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Variational Reduced-Density-Matrix Theory Applied to the Potential Energy Surfaces of Carbon Monoxide in the Presence of Electric Fields†

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The variational optimization of the energy with respect to the two-electron reduced-density matrix (2-RDM), constrained by *N*-representability conditions, can determine the shape of molecular potential energy surfaces with useful accuracy. In this paper, we apply the 2-RDM method with a first-order optimization algorithm [Mazziotti, D. A. *Phys. Rev. Lett.* **2004**, *93*, 213001] to investigating the potential energy surfaces of carbon monoxide in the presence and absence of an electric field. Two beneficial characteristics of the 2-RDM method for computing potential energy surfaces include the following: (i) its ability to capture multireference effects without specifying any reference wave function or density matrix and (ii) its guarantee of a global energy minimum in the variational optimization. The 2-RDM method produces electronic ground-state energies with similar accuracy at equilibrium and nonequilibrium geometries in both the presence and the absence of the electric field. Computed dipole moments are similar in accuracy to the values from the computationally expensive configuration interaction with single, double, triple, and quadruple excitations. These surfaces have important applications in quantum molecular control theory.

I. Introduction

Measurements of the interaction of radiation and matter in experiments to explore blackbody radiation, the photoelectric effect, and the hydrogen spectrum led to the development of modern quantum theory.[1] The probing of matter by radiation is critical to understanding chemical structure and dynamics at the molecular level. However, modeling the interaction of a molecule with an electric field for use in dynamics and quantum control requires knowledge of accurate potential energy surfaces. Although surfaces may be generated from the fitting of spectroscopic data, the most accurate surfaces are generally computed through a repeated solution of the many-electron Schrödinger equation for approximate electronic energies and wave functions.[2] In the present paper, we explore the computation of the potential energy surfaces for carbon monoxide in the presence and absence of electric fields through the use of a variational two-electron reduced-density-matrix (2-RDM) method.[3−22]

Because the molecular Hamiltonian contains at most two-electron interactions, the ground-state energy of an *N*-electron system may be in principle determined from a knowledge of the two-electron reduced density matrix (2-RDM).[23] Variationally minimizing the ground-state energy as a function of the 2-RDM, however, requires that the 2-RDM be constrained by conditions to ensure that it is representable by an *N*-electron density matrix.[24] These constraints are called *N*-representability conditions, and the search for a manageable formulation of these conditions is known as the *N*-representability problem.[25,26] The variational calculation of the 2-RDM[5−22] has been achieved with useful accuracy by applying *N*-representability constraints known as positivity conditions[6,26−28] and solving the optimization by semidefinite programming. The research extends variational 2-RDM work in the 1970s[3,4] and research on the contracted Schrödinger equation.[29−33] Semidefinite programming[34−36] is a special type of constrained optimization in which the objective function is a linear function of several matrices that are constrained to be positive semidefinite. Calculations of Nakata et al.[7,9] and Mazziotti[8,10,12] employ primal-dual interior-point algorithms for semidefinite programming to compute the 2-RDM with useful accuracy for a number of atoms and molecules at both equilibrium and nonequilibrium geometries. Mazziotti[15,16] has developed a first-order algorithm that significantly decreases the floating-point and storage requirements and permits application of the method to larger molecules and basis sets. The first-order algorithm enables the calculations in this paper.

In the present work, the variational 2-RDM method with 2-positivity conditions is employed to obtain the potential energy surfaces of the carbon monoxide molecule in the presence and the absence of electric fields. Two important characteristics of the 2-RDM for these applications are (i) its ability to capture multireference effects without specifying any reference wave function or density matrix and (ii) its guarantee of a global energy minimum in the variational optimization. Because the positivity conditions treat correlation in a manner distinct from many-body perturbation theory, the variational 2-RDM method accurately treats regions of the potential energy surface, corresponding to bond stretching, where multiple references contribute. The global minimum in the 2-RDM method arises from a mathematical property of the semidefinite programming employed to perform the energy optimization. In both the presence and the absence of electric fields the 2-RDM method yields potential energy surfaces with useful accuracy. From the 2-RDM, both one- and two-electron properties may also be evaluated. The dipole moment of carbon monoxide is computed for different bond lengths, and the resulting 2-RDM moments are compared to those from truncated and full configuration-interaction calculations. Calculating potential energy surfaces

