Considerations on describing non-singlet spin states in variational second order density matrix methods

Helen van Aggelen, Brecht Verstichel, Patrick Bultinck, Dimitri Van Neck, and Paul W. Ayers

Citation: J. Chem. Phys. **136**, 014110 (2012); doi: 10.1063/1.3672087
View online: http://dx.doi.org/10.1063/1.3672087
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v136/i1
Published by the American Institute of Physics.

Considerations on describing non-singlet spin states in variational second order density matrix methods

Helen van Aggelen,[1,a),b)] Brecht Verstichel,[2,a)] Patrick Bultinck,[1,a)] Dimitri Van Neck,[2,a)] and Paul W. Ayers[3]
[1]*Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 S3, 9000 Ghent, Belgium*
[2]*Center for Molecular Modelling, Ghent University, Proeftuinstraat 86, 9000 Ghent, Belgium*
[3]*Department of Chemistry, Mc Master University, L8S 4M1, Hamilton, Ontario, Canada*

(Received 2 September 2011; accepted 5 December 2011; published online 5 January 2012)

Despite the importance of non-singlet molecules in chemistry, most variational second order density matrix calculations have focused on singlet states. Ensuring that a second order density matrix is derivable from a proper *N*-electron spin state is a difficult problem because the second order density matrix only describes one- and two-particle interactions. In pursuit of a consistent description of spin in second order density matrix theory, we propose and evaluate two main approaches: we consider constraints derived from a pure spin state and from an ensemble of spin states. This paper makes a comparative assessment of the different approaches by applying them to potential energy surfaces for different spin states of the oxygen and carbon dimer. We observe two major shortcomings of the applied spin constraints: they are not size consistent and they do not reproduce the degeneracy of the different states in a spin multiplet. First of all, the spin constraints are less strong when applied to a dissociated molecule than when they are applied to the dissociation products separately. Although they impose correct spin expectation values on the dissociated molecule, the dissociation products do not have correct spin expectation values. Secondly, both under "pure spin state conditions" and under "ensemble spin state" conditions is the energy a convex function of the spin projection. Potential energy surfaces for different spin projections of the same spin state may give a completely different picture of the molecule's bonding. The maximal spin projection always gives the most strongly constrained energy, but is also significantly more expensive to compute than a spin-averaged ensemble. In the dissociation limit, both the problem of nondegeneracy of equivalent spin projections, size-inconsistency and unphysical dissociation can be corrected by means of subspace energy constraints.
 [doi:10.1063/1.3672087]

I. INTRODUCTION

Electronic spin lies at the heart of chemistry. The surprisingly simple quantum chemical description of spin has helped us to understand the most fundamental properties of matter.[1,2] However, when we do not wish to work with the full wavefunction, which is an impractical mathematical object, and work with more compact variables instead, describing spin is problematic. In density functional approximations (DFA), one often resorts to symmetry breaking.[3] A recent approach by Yang *et al.* adjusts DFA functionals to correct the origin of the problems that arise in describing spin, the concave relationship between the energy and fractional $\hat{S}_z$ expectation values.[4,5]

Although variational second order density matrix (v2DM) theory is typically a ground state method, it can be applied to find the lowest-energy state for a given spin state. Nonetheless, the problem of describing non-singlet spin states in v2DM theory has received little attention, although Valdemoro and co-workers have made a thorough study of spin purification procedures in the context of the contracted Schrödinger equation.[6,7] Mazziotti has pointed out the advantages of spin and spatial symmetry adaptation, providing a framework for singlet and non-singlet state calculations in a spin adapted basis in v2DM theory, but illustrates them only with singlet state calculations.[8,9] Very little about non-singlet state v2DM calculations has appeared in the literature.[10] An approach taken by Hammond and Mazziotti avoids the problem of dealing with a non-singlet spin states by coupling them to an overall singlet state.[10] However, because of the inherent size-inconsistency of approximate *N*-representability constraints (and, more importantly, of approximate *S*-representability constraints, as we will show here) and their tendency to allow fractional charges in non-interacting systems,[11–13] this approach is problematic.

A consistent treatment of non-singlet spin states in v2DM theory has not emerged yet but is much needed, not only because many important molecules are non-singlet states in their ground state but also because many singlet molecules dissociate into products in non-singlet states. Spin may therefore help us understand and solve size-consistency and dissociation issues.

For this reason, we propose several strategies to describe spin in variational 2DM approaches and compare their benefits and drawbacks. We consider two main approaches to derive constraints on the second order density matrix (2DM): from an *N*-electron pure spin state with fixed spin quantum

[a)]Member of the Ghent-Brussels QC-MM alliance.
[b)]Electronic mail: helen.vanaggelen@ugent.be.

numbers S and M and from an ensemble of N-electron spin states with different spin projection M. Section III discusses briefly which constraints follow directly from the N-electron state's spin properties when it is a pure spin state and when it is an ensemble spin state. Section V analyses both approaches by applying them to the potential energy graph of non-singlet molecules, the carbon dimer, and the oxygen dimer. First of all, Sec. II places the problem of describing spin in the context of practical v2DM methods.

II. *N*-REPRESENTABILITY CONDITIONS

Variational second order density matrix theory aims to replace the wavefunction by the second order density matrix as variable in a variational optimization, driven by the property that the 2DM fully describes all one- and two-electron interactions.[14,15] However, as the method avoids to make any reference to a wavefunction for the system, it cannot guarantee that there exists an antisymmetrical positive semidefinite Nth order density matrix from which the resulting 2DM can be derived,[16,17]

$$\Gamma_{i_1 i_2 j_1 j_2} = \frac{1}{(N-2)!} \sum_{i_3 \ldots i_N} \Gamma^{(N)}_{i_1 i_2 i_3 \ldots i_N \; j_1 j_2 i_3 \ldots i_N},$$

unless necessary and sufficient conditions to ensure so are imposed. Any 2DM that has a preimage in the set of antisymmetrical positive semidefinite Nth order density matrices under this contraction describes a physically correct electron pair distribution and is "ensemble N-representable".[16,18] Because the known necessary and sufficient conditions for N-representability are harder than full-CI from the complexity point of view,[19] only a limited set of necessary conditions is imposed in practice.[16,20,21] This, of course, results in optimizing over too large a variational space, hence convergence to a lower bound energy to the exact energy. In this work, we chose to impose only 2-index conditions on the 2DM, because including higher order conditions makes the calculations too expensive.

The most important necessary N-representability constraints on the 2DM are the so-called P-, Q-, and G-condition.[16,20,21] They impose positive-semidefiniteness of the 2DM in the basis of particle-particle, hole-hole, and particle-hole states. They are linearly interdependent through the anticommutator relationships for creation and annihilation operators.

P-condition: $\Gamma \succeq 0$ with $\Gamma_{ijkl} = \langle \Psi | a_k^\dagger a_l^\dagger a_j a_i | \Psi \rangle$.

