap) and orbital interchanges within a set (swapping of complex stars). We have seen that the entire interaction disappears when one of the geminals describes a broken bond, so F_D should contain factors that go to 0 when the respective geminal describes bond breaking. Finally, a concrete function of the ONs has to be chosen. In DMFT, there are two commonly used power factors: the linear product of occupation numbers and the square root of this product. The first one is used for HF like interactions, while the second one is used for the description of correlation. Since we are describing correlation, the second form will be selected (we will use 4 occupation numbers here instead of the usual 2 since we are working with 4 different orbitals). If one takes all of these restrictions into consideration, one arrives at the following expression for F_D:

$$F_D(n_i, n_a, n_j, n_b) = 8 f_{iajb} P_d(n_i \cdot n_a) P_d(n_j \cdot n_b) \sqrt{n_i n_a n_j n_b}, \quad (24)$$

where f_{iajb} is the phase factor that ensures that the $F_D(n_i, n_a, n_j n_b) D_{ia,jb}$ product gives a negative (energy lowering) contribution to W. This phase factor is required since the signs of the orbitals (phases) determine the sign of the integral, and this leaves us with an inadequate amount of parameters to ensure that the interaction is always negative for many geminal systems. In the case of CI calculations, one would be able to select the correct sign by simply changing the sign of the CI coefficient. The factor of 8 is present due to 2RDM symmetry considerations (see above). The Padé approximant P_d is given by

$$P_d(x) = \alpha \left(1 - \frac{\beta x^2}{1 + \beta x^2}\right). \quad (25)$$

This approximant goes to zero when the product of occupations x is at its largest; this occurs when both of the occupation numbers belonging to the same geminal are close to half occupancy. The "point" at which the Padé approximants start quenching the 2RDM elements is regulated by the parameter β. The Padé approximant also contains a prefactor scaling parameter α. One could in principle try to choose this parameter in such a way that it effectively absorbs all missing correlation, even if it means that the physics is completely eschewed. To avoid this, one should take a look at the value of this parameter if one tries to generate the CI 2RDM values when using the CI NO occupation numbers. This yields an acceptable value of around 1.1-1.5 for α and will serve as a boundary condition for our parameter optimization. Before we look at the optimization and calculation results, we will build a functional that can also fix the multibond dissociation problem.

B. Taking care of multibond breaking

As we have seen in our analysis, the standard APSG functional is not able to describe multibond breaking correctly because it is missing half of the exchange between the unpaired electrons, assuming that all of the unpaired electrons have the same spin direction; i.e., the fragments are in a high spin configuration. CI calculations fix this exchange by using a set of non-JKL integrals that have the same value as the intergeminal exchange integrals at the dissociation limit while still maintaining the correct singlet state of the total system.[46] No correction is needed in case one is at the equilibrium distance. In case of intermediate distances, it will be a bit harder to describe this interaction faithfully due to the fact that the various non-JKL 2RDM elements and their respective integrals act as distinct entities at these distances. One could use an unrestricted calculation to solve this problem;[47] however, unrestricted DMFT calculations are still in their infancy.[48] It is also more appealing to avoid the arbitrariness and loss of proper state and spin symmetry of unrestricted treatments. Instead, we will use the most simple closed shell approach possible to this problem: an exchange (K) only correction is added to the ELS-D functional. We know the behavior of the equilibrium and dissociation limits; the intermediate behavior will be modelled by parametrization. The functional will be designated as ELS-D-M(ultibond) and is given by the following expression:

$$W^{ELS-D-M} = W^{ELS-D} + \sum_{S_g} \sum_{S_h \neq S_g} \sum_{i \in S_g} \sum_{j \in S_h} F_M(n_i, n_j) K_{ij}, \quad (26)$$