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for a molecule in the presence of an electric field has important applications to molecular optimal control theory.[37−39]

II. Theory

After describing the essential ingredients of variational 2-RDM theory, we discuss two significant features of the 2-RDM method for the description of potential energy surfaces in the presence and absence of electric fields: (i) independence of the 2-RDM method from a mean-field reference both in the *N*-representability conditions and in the initial 2-RDM guess and (ii) the guarantee of a global minimum within semidefinite programming which forestalls the calculation of spurious potential energy surfaces.

A. Variational 2-RDM Method. Because electrons in an atom or molecule interact pairwise, the energy of an *N*-electron system may be expressed as a linear functional of the 2-electron RDM (${}^2D$)[23]

$$E = \sum_{i,j,k,l} {}^2K^{i,j}_{k,l} \langle \psi | \hat{a}^\dagger_i \hat{a}^\dagger_j \hat{a}_l \hat{a}_k | \psi \rangle = \mathrm{Tr}[{}^2K\, {}^2D] \tag{1}$$

where ${}^2K$ is the 2-electron reduced Hamiltonian whose matrix elements in a spin−orbital basis are given by

$${}^2K^{i,j}_{k,l} = \frac{1}{N-1}(\delta^i_k \langle j|\hat{h}|l\rangle + \delta^j_l \langle i|\hat{h}|k\rangle) + \langle ij|\hat{V}_{\mathrm{int}}|lk\rangle \tag{2}$$

In eq 2, $\hat{h}$ is a one-electron operator, representing the kinetic and nucleus-electron attraction contributions to the total energy as well as the interaction between electrons and an electric field and $\hat{V}_{\mathrm{int}}$ is a two-electron operator that describes the electron−electron repulsion. Equation 1 suggests that the ground-state energy may be obtained by straightforward minimization with respect to the 2-RDM matrix elements. Not every 2-RDM, however, corresponds to an *N*-electron wave function. To ensure that the 2-RDM is derivable from an *N*-electron wave function, *N*-representability constraints[26] need to be imposed on the 2-RDM.

Some necessary constraints on ${}^2D$[26] are that it must be (i) positive semidefinite (its eigenvalues nonnegative), (ii) Hermitian, (iii) normalized, and (iv) antisymmetric with particle exchange. Further restrictions may be derived by considering the positivity of the $p + 1$ distinct metric (or overlap) matrices associated with *p*-electron operators. For $p = 2$, we obtain the 2-positivity conditions[6] that enforce the positivity of the 2-electron (${}^2D$), the 2-hole (${}^2Q$), and G (${}^2G$) metric matrices

$$\begin{aligned} {}^2D^{i,j}_{k,l} &= \langle \psi | \hat{a}^\dagger_i \hat{a}^\dagger_j \hat{a}_l \hat{a}_k | \psi \rangle \\ {}^2Q^{i,j}_{k,l} &= \langle \psi | \hat{a}_i \hat{a}_j \hat{a}^\dagger_l \hat{a}^\dagger_k | \psi \rangle \\ {}^2G^{i,j}_{k,l} &= \langle \psi | \hat{a}^\dagger_i \hat{a}_j \hat{a}^\dagger_l \hat{a}_k | \psi \rangle \end{aligned} \tag{3}$$