Q-condition: $Q(\Gamma) \succeq 0$ with $Q(\Gamma)_{ijkl} = \langle \Psi | a_k a_l a_j^\dagger a_i^\dagger | \Psi \rangle$.

G-condition: $G(\Gamma) \succeq 0$ with $G(\Gamma)_{ijkl} = \langle \Psi | a_k^\dagger a_l a_j^\dagger a_i | \Psi \rangle$.

In addition to these semidefinite constraints, antisymmetry, Hermiticity, and spatial symmetry are imposed on the 2DM by construction. Another type of Hamiltonian-dependent N-representability constraint that will be considered is a non-convexity condition on the energy of subspaces of the one-particle basis space for fractional numbers of electrons in the subspace. This type of constraint has been introduced in previous work, and has been shown to correct size-consistency defects and produce correctly charged dissociation products.[12,13]

III. *S*-REPRESENTABILITY CONDITIONS

Analogously to the concept of N-representability, *S-representability* refers to the property that a density matrix is reducible from a proper N-electron spin state. Because the 2DM only carries information on one- and two-particle interactions, ensuring S-representability is a difficult problem. For instance, for the $\hat{S}^2$ operator, only the expectation value can be imposed explicitly, which does not guarantee that the state described by the variationally optimized 2DM is an eigenfunction of $\hat{S}^2$. We discern two types of constraints: spin symmetry adaptation of the two-particle (tp) basis, which is imposed by construction, and equality constraints derived from the action of spin operators on the N-electron state, which are imposed by projection in the variational optimization.

A. Spin symmetry adaptation

The 2DM can be expressed in spin-coupled basis, which is a basis for the tp state that satisfies the commutation relationships of a proper spin state under $\hat{S}_z$, $\hat{S}^+$, and $\hat{S}^-$.[8] Expressing the 2DM in a spin-coupled basis makes it easier to exploit additional symmetries for states with zero spin projection ($M_s = 0$) or zero spin ($S = 0$). For most spin states, spin symmetry adaptation is not an active constraint, because energy minimization under the driving force of a spinless Hamiltonian and constraints with the correct spin symmetry leads to a 2DM with correct spin symmetry. For singlet states, however, spin symmetry adaptation truly constrains the energy.

Spin coupled tp creation operators $\hat{A}^{SM_s}$ that form a basis for the 2DM can be composed from two particle creation operators $a_k^\dagger a_l^\dagger$ with suitable normalization through

$$\hat{A}^{0\,0}_{kl} = \frac{1}{\sqrt{2(1+\delta_{kl})}} (a_k^\dagger a_{\bar{l}}^\dagger + a_l^\dagger a_{\bar{k}}^\dagger),$$

$$\hat{A}^{1-1}_{kl} = a_{\bar{k}}^\dagger a_{\bar{l}}^\dagger,$$

$$\hat{A}^{1\,0}_{kl} = \frac{1}{\sqrt{2}} (a_k^\dagger a_{\bar{l}}^\dagger - a_l^\dagger a_{\bar{k}}^\dagger),$$

$$\hat{A}^{1\,1}_{kl} = a_k^\dagger a_l^\dagger,$$

where bars on the orbital indices are used to discern beta spin orbitals from alpha spin orbitals. Once coupled to tp creation operators $\hat{A}^{SM_s}_{kl}$ that are proper spin functions, the symbols denoting the individual spins of the single-particle (sp) orbitals are redundant and will thus be omitted. The operator $\hat{A}^{0\,0}_{kl}$ generates a singlet pair state and the operators $\hat{A}^{1-1}_{kl}$, $\hat{A}^{1\,0}_{kl}$, and $\hat{A}^{1\,1}_{kl}$ generate a triplet pair state. In general, elements $ijkl$ of the 2DM in the spin coupled basis are therefore

$$\langle \Psi | \hat{A}^{S_2\;M_2}_{kl} \left(\hat{A}^{S_1\;M_1}_{ij} \right)^\dagger | \Psi \rangle,$$

although spin symmetry implies that only certain combinations of S_2, S_1 and M_2, M_1 can couple to a non-zero element. First of all, the 2DM must be diagonal in the spin projection

of the tp state, $M_1 = M_2$. Hence in general it has three non-zero spin blocks which can be labeled according to the spin eigenvalues S_1, S_2 and the mutual spin projection $M_1 = M_2 \equiv M'$ of the spin-coupled tp state, so we introduce the notation

$$\Gamma_{ijkl}^{S_1 S_2\ M'} = \langle \Psi | \hat{A}_{kl}^{S_2, M'} \left(\hat{A}_{ij}^{S_1\ M'}\right)^\dagger | \Psi \rangle$$
$$\text{for } M' = -\min(S_1, S_2), 0, \min(S_1, S_2). \tag{1}$$

As for the coupling of the spins S_1 and S_2 of the two-particle/hole creation and annihilation operator, there are several possibilities, depending on the molecular state $|\Psi\rangle$ under consideration.

1. Pure spin states

For a pure spin state $|\Psi\rangle = |SM\rangle$, the formula for the spin-coupled 2DM (1) leads to the following block structures.

I. For a singlet state, there are only two linearly independent blocks in the 2DM, a "singlet" block with $S_1 = S_2 = 0$ and a "triplet" block with $S_1 = S_2 = 1$.

$$S = 0,\ M = 0: \begin{pmatrix} \Gamma^{00\ 0} & 0 \\ 0 & \Gamma^{11\ 0} = \Gamma^{11\ 1} = \Gamma^{11\ -1} \end{pmatrix}. \tag{2}$$

II. For the zero projection of a non-singlet state, the structure of the 2DM in spin coupled basis is

$$S \neq 0,\ M = 0: \begin{pmatrix} \Gamma^{00\ 0} & 0 & 0 \\ 0 & \Gamma^{11\ 0} & 0 \\ 0 & 0 & \Gamma^{11\ 1} = \Gamma^{11\ -1} \end{pmatrix}. \tag{3}$$

The reason that the blocks $\Gamma^{10\,0}$ and $\Gamma^{01\,0}$ are zero is that we consider spin free Hamiltonians with a spatially non-degenerate ground state. In this case, the wave function with $M = 0$ must be symmetric under the replacement of all electron spin projections from α to β and vice versa.

III. For any other non-zero spin state, the 2DM is only diagonal in the spin projection of the tp basis. It thus has a structure

$$S \neq 0,\ M \neq 0: \begin{pmatrix} \Gamma^{00\ 0} & \Gamma^{01\ 0} & 0 & 0 \\ \Gamma^{10\ 0} & \Gamma^{11\ 0} & 0 & 0 \\ 0 & 0 & \Gamma^{11\ 1} & 0 \\ 0 & 0 & 0 & \Gamma^{11\ -1} \end{pmatrix}. \tag{4}$$

2. Ensemble spin states

In contrast to a pure spin state 2DM, the 2DM for an ensemble spin state does not need to have a block structure by spin symmetry, although in practice any v2DM calculation on such a system under the usual spin constraints, which do have a spin block structure, will return a 2DM with the same block structure.

