Linearized Coupled Cluster Corrections to Antisymmetrized Product of Strongly Orthogonal Geminals: Role of Dispersive Interactions

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ABSTRACT: A linearized Multireference Coupled Cluster (MR-LCC) theory is formulated based on the Antisymmetrized Product of Strongly Orthogonal Geminals (APSG) reference state. The role of dispersive interbond interactions is discussed. The presented theory has led to qualitatively correct potential curves for the case when both OH bonds dissociate in H_2O, a result that cannot be achieved by adding only perturbative corrections to APSG. The potential curve obtained for the He···He problem practically coincides with the full CI (FCI) result, showing the unexpected accuracy of the MR-LCC approach in this case.

$$|\Psi\rangle = (1 + \hat{T})|\text{APSG}\rangle$$

1. INTRODUCTION

Reference states in quantum chemical calculations are used as zeroth order states obtained at a simpler level to be corrected by perturbative or more sophisticated theories. Coupled Cluster (CC) theory,[1−6] for example, offers a powerful tool to describe molecular electronic structure for single reference (SR) problems, i.e. when the electronic wave function can be qualitatively described by a single Slater determinant. Many chemical processes require the use of two or more determinants even for a qualitative description. Just like Multireference (MR) Perturbation Theory (PT),[7−15] the MR generalization of CC theory is a widely discussed problem, for which several ideas have been proposed, each having their advantages and disadvantages.[16−33]

A central problem in MR-CC theory is the construction of permitted excitations and their amplitudes by ensuring the same number of amplitude equations as the number of unknowns, preserving at the same time the commutation of excitation operators. The latter condition is essential to ensure extensivity manifested in the SR case by the ansatz

$$|\Psi\rangle = e^{\hat{T}}|\text{HF}\rangle$$

where $|\text{HF}\rangle$ is the SR state (typically the Hartree−Fock determinant) and $\hat{T}$ is the excitation operator

$$
\begin{aligned}
\hat{T} &= \hat{T}_1 + \hat{T}_2 + ... \\
&= \sum_i^{occ} \sum_p^{virt} t_i^p p^+ i^- + \sum_{i<j}^{occ} \sum_{p<q}^{virt} t_{ij}^{pq} p^+ q^+ j^- i^- + ...
\end{aligned}
\tag{1}
$$

where $i, j,...$ refer to occupied and $p, q,...$ refer to virtual indices relative to the Fermi vacuum $|\text{HF}\rangle$ and $\hat{T}_1, \hat{T}_2...$ describe single, double,... excitations, respectively. Creation/annihilation indices categorized into disjoint subsets results in the important fact that terms in $\hat{T}_1, \hat{T}_2...$ commute, ensuring extensivity of CC corrections. The simple categorization is clearly impossible if the reference state consists of several determinants. Of possible workarounds, we mention the Jeziorski−Monkhorst ansatz[34]

$$|\Psi\rangle = \sum_\mu C_\mu e^{\hat{T}_\mu}|\Phi_\mu\rangle$$

which deals with the MR reference state $|\Phi\rangle = \Sigma_\mu C_\mu|\Phi_\mu\rangle$, and cluster operators $\hat{T}_\mu$ are defined similarly to eq 1, the occupancies referring to that of $|\Phi_\mu\rangle$. Special attention has to be paid in these theories to eliminate possible redundancies in excitations and amplitudes.[35] One may obtain a theory free of the redundancy problem by picking up a dominant component $|\Phi_0\rangle$ in $|\Phi\rangle$ and define occupancies with respect to this pivot determinant.[36−38] The coupled-cluster correction developed specifically for the GVB wave function by Head-Gordon and Voorhis also relies on the concept of the pivot.[39−41] The alternative approach of devising an internally contracted theory has received much interest lately.[42−45]

The MR problem leads to complications also in PT. In SR-PT, the formalism remains simple since $|\text{HF}\rangle$ and excited determinants altogether form eigenvectors of a one-body operator, the Fockian ($\hat{F}$). If the reference state $|\Phi\rangle$ is of multireference character, no one-body operator emerges as a zero-order Hamiltonian, whose eigenvectors could be easily constructed. To resolve this problem, Dyall[46] was the first to propose the use of a two-body zero-order Hamiltonian. In our laboratory,[47−51] we have developed a MRPT using this philosophy applied to the APSG[52−62] reference state.

A method "between" simple PT and the more sophisticated CC theory is Linearized Coupled Cluster (LCC) formulation.[63−69] It emerges from CC by dropping all nonlinear terms in the amplitude equations. It was shown that LCC equations can also be derived by optimizing the partition via level shifts in a PT framework.[70,71] This latter statement holds in both the SR and MR cases.[70−73]

The present paper outlines a linearized CC (LCC) theory based on the APSG reference state. The formulation ensures extensivity, provides a uniquely soluble set of amplitude equations, and is free from the deficiencies of the PT presented in ref 51 concerning the description of simultaneous single bond dissociations. Our theory is related to that of Li et al.,[74,75] with notable differences. The present formulation relies strongly on the quasi-particle picture of geminals[47−50,76−85] and strictly maintains the size-consistency of the approach.

