

A new approach for the two-electron cumulant in natural orbital functional theory.

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Abstract

The cumulant expansion gives rise to an useful decomposition of the two-matrix \mathbf{D} in which the pair correlated matrix (cumulant) is disconnected from the antisymmetric product of the one-matrices $\mathbf{\Gamma}$. A new explicit antisymmetric approach for the two-particle cumulant matrix in terms of two symmetric matrices, $\mathbf{\Delta}$ and $\mathbf{\Lambda}$, as functionals of the occupation numbers is proposed for singlet ground states of closed-shell systems. It produces a natural orbital functional that reduces to the exact expression for the total energy in two-electron systems. The functional form of matrix $\mathbf{\Lambda}$ is readily generalized to any system with an even number of electrons. The diagonal elements of $\mathbf{\Delta}$ equal the square of the occupation numbers, and the N-representability positivity necessary conditions of the two-matrix impose several bounds on the off-diagonal elements of matrix $\mathbf{\Delta}$. The well-known mean value theorem and the partial sum rule obtained for the off-diagonal elements of $\mathbf{\Delta}$ provide a prescription for deriving a practical functional. In particular, when the mean values $\{J_i^*\}$ of the Coulomb interactions $\{J_{ij}\}$ for a given orbital i taking

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over all orbitals $j \neq i$ are assumed to be equal $\{K_{ii}/2\}$, a functional close to self-interaction-corrected GU functional is obtained, but the two-matrix fermionic antisymmetric holds. An additional term for the matrix elements of \mathbf{A} between HF occupied orbitals is proposed to ensure a correct description of the occupation numbers for the lowest occupied levels. The functional is tested in fully variational finite basis set calculations of 57 molecules. It gives reasonable molecular energies at the equilibrium geometries. The calculated values of dipole moments are in good agreement with the available experimental data.

Key words: natural orbital functional, cumulant, reduced density matrix, dipole moment, electron correlation energies

I. INTRODUCTION

The idea of a one-particle reduced density matrix (one-matrix) $\mathbf{\Gamma}$ functional appeared some decades ago [1]. More recently, several functionals of the natural orbitals and their occupation numbers have been proposed [2] - [11]. A major advantage of the method is that the kinetic energy and the exchange energy are explicitly defined using the one-matrix and do not require the construction of a functional. The unknown functional only needs to incorporate electron correlation. Moreover, the one-matrix is a much simpler object than the N-particle wave function, and the ensemble N-representability conditions that have to be imposed on variations of $\mathbf{\Gamma}$ are well-known [12]. Finally, the natural orbital functional (NOF) incorporates fractional occupation numbers in a natural way, which provides a correct description of both dynamical and nondynamical correlation.

A NOF requires an expression of the two-particle reduced density matrix (two-matrix) \mathbf{D} in terms of the one-matrix $\mathbf{\Gamma}$. Such reconstruction of the two-matrix can be achieved using the well-known cumulant expansion of \mathbf{D} [13]. In this paper, we propose an explicit antisymmetric form for the two-particle cumulant matrix. By employing an antisymmetric ansatz for the two-matrix we can obtain a correct description of the pair density for parallel-spin electrons, which is poorly described by its predecessor [11].

Unlike density functional theory (DFT), density matrix functional theory affords an exact energy functional for two-electron systems [14,6]. The ansatz presented here can be reduced to this exact expression providing the specific form of the cumulant matrix in the two-electron case. This functional form can be readily generalized to any N-electron system, but the off-diagonal elements of a symmetric matrix $\mathbf{\Delta}$ remain unknown. On the other hand, several constraints for these magnitudes can be achieved via some known positivity conditions. In the present work, we analyze the D-, G- and Q-conditions of two-matrix N-representability, and establish several bounds on the off-diagonal elements of matrix $\mathbf{\Delta}$.

In order to develop a practical method, a further approximation is assumed. Instead of approach off-diagonal elements of $\mathbf{\Delta}$ considering constraints imposed by positivity conditions, we approximate the term which involves matrix $\mathbf{\Delta}$ by employing the well-known mean value theorem and the partial sum rule obtained for this matrix. This leads to a total energy close to the self-interaction-corrected Hartree functional proposed by Goedecker and Umrigar (GU) [6]. GU functional is not antisymmetric assuming a Hartree-product form for the opposite spin component of \mathbf{D} , so it does not afford an N-representable two-matrix [15]. In contrast to this reconstruction, the current proposal can satisfy not only the Hermiticity and particle permutation conditions, but also the trace relation and positivity conditions of the two-matrix. Besides, it appears to reproduce properly the occupation numbers for lower occupied levels.

We start with a presentation of the basic concepts and notations relevant to natural orbital functional theory (Section II). We then present our ansatz for the two-electron cumulant matrix (Section III). The two- and N-electron cases, as well as the N-representability

of the functional are discussed in detail here. The following section is devoted to our further simplification in order to accomplish a practical functional (Section IV). We end with a short presentation of the methodological details (Section V) and some results for selected molecules (Section VI).

II. BASIC CONCEPTS AND NOTATIONS

A. General formalism

We consider an N-electron Coulombic system described by the Hamiltonian

$$\widehat{H} = \sum_{ij} h_{ij} \widehat{\Gamma}_{ji} + \sum_{ijkl} \langle ij|kl \rangle \widehat{D}_{kl,ij} \quad (1)$$

where h_{ij} denote the one-electron matrix elements of the core-Hamiltonian,

$$h_{ij} = \int \int d\mathbf{x} \chi_i^*(\mathbf{x}) \left[-\frac{1}{2} \nabla^2 - \sum_I \frac{Z_I}{|\mathbf{r} - \mathbf{r}_I|} \right] \chi_j(\mathbf{x}) \quad (2)$$

and $\langle ij|kl \rangle$ denote the two-electron matrix elements of the Coulomb interaction

$$\langle ij|kl \rangle = \int \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) r_{12}^{-1} \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2) \quad (3)$$

Atomic units are used. Here and in the following $\mathbf{x} \equiv (\mathbf{r}, \mathbf{s})$ stands for the combined spatial and spin coordinates, \mathbf{r} and \mathbf{s} , respectively. The spin-orbitals $\{\chi_i(\mathbf{x})\}$ constitute a complete orthonormal set of single-particle functions,

$$\langle \chi_i | \chi_j \rangle = \int d\mathbf{x} \chi_i^*(\mathbf{x}) \chi_j(\mathbf{x}) = \delta_{ij} \quad (4)$$

with an obvious meaning of the Kronecker delta δ_{ij} . The one- and two-particle density matrix operators,

$$\widehat{\Gamma}_{ji} = \widehat{a}_j^\dagger \widehat{a}_i \quad (5)$$

and

$$\widehat{D}_{kl,ij} = \left(\frac{1}{2} \right) \widehat{a}_k^\dagger \widehat{a}_l^\dagger \widehat{a}_j \widehat{a}_i \quad (6)$$

are constructed from the familiar creation and annihilation operators, $\{\hat{a}_i^\dagger\}$ and $\{\hat{a}_i\}$ [16], respectively, associated with the set of spin-orbitals $\{\chi_i(\mathbf{x})\}$.

