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Variational second order density matrix study of F_3^-: Importance of subspace constraints for size-consistency

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Variational second order density matrix theory under "two-positivity" constraints tends to dissociate molecules into unphysical fractionally charged products with too low energies. We aim to construct a qualitatively correct potential energy surface for F_3^- by applying subspace energy constraints on mono- and diatomic subspaces of the molecular basis space. Monoatomic subspace constraints do not guarantee correct dissociation: the constraints are thus geometry dependent. Furthermore, the number of subspace constraints needed for correct dissociation does not grow linearly with the number of atoms. The subspace constraints do impose correct chemical properties in the dissociation limit and size-consistency, but the structure of the resulting second order density matrix method does not exactly correspond to a system of noninteracting units. © *2011 American Institute of Physics*. [doi:10.1063/1.3532409]

I. INTRODUCTION

Heteronuclear diatomic molecules do not dissociate into fractionally charged atoms. As simple as this fact is, it is far less straightforward to establish in reduced density matrix theories. Yet, such fundamental physical properties are needed to make them applicable to geometries other than the equilibrium structure. Nonequilibrium structures like molecules with stretched or partly broken bonds, such as reaction intermediates or dissociation products, play an important role in chemical processes. Despite numerous efforts, they still cause problems in density functional approximations[1–4] and density matrix functional theory.[5–7] The variational P-, Q-, and G-conditioned second order density matrix method [v2DM(PQG)] also fails in this respect.[8–10] Although this method cannot be expected to be fully size-consistent because the 2DM is not a separable quantity under a strict subset of N-representability conditions,[11,12] its failure in describing dissociating chemical systems is dramatic. Even with three-index constraints [v2DM(PQGT)] the dissociation problem persists.[8] But, unlike density functional theory (DFT) and density matrix functional theory (DMFT), there is a straightforward approach to solve the problem because the 2DM fully determines the energy in a known manner. We exploited this property and introduced linear constraints on the energy of subspaces of the one-particle basis space for the molecule,[13] defined as the set of basis functions centered on a particular atom, to solve the dissociation problem. These subspace constraints are a physical expression of the notion of separability in chemistry and can be generalized to subspaces with any other topology.

Our objective is to clarify some practically and conceptually important aspects related to the application of these subspace constraints. First of all, the number of possible subspaces that can be composed of all basis functions centered on one or more atoms in an M-atomic system, namely $2^M - 2$, scales exponentially with the size of the molecule. In practice, however, some subspace constraints may not be active. Which of them are active depends on the geometry and nature of the system. How fast does the number of practically relevant, i.e., active, subspace constraints grow with the number of atoms in the molecule? And can these constraints be identified beforehand? This paper addresses this issue using a chemically relevant case, the potential energy surface (PES) of the triatomic F_3^- ion. Second, what is the relationship between the subspace constraints and size-consistency? Is the subspace- and P-, Q-, G-constrained 2DM consistent with a system of noninteracting units? The last paragraph of Sec. IV explores the connection between the subspace constraints, size-consistency, and separability in the variational 2DM method.

II. THEORETICAL BACKGROUND

Variational second order density matrix theory relies only on the 2DM to describe a physical system and obtains a 2DM by variational optimization. Early experiments using this method pointed out the need for additional constraints on the 2DM during the optimization, the so-called N-representability constraints.[14,15] These constraints ensure that the optimization is carried out exclusively over 2DM's derivable from a proper N-fermion state. Because no simple general expression is known for the necessary and sufficient conditions for N-representability, only certain necessary conditions are imposed in practical optimization schemes,

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resulting in a lower bound to the exact energy. Here, the standard two-positivity conditions are imposed. They require positive-semidefiniteness of the 2DM (particle–particle matrix),[14] the hole–hole matrix,[16] and the particle–hole matrix,[16] denoted Γ, $Q(\Gamma)$, and $G(\Gamma)$, respectively. The matrices $Q(\Gamma)$ and $G(\Gamma)$ are linear functions of the 2DM Γ. The setup of our linear semidefinite program for an N-electron system is

$$\min\ E = tr[H\Gamma], \tag{1}$$

under the conditions

$$tr\ \Gamma = N(N-1), \tag{2}$$

$$\Gamma \succeq 0, \tag{3}$$

$$Q(\Gamma) \succeq 0, \tag{4}$$

$$G(\Gamma) \succeq 0. \tag{5}$$

In addition, antisymmetry of the sp basis, Hermiticity, and spatial symmetry requirements on the 2DM are exploited.

The set of necessary conditions (3)–(5) can be extended with linear subspace constraints, as introduced by Verstichel *et al.*[13] to improve the description of long-distance interactions. These constraints were inspired by the observation of fractionally charged dissociation products in heteronuclear diatomics under two-positivity conditions.[8] The occurrence of fractionally charged dissociation products can be attributed to the strictly convex relationship between the energy and the number of electrons on the atom, which is ultimately a result of imposing necessary but not sufficient conditions for N-representability. In any exact theory, the relationship between the energy and the number of electrons is piecewise linear.[17] The strictly convex relationship between the energy and the number of electrons in the v2DM(PQG) method has a profound influence on dissociation: if the sum of the atomic energies becomes a strictly convex function of the number of electrons on one of the atoms (for a fixed total electron number), it will reach a minimum for a fractional number of electrons on each atom. Even more so, we observed that this minimum almost coincides with the number of electrons on one of the molecular dissociation products, which confirms the causal connection.[8] The strictly convex relationship between energy and number of electrons thus explains the occurrence of fractional charges on the dissociation products under energy minimization. Of course, fractionally charged dissociation species are not always unphysical. They occur naturally when several symmetry-equivalent charged species are formed upon dissociation. In heteronuclear diatomics, however, they are unjustified.