Another difference is the way geminal subspaces are chosen: we start from localized molecular orbitals and optimize them variationally, while Li et al.[74,75] use the "maximum similarity rule" introduced in ref 74.

2. THEORETICAL BACKGROUND

2.1. Geminals. A generalization of the one-determinant Hartree−Fock wave function is the Antisymmetrized Product of Strongly Orthogonal Geminals (APSG) wave function composed of two-electron orbitals ψ_i:

$$|\Psi\rangle = \psi_1^+ \psi_2^+ ... \psi_N^+ |\text{vac}\rangle \quad (2)$$

The two-electron operators (ψ_i^+) create *geminals*, and they are expanded in terms of one-electron operators corresponding to spin orbital χ_μ:

$$\psi_i^+ = \sum_{\mu < \nu} C_{\mu\nu}^i \chi_\mu^+ \chi_\nu^+ \quad (3)$$

In this respect, expression 2 is a multideterminantal wave function in terms of one-electron orbitals containing some proportion of the correlation effects. Because of the special structure of eqs 2 and 3, this is called *intrageminal correlation*.

The two-electron orbitals $\psi_i(1,2) = \psi_i^+|\text{vac}\rangle$ are constrained to satisfy the strong orthogonality condition

$$\int \psi_i(1, 2) \, \psi_k(1, 2) \, dr_1 = 0 \quad i \neq k \quad (4)$$

which, according to Arai,[86] is equivalent to expanding the geminals in mutually exclusive subsets of one-electron orbitals, called Arai subspaces.

In APSG theory, both the geminal coefficients $C_{\mu\nu}^i$ and one-electron basis orbitals χ_μ are optimized variationally, the latter via an MCSCF-type iteration. The geminal coefficients come from solving the set of self-consistent equations arising from the variational principle:

$$\hat{H}_i^{\text{eff}} \psi_i^p = E_i^p \psi_i^p \quad (5)$$

where i is the geminal index, $p \in \{0, 1, ..., n_i\}$ is the state index, and $\hat{H}_i^{\text{eff}}$ is an effective Hamiltonian defined over the spin orbital basis functions assigned to geminal i:

$$\hat{H}_i^{\text{eff}} = \sum_{\mu,\nu \in i} h_{\mu\nu}^{\text{eff}} \chi_\mu^+ \chi_\nu^- + \frac{1}{2} \sum_{\mu,\nu,\lambda,\sigma \in i} [\mu\nu|\lambda\sigma] \chi_\mu^+ \chi_\nu^+ \chi_\sigma^- \chi_\lambda^- \quad (6)$$

In the above formula $\mathbf{h}^{\text{eff}}$ is the "effective core" responsible for the intergeminal electrostatic and exchange interaction:

$$h_{\mu\nu}^{\text{eff}} = h_{\mu\nu} + \sum_{k \neq i} \sum_{\lambda,\sigma} P_{\lambda\sigma}^{k0} [\mu\lambda||\nu\sigma]$$

where $P_{\lambda\sigma}^{k0}$ is the density matrix of the ground-state geminal ψ_k^0:

$$P_{\lambda\sigma}^{k0} = \langle \psi_k^0 | \chi_\sigma^+ \chi_\lambda^- | \psi_k^0 \rangle \quad (7)$$

and $[\mu\lambda||\nu\sigma]$ is the antisymmetrized two-electron integral written in the $[12||12]$ convention. For more details, we refer to ref 61.

2.2. Perturbation Theory Based on Geminals. While APSG theory includes only intrageminal correlation effects, intergeminal corrections can be introduced via perturbation theory.[47−51] The basic concepts of this formulation are summarized below. We start from the second quantized

Hamiltonian written in terms of the energy-optimized spatial orbitals

$$\hat{H} = \sum_{m,n} \sum_\sigma h_{mn} m_\sigma^+ n_\sigma^- + \frac{1}{2} \sum_{m,n,l,s} \sum_{\sigma,\sigma'} [mn|ls] m_\sigma^+ n_{\sigma'}^+ s_{\sigma'}^- l_\sigma^- \quad (8)$$

where m, n, l, and s stand for the spatial part and σ and σ' for the spin part of spin orbital χ_μ. Because of strong orthogonality, each basis orbital belongs to one of the mutually exclusive orbital subsets. So instead of the sum over basis orbitals, we can introduce first a summation over the subsets (geminals) i, then a summation over the orbitals m belonging to that specific subset:

