Subspace constraints for size-consistent potential energy surfaces of small molecules in variational second order density matrix theory

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Variational second order density matrix theory under '2-positivity' tends to dissociate molecules into unphysical fractionally charged products with too low energies. We aim to construct a qualitatively correct potential energy surface for \( \text{F}_3^- \) by applying subspace energy constraints on mono- and diatomic subspaces of the molecular basis space. Mono-atomic 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 DM2 does not exactly correspond to a system of non-interacting units.

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. Non-equilibrium 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]. Variational P-,Q- and G-conditioned second order density matrix theory (DM2(PQG)) also fails in this respect [8–10]. But, unlike DFT and DMFT, there is a straightforward approach to solve the problem because the DM2 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 [11], 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 $\text{F}_3^-$ ion. Secondly, what is the relationship between the subspace constraints and size-consistency? Is the subspace- and P-,Q-,G-constrained DM2 consistent with a system of non-interacting units? The last paragraph explores the connection between the subspace constraints, size-consistency and separability in the variational DM2 method.

II. THEORETICAL BACKGROUND

Variational second order density matrix theory relies on the DM2 only to describe a physical system, and obtains a DM2 by variational optimization. Early experiments using this method pointed out the need for additional constraints on the DM2 during the optimization, the so called N-representability constraints[12][13]. These constraints ensure that the optimization is carried out exclusively over DM2’s derivable from a proper wave function for the N-electron system. 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, resulting in a lower bound to the exact energy. Here, the standard 2-positivity conditions are imposed. They require positive-semidefiniteness of the DM2 (particle-particle matrix), the hole-hole matrix, and the particle-hole matrix, denoted $\Gamma$, $Q(\Gamma)$ [12], and $G(\Gamma)$ [14], respectively. The latter notation stresses the linear dependence of the Q- and G-matrix on the DM2 $\Gamma$. The setup of our linear semidefinite program for an N-electron system is

$$\min E = \text{tr}[H\Gamma] \quad (1)$$

$$\text{tr} \quad \Gamma = N(N-1) \quad (2)$$

$$\Gamma \succeq 0 \quad (3)$$

$$Q(\Gamma) \succeq 0 \quad (4)$$

$$G(\Gamma) \succeq 0 \quad (5)$$

In addition, antisymmetry of the sp basis, Hermiticity and spatial symmetry requirements on the DM2 are exploited.

The set of necessary conditions (3)-(5) can be extended with linear subspace constraints, as introduced by Verstichel et al. [11] to improve the description of long-distance interactions. These constraints were inspired by the observation of fractionally charged dissociation products in heteronuclear diatomics[8]. Their fractional charge almost coincided with the minimum of the the strictly convex relationship between the sum of the atomic energies and the charge on one of the atoms, for a fixed total number of electrons. This relationship is very often strictly convex, because the atomic energies for most atoms are strictly convex functions of the charge on the atom. Ultimately, this is a result of imposing necessary but not sufficient conditions for N-representability. 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.

Separability constraints offer a computationally cheap solution to this problem. Their theoretical justification is built on the property that any subspace DM1 and DM2 must be fractional N-representable [11]. 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:

$$\text{tr}[H_A \Gamma] \geq \min_{\{x_i\},i=0,\infty} \sum_{i=0}^{\infty} x_i E_{N_i}^{\text{exact}} \geq \min_{\{x_i\},i=0,\infty} \sum_{i=0}^{\infty} x_i E_{N_i}^{DM2}$$

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 DM2 energies for the same system. The weights $\{x_i\}$ represent a physical ensemble for the system if they satisfy the relations

$$0 \leq x_i \leq 1 \quad i = 0, \ldots, \infty$$

$$\sum_{i=0}^{\infty} x_i = 1$$

$$\sum_{i=0}^{\infty} x_i N_i = N_A$$

The objective will therefore be to minimize the molecular energy subject to (3)-(9). Obviously, generally holding constraints must be based on the lowest energy ensemble of states with weights $x_i$ that corresponds to a total number of electrons $N_A$. If the set of energies $E_i, i = 1, \infty$ 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 $i=N$ and $i=N+1$ in equations (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 non-zero, expressions (8) and (9) are bounded. In summary, under the above assumptions, the constraint reduces to

$$\text{tr}[H_A \Gamma] \geq (N+1-N_A)E_N + (N_A-N)E_{N+1}$$

To compose the constraint equations 10, the energy of the subspace for $N$, $N+1$ electrons needs be calculated before the actual molecular DM2(PQG/subspace) calculation.