In an exact theory improper fractionally charged dissociation products cannot occur because the piece-wise linear relationship between energy and electron number ensures the minimum energy always corresponds to an integer electron number.[17] Separability constraints offer a computationally cheap way to impose this behavior. They aim to correct the dissociation problem by forcing the energy of atomic subspace in the molecule to lie above the piece-wise linear graph determined by the v2DM(PQG) energies for integer number of electrons. Their theoretical justification is built on the property that any pair of subspace 1DM and 2DM must be fractional N-representable.[13] By the definition of N-representability, the following must hold for any Hamiltonian H^A acting on the subspace A with N_A electrons, expressed here in MO basis space:

$$\begin{aligned} tr[H^A\Gamma] &\geq \underbrace{\min}_{\{x_{n_i}\}} \sum_{i=0}^{\infty} x_{n_i} E_{n_i}^{\text{exact}} \\ &\geq \underbrace{\min}_{\{x_{n_i}\}} \sum_{i=0}^{\infty} x_{n_i} E_{n_i}^{\text{2DM}}, \end{aligned} \tag{6}$$

where the $E_{n_i}^{\text{exact}}$ are exact ground state energies for the Hamiltonian H^A acting on a system with an integer number n_i electrons, which are greater than the 2DM energies for the same system. The weights $\{x_{n_i}\}$ represent a physical ensemble for the system if they satisfy the relations

$$0 \leq x_{n_i} \leq 1 \quad i = 0, \ldots \infty, \tag{7}$$

$$\sum_{i=0}^{\infty} x_{n_i} = 1, \tag{8}$$

$$\sum_{i=0}^{\infty} x_{n_i} n_i = N^A. \tag{9}$$

The objective will, therefore, be to minimize the molecular energy subject to Eqs. (3)–(9). Even though the indices in formulae (7)–(9) run over all positive integers, usually two low lying states with integer particle numbers N and $N+1$ determine the ground-state energy of an ensemble with $N < N^A < N+1$ electrons. If the set of energies E_{n_i}, $i = 1, \infty$ with $N^A \in [N, N+1]$ is a convex set, the lowest energy ensemble is a linear combination of the states with N and N+1 electrons. The assumption of convexity of the set of energies is reasonable; we have never encountered a violation. Consequently, only two indices $n_i = N$ and $n_i = N+1$ in Eqs. (7)–(9) are practically relevant. All other weights x_i with $i \neq N, N+1$ are zero and the weights x_N and x_{N+1} are completely determined by relation (9), which implies that $Nx_N + (N+1)x_{N+1} = N^A$. Since only x_N and x_{N+1} are nonzero, expressions (8) and (9) are bounded. In summary, under the above assumptions, the constraint reduces to

$$tr[H^A\Gamma] \geq \ (N+1-N^A)E_N + (N^A-N)E_{N+1}. \tag{10}$$

To compose the constraint Eq. (10), the energy of the subspace for N, N+1 electrons needs be calculated before the actual molecular v2DM(PQGs) calculation. References 8 and 13 offer a more elaborate explanation on subspace constraints.

The subspace constraints impose a lower bound on the energy of a dissociated system. Is this enough to ensure the resulting 2DM corresponds to a system of non-interacting units? The requirement that the 2DM of a system of non-interacting units must be separable into 2DMs for each unit defines several relationships, which will be verified in the last paragraph of Sec. IV.

For simplicity, we will only consider relationships for nondegenerate dissociated states. The 2DM of a nondegenerate system of two spatially infinitely separated atoms or molecules A and B determines the energy through

$$E = tr\,[V^{AAAA}\Gamma^{AAAA}] + tr\,[V^{BBBB}\Gamma^{BBBB}] + tr\,[h^{AA}\gamma^{AA}] + tr\,[h^{BB}\gamma^{BB}], \tag{11}$$

where V^{AAAA} and V^{BBBB} contain the electron–electron repulsion integrals between orbitals centered on A and B, respectively, and h^{AA} and h^{BB} contain the one-electron integrals between orbitals centered on A and B. The 1DM and 2DM for such a system must have the block structure

$$\gamma = \begin{pmatrix} \gamma^{AA} & 0 \\ 0 & \gamma^{BB} \end{pmatrix},$$

$$\Gamma = \begin{pmatrix} \Gamma^{AAAA} & 0 & 0 \\ 0 & \Gamma^{BBBB} & 0 \\ 0 & 0 & \Gamma^{ABAB} \end{pmatrix}, \tag{12}$$