Because the different spin projections are degenerate for the spinless Hamiltonians considered, a general wavefunction for a spin-S state can be written

$$|\Psi\rangle = \sum_{M=-S}^{S} c_M |SM\rangle \qquad \text{with} \quad \sum_M c_M^2 = 1.$$

Therefore the elements $ijkl$ of an ensemble 2DM composed of these wavefunctions may have the form

$$\Gamma_{ijkl}^{S_1 S_2\ M_1 M_2} = \sum_n w_n \sum_{M, M'=-S}^{S} c_M^n c_{M'}^n \langle SM' | \hat{A}_{kl}^{S_2\ M_2} \times \left(\hat{A}_{ij}^{S_1\ M_1}\right)^\dagger | SM \rangle,$$

with $w_n \geq 0, \sum_n w_n = 1$, such that $\langle \hat{S}_z \rangle = \sum_n w_n \sum_M (c_M^n)^2 M$. This form of 2DM in general does not lead to a block diagonal structure. In contrast to the pure spin state case, even the off-diagonal blocks with $M_1 \neq M_2$ may be non-zero because of a contribution from the transition density matrix elements $\langle SM' | \hat{A}_{kl}^{S_2\ M_2} (\hat{A}_{ij}^{S_1\ M_1})^\dagger | SM \rangle$ with $M \neq M'$.

However, in order to reduce computational cost and save memory, the 2DM may be restricted to have the same symmetry as a corresponding pure state would have, since this is a valid, albeit not necessary, representation of the spin state. We will therefore consider the same block structure as (3) and (4) for non-singlet ensemble spin states. A special case arises when the spin-averaged ensemble

$$\frac{1}{2S+1} \sum_{M=-S}^{S} \langle SM | \hat{A}_{kl}^{S_2\ M_2} \left(\hat{A}_{ij}^{S_1\ M_1}\right)^\dagger | SM \rangle \tag{5}$$

is considered. This composition of the ensemble leads to a spin block structure that is similar to that of a singlet state (2).[22]

B. Constraints derived from the action of spin operators $\hat{S}^2$, $\hat{S}_z$, $\hat{S}^+$, and $\hat{S}^-$ on the N-electron state

1. Pure spin states

The following constraints can be derived from the properties of a pure spin state wavefunction under the operators $\hat{S}^2$, $\hat{S}_z$, $\hat{S}^+$, and $\hat{S}^-$.

1. The "contraction" condition expresses that for any pure spin state

$$(N\ \hat{S}_z - M\ \hat{N}) |\Psi^{SM}\rangle = 0. \tag{6}$$

where $\hat{N}$ is the electron number operator and N is the number of electrons. This condition implies that the vector corresponding to this operator lies in the nullspace of the $M_1 = M_2 = 0$ block of the G-matrix:

$$\forall k, l: \ \sum_i N\ G_{iikl}^{10\ 0} - 2M\ G_{iikl}^{00\ 0} = 0, \tag{7}$$

$$\sum_i N\ G_{iikl}^{11\ 0} - 2M\ G_{iikl}^{10\ 0} = 0. \tag{8}$$

This condition ensures that the spin blocks of the 1DM can be derived from the 2DM both by contraction over α orbital indices and by contraction over β orbital indices. It thus imposes $K(K+1)$ conditions on the DM2, with K the sp basis size, although the number of practically relevant conditions is less if spatial symmetry is taken into account. It also ensures that the variance of the $\hat{S}_z$ operator vanishes for a pure spin state. As is obvious from formula (6), it implies correct $\hat{S}_z$ expectation value, and together with the normalization of the whole 2DM, $tr\Gamma = N(N-1)$, it implies normalization of the spin blocks to

$$tr\ \Gamma^{11\ 1} = \frac{1}{2}\left(\frac{N}{2}+M\right)\left(\frac{N}{2}+M-1\right), \quad (9)$$

$$tr\ \Gamma^{11\ -1} = \frac{1}{2}\left(\frac{N}{2}-M\right)\left(\frac{N}{2}-M-1\right), \quad (10)$$

$$tr\ \Gamma^{11\ 0} + tr\ \Gamma^{00\ 0} = \left(\frac{N}{2}+M\right)\left(\frac{N}{2}-M\right). \quad (11)$$

2. The maximal spin projection for a spin-S state, $M = S$, must satisfy the condition

$$\hat{S}^+|\Psi^{SM}\rangle = 0. \quad (12)$$

This condition forces the vector corresponding to the $\hat{S}^+$ operator to lie in the nullspace of the $G^{11\ 1}$ block of the G-matrix:

$$\forall k,l: \ \sum_i G^{11\ 1}_{iikl} = 0, \quad (13)$$

which implies K^2 additional conditions on the 2DM. Along with the contraction condition, it imposes correct $\hat{S}^2$ expectation value.

3. A smaller spin projection of a spin-S state, $|M| < S$, must satisfy

$$\forall k,l: \ (S-M)(S+M+1)\sum_i G^{11\ 1}_{iikl} = (S+M)(S-M+1)\sum_i G^{11\ -1}_{iikl}, \quad (14)$$

because the sums of G-matrix elements appearing in this expression can be identified as the first order transition density matrix elements involving the states $|SM-1\rangle, |SM\rangle, |SM+1\rangle$,

$$\sum_i G^{11\ 1}_{iikl} = \langle\Psi^{SM}|a_k^\dagger a_l S^+|\Psi^{SM}\rangle \quad (15)$$

$$= \sqrt{(S-M)(S+M+1)}\langle\Psi^{SM}|a_k^\dagger a_l|\Psi^{SM+1}\rangle, \quad (16)$$

$$\sum_i G^{11\ -1}_{iikl} = \langle\Psi^{SM}|a_k^\dagger a_l S^-|\Psi^{SM}\rangle \quad (17)$$

$$= \sqrt{(S+M)(S-M+1)}\langle\Psi^{SM}|a_k^\dagger a_l|\Psi^{SM-1}\rangle, \quad (18)$$

which are related, as expressed by the Wigner-Eckart theorem, yielding the condition (14). The condition (13) for maximal spin projection is a special case of this condition. Just like the maximal spin projection condition (13), it imposes K^2 additional conditions on the 2DM and imposes correct $\hat{S}^2$ expectation value when combined with the contraction condition, except for states with zero spin projection. In those cases, the condition (14) is already satisfied by the zero spin projection's symmetry. Correct $\hat{S}^2$ expectation value then needs to be imposed additionally.