A quantum mechanical pure state of our N-particle system can be characterized by a normalized wave function Ψ or a system density matrix Γ_N

$$\Gamma_N(\mathbf{x}'_1, \mathbf{x}'_2, \dots, \mathbf{x}'_N; \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \Psi^*(\mathbf{x}'_1, \mathbf{x}'_2, \dots, \mathbf{x}'_N) \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \quad (7)$$

The expectation value of the Hamiltonian (1) for the state Ψ is then

$$E = \sum_{ij} h_{ij} \Gamma_{ji} + \sum_{ijkl} \langle ij|kl \rangle D_{kl,ij} \quad (8)$$

where the one- and two-particle reduced density matrices, or briefly the one- and two-matrices, are defined as

$$\Gamma_{ji} = \langle \Psi | \hat{\Gamma}_{ji} | \Psi \rangle \quad (9)$$

$$D_{kl,ij} = \langle \Psi | \hat{D}_{kl,ij} | \Psi \rangle \quad (10)$$

According to expression (8) the energy E of a state Ψ is an exactly and explicitly known functional of Γ and \mathbf{D} .

The reduced density matrices satisfy important sum rules [17]. The trace of the one-matrix equals the number of electrons

$$\text{Tr } \Gamma = \sum_i \Gamma_{ii} = N \quad (11)$$

and the trace of the two-matrix gives the number of electron pairs in the system

$$\text{Tr } \mathbf{D} = \sum_{ij} D_{ij,ij} = \frac{N(N-1)}{2} = \binom{N}{2} \quad (12)$$

Their diagonal elements in the coordinate-space representation are always nonnegative, since $\Gamma(\mathbf{x}_1; \mathbf{x}_1)$ is related to the probability of finding one electron at \mathbf{x}_1 , and $D(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1, \mathbf{x}_2)$ is related to the probability of finding one electron at \mathbf{x}_1 and another at \mathbf{x}_2 .

\mathbf{D} satisfies several relations which follow directly from the anticommutation rules and the Hermiticity of the operators $\{\hat{a}_i^\dagger\}$ and $\{\hat{a}_i\}$, namely, the Hermiticity,

$$D_{kl,ij} = D_{ij,kl}^* \quad (13)$$

and the antisymmetry,

$$D_{kl,ij} = -D_{lk,ij} = -D_{kl,ji} = D_{lk,ji} \quad (14)$$

There is an important contraction relation between one- and two-matrices that is in agreement with the previous normalization (11)-(12),

$$\Gamma_{ji} = \frac{2}{N-1} \sum_k D_{jk,ik} \quad (15)$$

This implies that the energy functional (8) is just of the two-matrix, because \mathbf{D} determines $\mathbf{\Gamma}$. Attempts to determine the energy by minimizing $E[\mathbf{D}]$ are complicated due to the lack of a simple set of necessary and sufficient conditions for ensuring that the two-matrix corresponds to an N-particle wave function (the N-representability problem) [12]. Alternatively, the last term in Eq. (8) can be replaced by an unknown functional of the one-matrix [18],

$$E[\mathbf{\Gamma}] = \sum_{ij} h_{ij} \Gamma_{ji} + V_{ee}[\mathbf{\Gamma}] \quad (16)$$

The functional $V_{ee}[\mathbf{\Gamma}]$ is universal in the sense that it is independent of the external field. Its properties are well-known [19]. However, it is highly difficult to approximate because what we have done is to change the variational unknown from the complicated many-variable function Ψ to a single one-matrix $\mathbf{\Gamma}$.

The one-matrix $\mathbf{\Gamma}$ can be diagonalized by a unitary transformation of the spin-orbitals $\{\chi_i(\mathbf{x})\}$ with the eigenvectors being the natural spin-orbitals and the eigenvalues $\{n_i\}$ representing the occupation numbers of the latter,

$$\Gamma_{ji} = n_i \delta_{ji} \quad (17)$$

In the following, all representations used are assumed to refer to this basis. Accordingly, the energy functional is determined by the natural orbitals and their occupation numbers, i.e., $E[\{n_i, \psi_i\}]$. In addition, we assume all orbitals to be real.

B. Restricted formalism

The Hamiltonian (1) is spin independent, so only density matrix blocks that conserve the number of each spin type are nonvanishing. Specifically, the one-matrix has two nonzero blocks, an α block (Γ^α) and a β block (Γ^β),

$$\Gamma_{ji}^{\alpha\alpha} \neq 0, \quad \Gamma_{ji}^{\beta\beta} \neq 0, \quad (18)$$

and the two-matrix has three nonzero blocks, an $\alpha\alpha$ block ($\mathbf{D}^{\alpha\alpha}$), an $\alpha\beta$ block ($\mathbf{D}^{\alpha\beta}$) and a $\beta\beta$ block ($\mathbf{D}^{\beta\beta}$),

$$D_{kl,ij}^{\alpha\alpha,\alpha\alpha} \neq 0, \quad D_{kl,ij}^{\alpha\beta,\alpha\beta} \neq 0, \quad D_{kl,ij}^{\beta\beta,\beta\beta} \neq 0, \quad (19)$$

The set of spin-orbitals $\{\chi_i(\mathbf{x})\}$ is split here into two subsets: $\{\psi_i^\alpha(\mathbf{r})\alpha(\mathbf{s})\}$ and $\{\psi_i^\beta(\mathbf{r})\beta(\mathbf{s})\}$. In the case of spin compensated systems, the two blocks of the one-matrix are the same ($\Gamma^\alpha = \Gamma^\beta$), i.e.,

$$n_i^\alpha = n_i^\beta = n_i, \quad \psi_i^\alpha(\mathbf{r}) = \psi_i^\beta(\mathbf{r}) = \psi_i(\mathbf{r}) \quad (20)$$

The trace of the one-matrix (11) becomes

$$2 \sum_i n_i = N \quad (21)$$

For singlet states, the first and the last blocks of the two-matrix are also equal ($\mathbf{D}^{\alpha\alpha} = \mathbf{D}^{\beta\beta}$), so in this work we deal only with $\mathbf{D}^{\alpha\alpha}$ and $\mathbf{D}^{\alpha\beta}$. The parallel-spin component $\mathbf{D}^{\alpha\alpha}$ is antisymmetric, but $\mathbf{D}^{\alpha\beta}$ possess no special symmetry. Each of these two-matrix blocks must contract to the appropriate one-matrix block, namely

$$\sum_k D_{jk,ik}^{\alpha\alpha} = \frac{(N-2)}{4} \Gamma_{ji}^{\alpha\alpha} = \frac{(N-2)}{4} n_i \delta_{ji} \quad (22)$$

$$\sum_k D_{jk,ik}^{\alpha\beta} = \frac{N}{4} \Gamma_{ji}^{\alpha\alpha} = \frac{N}{4} n_i \delta_{ji} \quad (23)$$

It is readily demonstrated that the sum rules (22) and (23) are compatible with the Eq. (15). The traces of these two-matrix components read

$$Tr \mathbf{D}^{\alpha\alpha} = \frac{N(N-2)}{8}, \quad Tr \mathbf{D}^{\alpha\beta} = \frac{N^2}{8} \quad (24)$$

The singlet spin-compensated systems only will be considered in the rest of the paper.