$$\sum_m \equiv \sum_i \sum_{m \in i}$$

leading to a natural separation of the full Hamiltonian 8 in geminal indices:[47,48]

$$\hat{H} = \sum_i \hat{H}_i + \sum_{i,j}{}' \hat{H}_{ij} + \sum_{i,j,k}{}' \hat{H}_{ijk} + \sum_{i,j,k,l}{}' \hat{H}_{ijkl}$$

where the prime after the sums indicates that the summation indices cannot coincide. The one-geminal Hamiltonian will obviously be

$$\hat{H}_i = \sum_{m,n \in i} \sum_\sigma h_{mn} m_\sigma^+ n_\sigma^-$$
$$+ \frac{1}{2} \sum_{m,n,l,s \in i} \sum_{\sigma,\sigma'} [mn|ls] m_\sigma^+ n_{\sigma'}^+ s_{\sigma'}^- l_\sigma^-$$

The two-geminal part becomes[48]

$$\hat{H}_{ij} = \hat{H}_{1\text{-CT}} + \hat{H}_{\text{disp}} + \hat{H}_{2\text{-CT}}$$

where the terms refer to different "geminal−geminal interactions." The first term decreases the electron number by one on one geminal while increasing it by one on the other; this is a "delocalization interaction" or a "one electron charge transfer" (1-CT) term:

$$\hat{H}_{1\text{-CT}} = \sum_{m \in i} \sum_{n \in j} \sum_\sigma h_{mn} m_\sigma^+ n_\sigma^-$$
$$+ \sum_{m,n,l \in i} \sum_{s \in j} \sum_{\sigma,\sigma'} [mn|ls] m_\sigma^+ n_{\sigma'}^+ s_{\sigma'}^- l_\sigma^-$$
$$+ \sum_{m,l,s \in i} \sum_{n \in j} \sum_{\sigma,\sigma'} [mn|ls] m_\sigma^+ n_{\sigma'}^+ s_{\sigma'}^- l_\sigma^-$$

The second term does not change the electron number on the geminals; it describes "dispersive interaction":

$$\hat{H}_{\text{disp}} = \frac{1}{2} \sum_{m,s \in i} \sum_{n,l \in j} \sum_{\sigma,\sigma'} ([mn|ls] m_\sigma^+ n_{\sigma'}^+ s_{\sigma'}^- l_\sigma^- - [mn|sl] m_\sigma^+ n_{\sigma'}^+ s_\sigma^- l_{\sigma'}^-) \quad (9)$$

The last term of the two-geminal Hamiltonian annihilates both electrons on one geminal while putting two extra electrons on the other geminal, it is a "two electron charge transfer term" (2-CT):

$$\hat{H}_{2\text{-CT}} = \frac{1}{2} \sum_{m,n \in i} \sum_{l,s \in j} \sum_{\sigma,\sigma'} [mn|ls] m_\sigma^+ n_{\sigma'}^+ s_{\sigma'}^- l_\sigma^-$$

Similar formulas can be derived for the three- and four-geminal Hamiltonian as well. With these formulas, a standard Rayleigh–Schrödinger PT can be outlined with $\hat{H}_0 = \sum_i \hat{H}_i^{\mathrm{eff}}$ (cf. eq 6) being the zero-order Hamiltonian, and $\hat{H} - \hat{H}_0$ being the perturbation operator.[48,50] Of various possible corrections, we detail here the second order dispersion correction emerging from the perturbation operator of eq 9:

$$
E_{\mathrm{disp}}^{(2)} = -\sum_{\substack{i,j \\ i<j}} \sum_{\substack{p,q \\ S^{p,q}=0}}^{S^{p,q}=0} \frac{\left| \sum_{m,s\in i} \sum_{n,l\in j} \left([mn|sl] - \frac{1}{2}[mn|ls] \right) P_{sm}^{ip} P_{ln}^{jq} \right|^2}{E_j^q + E_i^p - E_i^0 - E_j^0}
$$
$$
-\frac{1}{4} \sum_{\substack{i,j \\ i<j}} \sum_{\substack{p,q \\ M_S^{p,q}=0}}^{S^{p,q}=1;} \frac{\left| \sum_{m,s\in i} \sum_{n,l\in j} [mn|ls] P_{sm}^{ip} P_{ln}^{jq} \right|^2}{E_j^q + E_i^p - E_i^0 - E_j^0}
$$
$$
-\sum_{\substack{i,j \\ i<j}} \sum_{\substack{p,q \\ M_S^p + M_S^q=0}}^{M_S^{p,q}=\pm1;} \frac{\left| \sum_{m,s\in i} \sum_{n,l\in j} [mn|ls]^{\pm} P_{sm}^{ip\mp} P_{ln}^{jq} \right|^2}{E_j^q + E_i^p - E_i^0 - E_j^0} \tag{10}
$$