2. Ensemble spin states

Unless a specific composition of the ensemble is assumed, there are few obvious generally holding constraints that derive from the wavefunctions that make up the ensemble. Imposing the total spin of the ensemble is limited to specifying its correct expectation value. Similarly, the $\hat{S}_z$ expectation value of the ensemble can be fixed.

1. Correct $\hat{S}^2$ expectation value is imposed through the generally holding formula

$$\langle\hat{S}^2\rangle = \frac{N}{4}(N+2) - tr\Gamma^{000} = S(S+1). \quad (19)$$

2. Correct $\hat{S}_z$ expectation value is imposed, $\langle\hat{S}_z\rangle = \sum_n w_n \sum_{M=-S}^{S}(c_M^n)^2 M$.

If the $\hat{S}_z$ expectation value is not specified, the symmetry present in the spinless Hamiltonian will lead to a zero expectation value.

Finally, in order to compare molecular dissociation products to the dissociation products calculated separately, we also consider them under correct $\hat{S}_z$ expectation value only, since imposing correct $\hat{S}^2$ expectation value does not guarantee correct $\hat{S}^2$ expectation value on the molecular dissociation products.

IV. COMPUTATIONAL AND ALGORITHMIC DETAILS

All calculations are done in the double zeta basis set D95V as specified in GAUSSIAN 03.[23] Reference full configuration interaction calculations with core electrons frozen (FCI(FC)) are carried out with GAMESS.[24] The potential energy graphs are composed from single point calculations. For the FCI(FC) potential energy graphs, the lowest energy state with the specified spin S is selected at each bond length.

To carry out the variational optimization of the 2DM under semidefinite constraints, we have adjusted our classical barrier method to a modified barrier method, which enjoys faster convergence.[25]

V. RESULTS AND DISCUSSION

In order to examine the strength of the spin conditions discussed above, we have applied them to the potential energy graph for the carbon and oxygen dimer for several spin states and their different spin projections. The singlet, triplet,

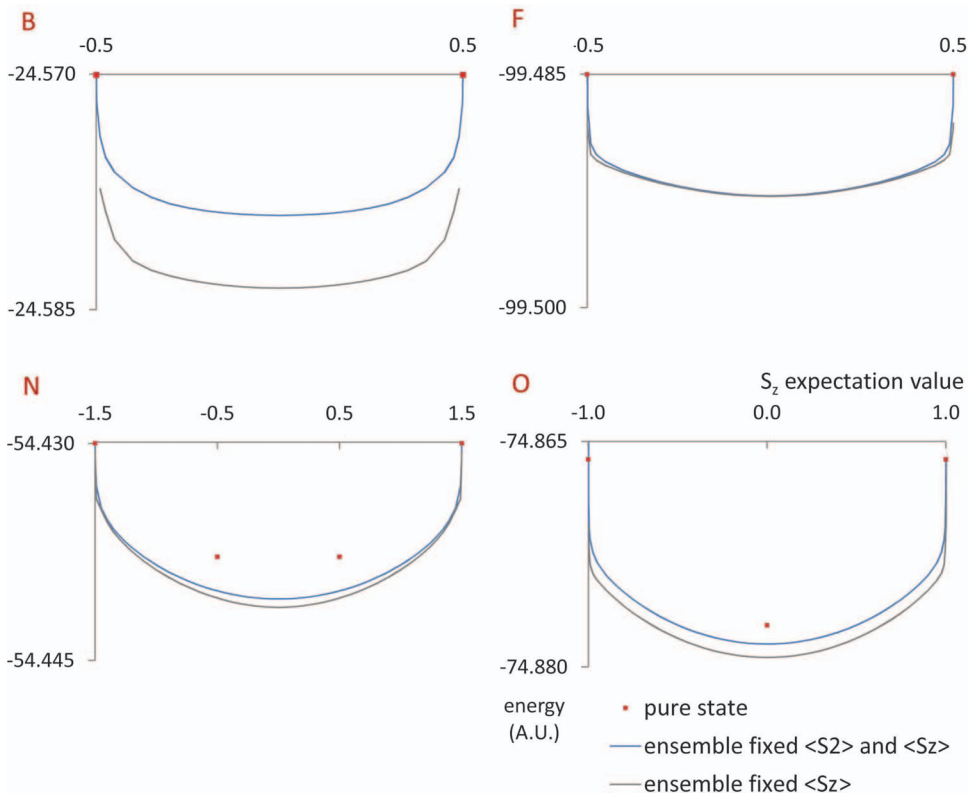

FIG. 1. The v2DM(PQG) energy, shown for the atoms boron, fluorine, nitrogen, and oxygen, is a convex function of the $\hat{S}_z$ expectation value under both pure spin state and ensemble spin state conditions. The maximal spin projection has the highest energy, even when only the $\hat{S}_z$ expectation value is imposed. The $\langle \hat{S}_z \rangle = 0$ energy without additional spin constraints is equivalent to the energy of a spin unconstrained problem, due to the spin independence of the Hamiltonian.

and quintuplet states must become degenerate in the dissociation limit. Because these systems are homonuclear, they do not suffer from dissociation into fractionally charged products under 2-positivity conditions.[12,26] These systems therefore make a good test case for examining several issues regarding spin:

Overall, are the proposed spin constraints capable of reproducing the characteristics of the potential energy graphs for different spin states and spin projections?

How do "pure spin state" constraints compare to "ensemble spin state" constraints?

How do different spin projections relate to each other?

How do spin constraints in the dissociation limit compare to those at short bond lengths? Are they equally strong at all bond lengths?

In earlier work on atomic systems,[22] we have reported calculations that assumed an ensemble resulting in a zero $\hat{S}_z$ expectation value for non-singlet spin states, and compared these to calculations for the pure spin state with maximal spin projection. A more detailed comparison of both the pure spin state approach and the ensemble spin state approach over the whole range of possible $\hat{S}_z$ expectation values for several non-singlet atoms (Figure 1) and for potential energy graphs of the lowest energy spin states of the oxygen and carbon dimer (Figures 2 and 5) reveals some more interesting features.

As a first key observation, no degeneracy for different spin projections of the same spin state is observed. This shortcoming was also noticed by Nakata.[27]

In fact, both in the pure spin state approach and in the ensemble spin state approach, the energy is convex with respect to the $\hat{S}_z$ expectation value (Figure 1). Interestingly, this is exactly the opposite behavior from that observed in DFA.[4] So the v2DM energy is not only convex with respect to the fractional electron number in between two consecutive integer electron numbers, as observed in previous work[11] but also with respect to fractional $\hat{S}_z$ expectation value in between two consecutive allowed pure state spin projections. The v2DM calculations for the maximal spin projection give the highest energy, both under pure spin state constraints (Sec. III B 1) and ensemble spin state constraints (Sec. III B 2).