where the superscripts denote the atom/molecule on which the orbital is centered (the orbitals that form the basis are assumed localized on either A or B). Moreover, since the wavefunction for such a noninteracting system is of the form $\Psi = \mathcal{A}\left\{\Psi^A(x_1,\ldots x_{N^A})\Psi^B(x_{N^A+1},\ldots,x_{N^A+N^B})\right\}$, where $\mathcal{A}$ is an antisymmetrizer, the elements of the Γ^{ABAB} block must satisfy

$$\Gamma^{ABAB}_{ijkl} = \left\langle \Psi^A\Psi^B \middle| a_k^+ a_l^+ a_j a_i \middle| \Psi^A\Psi^B \right\rangle = \gamma^{AA}_{ik}\gamma^{BB}_{jl} \tag{13}$$

or, the weaker contraction condition that is implied by Eq. (13)

$$\gamma^{AA}_{ik} = \frac{1}{N_A - 1}\sum_j \Gamma^{AAAA}_{ijkj} = \frac{1}{N_B}\sum_j \Gamma^{ABAB}_{ijkj}, \tag{14}$$

$$\gamma^{BB}_{ik} = \frac{1}{N_B - 1}\sum_j \Gamma^{BBBB}_{ijkj} = \frac{1}{N_A}\sum_j \Gamma^{ABAB}_{jijk}, \tag{15}$$

where $N^A = tr[\gamma^{AA}]$, $N^B = tr[\gamma^{BB}]$. Equation (13) states that the cumulant block $\Delta^{ABAB}_{ijkl} = \Gamma^{ABAB}_{ijkl} - \gamma^{AA}_{ik}\gamma^{BB}_{jl} + \gamma^{AB}_{il}\gamma^{BA}_{jk}$ is identically zero, indicating that the cumulant is additively separable and that electrons on separated systems are uncorrelated.

III. COMPUTATIONAL DETAILS AND NOTATION

We developed a logarithmic barrier-type optimization program,[18] using a Newton–Raphson/MINRES method for the inner iterations, to carry out the semidefinite optimization. It optionally includes subspace constraints by means of an additional logarithmic barrier term. We will use the notation "v2DM(PQG)" to denote the variational 2DM method under two-positivity conditions and "v2DM(PQGs)" to denote its extension with subspace constraints. Using the v2DM(PQG) method, we scanned the potential energy surface of F_3^- in the D95V basis set as defined in GAUSSIAN03.[19] The lowest-energy reaction path for the reaction of F^- with F_2 is collinear;[20,21] therefore, only two variables, the bond lengths R_1 and R_2, are needed to construct the potential energy surface. All calculations on the F_3^- system were constrained to singlet spin states. The calculations on the mono- and diatomic subspaces were performed without constraints on spin. The calculations on the diatomic subspaces do not include constraints on the atomic subspaces within the diatomic subspace.

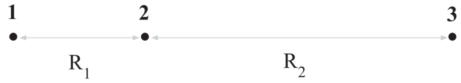

FIG. 1. Numbering of the atoms and bond lengths of F_3^- used throughout the paper.

Multireference configuration interaction with frozen core (MRCI) reference values were calculated with MOLPRO.[22] The configurations in the MRCI expansion were determined by a preceding full-valence complete active space self-consistent field (CASSCF), with an active space of 22 electrons and all 12 valence orbitals, except that the molecular orbitals were taken from an analogous CASSCF calculation for the neutral species with optimized doubly-occupied inactive orbitals (mostly 1s core).

Bond lengths and numbering of the atoms is done as indicated in Fig. 1. We introduce a short notation to characterize the subspace constraints used. The symbol C_i denotes a constraint on the monoatomic subspace that includes all basis functions centered on atom i; C_{ij} denotes a constraint on a diatomic subspace that includes all basis functions centered on atom i and j. For example, C_{13} denotes a constraint on the energy of the subspace spanned by all basis functions centered on the two fluorine atoms that are farthest apart.

IV. RESULTS AND DISCUSSION

The shape of PES calculated with the variational v2DM(PQG) method is severely incorrect, especially for molecular geometries with one or more stretched bonds. It is compared to that of an accurate MRCI PES in Figs. 2 and 3. Both graphs are composed of nonequidistant data points and show an equally large interval on the energy axis, which is truncated to enhance visibility of the bonding region. There are two striking differences between the two PES. First of all, the 2DM method yields a more shallow well corresponding to the formation of the F_3^- anion, with a minimum at a somewhat larger bond length compared to MRCI (1.9 Å for 2DM theory versus 1.8 Å for MRCI). Second, in the outer regions of the v2DM(PQG) potential energy surface, describing the dissociation of the F_3^- ion, the energy does not increase but rather decreases. The decrease in energy upon dissociation is so strong that the optimal F_3^- geometry is only a local minimum in the 2DM potential energy surface. The cause of this problem is clear from previous work on diatomic molecules:[9] the dependence of the v2DM(PQG) energy on the number of electrons is strictly convex in most atoms, so the dissociating system may reach a lower energy by allowing a fractional number of electrons on both atoms. Unless the decrease in