The above metric matrices are linearly dependent, and the following mapping relations between them may be derived by rearranging the creation/annihilation operators:

$${}^2Q^{i,j}_{k,l}/2 = (\delta^i_k - 2\,{}^1D^i_k) \wedge \delta^j_l + {}^2D^{i,j}_{k,l}/2 \tag{4}$$

and

$${}^2G^{i,j}_{k,l} = \delta^k_i\, {}^1D^j_l - {}^2D^{k,j}_{i,l} \tag{5}$$

where the 1-RDM arises from the integration (or contraction in a matrix representation) of the 2-RDM

$${}^1D^i_k = \frac{1}{N-1} \sum_j {}^2D^{i,j}_{k,j} \tag{6}$$

and the symbol $\wedge$ denotes the antisymmetric tensor product known as the Grassmann wedge product.[31] Because 2-positivity is not sufficient for the *N*-representability of molecular 2-RDMs, the set of 2-positive RDMs is larger than the *N*-representable set, and variational RDM calculations with 2-positivity constraints yield lower bounds to the exact energies (i.e., energies obtained from full-configuration-interaction calculations) in finite basis sets. The 2-positivity conditions, although only necessary for *N*-representability, have been shown to yield accurate ground-state energies for molecules at equilibrium and nonequilibrium geometries.[6−19]

B. Zero-Reference Method. The variational 2-RDM method does not depend on a mean-field reference wave function or 2-RDM in either its *N*-representability conditions or its initial guess. Approximate many-body wave function methods use one or more mean-field references to parametrize the Hilbert space of many-electron excitations. In contrast, the *N*-representability conditions in eq 3, known as 2-positivity constraints, do not depend on any reference wave function or density matrix. They define a convex set that includes all mean-field and correlated *N*-electron wave functions. Because the 2-positive set of 2-RDMs yields the exact 2-RDM for all Hamiltonians with just one-body terms, the *N*-representability conditions account for all mean-field references. On the other hand, because the *N*-representability conditions do not explicitly use any mean-field reference wave function or 2-RDM, we can also say that the variational 2-RDM method is a zero-reference method. The 2-RDM method can also be designed to be independent of any reference in the initial guess through the selection of the initial elements of the 2-RDM by a random number generator. The ability to treat multiple references without specifying any reference is especially useful for studying potential energy surfaces where multiple references contribute at stretched geometries. Calculations with the 2-RDM method indicate that it yields similar accuracy at both equilibrium and nonequilibrium geometries.

C. Global Energy Minimum. Electronic structure methods may be classified as variational or nonvariational. The RDM method employed in this work belongs to the former class since it computes the energy by minimizing the energy expression in eq 1 with respect to the elements of the 2-RDM. Unlike traditional variational wave function calculations, the 2-RDM method yields a lower bound on the exact ground-state energy within a given one-electron basis set. The 2-RDM energy optimization belongs to a special class of optimization known as semidefinite programming.[34,35]

The general semidefinite optimization may be expressed in its primal form

$$\begin{gathered} \text{minimize } \langle c|x\rangle \\ \text{such that } A|x\rangle = |b\rangle \\ M(x) \geq 0 \end{gathered} \tag{7}$$

where the vector $|c\rangle$ defines the unconstrained system, the vector $|b\rangle$ and matrix A enforce the linear constraints upon the primal solution $|x\rangle$, and the operator M maps the vector $|x\rangle$ onto the matrix $M(x)$ which is kept positive semidefinite. Similarly, in its dual formulation we have

$$\text{maximize } \langle b|y\rangle$$
$$\text{such that } |z\rangle = |c\rangle - A^{\mathrm{T}}|y\rangle$$
$$M(z) \geq 0 \tag{8}$$

where $|y\rangle$ is the dual solution and the matrix $M(z)$ is restricted to have nonnegative eigenvalues. For feasible solutions (i.e., the constraints in eqs 7 and 8 are satisfied), the primal and dual solutions yield upper and lower bounds on the objective function, respectively. Under mild assumptions,[34] the primal and dual solutions to the objective become equal at the optimal solution vectors ($\langle c|x_{\mathrm{opt}}\rangle = \langle b|y_{\mathrm{opt}}\rangle$), and the vanishing of the difference between the primal and dual solutions, known as the duality gap, guarantees a global extremum.