where E_i^p are the eigenvalues of the geminal Hamiltonian 5, S^p and M_S^p stand for the quantum number of two-electron $\hat{S}^2$ and $\hat{S}_z$ operators corresponding to the pth state of the geminal, and P_{ms}^{ip} is an element of the transition density matrix defined as

$$
P_{sm}^{ip} = \sum_\sigma \langle \psi_i^0 | m_\sigma^+ s_\sigma^- | \psi_i^p \rangle
$$

and $^{\pm}P_{sm}^{ip}$ is the spin-flip transition density matrix:

$$
^{\pm}P_{sm}^{ip} = \sum_\sigma \langle \psi_i^0 | m_\sigma^+ s_{\bar\sigma}^- | \psi_i^p \rangle
$$

with ψ_i^p being the $M_S = 0$ spin-polarized triplet geminal, $+$ referring to $M_S = +1$ and $-$ referring to $M_S \neq -1$. (Note that in previous papers[48–50] the second order correction eq 10 was displayed erroneously.)

It is apparent that this formula has a serious drawback: it exhibits a singularity when the ground states of two geminals, e.g. i and j, become degenerate, $E_i^p = E_i^0$ and $E_j^q = E_j^0$. This is perfectly the case when i and j label two dissociating bonds (geminals). As shown in ref 51, this feature makes the second order formula inapplicable to describing processes like the symmetric dissociation of H_2O, see also curve "APSG + PT2" in Figure 2.

In what follows, we elaborate a theory free from this deficiency.

3. MR-LCC THEORY WITH THE APSG REFERENCE STATE

Here, we investigate whether an MR-LCC treatment can cure the problem of dispersion correction for simultaneous dissociation of two single bonds. Previously, an MR-LCC formulation was used to describe "one-electron delocalization" corrections.[84]

The time-independent Schrödinger equation with the exponential CC ansatz is written with the APSG reference state as

$$
\hat{H} e^{\hat{T}} | \mathrm{APSG} \rangle = E e^{\hat{T}} | \mathrm{APSG} \rangle
$$

Projecting the Schrödinger equation by $\langle \mathrm{APSG} | e^{-\hat{T}}$ and using the fact that the APSG wave function is normalized, the following energy equation is obtained:

$$
\langle \mathrm{APSG} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \mathrm{APSG} \rangle = E \tag{11}
$$

Restricting ourselves to Linearized Coupled Cluster (LCC) approximation means a truncation of the Baker–Campbell–Hausdorff expansion after the second term (linear in $\hat{T}$):

$$
e^{-\hat{T}} \hat{H} e^{\hat{T}} \approx \hat{H} + [\hat{H}, \hat{T}] \tag{12}
$$

The cluster operator can be expanded in terms of excitation operators $\hat{X}_k$:

$$
\hat{T} = \sum_k t_k \hat{X}_k \tag{13}
$$

where $\hat{X}_k$ will be specified later, and t_k's are the "amplitudes" for which the MR-LCC amplitude equations are to be solved. Multiplying the coupled cluster Schrödinger equation

$$
e^{-\hat{T}} \hat{H} e^{\hat{T}} | \mathrm{APSG} \rangle = E | \mathrm{APSG} \rangle
$$

from the left by $\langle \mathrm{APSG} | X_j^\dagger$ and applying the linearization approximation 12, we obtain

$$
\langle \mathrm{APSG} | \hat{X}_j^\dagger [\hat{T}, \hat{H}] | \mathrm{APSG} \rangle = \langle \mathrm{APSG} | \hat{X}_j^\dagger \hat{H} | \mathrm{APSG} \rangle
$$

assuming $X_j^\dagger | \mathrm{APSG} \rangle = 0$. Substituting the expansion of the cluster operator 13, we get a linear equation system for the cluster amplitudes t_i

$$
\sum_i \underbrace{\langle \mathrm{APSG} | \hat{X}_j^\dagger (\hat{X}_i \hat{H} - \hat{H} \hat{X}_i) | \mathrm{APSG} \rangle}_{A_{ji}} t_i = \underbrace{\langle \mathrm{APSG} | \hat{X}_j^\dagger \hat{H} | \mathrm{APSG} \rangle}_{b_j} \tag{14}
$$

symbolized by

$$
\mathbf{At} = \mathbf{b}
$$

These are the MR-LCC amplitude equations.