where $F_M(n_i, n_j)$ is the functional factor that we are going to choose and optimize. Just like for the dynamical correlation case, we do not really have a simple wave function form that we can exploit. We do however have an excellent DMFT base factor that was not mentioned in Sec. IV A: the symmetrical occupation-hole product $n_i(1 - n_i)n_j(1 - n_j)$. The square root of this product was first used by Csanyi and
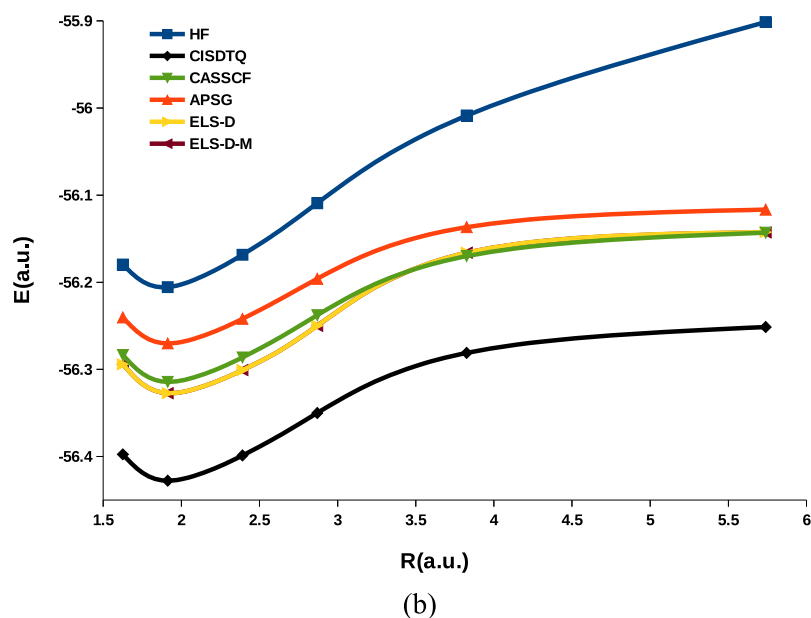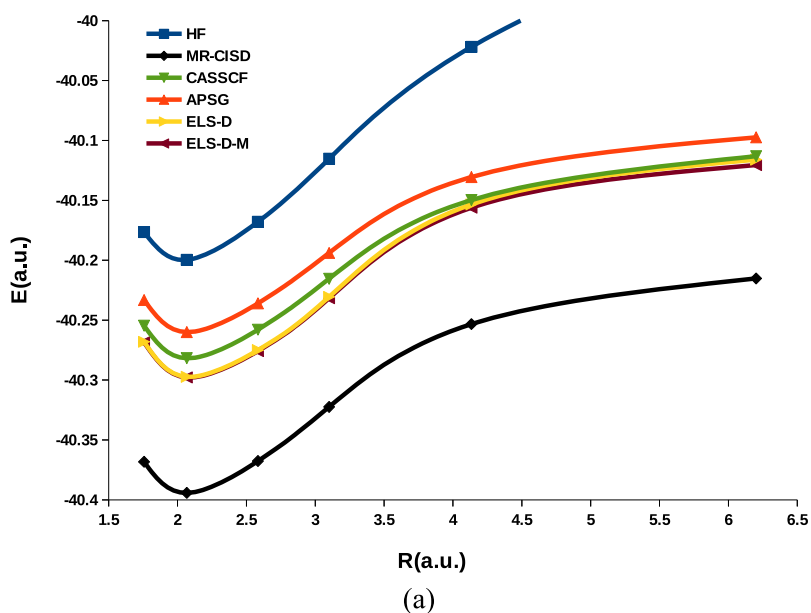

FIG. 2. Potential energy curves for CH_4 and NH_3 (single bond stretching). (a) CH_4. (b) NH_3.

Arias in their corrected-Hartree-Fock functional[6] and has since been used in many other functionals. One would think that the linear version of this product (with a suitable prefactor) would be the best choice since it will have a nearly negligible contribution at equilbrium distances and it will have a full contribution in case both orbitals have half occupation. However, trial calculations have shown that this only works very well for equilibrium distance and the dissociation limit, but it fails to generate an adequate amount in the intermediate regime. So we will have to use the square root version in order to generate a larger contribution in the intermediate regime. The downside of using this is that it generates a large amount of unwanted "dynamical" correlation at equilibrium distance and between non-bond breaking geminals at larger distances as well. In order to counter this unwanted correlation, a modulation factor has to be added. If one takes all of these things into account, one arrives at the following expression:

$$F_M(n_i, n_j)$$
$$= -P_m(n_i(1 - n_i))P_m(n_j(1 - n_j))\sqrt{n_i(1 - n_i)n_j(1 - n_j)},$$
(27)

where P_m is the Padé approximant given by

$$P_m(x) = (1 + \frac{16}{\gamma})\frac{\gamma x^2}{1 + \gamma x^2}.$$
(28)

The first term ensures normalization to 1 when an orbital's occupancy is half, and the second part is the modulation factor that ensures that the newly added exchange will not be added to non-bond breaking geminal intergeminal interactions.