The subspace constraints impose a lower bound on the energy of a dissociated system. Is this enough to ensure the resulting DM2 corresponds to a system of non-interacting units? The requirement that the DM2 of a system of non-interacting units must be separable into DM2’s for each unit defines several relationships, which will be verified in the last paragraph.

For simplicity, we will only consider relationships for non-degenerate dissociated states. The DM2 of a non-degenerate system of two spatially infinitely separated atoms or molecules A and B determines the energy through

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

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 DM1
and DM2 for such a system must have the block structure

\[ \gamma = \begin{pmatrix} \gamma^{AA} & 0 \\ 0 & \gamma^{BB} \end{pmatrix}, \quad \Gamma = \begin{pmatrix} \Gamma^{AAAA} & 0 & 0 \\ 0 & \Gamma^{BBBB} & 0 \\ 0 & 0 & \Gamma^{ABAB} \end{pmatrix} \] (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 non-interacting system is of the form \( \Psi = A \{ \Psi^{A}(x_{1}, \ldots x_{N_{A}}) \} \Psi^{B}(x_{N_{A}+1}, \ldots, x_{N_{A}+N_{B}}) \) where \( A \) is an antisymmetrizer, the elements of the \( \Gamma^{ABAB} \) block must satisfy

\[ \Gamma^{ABAB}_{ijkl} = \langle \Psi^{A}\Psi^{B}|a_{k}^{+}a_{l}^{+}a_{j}a_{i}|\Psi^{A}\Psi^{B} \rangle = \gamma^{AA}_{ik}\gamma^{BB}_{jl} \] (13)

or, the weaker contraction condition which is implied by (13)

\[ \gamma^{AA}_{ik} = \frac{1}{N_{A}-1} \sum_{j} \Gamma^{AAAA}_{ijkj} = \frac{1}{N_{B}} \sum_{j} \Gamma^{ABAB}_{ijkj} \] (14)

\[ \gamma^{BB}_{ik} = \frac{1}{N_{B}-1} \sum_{j} \Gamma^{BBBB}_{ijkj} = \frac{1}{N_{A}} \sum_{j} \Gamma^{ABAB}_{jijk} \] (15)

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.

Computational details and notation

We developed a logarithmic barrier type optimization program[15], 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 'DM2(PQG)' to denote the variational DM2 method under 2-positivity conditions and 'DM2(PQG/subspace)' to denote its extension with subspace constraints. Using the DM2(PQG) method, we scanned the potential energy surface of \( F_{3}^- \) in the D95V basis set as defined in Gaussian03 [16]. The lowest-energy reaction path for the reaction of \( F^- \) with \( F_2 \) is collinear [17, 18]; 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.

MRCI reference values were calculated with MOLPRO [19]. David, could you specify this? The 1s orbitals were frozen in the MRCI calculation and the configurations in the MRCI expansion were determined by a preceding full-valence CASSCF, with an active space of 22 electrons and all 12 valence orbitals and optimized doubly-occupied inactive orbitals (mostly 1s core).

Bond lengths and numbering of the atoms is done as indicated in figure 1. We introduce a short notation to characterize the subspace constraints used. The symbol \( C_i \) denotes a constraint on the mono-atomic 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 the two fluorine atoms that are farthest apart.