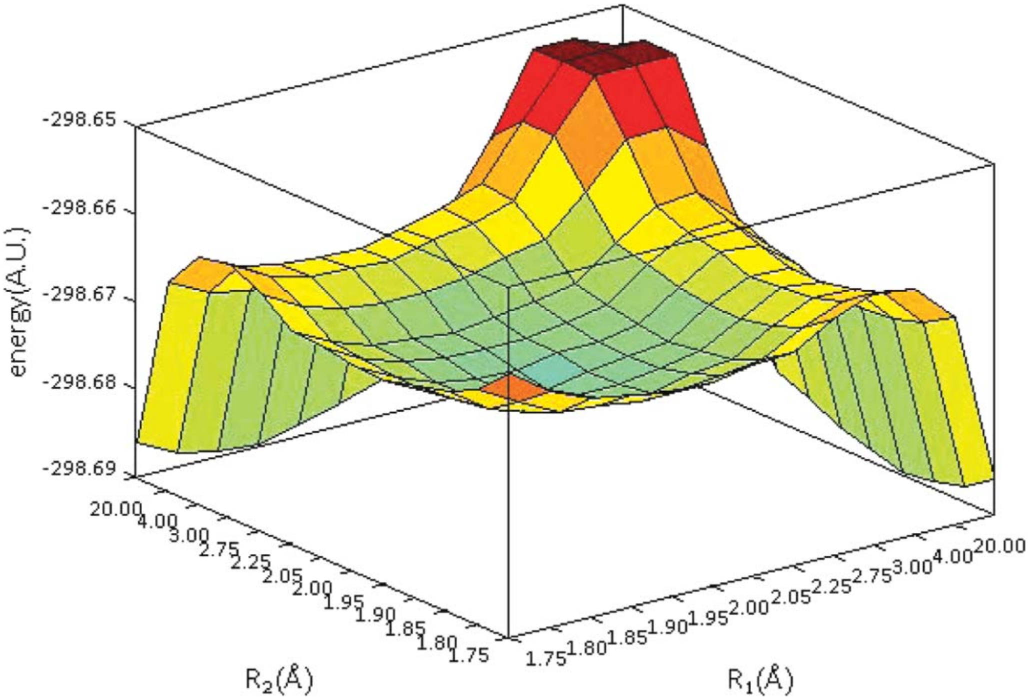

FIG. 2. The outer regions of the potential energy surface of F_3^- obtained with the v2DM(PQG) method, corresponding to geometries with dissociated bonds, erroneously decrease in energy.

energy caused by allowing a fractional charge on one atom is countered by a bigger increase in energy for the corresponding fractional charge on the other atom, the molecule will incorrectly dissociate into fractionally charged atoms. The v2DM(PQG) method thus often leads to unphysical fractionally charged dissociated states with too low an energy. This explains the additional potential energy wells at long bond lengths in the 2DM PES for the F_3^- molecule.

The subspace constraints only affect molecular structures with large bond lengths. They aim to solve the aforementioned dissociation problem by constraining the energy of mono- or diatomic subspaces in the molecule to lie above the lowest ensemble energy for the isolated subspace with the same fractional number of electrons as the subspace in the molecule. The lowest energy dissociated state will then be automatically obtained at integer occupations on the atoms

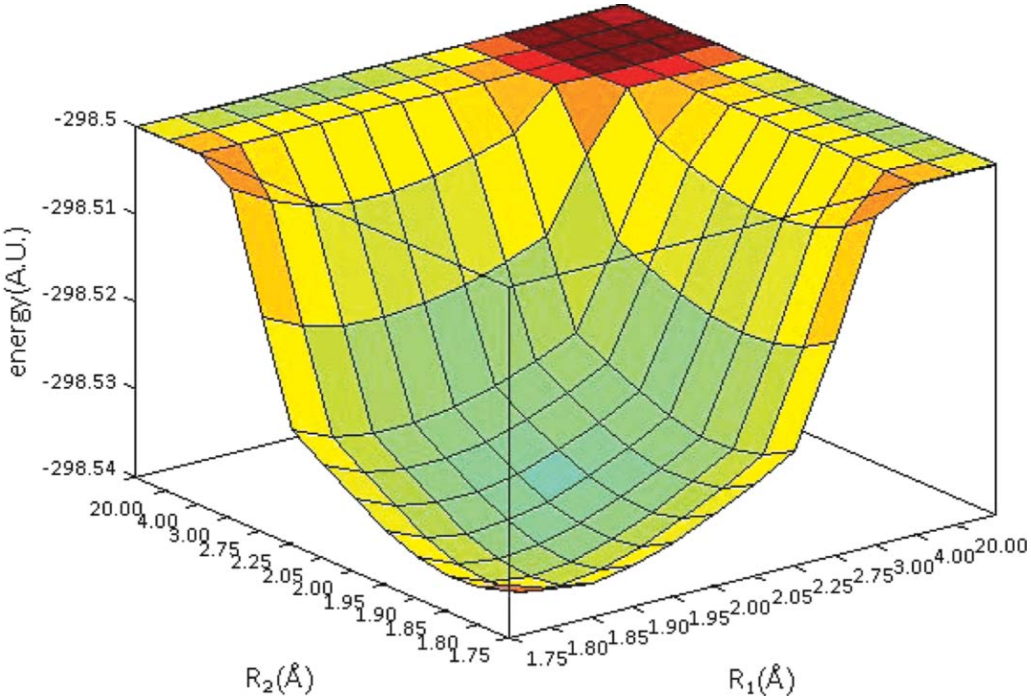

FIG. 3. A reference potential energy surface of F_3^-, obtained with MRCI, shows the correct shape of the potential energy surface.