III. THE TWO-MATRIX

A. Cumulant of the two-matrix

It remains to find approximations for the unknown functional $V_{ee}[\Gamma]$. To this end, we use here a reconstructive functional $\mathbf{D}[\Gamma]$, that is, we express the elements $D_{kl,ij}$ in terms of the Γ_{ji} . We neglect any explicit dependence of \mathbf{D} on the natural orbitals themselves because the energy functional (8) has already a strong dependence on the natural orbitals via the one- and two-electron integrals. Let's consider the following well-known [13] decomposition of \mathbf{D} :

$$D_{kl,ij}^{\alpha\alpha} = \frac{1}{2} \left(\Gamma_{ki}^{\alpha} \Gamma_{lj}^{\alpha} - \Gamma_{kj}^{\alpha} \Gamma_{li}^{\alpha} + \lambda_{kl,ij}^{\alpha\alpha} \right) = \frac{n_j n_i}{2} (\delta_{ki} \delta_{lj} - \delta_{kj} \delta_{li}) + \lambda_{kl,ij}^{\alpha\alpha} \quad (25)$$

$$D_{kl,ij}^{\alpha\beta} = \frac{1}{2} \left(\Gamma_{ki}^{\alpha} \Gamma_{lj}^{\beta} + \lambda_{kl,ij}^{\alpha\beta} \right) = \frac{1}{2} \left(n_j n_i \delta_{ki} \delta_{lj} + \lambda_{kl,ij}^{\alpha\beta} \right) \quad (26)$$

where λ is the cumulant matrix. It should be noted that matrix elements of λ are nonvanishing only if all its labels refer to partially occupied natural orbitals with occupation number different from 0 or 1 [13]. It can be easily shown from Eqs. (22) and (23), taking into account the normalization condition for the one-matrix (21), that spin components of λ fulfill the following sum rules:

$$\sum_k \lambda_{jk,ik}^{\alpha\alpha} = n_i (n_i - 1) \delta_{ji} \quad (27)$$

$$\sum_k \lambda_{jk,ik}^{\alpha\beta} = 0 \quad (28)$$

The first two terms on the rhs of Eq. (25) together satisfy property (14) of $\mathbf{D}^{\alpha\alpha}$. Therefore, the matrix $\lambda^{\alpha\alpha}$ should be antisymmetric too. In general, the cumulant has a dependence of four indices and direct computation with such quantities is infeasible to be applied to large systems. In this work, we consider the following parallel component of the cumulant matrix:

$$\lambda_{kl,ij}^{\alpha\alpha} = -\frac{\Delta_{ji}}{2} \delta_{ki} \delta_{lj} + \frac{\Delta_{ji}}{2} \delta_{kj} \delta_{li} \quad (29)$$

where Δ is a symmetric matrix. The sum rule (27) and the approximate ansatz (29) imply the constraint

$$\sum_j' \Delta_{ji} = n_i(1 - n_i) \quad (30)$$

The prime indicates that the $i = j$ term is omitted. For $\lambda^{\alpha\beta}$, we can achieve a suitable approximation if we replace the second term in Eq.(29) by the dependence obtained in the improved Bardeen-Cooper-Schrieffer (IBCS) method [20], namely

$$\lambda_{kl,ij}^{\alpha\beta} = -\frac{\Delta_{ji}}{2}\delta_{ki}\delta_{lj} + \frac{\Pi_{ki}}{2}\delta_{kl}\delta_{ij} \quad (31)$$

where we have introduced a new symmetric matrix Π . For convenient purposes as we see below, we define the matrix Π in terms of a new symmetric matrix Λ :

$$\Pi_{ki} = n_k n_i - \Delta_{ki} - \Lambda_{ki} \quad (32)$$

Combining Eqs. (28), (30), (31) and (32) results in

$$2\Delta_{ii} + \Lambda_{ii} = 2n_i^2 - n_i \quad (33)$$

Using Eqs. (17), (20), (25), (26), (29), (31) and (32) the energy Eq. (8) reads as

$$E = 2 \sum_i n_i h_{ii} + \sum_{ij} (n_j n_i - \Delta_{ji}) (2J_{ij} - K_{ij}) + \sum_{ij} (n_j n_i - \Delta_{ji} - \Lambda_{ji}) L_{ij} \quad (34)$$

with $J_{ij} = \langle ij|ij \rangle$, $K_{ij} = \langle ij|ji \rangle$ and $L_{ij} = \langle ii|jj \rangle$, see Eq. (3) with $\chi_i(\mathbf{x})$ replaced by $\psi_i(\mathbf{r})$. Note that if $\Delta_{ji} = 0$ and $\Lambda_{ji} = n_j n_i$ (so $\Pi_{ji} = 0$), then the reconstruction proposed here yields the Hartree-Fock (HF) case as expected. Taking into account that $L_{ij} = K_{ij}$ for real orbitals, the expression (34) can be rewrite as

$$E = 2 \sum_i n_i h_{ii} + 2 \sum_{ij} (n_j n_i - \Delta_{ji}) J_{ij} - \sum_{ij} \Lambda_{ji} K_{ij} \quad (35)$$

B. Two-electron systems

NOF theory provides an exact energy functional for two-electron systems [14,6]. In the weak correlation limit, the total energy is given by

$$E = 2 \sum_{i=1}^{\infty} n_i h_{ii} + n_1 K_{11} - 2 \sum_{i=2}^{\infty} \sqrt{n_1 n_i} K_{i1} + \sum_{i,j=2}^{\infty} \sqrt{n_j n_i} K_{ij} \quad (36)$$

As can be seen from Eq. (36), the dependence of \mathbf{D} on the natural occupations requires a distinction between HF occupied and virtual orbitals.