In the variational 2-RDM method with 2-positivity, the solution $|x\rangle$ of the primal program is a vector of the three metric matrices from the 2-RDM, the ${}^2D$, the ${}^2Q$, and the ${}^2G$ matrices

$$M(x) = \begin{pmatrix} {}^2D & 0 & 0 \\ 0 & {}^2Q & 0 \\ 0 & 0 & {}^2G \end{pmatrix} \tag{9}$$

the vector $|c\rangle$ holds specific information about the quantum system in the form of the two-particle reduced Hamiltonian

$$M(c) = \begin{pmatrix} {}^2K & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{10}$$

and the matrix A and the vector $|b\rangle$ contain the linear mappings among the ${}^2D$, ${}^2Q$, and ${}^2G$ matrices in eqs 4 and 5, the contraction [eq 6 and trace conditions ($\mathrm{Tr}({}^1D) = N$)], as well as any spin constraints. The constraint $M(x) \geq 0$ in eq 7 restricts the ${}^2D$, ${}^2Q$, and ${}^2G$ matrices to be positive semidefinite.

Because variational RDM theory belongs to the class of positive semidefinite optimization problems, the ground-state energy calculated by minimizing eq 1 with respect to the 2-RDM elements will be a unique global minimum regardless of the initial guess for the 2-RDM. For example, one may initiate the energy minimization procedure with either a density matrix from a Hartree−Fock (RHF) calculation or even a positive semidefinite two-electron density matrix constructed from random numbers. In methods such as coupled cluster which solve a system of nonlinear equations there exist a family of mathematical solutions, and at geometries far from equilibrium, the ground-state energies that are computed can be significantly influenced by the initial guess for the parameters of the wave function. Variational RDM calculations of Nakata et al.[7,9] and Mazziotti[8,10,12] employed primal-dual interior-point algorithms, such as SDPA,[40] SeDuMi,[41] and SDPT3,[42] to obtain the ground-state energy; however, large computational requirements, in particular memory and floating-point operation scaling (r^8 and r^{16} respectively), limited applications to small molecules in minimal basis sets. Mazziotti has implemented a first-order nonlinear algorithm[15,16] that dramatically reduces the storage requirements and the floating-point operations of the variational 2-RDM method. Memory storage and floating-point operations scale as r^4 and r^6 in the first-order nonlinear algorithm.

III. Applications

After summarizing computational details and N-representability conditions, we discuss results for the potential energy surface of carbon monoxide in the presence and the absence of electric fields.

A. Computational Details. To evaluate the accuracy of the variational 2-RDM method for carbon monoxide, we employ the valence double-ζ basis set[43] for which a solution of the Schrödinger equation by full configuration interaction (FCI) can be performed. All calculations use the abelian C_{2v} group with the bond axis along the z axis. The carbon atom is located at the origin with the oxygen lying on the positive z axis. The core 1s orbitals on the carbon and oxygen are frozen, but all virtual orbitals are correlated. Ground-state energies are evaluated for the range 0.9075 Å $\leq R \leq$ 3.63 Å, where R is the carbon monoxide nuclear separation, and the equilibrium bond length (R_e) is 1.21 Å. Energies from restricted Hartree−Fock, several levels of coupled cluster,[44] such as CCSD, CCSD(T), and CR−CCSD(T), and second-order multireference perturbation theory (MRPT2) with an active space of eight orbitals are evaluated at 46 nuclear separations (starting at $R = 0.9075$ Å) in increments of 0.0605 Å. All coupled cluster computations use the previously converged amplitudes as the initial guess, and orbital rotations are restricted in order to prevent sign changes in the coupled cluster amplitudes. Energies from wave function methods and the one- and two-electron integrals necessary for the formation of ${}^2K$ in eq 2 are computed with the GAMESS[45] quantum chemistry package.

B. Summary of *N*-Representability Conditions. The following N-representability conditions on the 2-RDM are imposed:

(1) Hermiticity of the 2-RDM:

$${}^2D^{i,j}_{k,l} = {}^2D^{k,l}_{i,j} \tag{11}$$

(2) Antisymmetry of upper and lower indices

$${}^2D^{i,j}_{k,l} = -{}^2D^{j,i}_{k,l} = -{}^2D^{i,j}_{l,k} = {}^2D^{j,i}_{l,k} \tag{12}$$

enforced by storing the 2-RDM with basis functions $\tilde{\phi}_{i,j} = 1/\sqrt{2}(\phi_{i,j} - \phi_{j,i})$.