The pure spin state constraints are especially strong compared to the ensemble spin state constraints near zero spin projection. In fact, as $M \rightarrow S$, the v2DM energy under ensemble spin constraints converges practically to that of the pure state maximal spin projection. For near-zero spin projections, however, the ensemble spin state conditions give a much lower energy. Even more so, the $\langle \hat{S}_z \rangle = 0$ condition does not improve the energy at all. Due to the spin independence of the Hamiltonian, the $\langle \hat{S}_z \rangle = 0$ condition without reinforcement by other spin conditions, is equivalent to not imposing any spin condition.

A second key observation is that the spin constraints are not size-consistent: the constraints on the molecular system do not imply equivalent spin constraints on the dissociation products.

The $\hat{S}_z$ expectation values of the dissociation products, being a one-electron property, are fixed to half the

TABLE I. The properties of the dissociated atoms in the oxygen dimer in the dissociation limit, denoted by the superscript "*atom*," are remarkably similar for molecular states that lead to dissociated atoms with the same spin projection, both when pure spin state conditions are imposed and when only spin projection is specified (column "not fixed"). This illustrates the inability of the pure state spin constraints to treat spin in a size-consistent manner.

Molecular state $\|S0\rangle$				
S	0	1	2	Not fixed
E^{atom}	−74.8809	−74.8809	−74.8808	−74.8809
$\langle\hat{S}_z\rangle^{atom}$	0.00	0.00	0.00	0.00
$\langle\hat{S}_z^2\rangle^{atom}$	0.68	0.45	0.28	0.68
$\langle\hat{S}^-\hat{S}^+\rangle^{atom}$	1.36	1.59	1.76	1.36
$\langle\hat{S}^2\rangle^{atom}$	2.04	2.04	2.04	2.04
Molecular state $\|S1\rangle$				
S		1	2	Not fixed
E^{atom}		−74.8794	−74.8793	−74.8795
$\langle\hat{S}_z\rangle^{atom}$		0.50	0.50	0.50
$\langle\hat{S}_z^2\rangle^{atom}$		0.51	0.48	0.69
$\langle\hat{S}^-\hat{S}^+\rangle^{atom}$		1.03	1.07	0.85
$\langle\hat{S}^2\rangle^{atom}$		2.04	2.05	2.04
Molecular state $\|S2\rangle$				
S			2	Not fixed
E^{atom}			−74.8718	−74.8725
$\langle\hat{S}_z\rangle^{atom}$			1.00	1.00
$\langle\hat{S}_z^2\rangle^{atom}$			1.01	1.01
$\langle\hat{S}^-\hat{S}^+\rangle^{atom}$			0.05	0.05
$\langle\hat{S}^2\rangle^{atom}$			2.06	2.06

homonuclear molecule's $\hat{S}_z$ expectation value, but none of their other spin properties is determined by the spin constraints on the molecule. Of course, even when the molecule is constrained to be a pure spin state, the dissociation products need not be pure spin states, but they need to be proper ensemble spin states at least. The applied spin constraints, however, lead to dissociated oxygen atoms with $\hat{S}^2$ expectation values around 2.05. Moreover, the effect of imposing spin constraints on the dissociated molecule should be equivalent to imposing them on the dissociation products separately in order to produce size-consistent energies, but this is not true for the applied spin constraints (Table II). In fact, the dissociated oxygen atoms have similar energy and $\hat{S}^2$ expectation value under the pure spin state conditions to a calculation constrained only to have the same $\hat{S}_z$ expectation value (Table I). However, when the pure spin state constraints are imposed in separate calculations on the isolated oxygen atoms, they increase the energy significantly compared to a calculation that only imposes $\hat{S}_z$ expectation value (Table II). This illustrates the discrepancies between imposing the spin constraints on the dissociated molecule as a whole and imposing them on each dissociated atom separately.

The absence of degeneracy between different spin projections of the same spin state may have far reaching implications on chemical calculations. Non-interacting states that can couple to different degenerate spin states, such as dissociated molecules, may not be treated on equal footing. Consider for example two triplet oxygen atoms, infinitely far apart. The two states can couple to either a singlet, triplet, or quintuplet state. Theoretically, all three spin states, and all of their spin projections, are energetically equivalent. So the singlet, triplet, and quintuplet oxygen dimer should yield the same energy in the dissociation limit. Unfortunately, under the pure state spin constraints only the zero spin projection gives the same dissociation limit for all spin states (Figures 2 and 3) because, for each of the spin states, the zero spin projection leads to dissociated atoms with zero spin projections in a homonuclear molecule. The maximal spin projections for the singlet, triplet, and quintuplet lead to significantly different dissociation limits. The different spin projections of the resulting dissociated atoms seem to be the main cause of these energy differences in the dissociation limit: the energies of the dissociated molecules under maximal spin projection conditions are very similar to those constrained to the same $\hat{S}_z$ expectation value only (Figures 4 and 5).

TABLE II. The pure state spin constraints are much stronger when imposed on the triplet atoms separately, as shown in this table, than when they are imposed on the dissociated singlet, triplet or quintuplet oxygen dimer (shown in Table I), even though they should be equivalent to be size-consistent.

Atomic state $\|S0\rangle$			Atomic state $\|S1\rangle$		
S	2	Not fixed	S	2	Not fixed
E^{atom}	−74.8772	−74.8794	E^{atom}	−74.8662	−74.8706
$\langle\hat{S}_z\rangle^{atom}$	0.00	0.00	$\langle\hat{S}_z\rangle^{atom}$	1.00	1.00
$\langle\hat{S}_z^2\rangle^{atom}$	0.00	0.69	$\langle\hat{S}_z^2\rangle^{atom}$	1.00	1.01
$\langle\hat{S}^-\hat{S}^+\rangle^{atom}$	2.00	1.37	$\langle\hat{S}^-\hat{S}^+\rangle^{atom}$	0.00	1.05
$\langle\hat{S}^2\rangle^{atom}$	2.00	2.06	$\langle\hat{S}^2\rangle^{atom}$	2.00	2.06

None of the spin constraints applied to different spin projections of the lowest-lying spin states of the oxygen and carbon dimer gives a truly satisfying picture of the molecule's properties.

The zero spin projection constraints treat all spin states equivalently in the dissociation limit, but fail to reproduce the correct features of the potential energy graphs for the different spin states. Most remarkably, they produce a triplet potential energy graph that is lower than the singlet potential energy graph for the carbon dimer, in contradiction with FCI(FC) results (Figure 6). In case of the oxygen dimer, they make the quintuplet state much too strongly binding (Figure 7).