Since $\mathbf{D}^{\alpha\alpha} = 0$ for $N = 2$, one easily deduces from Eqs. (25) and (29) that $\Delta_{ji} = n_j n_i$. Consequently, it is not difficult to see from Eqs. (26), (31) and (32) that $\mathbf{D}^{\alpha\beta}$ nonzero elements have the form $D_{jj,ii}^{\alpha\beta} = -\Lambda_{ji}/2$. Thus, the total energy (35) turns into

$$E = 2 \sum_i n_i h_{ii} - \sum_{ij} \Lambda_{ji} K_{ij} \quad (37)$$

From the requirement that for any two-electron system the expression (37) should yield Eq. (36), one has to set

$$\Lambda_{ji} = \text{sign}(\Lambda_{ji}) \sqrt{n_j n_i}, \quad \text{sign}(\Lambda_{ji}) = \left\{ \begin{array}{l} -1 \text{ if } i = 1, j = 1 \\ +1 \text{ if } i = 1, j \geq 2; \quad i \geq 2, j = 1 \\ -1 \text{ if } i \geq 2, j \geq 2 \end{array} \right\} \quad (38)$$

It is worth noting that the chosen Δ and Λ satisfy the constraints (30) and (33). Moreover, the sign rule (38) also holds true for systems where the largest occupation deviates significantly from one, indicating that it may be possibly valid for arbitrary correlation strengths [6].

C. N-electron systems

The expression (38) suggests the following functional form for $\{\Lambda_{ji}\}$:

$$\Lambda_{ii} = -n_i \quad (39)$$

$$\Lambda_{ji} = \text{sign}(\Lambda_{ji})\sqrt{n_j n_i} \quad \text{if } i \neq j \quad (40)$$

where

$$\text{sign}(\Lambda_{ji}) = \left\{ \begin{array}{l} +1 \text{ if } i \leq nco, j \leq nco \\ +1 \text{ if } i \leq nco, j > nco; \quad i > nco, j \leq nco \\ -1 \text{ if } i > nco, j > nco \end{array} \right\} \quad (41)$$

Here, the number of HF closed shells is denoted nco . Inserting Eq. (39) into the equality (33), affords

$$\Delta_{ii} = n_i^2 \quad (42)$$

By taking into account Eqs. (39) and (42), the energy functional (35) can be expressed as

$$E = \sum_i n_i (2h_{ii} + K_{ii}) + 2 \sum'_{ij} (n_j n_i - \Delta_{ji}) J_{ij} - \sum'_{ij} \Lambda_{ji} K_{ij} \quad (43)$$

Unfortunately, $\Delta_{ji} = n_j n_i$, taken from the $N = 2$ case, violates the sum rule (30) in the general case of $N > 2$. This means that the functional form of nondiagonal elements of Δ is unknown for N-electron systems, as yet. Nevertheless, some constraints can be achieved for these quantities using known necessary conditions of two-matrix N-representability.

D. N-representability

The one-matrix and the functional N-representability problems are entirely different. Restriction of the occupation numbers $\{n_i\}$ to the range $0 \leq n_i \leq 1$ represents a necessary and sufficient condition for ensemble N-representability of the one-matrix [12]. However, the functional N-representability refers to the conditions that guarantee the one-to-one correspondence between $E[\Psi]$ and $E[\Gamma]$, which is a related problem to the N-representability of the two-matrix. Therefore, any approximation for $V_{ee}[\{n_i, \psi_i\}]$ must comply at least with the known necessary conditions for the N-representability of the two-matrix [21].

The so called D-, G- and Q-conditions state that the two-electron density matrix, Eq. (10), the electron-hole density matrix \mathbf{G} ,

$$G_{kl,ij} = \frac{1}{2} \langle \Psi | \hat{a}_k^\dagger \hat{a}_l \hat{a}_j^\dagger \hat{a}_i | \Psi \rangle \quad (44)$$

and the two-hole density matrix \mathbf{Q} ,

$$Q_{kl,ij} = \frac{1}{2} \langle \Psi | \hat{a}_k \hat{a}_l \hat{a}_j^\dagger \hat{a}_i^\dagger | \Psi \rangle \quad (45)$$

must be positive semidefinite. There are also other two necessary conditions for the N-representability of a fermion two-matrix which were named B- and C-conditions. A discussion of relations among these *positivity* conditions is given in Ref. [22].

Using the anticommutation relations for creation and annihilation operators and definitions of the one- and two-matrices given in Eqs. (9) - (10), the spin component matrices of \mathbf{G} and \mathbf{Q} can be derived from the matrices \mathbf{D} and $\mathbf{\Gamma}$ as follows:

$$G_{kl,ij}^{\alpha\alpha} = \frac{1}{2} \delta_{lj} \Gamma_{ki}^\alpha - D_{kj,il}^{\alpha\alpha} \quad (46)$$

$$G_{kl,ij}^{\alpha\beta} = \frac{1}{2} \delta_{lj} \Gamma_{ki}^\alpha - D_{kj,il}^{\alpha\beta} \quad (47)$$

$$Q_{kl,ij}^{\alpha\alpha} = \frac{1}{2} \left(\delta_{ki} \delta_{lj} - \delta_{ki} \Gamma_{jl}^\alpha - \delta_{lj} \Gamma_{ik}^\alpha - \delta_{kj} \delta_{li} + \delta_{kj} \Gamma_{il}^\alpha + \delta_{li} \Gamma_{jk}^\alpha \right) + D_{ij,kl}^{\alpha\alpha} \quad (48)$$

$$Q_{kl,ij}^{\alpha\beta} = \frac{1}{2} \left(\delta_{ki} \delta_{lj} - \delta_{ki} \Gamma_{jl}^\beta - \delta_{lj} \Gamma_{ik}^\alpha \right) + D_{ij,kl}^{\alpha\beta} \quad (49)$$

A matrix is positive semidefinite if, and only if, all of its eigenvalues are non-negative. The solution of the eigenproblem for $\mathbf{D}^{\alpha\alpha}$ is readily carried out, yielding the following set of eigenvalues:

$$d^{\alpha\alpha} = \{0, \quad n_j n_i - \Delta_{ji}\}, \quad j \neq i \quad (50)$$

For more details, the reader can find an analogous derivation in Ref. [15]. $\mathbf{D}^{\alpha\beta}$ consists of 1×1 blocks, along with a single $R \times R$ block, where R is the number of orbitals. The latter has elements

$$D_{ii,jj}^{\alpha\beta} = \frac{1}{2} (n_j n_i - \Delta_{ji} - \Lambda_{ji}) \quad (51)$$

The 1×1 blocks have elements $D_{ij,ij}^{\alpha\beta}$, for $j \neq i$, and thus yield eigenvalues

$$d_{ji}^{\alpha\beta} = \frac{1}{2} (n_j n_i - \Delta_{ji}) \quad (52)$$

To sum up, we have analytic expressions for all eigenvalues of \mathbf{D} , except those arising from the single $R \times R$ block. Consequently, our reconstructive functional satisfies the D-condition ($d \geq 0$) if $\Delta_{ji} \leq n_j n_i$ and the $R \times R$ block of $\mathbf{D}^{\alpha\beta}$ is positive.