(3) Trace conditions on the spin-blocks of the 2-RDM:

$$N_s(N_s - 1) = \sum_{i,j} {}^2D^{i,\alpha;j,\alpha}_{i,\alpha;j,\alpha}$$
$$N_s{}^2 = \sum_{i,j} {}^2D^{i,\alpha;j,\beta}_{i,\alpha;j,\beta} \tag{13}$$

where roman and Greek letters indicate spatial and spin−orbitals respectively and $N_s = N/2$.

(4) Closed-shell spin conditions:

$${}^2D^{i,\alpha;j,\beta}_{k,\alpha;l,\beta} = {}^2D^{j,\alpha;i,\beta}_{l,\alpha;k,\beta}$$
$$\sum_{i,j} {}^2D^{i,\alpha;j,\beta}_{j,\alpha;i,\beta} = N_s \tag{14}$$

(5) Positivity of the three different representations of the 2-RDM in eq 3.

(6) Mapping conditions between ${}^2D$, ${}^2Q$, and ${}^2G$.

(7) Contraction of the 2-RDM onto the 1-RDM:

$$(N_s - 1)\,{}^1D^{i,\alpha}_{j,\alpha} = \sum_k {}^2D^{i,\alpha;k,\alpha}_{j,\alpha;k,\alpha}$$
$$N_s\,{}^1D^{i,\alpha}_{j,\alpha} = \sum_k {}^2D^{i,\alpha;k,\beta}_{j,\alpha;k,\beta} \tag{15}$$

TABLE 1: Error in the 2-RDM* Ground-State Energies Reported for Various Bond Lengths Relative to FCI for CO without an Electric Field[a]

	energy (H)			energy error (mH)		
R	FCI	2-RDM*	CCSD	CCSD(T)	CR−CCSD(T)	MRPT2
0.9075	−112.6309	9.8	4.5	0.8	1.3	10.1
1.1495	−112.8969	3.2	9.5	1.4	3.1	10.0
1.2100	−112.8977	1.7	11.3	1.7	3.8	9.9
1.2705	−112.8882	0.2	13.4	1.9	4.6	9.8
1.7545	−112.7291	−11.6	36.7	1.2	15.4	7.6
2.1780	−112.6365	−20.1	23.3	−177.4	−44.9	4.9
2.7830	−112.5897	−13.9	44.7	−453.1	23.9	14.2
3.2065	−112.5821	−6.9	59.6	−537.4	43.2	10.1
3.6300	−112.5796	−3.3	63.9	−548.5	47.9	8.6

[a] The maximum deviation of the 2-RDM* energies is half as large as the maximum deviation in any of the coupled cluster methods. The two core 1s orbitals are frozen. The 2-RDM* energies are obtained from a shift of 43.93 milliHartrees.

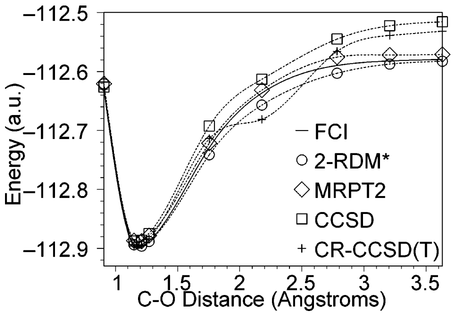

Figure 1. Comparison of the 2-RDM*, coupled-cluster, MRPT2, and FCI potential energy surfaces of CO where all valence electrons are correlated. 2-RDM* and MRPT2 accurately describe the features of the FCI potential energy surface. The CCSD and CR−CCSD(T) potential energy surfaces display an unphysical “hump” near 2.2 Å.