C. Tests of the ELS-D-M functional

We will now move on to applying these functionals to our prototype molecules. The following values were used for the parameters: $\alpha = 1.25$, $\beta = 750$, and $\gamma = 1500$. These values were
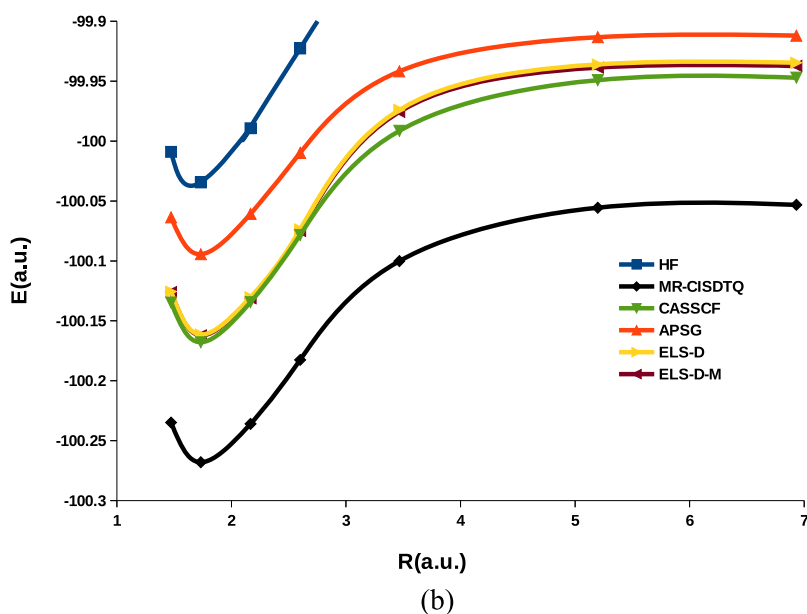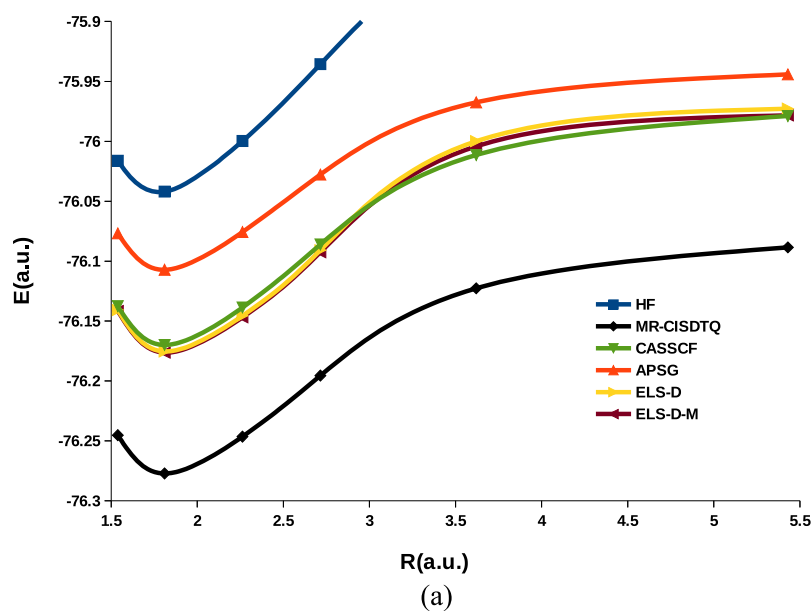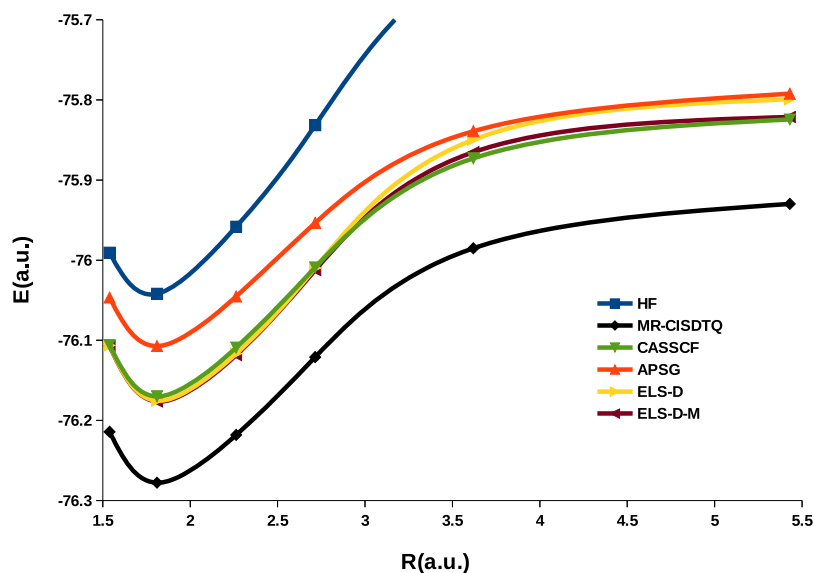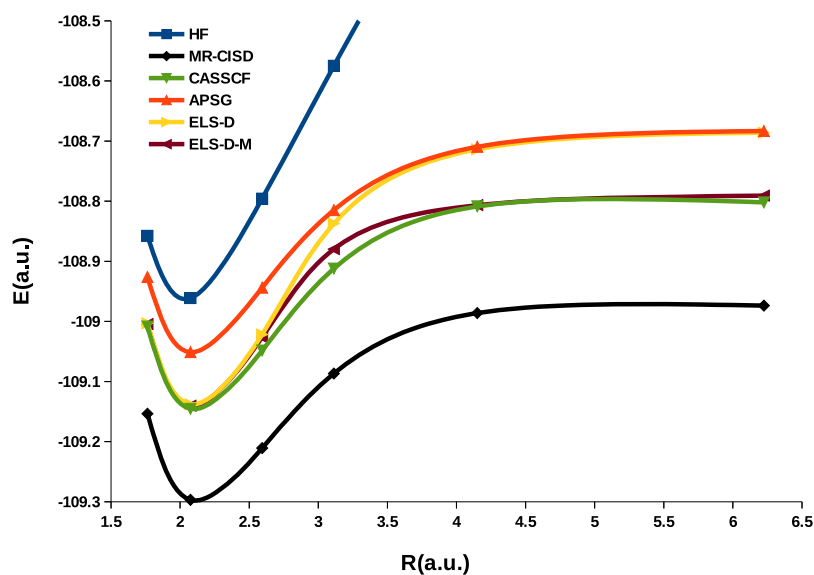