Introducing the abbreviation $\Omega_{ji} = 1 - n_j - n_i + n_j n_i$, and considering that \mathbf{Q} has the same block structure as \mathbf{D} , one has the following set of analytic eigenvalues:

$$q = \left\{ 0, \quad \Omega_{ji} - \Delta_{ji}, \quad \frac{\Omega_{ji} - \Delta_{ji}}{2} \right\}, \quad j \neq i \quad (53)$$

Accordingly, if one takes $\Delta_{ji} \leq \Omega_{ji}$, and the $R \times R$ block of $\mathbf{Q}^{\alpha\beta}$ is positive, the Q-condition is fulfilled. It is easy to verify that D-condition is more restrictive than Q-condition for Δ_{ji} between HF virtual orbitals (occupation numbers are close to zero), whereas for elements between HF occupied levels the Q-condition is predominant.

Finally, we consider \mathbf{G} . The spin component $\mathbf{G}^{\alpha\alpha}$ contains also a single block $R \times R$, for which the eigenvalues have no analytic expression, and 1×1 blocks. These latter blocks contribute eigenvalues

$$g_{ji}^{\alpha\alpha} = \frac{1}{2} (n_i - n_j n_i + \Delta_{ji}), \quad j \neq i \quad (54)$$

From Eq. (54), it is evident that $g_{ji}^{\alpha\alpha} \geq 0$ if $\Delta_{ji} \geq n_i (n_j - 1)$. This inequality is easy to satisfy on the domain of allowed occupation numbers ($n_j \leq 1$) if we consider non-negative Δ_{ji} .

The opposite spin component consists entirely of 1×1 blocks $G_{ii,ii}^{\alpha\beta} = 0$, and 2×2 blocks

$$\begin{pmatrix} G_{ij,ij}^{\alpha\beta} & G_{ij,ji}^{\alpha\beta} \\ G_{ji,ij}^{\alpha\beta} & G_{ji,ji}^{\alpha\beta} \end{pmatrix} \quad (55)$$

After some straightforward algebra, it can be shown that blocks (55) afford the eigenvalues

$$g_{ji}^{\alpha\beta} = \frac{n_j + n_i}{4} + \frac{\Delta_{ji} - n_j n_i}{2} \pm \frac{1}{4} \sqrt{(n_j - n_i)^2 + 4(n_j n_i - \Delta_{ji} - \Lambda_{ji})^2} \quad (56)$$

In order to ensure that $g_{ji}^{\alpha\beta} \geq 0$, the expression (56) gives rise to the inequality

$$\Delta_{ji} \leq n_j n_i + \frac{n_j n_i - \Lambda_{ji}^2}{2\Lambda_{ji} - n_j - n_i} \quad (57)$$

IV. A PRACTICAL FUNCTIONAL

To obtain the NOF for a system of N electrons, one may attempt to approximate off-diagonal elements of $\mathbf{\Delta}$ considering the sum rule (30) and constraints imposed by the D-, G- and Q-conditions. However, it is not evident how to approach Δ_{ji} , for $j \neq i$, in terms of the occupation numbers. Due to this fact, let's rewrite the energy term in Eq. (43) which involves Δ_{ji} as

$$\sum'_{ij} \Delta_{ji} J_{ij} = \sum_i J_i^* \sum'_j \Delta_{ji} \quad (58)$$

where J_i^* denotes the mean value of the Coulomb interactions J_{ij} for a given orbital i taking over all orbitals $j \neq i$. From the property shown in Eq. (30) follows immediately

$$\sum'_{ij} \Delta_{ji} J_{ij} = \sum_i n_i (1 - n_i) J_i^* \quad (59)$$

Inserting this expression into Eq. (43), one obtains

$$E = \sum_i (2n_i h_{ii} + n_i^2 K_{ii}) + \sum'_{ij} (2n_j n_i J_{ij} - \Lambda_{ji} K_{ij}) + \sum_i n_i (1 - n_i) (K_{ii} - 2J_i^*) \quad (60)$$

A further simplification of our NOF is accomplished by setting $J_i^* \approx K_{ii}/2$, which produces

$$E = \sum_i (2n_i h_{ii} + n_i^2 K_{ii}) + \sum'_{ij} (2n_j n_i J_{ij} - \Lambda_{ji} K_{ij}) \quad (61)$$

Under these circumstances, the NOF (43) turns out to be identical with the self-interaction-corrected Hartree functional proposed by Goedecker and Umrigar [6] except for the choice of phases given by $sign(\Lambda_{ji})$. The functional form (40) for the matrix elements of \mathbf{A} between HF occupied orbitals gives a wrong description of the occupation numbers for the lowest occupied levels. They are identically equal to one. In order to ensure that these occupation numbers only are close to unity we assume the form (see, e.g., [5])

$$\Lambda_{ji} = \sqrt{n_j n_i} + \sqrt{(1 - n_j)(1 - n_i)} \quad \text{if } i \leq nco, j \leq nco, i \neq j \quad (62)$$

Let us apply the well-known procedure of taking molecular orbitals as linear combination of atomic orbitals (MO-LCAO),

$$\psi_i(\mathbf{r}) = \sum_{\nu} C_{\nu i} \varphi_{\nu}(\mathbf{r}) \quad (63)$$

The electronic energy (61) will then be a functional

$$E[\{\mathbf{C}_i\}, \{n_i\}] = \sum_{\nu\eta} \left\{ [2h_{\eta\nu} \Gamma_{\nu\eta} + \sum_i n_i^2 K_{\eta\nu}^i \Gamma_{\nu\eta}^i] + \sum_{ij}' [2n_j n_i J_{\eta\nu}^j - \Lambda_{ji} K_{\eta\nu}^j] \Gamma_{\nu\eta}^i \right\} \quad (64)$$

where it has been introduced the following matrices

$$\Gamma_{\nu\eta} = \sum_i n_i \Gamma_{\nu\eta}^i, \quad \Gamma_{\nu\eta}^i = C_{\nu i} C_{\eta i} \quad (65)$$

$$J_{\eta\nu}^j = \sum_{\lambda\mu} \langle \eta\mu | \nu\lambda \rangle \Gamma_{\lambda\mu}^j \quad (66)$$

$$K_{\eta\nu}^j = \sum_{\lambda\mu} \langle \eta\mu | \lambda\nu \rangle \Gamma_{\lambda\mu}^j \quad (67)$$

The orthonormality condition (4) reads as follows:

$$\sum_{\nu\mu} C_{\mu j} S_{\mu\nu} C_{\nu i} = \delta_{ji} \quad (68)$$

where $S_{\mu\nu} = \langle \varphi_{\mu} | \varphi_{\nu} \rangle$ is the overlap matrix.

V. METHODOLOGICAL DETAILS

Direct minimization of the energy functional of Eq. (64) is required, subject to the constraints:

1. The N-representability condition of the one-matrix ($0 \leq n_i \leq 1$).
2. The constant number of particles, Eq. (21).
3. The orthonormality condition, Eq. (68).