C. Results. *1. Potential Energy Surface in the Absence of an Electric Field.* Table 1 shows the error in the coupled-cluster [CCSD, CCSD(T), and CR−CCSD(T)] and 2-RDM* ground-state energies relative to FCI at selected bond lengths. Because the 2-RDM energies are consistently below the FCI values at all bond distances by approximately the same amount, the 2-RDM* energies are defined by adding the difference between the CCSD(T) and 2-RDM energies at $R = R_e = 1.21$ Å to the variational 2-RDM energy at each bond length. A similar correction has been employed in calculations of bond dissociation in the diatomic molecules N_2 and C_2[18] as well as several organic molecules.[17] The 2-RDM* energies are slightly above the FCI energies for geometries around the equilibrium configuration with the greatest error of −20.1 mH occurring at intermediate nuclear separations around $R = 2.1780$ Å. The errors in the CCSD energies increase from 4.5 mH at $R = 0.9075$ Å to 63.9 mH at $R = 3.63$ Å; the errors in CCSD(T) become large and negative between −177.4 mH and −548.5 mH for $R \in [2.178$ Å, 3.63 Å$]$, whereas the errors in the CR−CCSD(T) energies increase from 1.3 mH at $R = 0.9075$ Å to 47.9 mH at $R = 3.63$ Å except for an error of −44.9 mH at $R = 2.178$ Å. In Table 1, 2-RDM* and MRPT2 energies agree with the FCI energies within 14.2 and 20.1 mH, respectively. The curve from the 2-RDM* method in Figure 1 displays the proper features of the FCI potential energy surface and remains accurate at all bond lengths.

The initial guess for the coupled cluster solution at each iteration may be selected (or seeded) by two approaches: (i) setting all initial single and double transition amplitudes to zero at each point on the potential energy surface or (ii) using the converged amplitudes from the previous point computed on the potential energy surface. For N_2, which has been extensively treated in the literature, either choice produces the same results, but for CO, which has been discussed much less, the first seed approach yields mathematical solutions to the nonlinear coupled cluster equations for $R \geq 2.1175$ which are discontinuous from the solutions near equilibrium $R < 2.1175$. The coupled-cluster surface in ref 16, computed at only a few internuclear distances by the first seed, jumps to the second solution for $R \geq 2.1175$. The potential surface reported here is computed at a fine grid spacing in internuclear separation with the second seed. The 2-RDM method, because of the uniqueness of the variational 2-RDM energy, yields the same potential energy surfaces regardless of the initial guess for the 2-RDM.

TABLE 2: Error in the Dipole Moment in Atomic Units Relative to FCI from Variational 2-RDM Theory for Selected Bond Lengths for CO without an Electric Field[a]

	dipole moment		dipole error (a.u.)		
R (Å)	FCI	2-RDM	CISD	CISDT	CISDTQ
0.9075	0.3384	$1.42e-2$	$-1.51e-2$	$1.13e-2$	$-1.55e-3$
1.1495	0.0093	$2.44e-5$	$-1.72e-2$	$2.02e-2$	$-2.90e-3$
1.2100	−0.0710	$-3.85e-3$	$-1.53e-2$	$4.98e-2$	$-2.90e-3$
1.2705	−0.1475	$-1.03e-2$	$-1.23e-2$	$6.30e-2$	$-2.58e-3$
1.7545	−0.5313	$-6.43e-2$	$1.17e-1$	$2.17e-1$	$2.28e-2$
2.1780	−0.4572	$-2.28e-3$	$3.36e-1$	$1.02e-1$	$7.24e-2$

[a] The 2-RDM dipole moments are often as accurate as the dipole moments from configuration interaction with quadruple excitations.

The accuracy of the energy increases faster in wave function methods than the accuracy of other molecular properties. For example, a first-order wave function yields an energy correct through second order in perturbation theory. In contrast, because the 2-RDM energy is linear in the matrix elements in ${}^2D$, the errors in the 2-RDM from approximate N-representability conditions appear linearly in both the energy and other properties. Thus, a variational 2-RDM theory that gives accurate ground-state energies should also generate other properties such as the permanent dipole moment with similar accuracy. The error in the carbon monoxide dipole moment obtained from variational RDM theory is compared to several levels of truncated configuration-interaction (CI) results in Table 2. For the considered bond lengths, the RDM dipole moments are generally more accurate than CI with single and double excitations (CISD), with the maximum error in the RDM dipole being −0.0643 atomic units (a.u.). Adding triple excitations (CISDT) does not significantly improve the CI results, whereas the inclusion of quadruple excitations (CISDTQ) reduces the error in the dipole moment by a factor of 10. The RDM dipole moments are competitive with the values from the expensive CISDTQ wave function method which scales computationally as r.[12]