Before solving eq 14, a decision is to be made on the type of excitations included in the cluster operator. It is possible, e.g., to resort to dispersive amplitudes only. In this case, the excitations appearing in eq 13 are specified as

$$
\hat{T} = \sum_k^{\mathrm{disp}} t_k \hat{X}_k = \sum_{i<j} \sum_p^{n_i} \sum_q^{n_j} t_{ij}^{pq} \, \psi_{ip}^+ \psi_{jq}^+ \psi_{j0}^- \psi_{i0}^- \tag{15}
$$

In eq 15, p and q run over the excited states of geminals i and j, respectively (n_i is the number of excited states of geminal i), and ψ_{ip}^+ and ψ_{jp}^+ refer to the excited state creation operators of the corresponding geminal while ψ_{i0}^- and ψ_{j0}^- annihilate ground-state geminals (they are both solutions of eqs 5). When working with dispersive amplitudes only, it is the "dispersive" Hamiltonian which contributes to inhomogeneous vector $\mathbf{b}$ of the LCC equations. This is a direct consequence of the fact that $\hat{H}_{\mathrm{disp}}$ conserves the particle number on each of the geminals and so does the cluster operator 15. The dispersive PT correction of eq 10 is closely related to the dispersive-only MR-LCC theory: it arises by neglecting all off-diagonal terms in matrix $\mathbf{A}$ of eq 14.

With the eq 15 definition of the cluster operator, we have $\langle \mathrm{APSG} | \hat{T} = 0$; the energy formula 11 consequently simplifies to the form

$$
E = \langle \mathrm{APSG} | \hat{H} + \hat{H} \hat{T} | \mathrm{APSG} \rangle
$$

Terms of the BCH expansion with second or higher powers of $\hat{T}$ do not contribute to the energy, since the "dispersive" Hamiltonian can interact with two excited geminals at most.

On the basis of analogy with single reference LCC theory, one may include in the cluster operator all types of excitations which generate a function that has nonzero interaction with the APSG wave function via the Hamiltonian (the so-called first order interacting subspace). This treatment involves dispersive as well as charge transfer states; see ref 51 for a categorization of the various excitations. Parametrization of the cluster operator in terms of geminal creation/annihilation operators can be carried out analogously to the dispersive case. Alternatively, one may formulate the theory using determinantal and/or internally contracted excited states. As far as excited functions span the same space, their actual form is irrelevant, due to the invariance of LCC theory to a unitary transformation.[87]

4. APPLICATIONS

A numerical study on the performance of MR-LCC theory based on the APSG wave function is presented in this section, on the two-geminal example of two He atoms and the water molecule. The latter is treated in the frozen core approximation, hence involving four geminals. Apart from total energies, the second derivative of the potential curves at around equilibrium is also examined.

We study the influence of the dimension of Arai subspaces, the effect of dispersive excitations by themselves, and the role of excitations involving spin-polarized triplet geminals. The acronym "MRLCC|DISP" is used to refer to the dispersive parametrization 15 of the cluster operator. Dispersive excited states may involve spin-polarized triplet geminals (coupled to an overall singlet). When spin-polarized geminal states are omitted, "noSP" appears in the acronym. The abbreviation "MRLCC" refers to a calculation where all states constituting the first order interacting subspace (including dispersives) are considered when solving the MR-LCC equations. This approach is termed full MR-LCC at some points. Occasionally, the results are compared with the dispersive second-order PT correction of eq 10, denoted as "PT2." FCI values are used as a benchmark; in the case of water symmetric dissociation, FCI refers to frozen core full CI calculations.

4.1. The He···He Interaction. The interaction of two helium atoms is investigated in the cc-pVDZ basis set,[88] with all orbitals assigned to either of the geminals. This gives 5 as the dimension of each Arai subspace.

In Figure 1, the APSG energies are presented along with MR-LCC results as compared to the FCI energies. The MR-LCC curve is depicted by restricting the excitations to dispersive ones ("APSG-MRLCC|DISP"), as well as the full MR-LCC curve ("APSG-MRLCC").

Figure 1 reflects the fact that the APSG method describes only intrageminal correlation; thus it cannot describe intergeminal dispersion. (The shallow well depth apparent in Figure 1 is a genuine basis set superposition effect.) Adding the correction of dispersive amplitudes in an MR-LCC scheme, approximately half of the expected well depth is recapitulated. An interesting feature of this example is that a full MR-LCC calculation provides a potential curve which cannot be distinguished by visual inspection from the FCI result, the exact one in the given basis set. (The difference between these results appears in the ninth digit.) Intergeminal (in this example also interatomic) correlations tend to zero at infinite distance; the APSG energy therefore matches the FCI result in this limit.