One has to calculate the gradient of the functional both with respect to natural orbitals coefficients $\{\mathbf{C}_i\}$ and the occupation numbers $\{n_i\}$. Since the minimization with respect to occupations is much cheaper than with respect to the orbitals, one can decouple the variation of the occupation numbers from that of the natural orbitals, a procedure used by us in the IBCS method [20]. In the inner loop we find the optimal occupation numbers for a given set of orbitals under constraint 2. Bounds on the occupation numbers are enforced by setting $n_i = (\sin \gamma_i)^2$ and varying the γ_i without constraints. In the outer loop we minimize with respect to the orbital coefficients under the constraints 3 of mutual orthonormality. Both the inner- and outer-loop optimizations has been implemented using a sequential quadratic programming (SQP) method [23].

VI. RESULTS

In this section, calculations of total energies and dipole moments for selected molecules using contracted Gaussian basis sets 6-31G** [24] are presented. Computationally speaking, NOF theory in its current form is very demanding. Therefore, we have chosen a medium-size basis set for the calculations and we have compared the results with the results using other methods at the same level. We are aware of the fact that very large basis sets are required to estimate experimental values.

Among the approaches compared are the coupled cluster technique including all single and double excitations and a perturbational estimate of the connected triple excitations [CCSD(T)], as well as the Becke-3-Lee-Yang-Parr (B3LYP) density functional [25]. The CCSD(T) and B3LYP values were calculated with the GAUSSIAN 94 system of programs [26], using the basis set keyword 5D.

In Table I we report the values obtained for the total energies of 57 molecules, employing the experimental geometry [27,28]. For comparison, we have included into this Table the total energies calculated at the CCSD(T) and B3LYP levels.

[**TABLE I**]

According to Table I, the values we have obtained are more like CCSD(T) calculations, which are very accurate results for the basis-set correlation energies on these small molecules. The B3LYP values, as is well known, tend to be too low. We note that the percentage of the correlation energy obtained by CCSD(T) decreases as the number of electrons increases, whereas our functional keeps giving a slightly larger portion of the correlation energy (e.g. AlCl, SiS, P₂, SO₂, Cl₂).

For molecules with dipole moments (μ) different from zero, we have also evaluated this property (Table II). For comparison, we have included into this Table the available experimental data [29] of μ and those calculated with the GAUSSIAN 94 system of programs at the CCSD(T) and B3LYP levels.

[**TABLE II**]

The dipole moments obtained with the correlated methods are in good agreement with the experimental data considering the basis sets (6-31G**) used for these calculations. For the reported molecules, the correlated dipole moments are lower compared to HF μ , except for BCl, BF and CS. For PH₃ and SiH₂, we have to mention that B3LYP dipole moments are increased with respect to the HF result, whereas the NOF and CCSD(T) values continue being smaller than it. On the contrary, in the case of AlF molecule, the B3LYP method

decreases μ with respect to the HF value, whereas the NOF and CCSD(T) yield a higher dipole moment. Important cases are the CO and N₂O molecules for which the HF approximation gives a dipole moment in the wrong direction, whereas correlation methods approach it to the experimental value.

The quality of natural orbitals is critical for the accuracy of NOF theory. For example, in the case of CO molecule, we can achieve the sign inversion of the dipole moment ($\mu = 0.03$ Debyes) by adding only one basis function (6-311G**). One can hope to obtain a better agreement by improving further the basis sets.

VII. CONCLUDING REMARKS

Making use of the known cumulant expansion, it has been proposed a new reconstructive functional for the two-matrix. Its explicit antisymmetric form leads to a better description of the pair density for parallel-spin electrons with respect to our previous proposal. The dependence obtained in the improved Bardeen-Cooper-Schrieffer (IBCS) method was also considered for the opposite-spin component of the cumulant.

The functional given by Eq. (35) can be reduced to the exact energy expression for singlet ground states of two-electron closed-shell systems like H₂ or He. This permitted us to generalize its functional form for N-electron systems, except for the off-diagonal elements of a symmetric matrix Δ .

The fact that the N-representability conditions for the ensemble 1-matrix are known is not sufficient to ensure the N-representability of the functional, which is a related problem to the N-representability of the two-matrix. To this end, we discussed here the well-known necessary D-, G- and Q-conditions. The analytic determined eigenvalues provided rigorous bounds on the magnitudes $\{\Delta_{ji}\}$ to guarantee that our reconstructed functional satisfies these positivity conditions.

By considering the mean value theorem and the partial sum rule for matrix Δ , we achieved a practical functional which is close to the self-interaction-corrected GU functional.

Despite the previous reported N-representability violations of the GU functional, the cumulant expansion examined here can correct these positivity problems satisfying at the same time the trace relation of the two-matrix. On the other hand, our ansatz (62) reproduces properly the occupation numbers for lower occupied levels. An improvement of our approach requires better approximations for the mean values $\{J_i^*\}$ of the Coulomb interactions.

A representative set of 57 molecules was investigated. The comparison with other theoretical methods showed that the presented NOF provides total energies closer to accurate ab initio methods than to DFT energies. The agreement between theory and experiment for μ was satisfactory considering the basis sets used. The accuracy of dipole moments in all calculational approaches in present study appears to be comparable to each other. In conclusion, the encouraging results obtained in this work show that our NOF can be used in order to predict other properties.

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REFERENCES

- [1] Gilbert, T.L.; Phys. Rev. B 1975, 12, 2111; Donnelly, R.A.; Parr, R.G. J. Chem. Phys. 1978, 69, 4431; Valone, S.M. J. Chem. Phys. 1980, 73, 1344; 1980, 73, 4653; Lieb, E. H. Int. J. Quantum Chem. 1983, 24, 243; Zumbach, G.; Maschke, K. J. Chem. Phys. 1985, 82, 5604.
- [2] Goedecker, S.; Umrigar, C.J. Phys. Rev. Lett. 1998, 81, 866; Buijse, M.A.; Baerends, E.J. Mol. Phys. 2002, 100, 401.
- [3] Holas, A. Phys. Rev. A 1999, 59, 3454.
- [4] Cioslowski, J.; Pernal, K. J. Chem. Phys. 1999, 111, 3396.
- [5] Csanyi, G.; Arias, T. A. Phys. Rev. B 2000, 61, 7348.
- [6] Goedecker, S.; Umrigar, C. J. In: Cioslowski, J.; Ed. Many-Electron Densities and Reduced Density Matrices, Kluwer/Plenum: New York, 2000, p. 165.
- [7] Yasuda, K. Phys. Rev. A 2001, 63, 32517; Yasuda, K. Phys. Rev. Lett. 2002, 88, 053001.
- [8] Staroverov, V.N.; Scuseria, G.E. J. Chem. Phys. 2002, 117, 2489.
- [9] Csanyi, G.; Goedecker, S.; Arias, T. A. Phys. Rev. A 2002, 65, 032510.
- [10] Cioslowski, J.; Buchowiecki, M.; Ziesche, P. J. Chem. Phys. 2003, 119, 11570.
- [11] Piris, M.; Otto, P. Int. J. Quantum Chem. 2003, 94, 317; Piris, M.; Martinez, A.; Otto, P. Int. J. Quantum Chem. 2004, 97, 827; Piris, M.; Otto, P. Int. J. Quantum Chem. 2005, 102, 90; Leiva, P.; Piris, M. J. Mol. Struct.: THEOCHEM 2005, 719, 63.
- [12] Coleman, A. J. Rev. Mod. Phys. 1963, 35, 668.
- [13] Kutzelnigg, W.; Mukherjee, D. J. Chem. Phys. 1999, 110, 2800.
- [14] Kutzelnigg, W. Theor. Chim. Acta 1963, 1, 327.
- [15] Herbert, J.M.; Harriman, J.E. J. Chem. Phys. 2003, 118, 10835.