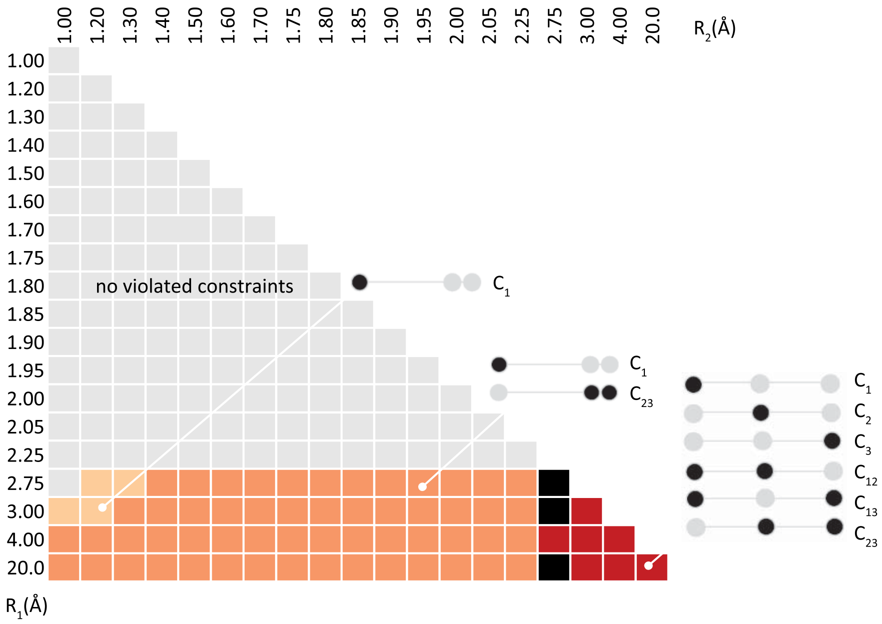

FIG. 4. Different combinations of subspace constraints are violated by the v2DM(PQG) calculations in different parts of the PES. While no subspace constraints are violated for geometries with only short bond lengths (indicated by light gray squares in the PES), all of them are violated by calculations on fully stretched geometries (indicated by red squares in the PES). A schematic representation indicates with black dots on which atom the basis functions that span the subspace of the violated constraints are centered. Black squares in the overview of the PES indicate geometries at which yet another combination of subspace constraints was violated.

(see Tables I and II). This constraint is already satisfied by v2DM(PQG) calculations for geometries with both bond lengths shorter than 2.75 Å (Fig. 4). The bond length of 2.75 Å marks the onset of the "long-distance behavior." The constraints that are violated in geometries with dissociated bonds largely obey the following trends. When only one bond (R_1) is dissociated, and the other bond (R_2) is relatively short, the v2DM(PQG) calculation only violates the C_1 and C_{23} constraints, which act on the spatially separated atomic and diatomic units in the system. When both bonds are dissociated, however, all constraints are violated by the v2DM(PQG) calculations.

The subspace constraints ensure correct dissociation of the F_3^- ion into F_2^- and F. Without subspace constraints, the

TABLE I. Subspace constraints on the atomic subspaces C_1, C_2, C_3 alone are not sufficient to ensure the energy (in atomic units) of systems with one dissociated bond ($R_1 = 20$ Å) and one short bond (R_2) equals the sum of the energies of the dissociated species. The set of constraints C_1, C_{23} on the two spatially separated units in the system, one diatomic and one atomic, is the smallest set of constraints that ensures the energy reproduces the sum of the energies of those units calculated separately—the energy difference between both is given in the last column denoted "Δ."

$R_1 = 20.0$ Å				
R_2(Å)	PQG	PQG/C$_1$, C$_2$, C$_3$	PQG/C$_1$, C$_{23}$	Δ
1.00	−298.1694	−298.1638	−298.1629	−0.0002
1.20	−298.4873	−298.4640	−298.4626	−0.0005
1.30	−298.5687	−298.5278	−298.5198	0.0000
1.40	−298.6234	−298.5726	−298.5486	0.0004
1.50	−298.6572	−298.6036	−298.5605	−0.0002
1.60	−298.6769	−298.6226	−298.5673	−0.0017
1.70	−298.6860	−298.6317	−298.5870	−0.0001
1.75	−298.6884	−298.6341	−298.5937	−0.0002
1.80	−298.6893	−298.6351	−298.5983	−0.0002
1.85	−298.6897	−298.6354	−298.6017	−0.0003
1.90	−298.6887	−298.6344	−298.6035	−0.0002
1.95	−298.6875	−298.6332	−298.6047	0.0002
2.00	−298.6860	−298.6317	−298.6052	0.0001
2.05	−298.6844	−298.6302	−298.6055	−0.0003
2.10	−298.6822	−298.6281	−298.6050	−0.0001
2.20	−298.6792	−298.6252	−298.6047	−0.0006

TABLE II. Subspace constraints on the atomic subspaces C_1, C_2, C_3 are not sufficient to ensure correct atomic (Mulliken, shown are those on F_1) populations on systems with one dissociated bond $R_1 = 20$ Å and one short bond R_2 ranging from 1.00 to 2.20 Å. The set of constraints C_1, C_{23} on the spatially separated units in the system—one diatomic and one atomic—is the smallest set of constraints that ensures a correct dissociation with integer charges on the dissociated species.