4.2. Symmetric Dissociation of Water. *4.2.1. Role of Dispersive Amplitudes.* As a second example, the symmetric
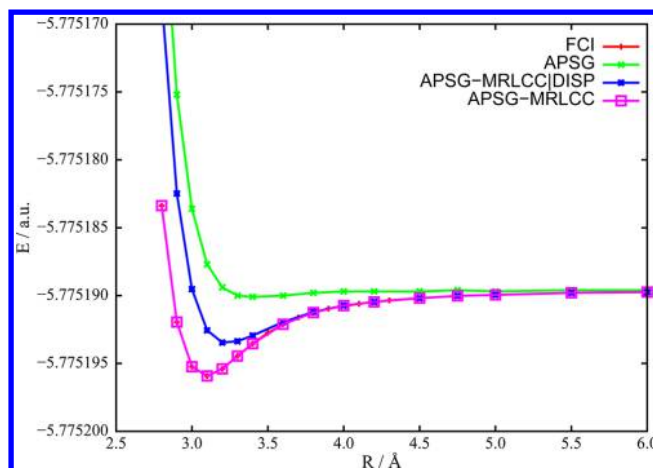

Figure 1. Energy of the helium dimer as a function of interatomic distance in the cc-pVDZ basis set. There are five functions on each helium in the APSG wave function. See text for acronyms.

dissociation of a water molecule is investigated. As seen in Figure 2, the APSG wave function alone describes this process
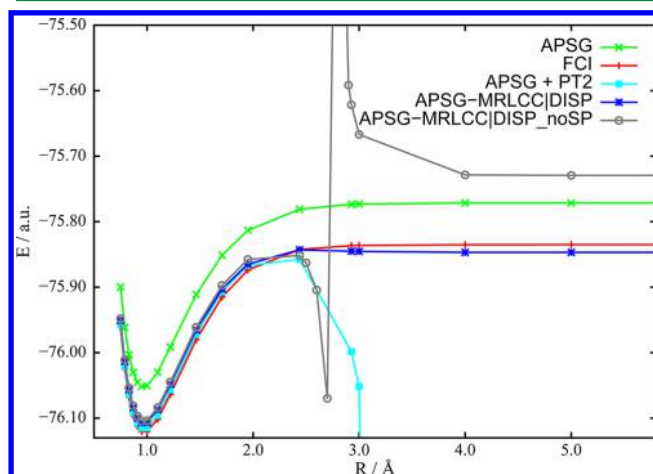

Figure 2. Water symmetric dissociation in 6-31G basis set with bond angle fixed at $\angle$ (H−O−H) = 110.6°. An APSG wave function is assumed as the reference. Frozen core approximation is applied. The APSG reference has four orbitals on the bonding and two on the nonbonding geminals. See text for acronyms.

qualitatively well. Second order dispersive perturbative corrections lead to a divergent energy curve, see "APSG + PT2" in Figure 2. This can be corrected if accounting for dispersive excitations by the MR-LCC theory: the curve "APSG-MRLCC|DISP" shows an acceptable agreement with a slight overestimation of the absolute energy for large OH distances. At around equilibrium, the second order results are closer to the FCI ones than those obtained by MR-LCC, see Figure 3. Having a closer look at the energy values, it is apparent that while CC-correction improves the absolute energies, it does not necessarily improve relative energies.

4.2.2. Role of Spin-Polarized States. Among dispersive amplitudes, those corresponding to spin-polarized excitations were found to have special importance. These are states that contain $\hat{X}_k$ excitation operators in eq 15 with $\psi_{ip}^+ = \Sigma_{m<n\in i} C_{mn}^{ip} m_\alpha^+ n_\alpha^+$ being an $M_S = +1$ geminal creation operator and $\psi_{jq}^+ = \Sigma_{m<n\in j} C_{mn}^{jq} m_\beta^+ n_\beta^+$ an $M_S = -1$ one, or vice versa. The two spin-polarized triplets with opposite M_S quantum numbers
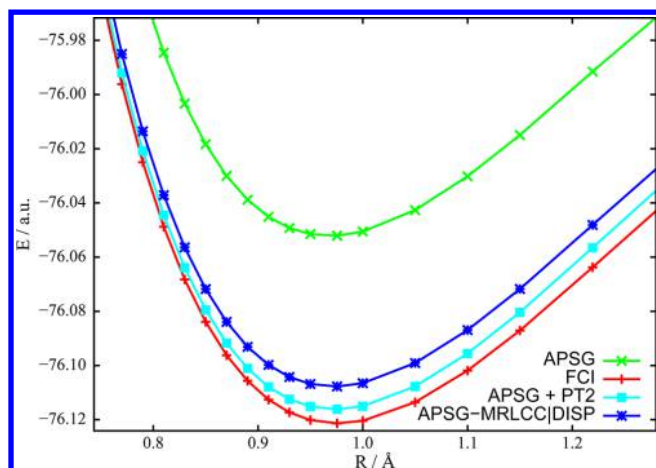
Figure 3. Water symmetric dissociation around equilibrium in 6-31G basis set. See text for acronyms and the legend of Figure 2 for other particulars.

can be coupled into a singlet four-electron state. Omitting these spin-flip triplets, one obtains the curve denoted by "APSG-MRLCC|DISP_noSP" in Figure 2. Apart from badly over-estimating the dissociation energy, this curve goes through a singularity at around 3.0 Å, rendering the potential curve meaningless. This is a typical example of an LCC singularity caused by a zero eigenvalue of coefficient matrix **A**.