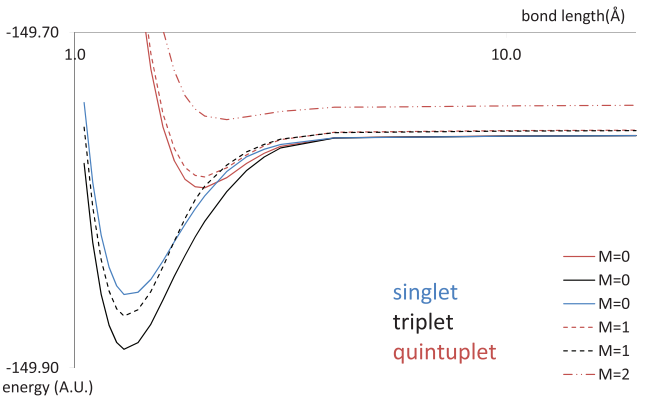

FIG. 2. The differences between the v2DM potential energy graph of the oxygen dimer under pure spin state conditions (Sec. III B 1) for different spin projections M of the same spin state S are remarkable. In the dissociation limit, the difference in the energy for different spin projections seems primarily attributable to the different $\hat{S}_z$ expectation value of the dissociated atoms because their energies are very similar to atomic energies obtained under the same $\hat{S}_z$ expectation value only (Table I).

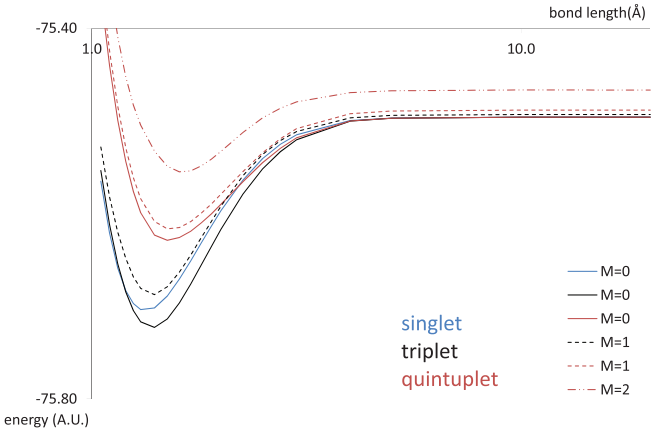

FIG. 3. Differences between the v2DM potential energy graph of the carbon dimer under pure spin state conditions (Sec. III B 1) for different spin projections M of the same spin state S are remarkable. In the dissociation limit, the difference in the energy for different spin projections seems primarily attributable to the different $\hat{S}_z$ expectation value of the dissociated atoms. Only the $S = 2, M = 1$ state gives atomic energies in the dissociation limit that are slightly higher than those obtained under $\langle \hat{S}_z \rangle = 1$.

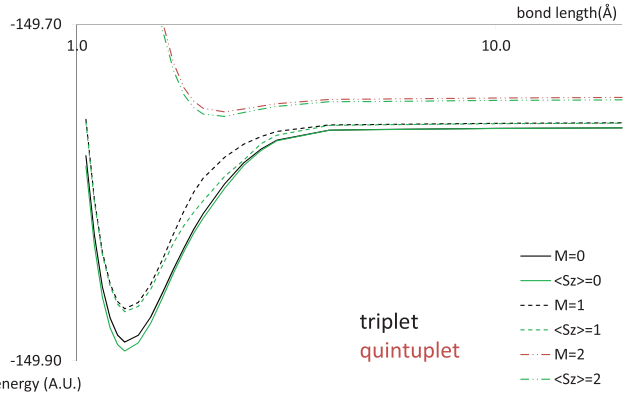

FIG. 4. Although both the v2DM(PQG) triplet and quintuplet potential energy graph (black, red) for the oxygen dimer should converge to the same dissociation limit, only the same spin projections converge to a very similar dissociation limit, which practically coincides with the dissociation limit under a constraint on $\hat{S}_z$ expectation value only, $\langle \hat{S}_z \rangle = M$ (green lines).

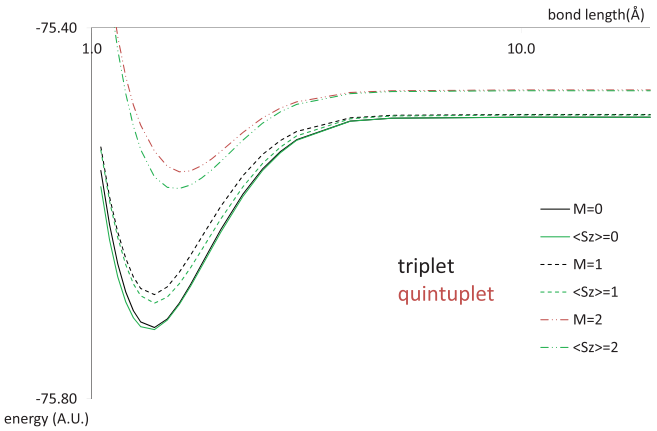

FIG. 5. Although both the v2DM(PQG) triplet and quintuplet potential energy graph (black, red) for the carbon dimer should converge to the same dissociation limit, only the same spin projections converge to a very similar dissociation limit, which practically coincides with the dissociation limit under a constraint on $\hat{S}_z$ expectation value only, $\langle \hat{S}_z \rangle = M$ (green lines).

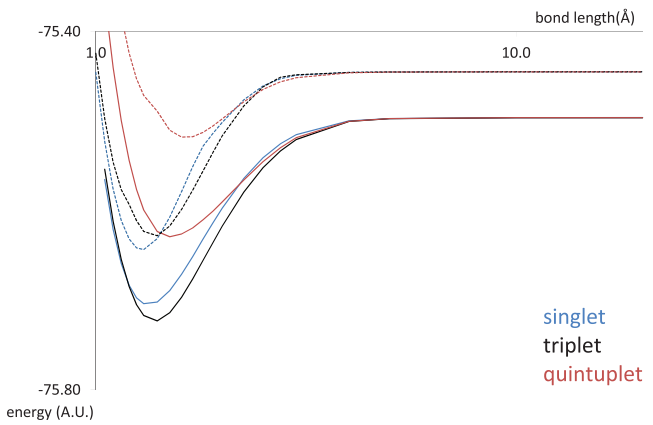

FIG. 6. The pure spin state conditions for the zero spin projection v2DM(PQG) potential energy graph (solid lines) of the carbon dimer singlet yield lower energies than those for the triplet around equilibrium bond length. Yet FCI(FC) calculations (dotted lines) prove that their relative order should be exactly opposite.

The maximal spin projection constraints give the most strongly constrained results, but do not reproduce degeneracy of the different spin states upon dissociation. They do give the lowest equilibrium energy for the singlet state of the carbon dimer (Figure 8), in agreement with FCI(FC) data, but they severely underestimate the singlet-triplet energy gap, in both the carbon and oxygen dimer (Figure 9).