FIG. 3. Potential energy curves for H_2O and FH (single bond stretching). (a) H_2O. (b) HF.

(a)

(b)

FIG. 4. Potential energy curves for N_2 and H_2O for multiple bond breaking (symmetrical stretch in H_2O). (a) H_2O symmetrical stretch. (b) N_2.

handpicked after several grid optimizations were performed for the target molecules (both in the aug-cc-pVDZ and 6-31G basis, all potential energy curves shown use the aug-cc-pVDZ basis). The potential energy curves for single bond breaking are shown in Figs. 2 and 3, while the potential energy curves for multibond breaking are shown in Fig. 4. The dissociation energies are shown in Table XI. The results for the Hartree-Fock (often truncated due to its extremely poor performance when bonds are broken), APSG (which reduces to generalized valence bond with perfect pairs, GVB-PP ≡ PNOF5, due to the PP set choice), ELS-D, and ELS-D-M functionals are shown. The CASSCF (active space uses the same number of orbitals as there are valence electrons) and MR-CI results are also depicted. The MR-CI curves simply serve as a reminder of how much correlation energy is still missing when truncating the active space. The CASSCF curves effectively serve as the true benchmark value for the approximate DMFT functionals that we are using here since they have the same PP active

space. The single bond curves [CH_4, NH_3, H_2O-single-bond (asymmetric stretch), FH] show similar trends. The ELS-D and ELS-D-M curves are quite close to the CASSCF curves and nearly on top of each other due to the lack of multibond breaking in these systems (Figs. 2 and 3). They generally

TABLE XI. Dissociation energies for various methods in kcal/mol. The dissociation limit is defined as the point where the bond is stretched to 3 times the equilibrium length (4 times for FH).

	HF	CI	CASSCF	APSG	ELS-D	ELS-D-M
CH4	178.8	112.3	105.8	102.0	113.7	111.2
NH3	190.9	110.7	107.4	96.4	116.0	115.8
H2O	209.9	118.4	119.9	102.3	127.1	124.2
FH	474.0	134.8	138.5	114.4	142.3	141.1
H2O 2b	368.2	218.3	216.8	197.6	236.0	222.7
N2	617.6	202.7	215.5	230.9	283.5	219.3

overestimate the correlation (compared with CASSCF) by a small amount in the equilibrium regime (except in the case of FH), and they underestimate it by a slight amount in the dissociation limit. The net effect is that the dissociation energies (Table XI) are very close to the CASSCF values. The ASPG functional treats the equilibrium and dissociated situations not so uniformly, and it generates relatively less of the correlation at equilibrium distance. The APSG functional therefore generates poor dissociation energies (too low) for the NH_3, H_2O, and HF molecules.