4.2.3. Role of Charge Transfer and Virtual Excitations. As Figures 2 and 3 reflect, dispersion correction alone is enough to describe water dissociation without a divergent potential energy surface. Moreover, dispersion correction accounts for much of the correlation effect in the example of Figure 2. This is not a general observation however; the error committed by "APSG-MRLCC|DISP" depends largely on the number of orbitals assigned to geminals. To show this, in the next example only two orbitals are assigned to the geminals describing the OH bonds, while lone pairs remain at the Hartree–Fock level, with only one function per geminal. This is called the Generalized Valence Bond (GVB) function[89] (also called as *best orbital description* in ref 53). In Figure 4, it is again visible that
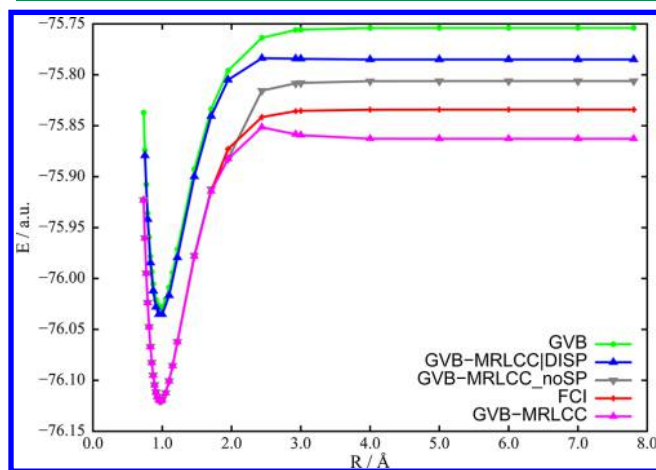

Figure 4. Water symmetric dissociation in the 6-31G basis set with bond angle fixed at $\angle$ (H−O−H) = 110.6°. A GVB wave function is assumed as the reference, and the frozen core approximation is applied. The GVB reference contains two orbitals on the bonding and one on the nonbonding geminals. See text for acronyms.

dispersive excitations described by MR-LCC give a qualitatively correct result. However the total energy shows hardly any improvement at around equilibrium, while a rough 40% of the error of GVB is accounted for in the dissociation limit.

Taking into account all excitations yielding the first order interacting subspace, the curve labeled "GVB-MRLCC" in Figure 4 is obtained. Apart from dispersion, this method takes into account the effect of "charge transfer" (i.e., annihilating one or two orbitals of a geminal and creating orbitals on other geminals and also excitations to those orbitals that do not belong to the subset of any of the geminals). Inspection of Figure 4 reveals that the total energy is much improved by "GVB-MRLCC" at around equilibrium. The curve however shows a hump at an intermediate bond distance and results in an overestimation of the correlation energy in the dissociation limit. It is interesting to investigate the effect of omitting spin-polarized excitations on the "GVB-MRLCC" results. The curve produced by this approach is labeled "GVB-MRLCC_noSP" in Figure 4. Apparently, removal of spin-polarized geminal states cures the shape of the potential energy curve. On the other hand, regarding the dissociation energy, neither "GVB-MRLCC" nor "GVB-MRLCC_noSP" is accurate. Figure 5 shows that at the equilibrium bond distance, we are quite close to the FCI results, while at an infinite distance, both approaches are erroneous by tens of millihartrees.
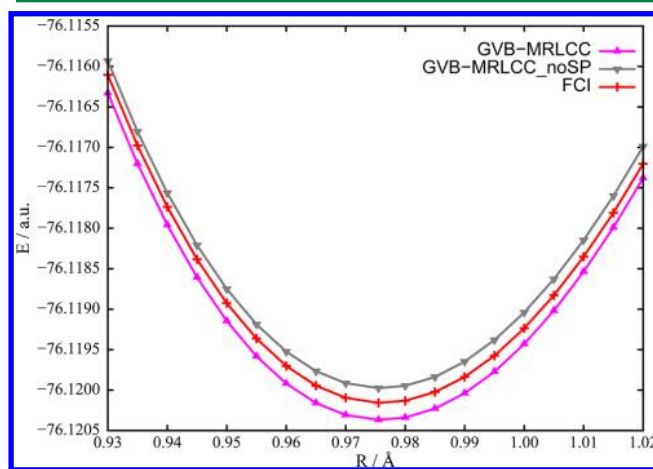

Figure 5. Water symmetric dissociation around equilibrium in 6-31G basis set. See text for acronyms and the legend of Figure 4 for other particulars.