The potential energy graph of the carbon dimer has also been computed in a 6-31G* basis set under singlet conditions by Gidofalvi and Mazziotti. The conditions they imposed on the singlet 2DM are equivalent to the conditions we use here, except that they did not explicitly impose the equivalence of the three triplet blocks of the 2DM in their early work.[28] The current comparison of the singlet potential energy graph with other spin states shows the subtle, but crucial, effect that spin constraints may have. Depending on the spin projection under consideration, the wrong spin state may be obtained as the lowest energy state under approximate spin constraints.

Imposing the conditions that describe a pure state maximal spin projection is theoretically the preferred method for describing spin because these conditions are the most

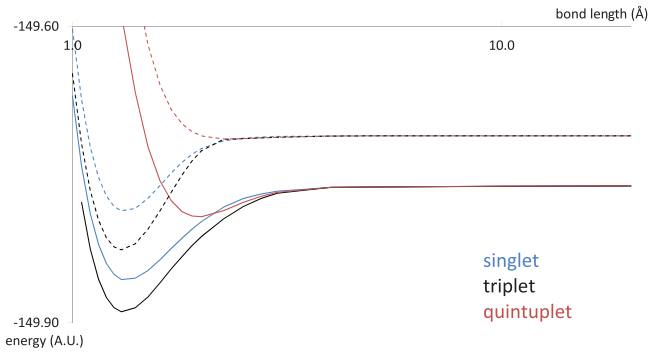

FIG. 7. The pure spin state conditions for the zero spin projection v2DM(PQG) potential energy graph (solid lines) treat all different spin states of the oxygen dimer equivalently in the dissociation limit. Yet they do not give a fully satisfying picture of its properties; the quintuplet state becomes much too strongly binding compared to FCI(FC) calculations (dotted lines).

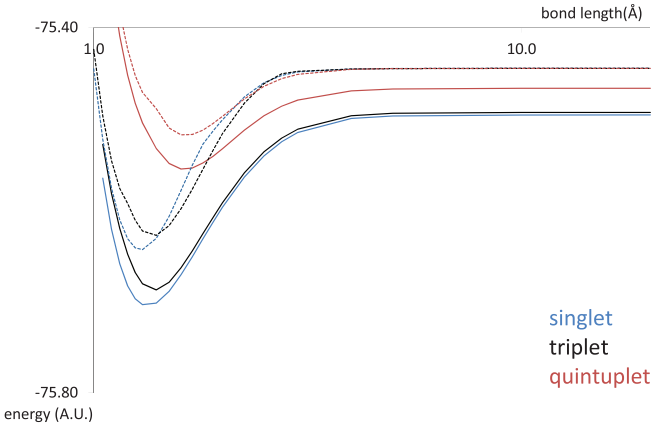

FIG. 8. The v2DM(PQG) potential energy graph (solid lines) for the maximal spin projections of the singlet, triplet, and quintuplet of the carbon dimer under pure spin state conditions (Sec. III B 1) are not equivalent in the dissociation limit. Nonetheless, they do give the correct order of singlet and triplet potential energy graph, similar to that in FCI(FC) calculations (dotted lines).

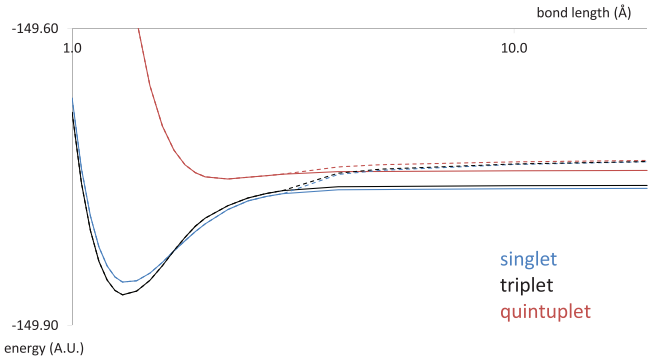

FIG. 10. When subspace constraints are imposed on the singlet, triplet, and quintuplet v2DM(PQG) potential energy graph under pure spin state conditions (Sec. III B 1), both the violation of size-consistency and the absence of degeneracy among dissociated states with different spin projections (solid lines) are corrected in the resulting potential energy graph (dotted lines). The shapes of the different spin surfaces remain poor, though, as can be seen by comparing to the FCI energies in Figure 9.

stringent, although they are also the most expensive in terms of computational cost. The pure state maximal spin projection constraints provide the most stringent lower bound on the energy and, moreover, give the correct relative order of the different spin projections for the carbon dimer. Although it does not seem straightforward to derive conditions that directly constrain non-maximal spin projections to the same extent, it is possible to derive a 2DM for a lower spin projection $M < S$ from the maximal spin projection $M = S$ by means of the Wigner-Eckart theorem.[29] By construction, the resulting 2DM for the $M < S$ spin projection will have the exact same energy as the maximal spin projection. This justifies the use of maximal spin projection conditions to get the strictest lower bound on the energy. Additionally, the inconsistencies that arise in the dissociation limit of the maximal spin projections of degenerate spin states, such as those occurring in the dissociation limit of the oxygen and carbon dimer, can be corrected by imposing subspace energy conditions.[12,13,30] At the same time, these constraints will correct size-consistency defects and incorrect dissociation—in contrast to the molecules under consideration here, non-homonuclear molecules generally dissociate into fractionally charged products in practical v2DM methods.[11]

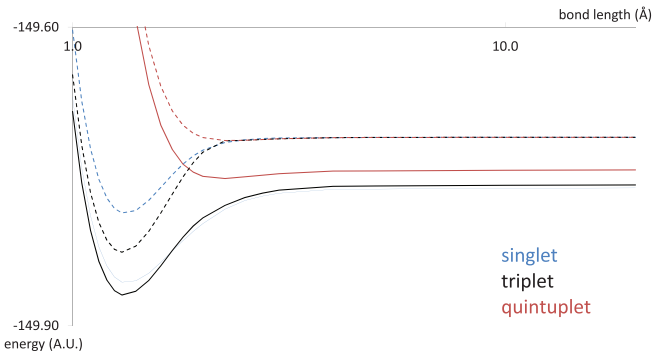

FIG. 9. The v2DM(PQG) potential energy graph (solid lines) for the maximal spin projections of the singlet, triplet, and quintuplet of the oxygen dimer under pure spin state constraints (Sec. III B 1) are not consistent: they do not converge to equivalent dissociated states. Moreover, they give a singlet-triplet gap that is much too small compared to FCI(FC) data (dotted lines).