The multibond curves (N_2, H_2O-symmetric stretch, Fig. 4) show the same kind of trends as the single bond curves. The only difference is related to the dissociation behavior of the ELS-D functional. It goes to the same dissociation limit as the APSG functional; this is caused by the fact that there is very little intergeminal dynamical correlation left to describe by the remaining two non-bond broken geminals. Furthermore the ELS-D and ELS-D-M curves now do not coincide in the dissociation limit. This is of course caused by the fact that the ELS-D functional does not have a multibond dissociation correction. In case of H_2O, only a single unpaired interaction has to be fixed, while a total of 6 unpaired interactions have to be corrected (3 per atom) for N_2. This explains the larger absolute energy difference between ELS-D and ELS-D-M in case of N_2. The ELS-D-M dissociation energy is very close to the CASSCF value (Table XI), again showing that the new functional is up to the task. It can be noted that in the case of N_2, the APSG functional happens to have a dissociation energy that is not extremely far away from the CASSCF value; this is accidental, and it basically fails to describe a large part of the physics that is involved in describing the N_2 dissociation curve.

V. CONCLUSIONS

The 2RDM (in the NO basis generated by MR-CI calculations) has been analyzed in this paper for the prototype molecules CH_4, NH_3, H_2O, FH, and N_2. The most important finding has been the essential role of dispersion type terms (non-JKL two-electron integrals) that describe the correlation between electrons in different geminals. Such terms describe an essential part of the dynamical correlation, namely the intergeminal attractive multipole-multipole interactions that arise from simultaneous single excitations on two geminals. If the distance between the two geminals is large, these are the well-known dispersion type interactions that give rise to van der Waals bonding. The essential deficiency of pure *JKL* functionals has been recognized for the first time precisely for the case of van der Waals bonding, in an analysis of the prototype He$_2$ system.[14] Naturally, such dispersion type interactions also occur between geminals in general molecules, and when the distance between the geminals is shorter than the typical van der Waals distance, the energetic effects of this dispersion type of electron correlation become much larger and have to be taken into account for reliable bond energies. The insights obtained have been used to generate new DMFT functionals. Benchmark CASSCF calculations have been performed, which have the same number of active orbitals as the DMFT calculations (the PP set,

i.e., equal to the number of valence electrons). The most advanced version of our functionals, ELS-D-M, is able, by incorporating the non-*JKL* terms in the functional, to reproduce the benchmark CASSCF potential energy curves. Of course these terms increase the computational effort. However, in our perfect pair scenario, only a single integral is required between each pair of geminals, reducing these additional costs significantly.

We also note that this is the first time that a DMFT functional has been able to produce all the essential physics for the multibond N_2 system. This was accomplished by adding a correction that ensures that, after the breaking of bonds, unpaired electrons on fragments feel the appropriate amount of exchange interaction (for a high-spin configuration). This multibond correction is only an exchange correction, so *JKL* functionals can easily incorporate this correction for ground state calculations. Both of these corrections are pairwise between geminals, so it is expected that the ELS-D-M functional is capable of providing a similar kind of performance for larger systems. However, the multibond correction might generate an incorrect amount of exchange compensation in case one of the fragments is not correctly described by a high spin configuration. The geminal nature of the functional could potentially generate some problems for delocalized systems. It is known from valence bond calculations that 2 orbital geminal systems are incapable of generating the correct equilibrium structure for benzene; the correct structure is obtained when enough intergeminal corrective terms are added.[49] The ELS-D-M functional does use additional correlation terms. However, some terms might still be missing, and the interaction strength (parameters) of the terms that we do use might favor a symmetry broken geometry. This will have to be investigated in the future.

The ELS-D and ELS-D-M functionals were able to increase the dynamical correlation energy from the 50%–60% (of the benchmark CASSCF correlation energy) generally obtained by APSG-PP to virtually all of the dynamical correlation energy obtained by the PP space CASSCF calculations. Still, the latter usually amounts to only 45%-50% of the total dynamical correlation energy as obtained by the MR-CI calculations. If we want to obtain a larger percentage of the total dynamical correlation energy, we need to incorporate more orbitals in the geminals in order to obtain more dynamical correlation per geminal and more intergeminal correlation energy by adding additional (dispersive) terms that contain these orbitals; see the discussion in Ref. 50. Another way of incorporating the effect of additional orbitals is to resort to perturbative treatments.

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