- [16] Szabo, A.; Ostlund, N.S. *Modern Quantum Chemistry*; McGraw-Hill: New York, 1989.
- [17] Davidson, E.R. *Reduced Density Matrices in Quantum Chemistry*; Academic Press: New York, 1976.
- [18] Levy, M. *Proc. Natl. Acad. Sci. U.S.A.* 1979, 76, 6062.
- [19] Levy, M. In: Erdahl, R.; Smith, V.H., Jr.; Eds. *Density Matrices and Density Functionals*, Reidel: Dordrech, 1987, p. 479.
- [20] Piris, M.; Cruz, R. *Int. J. Quantum Chem.* 1995, 53, 353; Piris, M. *J. Math. Chem.* 1999; 25, 47.
- [21] Coleman, A. J.; Yukalov, V. I. *Reduced Density Matrices: Coulson's Challenge*, Lecture Notes in Chemistry; Springer: Berlin, 2000.
- [22] Kummer, H. *Int. J. Quantum Chem.* 1977, 12, 1033.
- [23] Fletcher, R. *Practical Methods of Optimization*, 2nd Edition, John Wiley & Sons: New York, 1987.
- [24] Hariharan, P.C.; Pople, J.A. *Theoret. Chimica Acta* 1973, 28, 213; Francl, M.M.; Pietro, W.J.; Hehre, W.J.; Binkley, J.S.; Gordon, M.S.; DeFrees, D.J.; Pople, J.A. *J. Chem. Phys.* 1982, 77, 3654.
- [25] Levine, I. N. *Quantum Chemistry*, Prentice Hall: Upper Saddle River, New Jersey 07458, 2000.
- [26] Frisch, M. J. ; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez,

C.; Pople, J. A. GAUSSIAN 94 Inc. 1995, Pittsburgh PA.

[27] Hubert, K. P.; Herzberg, G. Molecular Spectra and Molecular Structure Vol. IV 1979, Van Nostrand Reinhold Company

[28] Bondybey, V. E. Chem. Phys. Lett. 1984, 109, 436; Stewart, J. J. P. J. Comp. Chem. 1989, 10, 221.

[29] Nelson Jr., R.D.; Lide, D.R. ; Maryott, A.A. Selected values of electric dipole moments for molecules in the gas phase 1967, NSRDS-NBS 10.

TABLE I. Total energies (E_{total}) in Hartrees.

| Molecule | HF^1 | $CCSD(T)^2$ | NOF^3 | $B3LYP^4$ |
|-------------------------------|-------------|-------------|-------------|-------------|
| AlCl | -701.446543 | -701.645139 | -701.723456 | -702.682030 |
| AlF | -341.405383 | -341.639667 | -341.660582 | -342.331111 |
| AlH | -242.438008 | -242.506581 | -242.525697 | -242.981911 |
| BCl | -484.105019 | -484.329332 | -484.376709 | -484.974255 |
| Be ₂ | -29.122716 | -29.224189 | -29.200175 | -29.343773 |
| BeH ₂ | -15.766705 | -15.829649 | -15.821505 | -15.917811 |
| BeO | -89.406757 | -89.648394 | -89.609227 | -89.898440 |
| BeS | -412.103398 | -412.284575 | -412.310091 | -412.894462 |
| BF | -124.101178 | -124.351814 | -124.346169 | -124.656132 |
| BH | -25.119105 | -25.206100 | -25.193976 | -25.288104 |
| C ₂ H ₂ | -76.820612 | -77.106349 | -77.069774 | -77.327715 |
| CH ₄ | -40.201379 | -40.388310 | -40.363928 | -40.523216 |
| Cl ₂ | -918.908639 | -919.198123 | -919.345443 | -920.341830 |
| CO | -112.736756 | -113.032821 | -113.020010 | -113.306694 |
| CO ₂ | -187.631787 | -188.113590 | -188.134537 | -188.577339 |
| CS | -435.302218 | -435.569554 | -435.601712 | -436.204876 |
| F ₂ | -198.669746 | -199.045358 | -199.109071 | -199.495477 |
| FCl | -558.816103 | -559.143280 | -559.244622 | -559.937606 |
| FH | -100.009834 | -100.198698 | -100.178202 | -100.425817 |
| H ₂ CO | -113.867947 | -114.202886 | -114.208902 | -114.500848 |
| H ₂ N ₂ | -109.997791 | -110.357170 | -110.370685 | -110.639297 |
| H ₂ O | -76.022615 | -76.228954 | -76.207940 | -76.417892 |
| H ₂ O ₂ | -150.769507 | -151.166824 | -151.202528 | -151.537846 |
| HBO | -100.166126 | -100.442361 | -100.419037 | -100.711017 |
| HCF | -137.753632 | -138.060398 | -138.086920 | -138.398508 |