$R_1 = 20.0$ Å			
R_2(Å)	PQG	PQG/C$_1$, C$_2$, C$_3$	PQG/C$_1$, C$_{23}$
1.00	9.98	10.00	10.00
1.20	9.84	9.98	10.00
1.30	9.72	9.87	10.00
1.40	9.62	9.70	10.00
1.50	9.55	9.58	9.99
1.60	9.49	9.50	9.13
1.70	9.46	9.44	9.01
1.75	9.45	9.42	9.00
1.80	9.44	9.41	9.00
1.85	9.44	9.39	9.00
1.90	9.43	9.38	9.00
1.95	9.43	9.37	9.00
2.00	9.43	9.37	9.00
2.05	9.43	9.36	9.00
2.10	9.42	9.35	9.00
2.20	9.42	9.34	9.00

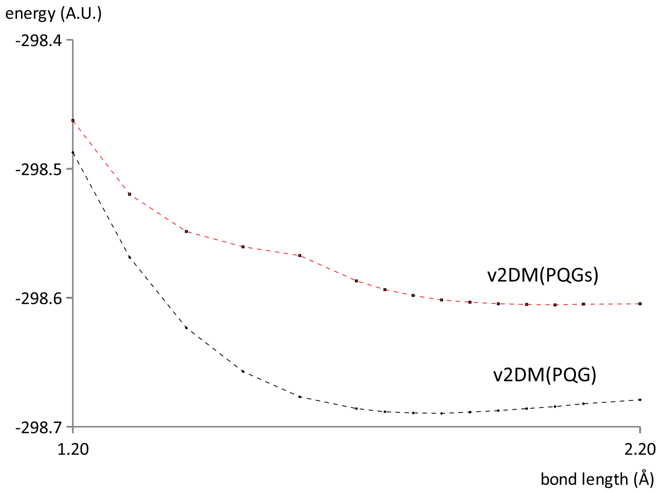

FIG. 5. The v2DM(PQGs) method applied to the cut of the PES of F_3^- with one bond length fixed at 20Å reveals the crossing between the two competitive dissociations $F_2 + F^-$ and $F_2^- + F$.

F_3^- ion dissociates into $F_2^{-0.56} + F^{-0.44}$, which is the minimum energy structure among all structures with one bond dissociated, shown in the lower graph of Fig. 6. In fact, all these structures with one short bond and one dissociated bond (20 Å) should have an electronic structure recognizable as either F_2+F^- or F_2^-+F. However, without subspace constraints, the electronic charge delocalizes over the dissociation species (Table II).

When all subspace constraints are imposed, the electronic charge becomes properly localized on the dissociation products (Table II). The energies of the structures with one short bond and one dissociated bond are then given by the uppermost graph in Fig. 5, which has a kink between 1.5 and 1.6 Å. At this point, the energy of the dissociation into $F_2^- + F$ becomes lower than that of the alternative dissociation $F_2 + F^-$. The minimum energy dissociation under the subspace constraints is $F_2^- + F$ with a bond length of 2.05 Å and charges –0.50 on both F atoms in the F_2^- molecule. These results agree with MRCI calculations, for which $F_2^- + F$ is also the lowest energy dissociation, with a bond length of 1.95 Å in the F_2^- molecule.

The set of subspace constraints acting on the spatially separate units in the system is the smallest set of subspace constraints that produces the correct dissociation in geometries with either short or dissociated bonds. Not all subspace constraints that are violated in the v2DM(PQG) calculation need be imposed in the v2DM(PQGs) calculation in order to obtain the correct dissociation. Some of them may overrule others, rendering them inactive in the resulting 2DM. For example, in the fully dissociated molecule, with three nuclei with large separations, all six subspace constraints are violated by v2DM(PQG). Nonetheless, the "diatomic" subspace constraints are unlikely to have a meaningful contribution over the atomic subspace constraints, since their own energy violates the atomic subspace constraints. Indeed, they are made redundant by the atomic subspace constraints (the red area in Fig. 5). For all systems with a single dissociated bond, consisting of a diatomic unit and an atomic unit at very large internuclear distance, there are only two active constraints: a constraint on the diatomic unit and a constraint on the atomic unit. Therefore, in systems composed of (poly-) atomic units that are widely separated, the necessary constraints for correct