2. Potential Energy Curves in the Presence of an External Electric Field. For carbon monoxide in an electric field with a strength of 0.10 a.u. applied in the negative and positive z directions Tables 3 and 4 report the errors in the 2-RDM*, coupled-cluster, and MRPT2 energies relative to FCI. For an electric field of strength 0.1 a.u. in the negative direction, the maximum deviations in the energies of 2-RDM* and MRPT2 from FCI are 7.6 and 14.0 mH, respectively. Figure 2 shows that for the electric field in the negative direction the CCSD, CR−CCSD(T), and 2-RDM* methods yield qualitatively similar potential energy surfaces that properly describe the main features of the FCI potential energy surface. The direction of the electric field affects the accuracy of the 2-RDM* energies much less than it affects the accuracy of the coupled cluster methods. For

TABLE 3: Error in the 2-RDM* Ground-State Energies Reported for Various Bond Lengths Relative to FCI for CO with an Electric Field of −0.10 au[a]

	energy (H)		energy error (mH)			
R	FCI	2-RDM*	CCSD	CCSD(T)	CR−CCSD(T)	MRPT2
0.9075	−112.6443	7.6	4.5	0.6	1.2	12.9
1.1495	−112.9641	3.0	7.6	1.1	2.3	13.9
1.2100	−112.9793	2.1	8.5	1.2	2.6	14.0
1.2705	−112.9843	1.3	9.5	1.3	3.0	13.9
1.7545	−112.9261	−3.4	21.1	4.9	8.0	9.0
2.1780	−112.8924	−7.0	30.1	16.6	18.7	2.4
2.7830	−112.9216	−4.0	24.8	7.3	15.6	3.6
3.2065	−112.9730	−2.9	22.2	−11.5	10.6	4.0
3.6300	−113.0337	−7.3	20.5	−57.2	5.9	7.1

[a] The two core 1s orbitals are frozen. The 2-RDM* energies are obtained from a shift of 44.05 milliHartrees (mH).

TABLE 4: Error in the 2-RDM* Ground-State Energies Reported for Various Bond Lengths Relative to FCI for CO with an Electric Field of 0.10 au[a]

	energy (H)		energy error (mH)			
R	FCI	2-RDM*	CCSD	CCSD(T)	CR−CCSD(T)	MRPT2
0.9075	−112.7161	13.5	4.3	1.0	1.5	9.5
1.1495	−112.9715	5.0	10.2	2.4	4.2	8.9
1.2100	−112.9711	3.0	12.4	3.0	5.3	8.8
1.2705	−112.9611	0.9	15.0	3.6	6.7	8.6
1.7545	−112.8306	−13.9	47.3	−10.8	26.0	6.8
2.1780	−112.8067	−12.5	88.6	−220.1	35.1	4.5
2.7830	−112.8666	7.8	184.2	−386.5	137.2	6.7
3.2065	−112.9257	16.1	236.4	−561.6	188.3	6.9
3.6300	−112.9900	19.8	276.1	−845.4	218.8	6.9

[a] The two core 1s orbitals are frozen. The 2-RDM* energies are obtained from a shift of 44.05 milliHartrees (mH).