**Results and discussion**

The shape of the potential energy surface (PES) calculated with the variational DM2(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 figures 2 and 3. Both graphs are truncated on the energy axis and show an equally large interval on the energy axis from a similar angle. There are two striking differences between both PES. First of all, the DM2 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 DM2 theory versus 1.8 Å for MRCI). Secondly, in the outer regions of the DM2(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 DM2 potential energy surface. The cause of this problem is clear from previous work on diatomic molecules[9]: the dependence of the DM2(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 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 DM2 (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 DM2 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 be concave. The lowest energy state will then be automatically obtained at integer occupations on the atoms. These constraints, however, are not violated by DM2(PQG) calculations on structures with both bond lengths shorter than 2.75 Å (figure ??). The bond length of 2.75 Å is a critical point. It signals the onset of the 'long-distance behavior'. The constraints that are violated in stretched geometries largely obey the following trends. When only one bond \((R_1)\) is dissociated, and the other bond \((R_2)\) is relatively short, the DM2(PQG) calculation only violates the \(C_1\) and \(C_{23}\) constraints, which act on the spatially separated atomic and diatomic unit in the system. When both bonds are dissociated, however, all constraints are violated by the DM2(PQG) calculations.

The subspace constraints ensure correct dissociation of the \(F^-_3\) ion into \(F^-_2\) and \(F\). Without subspace constraints, the \(F^-_3\) 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 figure 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 figure 6, which has a kink between 1.5 and 1.6 Å. At this point, the PES of the two competing
dissociations \( \text{F}_2 + \text{F}^- \) and \( \text{F}_2^- + \text{F} \) cross. The minimum energy dissociation under the subspace constraints is \( \text{F}_2^- + \text{F} \) with a bond length of 2.05 Å and charges -0.50 on both F atoms in the \( \text{F}_2^- \) molecule. These results agree with MRCI calculations, for which \( \text{F}_2^- + \text{F} \) is also the lowest energy dissociation, with a bond length of 1.95 Å in the \( \text{F}_2^- \) 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 DM2(PQG) calculation need be imposed in the DM2(PQG/subspace) calculation in order to obtain the correct dissociation. Some of them may overrule others, rendering them inactive in the resulting DM2. For example, in the fully dissociated molecule, with three nuclei with large separations, all six subspace constraints are violated by DM2(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 figure 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 with stretched bonds that are clearly dissociated the necessary constraints for correct dissociation each act on the subspace associated with a spatially separate unit of the system, 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 figure 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 DM2(PQG) PES, but do not alter results for bound systems with short bonds. 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 \( \text{F}_3^- \) (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 DM2(PQG/subspace) method still overestimates the bond strength compared to wavefunction based ab initio methods (table III). The subspace constraints do not alter the equilibrium \( \text{F}_3^- \) calculation and merely ensure the calculation on the dissociated system is 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 but do not impose the exact DM2 structure of a system of non-interacting units in the dissociation limit. Size-consistency is usually defined with respect to energy requirements in the context of wave function 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-VDZ basis using the DM2(PQG/subspace) method without spin constraints on the molecular and subspace calculations indicate that it is size-consistent. Besides yielding size-consistent energies, the DM2 for a
dissociated system must have a structure consistent with a system of non-interacting units, as explained section II. The correct structure is not guaranteed under necessary but not sufficient N-representability constraints. Although the variationally optimized DM2 under P-, Q- and G-condition has the correct block structure given by (12), the DM2 neither satisfies the condition on cumulant additivity (13), nor the weaker contraction condition (15), not even with subspace constraints. The differences $\Gamma^{ABAB}_{ijkl} - \gamma^{AA}_{ik} \gamma^{BB}_{jl}$ are typically of the order $10^{-2} - 10^{-5}$. The differences $(N_A - 1) \sum_j \Gamma^{ABAB}_{ijkl} - N_B \sum_j \Gamma^{AAAA}_{ijkl}$ 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 the DM2 is separable into DM2’s for the dissociation products.