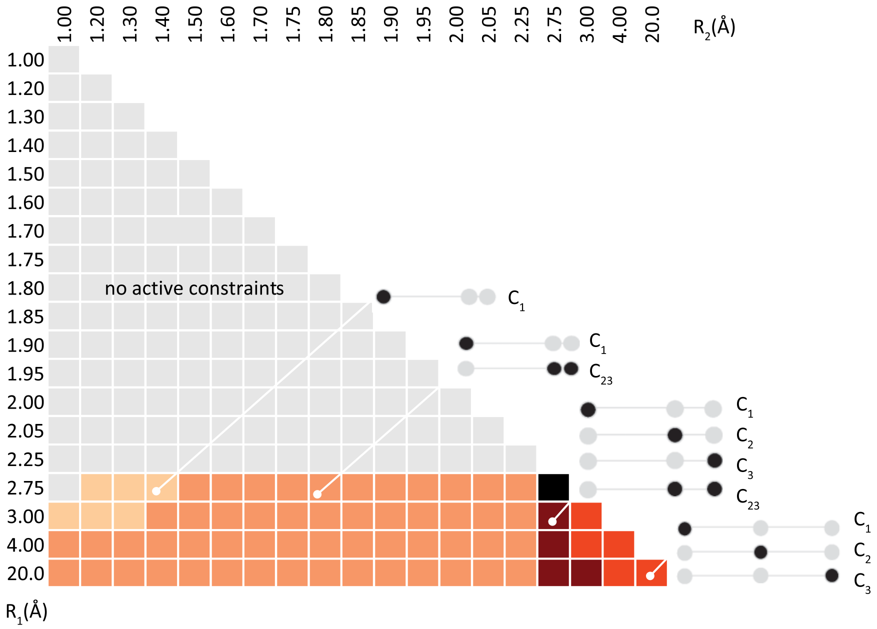

FIG. 6. Although all subspace constraints are violated by the v2DM(PQG) method for geometries with both bonds dissociated, only the atomic subspace constraints are active when imposed in the calculation (indicated by bright red squares in the PES). A schematic representation indicates with black dots on which atom the basis functions that span the subspace of the active constraints are centered. For geometries with either clearly dissociated or short bonds, the active constraints target subspaces that coincide with the spatially separate units of the system. However, in structures with stretched—but not yet dissociated—bonds more subspace constraints are active (indicated by dark red squares in the PES). Black squares indicate geometries at which yet another combination of subspace constraints was active.

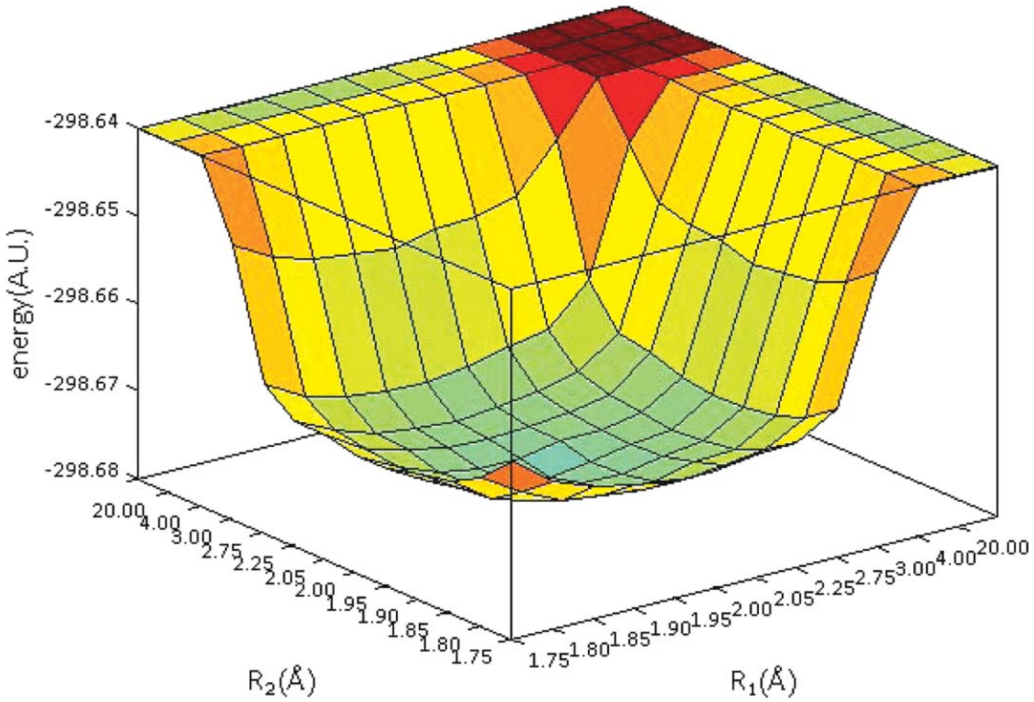

FIG. 7. Imposing all mono- and diatomic subspace constraints corrects the dissociative regions of the potential energy surface of F_3^- as compared with the v2DM(PQG) potential energy surface in Fig. 2.

dissociation act on the subspaces associated with the units, i.e., the subspace spanned by all basis functions centered on the atoms in the unit. Unfortunately, this does not hold for all geometries. In systems with bonds that are stretched but not clearly dissociated, around 2.75 Å, additional diatomic constraints may be active (the dark red area in Fig. 5). As a consequence, the number of active constraints does not always increase linearly with the size of the molecule.