Staying with a GVB reference function described above, Figure 6 displays the water dissociation profile calculated in the 6-31G* basis set. One can observe that "dispersive states" by themselves (GVB-MRLCC|DISP) produce a curve of qual-itatively correct shape, though minor improvement in total energy. When all states of the first-order interacting space are considered, we experience again a hump, but the effect in the polarized basis is considerably greater (GVB-MRLCC). The breakdown of the GVB-MRLCC curve at a large bond distance is similar to the behavior observed for the imperfect pairing (IPP) approximation by Head-Gordon and Voorhis.[39] The analysis of a two-geminal dissociation case has revealed that the reason behind the ill behavior of IPP is the presence of a spurious singlet−singlet coupling term in the wave function.[40] The reason for the erroneous curve obtained by GVB-MRLCC may also lie with the incorrect spin state of the fragments, as described by APSG in the dissociated limit. Omitting spin-
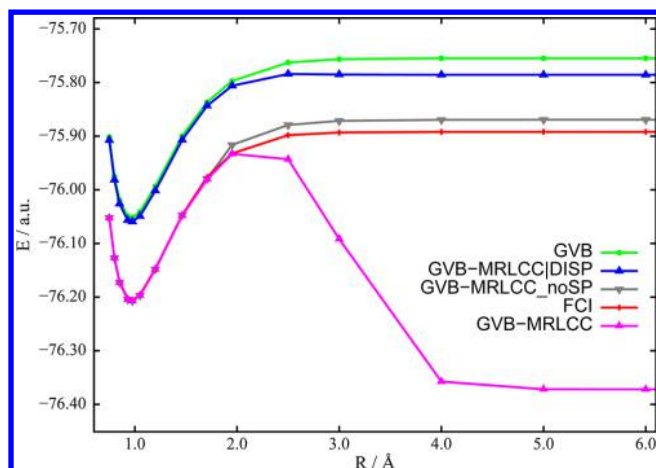
Figure 6. Water symmetric dissociation in 6-31G* basis set with bond angle fixed at $\angle(H-O-H) = 110.6°$. A GVB wave function is assumed as the reference, and the frozen core approximation is applied. The GVB reference contains two orbitals on the bonding and one on the nonbonding geminals. See text for acronyms.

polarized geminals (GVB-MRLCC_noSP) from the full MR-LCC treatment cures the shape of the curve on this example also.

4.2.4. Force Constants for Water. Table 1 shows force constants of the water molecule, calculated by taking five

Table 1. Force Constants for Water Symmetric Stretching in 6-31G Basis Set, $\angle (H-O-H) = 110.6°$[a]

method	force constant $[E_h/a_0^2]$
APSG	1.06
GVB	0.86
APSG + PT2	0.92
APSG-MRLCC|DISP	1.01
GVB-MRLCC	0.96
frozen core FCI	0.98

[a]See text for acronyms. GVB reference contains two orbitals on the bonding geminals and one on the nonbondings. APSG reference has four orbitals on the bonds and two on the nonbonding geminals.

equidistant points along the symmetric stretching, near equilibrium with a 2×10^{-4} Å difference in bond length. Either "APSG" or "GVB" is regarded as a reference. In the former case, each virtual orbital is given to one of the geminals (a full geminal calculation), while in case of "GVB" only two orbitals are assigned to the bonding geminals. Comparing force constants of the geminal based methods, we see that "APSG" overestimates the force constant; "GVB" does the opposite. Dispersive excitations described by MR-LCC (APSG-MRLCC\|DISP) give a better picture than a PT correction (APSG + PT2). Keeping the "GVB" function as the reference, a full MR-LCC correction considerably improves the results (GVB-MRLCC).

5. CONCLUSION

A linearized MR-LCC method based on the APSG reference state was introduced. The theory is size-extensive, and no redundancy problems appear. The system of amplitude equations is uniquely soluble. The theory is able to correct the deficiencies of the PT formulation based on the dispersive states, namely the incorrect description of simultaneous single

bond dissociations due to zero denominators in the dissociation limit. The addition of single and double excitations of the determinants present in the APSG reference further improves the results. In the case of the He⋯He interaction, the MR-LCC results get very close to the FCI calculations. Omission of the spin-polarized states from the dispersive coupled cluster method also leads to divergences in the symmetric dissociation of water. When performing full MR-LCC calculations (this case was investigated for the GVB wave function only), we experienced the opposite thing; spin-polarized triplet geminal states were responsible for incorrect dissociation behavior. Among the methods investigated, this latter one gives the smallest error. It is however necessary to perform further studies on a wider set of examples, before a decision on the preferred correction scheme to APSG could be made.

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Notes

The authors declare no competing financial interest.

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