Conclusions

Subspace constraints offer a computationally cheap way to obtain correct molecular dissociation of small molecules in variational DM2 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 atoms in an M-atomic molecule, or 2 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. Secondly, constructing the constraints requires separate calculations for each geometry of the multi-atomic subspaces. Multi-atomic 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 DM2 for a dissociated system obtained under these constraints does not exactly correspond to a system of non-interacting 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 DM2(PQG) method for geometries with short bonds.

Acknowledgements

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

FIG. 2: The outer regions of the potential energy surface of $F_3^-$ obtained with the DM2(PQG) method, corresponding to geometries with dissociated bonds, erroneously decrease in energy.

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 DM2(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.
FIG. 5: Although all subspace constraints are violated by the DM2(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. 6: The DM2(PQG/subspace) 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 $F_2^- + F$. 
FIG. 7: Imposing all mono- and diatomic subspace constraints corrects the dissociative regions of the potential energy surface of F$_3^-$ obtained with the DM2(PQG) method (cfr. figure 2)

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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 ($R_2 = 20\text{Å}$) and one short bond ($R_1$) equals the sum of the energies of the dissociated species. The set of constraints $C_{12}$, $C_3$ 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 ‘$\Delta$’.
\( R_1 = 20.0 \text{ Å} \) \( R_2(\text{Å}) \) PQG PQG/C\(_1\), C\(_2\), C\(_3\) PQG/C\(_1\), C\(_{23}\)

\begin{align*}
1.00 & \quad 9.98 & \quad 10.00 & \quad 10.00 \\
1.20 & \quad 9.84 & \quad 9.98 & \quad 10.00 \\
1.30 & \quad 9.72 & \quad 9.87 & \quad 10.00 \\
1.40 & \quad 9.62 & \quad 9.70 & \quad 10.00 \\
1.50 & \quad 9.55 & \quad 9.58 & \quad 9.99 \\
1.60 & \quad 9.49 & \quad 9.50 & \quad 9.13 \\
1.70 & \quad 9.46 & \quad 9.44 & \quad 9.01 \\
1.75 & \quad 9.45 & \quad 9.42 & \quad 9.00 \\
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2.10 & \quad 9.42 & \quad 9.35 & \quad 9.00 \\
2.20 & \quad 9.42 & \quad 9.34 & \quad 9.00 \\
\end{align*}

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 \( R_2 = 20 \text{Å} \) and one short bond \( R_1 \) ranging from 1.00 to 2.20 Å. The set of constraints \( C_{12}, C_3 \) 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.

\[
\begin{array}{cccc}
\text{MRCI(FC)} & \text{CCSD(FC)} & \text{DM2(PQG/subspace)} \\
\hline
\text{E(A.U.) R(Å)} & \text{E(A.U.) R(Å)} & \text{E(A.U.) R(Å)} \\
\text{F}_3^- & -298.5385 & 1.80 & -298.5792 & 1.75 & -298.6724 & 1.90 \\
\text{F}_2 & -198.9637 & 1.60 & -198.9652 & 1.52 & -199.0189 & 1.60 \\
\text{F}_2^- & -199.0404 & 1.95 & -199.0557 & 1.94 & -199.1125 & 2.00 \\
\text{F}_2^- + \text{F} & -298.5094 & -298.5260 & -298.6053 \\
\text{D}_e(\text{F}_2^-, \text{F}) & 0.0532 & 0.0671 \\
\text{D}_e(\text{F}, \text{F}, \text{F}^-) & 0.1353 & 0.1036 & 0.1426 \\
\end{array}
\]

TABLE III: The accuracy of the DM2(PQG/subspace) method remains poor, as the subspace constraints only correct for improper dissociation. The DM2(PQG/subspace) dissociation energies \( D_e \) for dissociation into \( \text{F}_2^- + \text{F} \) and \( \text{F} + \text{F} + \text{F}^- \) are substantially bigger than those obtained with CCSD and MRCI. MRCI calculations on the dissociated system \( \text{F}_2^- + \text{F} \) 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 DM2(PQG/subspace), determined in steps of 0.05 Å.