| Molecule | <i>HF</i> ¹ | <i>CCSD(T)</i> ² | <i>NOF</i> ³ | <i>B3LYP</i> ⁴ |
|------------------|------------------------|-----------------------------|-------------------------|---------------------------|
| HCl | -460.064368 | -460.221565 | -460.258382 | -460.797390 |
| HCN | -92.875178 | -93.181241 | -93.145714 | -93.421806 |
| HCP | -379.105181 | -379.377798 | -379.389201 | -379.992926 |
| HNO | -129.783338 | -130.149630 | -130.185528 | -130.467334 |
| HOF | -174.730223 | -175.113429 | -175.161571 | -175.524723 |
| HPO | -416.121769 | -416.441974 | -416.509129 | -417.135327 |
| Li ₂ | -14.865878 | -14.896032 | -14.887910 | -15.013967 |
| LiCl | -467.006944 | -467.157908 | -467.192191 | -467.792715 |
| LiF | -106.933139 | -107.126788 | -107.100782 | -107.416662 |
| LiH | -7.981141 | -8.008224 | -8.000625 | -8.082268 |
| LIOH | -82.908772 | -83.121379 | -83.095776 | -83.372938 |
| Mg ₂ | -399.187445 | -399.256740 | -399.282202 | -400.156464 |
| MgO | -274.322470 | -274.592547 | -274.561446 | -275.212883 |
| MgS | -597.077741 | -597.256828 | -597.302717 | -598.249807 |
| N ₂ | -108.941801 | -109.261984 | -109.241787 | -109.520563 |
| N ₂ O | -183.675227 | -184.203202 | -184.233374 | -184.656028 |
| Na ₂ | -323.681228 | -323.707095 | -323.717745 | -324.586846 |
| NaCl | -621.397562 | -621.546221 | -621.586299 | -622.556987 |
| NaF | -261.300190 | -261.491762 | -261.473972 | -262.156146 |
| NaH | -162.372474 | -162.400444 | -162.396537 | -162.852762 |
| NaOH | -237.278603 | -237.488190 | -237.469800 | -238.113220 |
| NH ₃ | -56.194962 | -56.399981 | -56.378970 | -56.556343 |
| O ₃ | -224.242821 | -224.867269 | -224.992524 | -225.400708 |
| P ₂ | -681.421021 | -681.667624 | -681.742405 | -682.683866 |
| PH ₃ | -342.452229 | -342.605974 | -342.635555 | -343.142663 |
| PN | -395.122081 | -395.425821 | -395.444920 | -396.057582 |

| Molecule | <i>HF</i> ¹ | <i>CCSD(T)</i> ² | <i>NOF</i> ³ | <i>B3LYP</i> ⁴ |
|------------------|------------------------|-----------------------------|-------------------------|---------------------------|
| SH ₂ | -398.673332 | -398.832641 | -398.871007 | -399.388424 |
| SiH ₂ | -290.001640 | -290.109244 | -290.137664 | -290.613330 |
| SiH ₄ | -291.229906 | -291.366504 | -291.394429 | -291.886230 |
| SiO | -363.776369 | -364.055966 | -364.079292 | -364.716360 |
| SiS | -686.438897 | -686.663532 | -686.742597 | -687.690102 |
| SO ₂ | -547.165010 | -547.686081 | -547.805959 | -548.579504 |

¹Hartree-Fock total energies.

²CCSD(T) total energies.

³Natural Orbital Functional total energies computed in this work.

⁴B3LYP total energies.

TABLE II. Dipole Moments (μ) in Debyes.

| Molecule | HF^1 | $CCSD(T)^2$ | $B3LYP^3$ | NOF^4 | Exp^5 |
|-------------------------------|--------|-------------|-----------|---------|---------|
| AlCl | 1.72 | 1.62 | 1.57 | 1.60 | - |
| AlF | 1.06 | 1.12 | 0.99 | 1.09 | 1.53 |
| AlH | 0.49 | 0.15 | 0.28 | 0.23 | - |
| BCl | 0.94 | 1.00 | 1.21 | 1.00 | - |
| BeO | 6.91 | 5.33 | 5.58 | 6.16 | - |
| BeS | 6.42 | 4.59 | 5.14 | 5.38 | - |
| BF | 0.87 | 0.88 | 1.10 | 0.96 | - |
| BH | 1.48 | 1.03 | 1.32 | 1.28 | - |
| CO | 0.33* | 0.07 | 0.10 | 0.07* | 0.11 |
| CS | 1.26 | 1.76 | 1.57 | 1.47 | 1.98 |
| FCl | 1.26 | 1.02 | 0.91 | 0.75 | 0.88 |
| FH | 1.98 | 1.87 | 1.82 | 1.84 | 1.82 |
| H ₂ CO | 2.75 | 2.18 | 2.17 | 2.36 | 2.33 |
| H ₂ O | 2.20 | 2.09 | 2.04 | 2.08 | 1.85 |
| H ₂ O ₂ | 1.86 | 1.75 | 1.72 | 1.65 | 2.20 |
| HBO | 3.11 | 2.38 | 2.45 | 2.70 | - |
| HCF | 1.45 | 1.23 | 1.34 | 1.22 | - |
| HCl | 1.48 | 1.37 | 1.43 | 1.30 | 1.08 |
| HCN | 3.23 | 2.88 | 2.88 | 3.01 | 2.98 |
| HCP | 0.71 | 0.65 | 0.71 | 0.59 | 0.39 |
| HNO | 2.02 | 1.63 | 1.61 | 1.61 | 1.67 |
| HOF | 2.24 | 1.98 | 1.96 | 1.85 | 2.23 |
| HPO | 2.93 | 2.24 | 2.01 | 2.33 | - |

| Molecule | <i>HF</i> ¹ | <i>CCSD(T)</i> ² | <i>B3LYP</i> ³ | <i>NOF</i> ⁴ | <i>Exp</i> ⁵ |
|------------------|------------------------|-----------------------------|---------------------------|-------------------------|-------------------------|
| LiCl | 7.43 | 7.05 | 6.91 | 7.21 | 7.13 |
| LiF | 6.20 | 5.86 | 5.62 | 6.01 | 6.33 |
| LiH | 5.89 | 5.58 | 5.58 | 5.75 | 5.88 |
| LIOH | 4.27 | 3.85 | 3.65 | 4.17 | 4.75 |
| MgO | 7.81 | 5.14 | 6.36 | 5.21 | - |
| MgS | 9.03 | 6.38 | 7.12 | 6.68 | - |
| N ₂ O | 0.60* | 0.07* | 0.01 | 0.03 | 0.17 |
| NaCl | 9.39 | 8.97 | 8.61 | 9.03 | 9.0 |
| NaF | 8.00 | 7.52 | 7.05 | 7.82 | 8.16 |
| NaH | 6.84 | 6.19 | 5.96 | 6.44 | - |
| NaOH | 6.33 | 5.85 | 5.48 | 6.11 | - |
| NH ₃ | 1.89 | 1.81 | 1.79 | 1.76 | 1.47 |
| O ₃ | 0.78 | 0.49 | 0.62 | 0.50 | 0.53 |
| PH ₃ | 0.80 | 0.80 | 0.96 | 0.60 | 0.58 |
| PN | 2.91 | 2.46 | 2.45 | 2.59 | 2.75 |
| SH ₂ | 1.38 | 1.30 | 1.41 | 1.19 | 0.97 |
| SiH ₂ | 0.49 | 0.31 | 0.52 | 0.23 | - |
| SiO | 3.36 | 2.59 | 2.60 | 2.81 | 3.10 |
| SiS | 2.51 | 1.53 | 1.74 | 1.84 | 1.73 |
| SO ₂ | 2.21 | 1.78 | 1.68 | 1.56 | 1.63 |

¹Hartree-Fock dipole moments.

²CCSD(T) dipole moments.

³B3LYP dipole moments.

⁴Natural Orbital Functional dipole moments computed in this work.

⁵Experimental dipole moments from ref. [29].

*This value has an opposite sign relative to the experimental value