The subspace constraints correct the shape of the dissociative regions of the v2DM(PQG) PES but do not alter results for bound systems with short bonds (see Fig. 7). They turn the previously observed potential energy wells at long bond lengths into proper potential walls, such that a single well remains, corresponding to the bound F_3^- (with $R_1 = R_2 = 1.9$ Å the global minimum). Moreover, they do not only correct the energy for geometries with one or more large bond lengths, but other chemical properties, such as dipole moments, as well. Nonetheless, the v2DM(PQGs) method still overestimates the bond strength compared to wavefunction based *ab initio* methods (Table III). The subspace constraints do not alter the equilibrium F_3^- calculation and merely ensure the calculation on the dissociated system is energetically equivalent to separate calculations on the dissociated units. In order to obtain more accurate chemical properties, constraints are needed that improve results for short bond lengths as well. A combination of higher-index constraints with subspace constraints should improve results for both short and long bond distances, but would be much more costly.

The subspace constraints impose size-consistency (Table I) but do not impose the exact 2DM structure of a system of noninteracting units in the dissociation limit. Size-consistency is usually defined with respect to energy requirements in the context of wavefunction based methods. A method is size-consistent if the energy of a system composed of two or more spatially separated units, infinitely far apart, equals the sum of the energies of the different units calculated separately. Calculations on a set of dissociated 14-electron diatomic molecules with bond lengths larger than 10^4 Å in the Cartesian cc-pVDZ basis indicate that including subspace constraints makes the v2DM(PQGs) size-consistent. Even though the energy of the dissociated system is completely consistent with the energies of the dissociation products calculated separately, the 2DM need not be. The 2DM for a dissociated system without any degeneracies, such as a dissociated system composed of two neutral closed-shell singlet atoms, must have a structure that is consistent with the 2DMs calculated separately for the

TABLE III. The accuracy of the v2DM(PQGs) method remains poor, as the subspace constraints only correct for improper dissociation. The v2DM(PQGs) dissociation energies D_e for dissociation into $F_2^- + F$ and $F + F + F^-$ are substantially bigger than those obtained with CCSD and MRCI. The MRCI calculations on the dissociated system $F_2^- + F$ did not converge properly, hence no value is specified for the dissociation energy. Equilibrium bond lengths R are, in the case of FCI(FC), MRCI(FC), and v2DM(PQGs), determined in steps of 0.05 Å.

	MRCI(FC)		CCSD(FC)		v2DM(PQGs)	
	E(a.u.)	R(Å)	E(a.u.)	R(Å)	E(a.u.)	R(Å)
F_3^-	−298.5385	1.80	−298.5792	1.75	−298.6724	1.90
F	−99.4690		−99.4703		−99.4928	
F^-	−99.5307		−99.5350		−99.5441	
F_2	−198.9637	1.60	−198.9652	1.52	−199.0189	1.60
F_2^-	−199.0404	1.95	−199.0557	1.94	−199.1125	2.00
$F_2^- + F$	−298.5094		−298.5260		−298.6053	
$D_e(F_2^-, F)$			0.0532		0.0671	
$D_e(F, F, F^-)$	0.1353		0.1036		0.1426	

dissociation products, as explained in Sec. II. The correct structure is not guaranteed under necessary but not sufficient N-representability constraints. Although the variationally optimized 2DM under P-, Q-, and G-condition has the typical block structure of a system of noninteracting units, given by Eq. (12), the 2DM neither satisfies the cumulant additivity condition (13), nor the weaker contraction condition (15), not even with subspace constraints. The maximum absolute eigenvalue of the cumulant block Δ^{ABAB} with entries $\Delta^{ABAB}_{ijkl} = \Gamma^{ABAB}_{ijkl} - \gamma^{AA}_{ik}\gamma^{BB}_{jl}$ is typically of the order 10^{-2}. The maximum absolute differences $(N_A - 1)\sum_j \Gamma^{ABAB}_{ijkj} - N_B \sum_j \Gamma^{AAAA}_{ijkj}$ with $N_A = tr[\gamma^{AA}]$ and $N_B = tr[\gamma^{BB}]$ are typically of the same order. The subspace constraints only act on the energy of the dissociated system, which is not enough to guarantee that the 2DM is separable into 2DMs for the dissociation products.

V. CONCLUSIONS

Subspace constraints offer a computationally cheap way to obtain correct molecular dissociation of small molecules in variational 2DM theory. Nonetheless, practical difficulties may arise when they are applied to larger systems. First of all, the number of subspace constraints needed to ensure correct dissociation does not always grow linearly with the number of atoms. In geometries with either clearly dissociated or short bonds, the correct dissociation can be obtained using only constraints on the spatially separated units in the system, which may include up to M-1 atoms in an M-atomic molecule, or two atoms in the F_3^- molecule examined here. However, this does not hold for all geometries. Additional constraints may be active in geometries with stretched, but not fully dissociated, bonds. Second, constructing the constraints requires separate calculations for each geometry of the multiatomic subspaces. Multiatomic subspaces may be needed because the correct dissociation cannot always be realized through constraints on the atomic subspaces only. Assembling the constraint data thus becomes a time-consuming process when applied to large PES. Finally, even though the subspace constraints allow for a size-consistent description of long-range electronic interactions, the structure of the 2DM for a dissociated system obtained under these constraints does not exactly correspond to a system of noninteracting units. Furthermore, the subspace constraints merely correct the faulty long-range behavior under the P-, Q-, and G-condition, they do not affect the accuracy of the v2DM(PQG) method for geometries with short bonds.

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