A spin condition can be incorporated indirectly into the subspace constraints by requiring that the energy of the subspace in the molecule must be at least equal to the energy of the lowest-energy spin state of the subspace treated as a separate system. Moreover, because of the lack of degeneracy in multiplets calculated with the v2DM method, the tightest constraint is obtained if the maximal spin projection is considered for the subspace system:

$$tr[H^A\Gamma] \geq E_0(H^A)|_{S=S_0,M=S},$$

with H^A a Hamiltonian matrix for the atomic or molecular subspace A expressed in the molecular basis space, $tr[H^A\Gamma]$ the energy of the subspace A in the molecule and $E_0(H^A)|_{S=S_0,M=S}$ the ground state v2DM energy for this atomic or molecular subspace calculated separately in the maximal spin projection of the lowest energy spin state S_0. Because the energy of the reference system A should be degenerate for different spin projections, considering the highest spin projection is fully justified. This constraint can be considered an extension of the "flat plane condition" developed by Yang *et al.* in DFA (Refs. 4 and 5) to v2DM theory.

Although this constraint ensures that the energy of maximal spin projections of degenerate spin states effectively becomes degenerate in the dissociation limit, it does not improve the poor relative position of the different spin states around equilibrium bond length, because the subspace constraints only become active upon dissociation (Figure 10).[12,13]

VI. CONCLUSIONS

Two main shortcomings concerning spin constraints in v2DM theory explain the incorrect features of the potential energy graphs of the carbon and oxygen dimer for different spin states. First of all, spin constraints on a system composed of non-interacting atoms or molecules do not imply equally strong constraints on the non-interacting atoms or molecules separately. They are therefore a source of size-inconsistency.

This shortcoming is inherent to the method and will be difficult to correct except through a "quick fix," like the subspace energy constraints introduced in previous work and applied to the potential energy graph of the oxygen dimer in Figure 10.

Secondly, the v2DM energy is a convex function of the $\hat{S}_z$ expectation value, with the highest energy for the maximal spin projection. The pure spin state conditions for the maximal spin projection are therefore the most stringent conditions on the 2DM that one can formulate directly in terms of the spin operators. An equivalent 2DM for a lower spin projection is derivable from the maximal spin projection by application of the Wigner-Eckart theorem. As a consequence of the lack of degeneracy between different spin projections of a multiplet, maximal spin projections of higher spin states are more severely constrained than those of lower spin states, which becomes especially apparent in the dissociation limit, where theoretically degenerate spin states fail to become degenerate in the v2DM method. These differences, together with size-consistency defects and incorrect dissociation, can also be fixed by means of subspace constraints.

Even though the pure spin state maximal spin projection conditions are the strongest, they are also significantly more expensive than the ensemble spin state conditions, because describing them requires about twice as much variables. The ensemble approach allows to consider a spin-averaged ensemble (5) with resulting $\langle \hat{S}_z \rangle = 0$, which has similar spin symmetry to the pure state singlet (2). This reduces the number of variables by about a factor 2. Given the typical scaling of $O(K^6)$ of semidefinite programs with basis set dimension K, this makes the ensemble approach considerably cheaper. Future work may therefore focus on ways of improving the spin-averaged ensemble approach, although the lack of knowledge about the pure states that make up the ensemble makes it difficult to derive stringent constraints that apply to it.

ACKNOWLEDGMENTS

We gratefully acknowledge FWO-Flanders and the research council of Ghent University for financial support and the Flemish Supercomputer Center for sharing their computer facilities. P.W.A. acknowledges support from NSERC and Sharcnet.

[1] R. McWeeny, *Spins in Chemistry* (Dover, New York, 1970).
[2] R. McWeeny and Y. Mizuno, Proc. R. Soc. London A **259**, 554 (1968).
[3] J. P. Perdew, A. Savin, and K. Burke, Phys. Rev. A **51**, 4531 (1995).
[4] A. J. Cohen, P. Mori-Sanchez, and W. Yang, J. Chem. Phys. **129**, 121104 (2008).
[5] D. Ess, E. Johnson, X. Hu, and W. Yang, J. Phys. Chem. A **115**, 76 (2011).
[6] D. R. Alcoba and C. Valdemoro, Int. J. Quant. Chem. **102**, 629 (2005).
[7] D. R. Alcoba, C. Valdemoro, L. M. Tel, and E. Perez-Romero, Phys. Rev. A **77**, 042508 (2008).
[8] G. Gidofalvi and D. A. Mazziotti, Phys. Rev. A **72**, 52505 (2005).
[9] D. A. Mazziotti, Phys. Rev. A **72**, 32510 (2005).
[10] J. R. Hammond and D. A. Mazziotti, Phys. Rev. A **73**, 012509 (2006).
[11] H. van Aggelen, P. Bultinck, B. Verstichel, D. Van Neck, and P. W. Ayers, Phys. Chem. Chem. Phys. **11**, 5558 (2009).
[12] B. Verstichel, H. van Aggelen, D. Van Neck, P. W. Ayers, and P. Bultinck, J. Chem. Phys. **132**, 114113 (2010).
[13] H. van Aggelen, B. Verstichel, P. Bultinck, D. Van Neck, P. W. Ayers, and D. L. Cooper, J. Chem. Phys. **134**, 054115 (2011).
[14] P. O. Löwdin, Phys. Rev. **97**, 1474 (1955).
[15] K. Husimi, Proc. Phys. Math. Soc. Jpn. **22**, 264 (1940).
[16] J. Coleman, Rev. Mod. Phys. **35**, 668 (1963).
[17] C. A. Coulson, Rev. Mod. Phys. **32**, 170 (1960).
[18] H. Kummer, J. Math. Phys. **8**, 2063 (1967).
[19] P. W. Ayers and E. Davidson, Adv. Chem. Phys. **134**, 443 (2007).
[20] C. Garrod and J. K. Percus, J. Math. Phys. **5**, 1756 (1964).
[21] R. M. Erdahl, Int. J. Quant. Chem. **13**, 697 (1978).
[22] B. Verstichel, H. van Aggelen, D. Van Neck, P. W. Ayers, and P. Bultinck, Phys. Rev. A **80**, 32508 (2009).
[23] M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Revision B.05, Gaussian, Inc., Wallingford, CT, 2004.
[24] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, J. Comput. Chem. **14**, 1347 (1993).
[25] M. Stingl, "On the solution of nonlinear semidefinite programs by augmented Lagrangian methods," Ph.D. dissertation (Shaker Verlag, Aachen, 2006).
[26] B. Verstichel, H. van Aggelen, D. Van Neck, and P. Bultinck, Comput. Phys. Commun. **182**, 1235 (2010).
[27] M. Nakata, in *Workshop on Quantum Marginals and Density Matrices* (Fields Institute, Toronto, 2009).
[28] G. Gidofalvi and D. A. Mazziotti, J. Chem. Phys. **122**, 194104 (2005).
[29] W. H. Dickhoff and D. V. Neck, *Many-Body Theory Exposed! Propagator Description of Quantum Mechanics in Many-Body Systems* (World Scientific, Singapore, 2005).
[30] H. van Aggelen, B. Verstichel, P. Bultinck, D. Van Neck, P. W. Ayers, and D. L. Cooper, J. Chem. Phys. **132**, 114112 (2010).