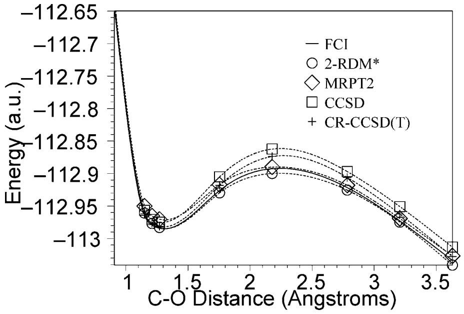

Figure 2. Comparison of the 2-RDM*, coupled-cluster, MRPT2, and FCI potential energy surfaces of CO in an electric field of −0.10 au where all valence electrons are correlated. 2-RDM*, CCSD, CR−CCSD(T), and MRPT2 accurately describe the shape of the FCI potential energy surface.

the field in the positive direction, all coupled cluster energies are accurate close to the equilibrium geometry, but as the bond length increases, their accuracy worsens. Both the CCSD and CR−CCSD(T) energies are several hundreds of mHs above the FCI for $R \geq 2.1780$ Å, and the CCSD(T) energy diverges for $R \geq 1.7545$ Å. The maximum deviations in the energies of 2-RDM* and MRPT2 from FCI are 19.8 mH and 9.5 mH, respectively. Although single-reference wave function methods have difficulty with the positive field, MRPT2 yields its best results in this case. Figure 3 shows that the 2-RDM* curve follows closely the FCI result.

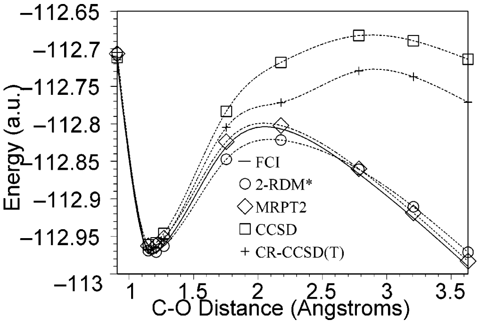

Figure 3. Comparison of the 2-RDM*, coupled-cluster, MRPT2, and FCI potential energy surfaces of CO in an electric field of 0.10 au where all valence electrons are correlated. Both the 2-RDM* and the MRPT2 methods accurately capture the bend in the potential energy surface at stretched geometries.

IV. Discussion and Conclusions

The variational 2-RDM method with 2-positivity conditions, implemented by a first-order nonlinear algorithm for semidefinite programming,[15,16] is applied to compute the ground-state potential energy surface of the carbon monoxide molecule in the absence and in the presence of electric fields. Even without an electric field, the calculation of the potential energy surface of the carbon monoxide molecule is a challenging task because proper treatment of the triple bond requires six-to-eight-particle excitations from a single Slater determinant or Hartree−Fock reference. We find that solving for the electronic structure of carbon monoxide in the presence of an electric field can either diminish or enhance the effects of the correlation along the bond dissociation curve. Modeling molecules within electric fields, therefore, provides a stringent test for electronic structure methods since we can increase the effects of correlation beyond their role in the absence of the field. Two advantages of the variational 2-RDM method for describing bond dissociation both with and without an electric field are as follows: (i) implicit treatment of both single- and multireference correlation effects without invoking either a Hartree−Fock reference or an active space of references and (ii) uniqueness of its energies and 2-RDMs from the guarantee within semidefinite programming that a solution is a global extremum.

Incorporating multireference correlation into a wave function requires including many-electron excitations from the Hartree−Fock reference determinant (single-reference methods) or few-electron excitations from a large, carefully selected set of reference determinants (multireference methods). Either approach must parametrize a wave function with all relevant many-electron excitations. In contrast, the variational 2-RDM performs the optimization on the space of two-electrons, more specifically, on the convex set of 2-RDMs satisfying the 2-positivity conditions. Because the set of 2-positive 2-RDMs contains the set of N-representable 2-RDMs, the 2-RDM is parametrized to represent on the two-electron space any correlated N-electron wave function. The 2-positivity conditions must be sufficiently stringent for a given type of two-body interaction to prevent significant contamination of the N-representable 2-RDM solution by non-N-representable 2-RDMs. Computational experience indicates that the 2-RDM method with 2-positivity conditions yields energies and properties of atoms and molecules with useful accuracy. Furthermore, the method's accuracy at equilibrium geometries where single-reference correlation dominates is similar to the method's accuracy at stretched geometries where multireference correlation effects are important.

The minimization of the energy with the 2-RDM method is a special optimization problem known as a semidefinite program. As explained earlier, under mild assumptions, a solution to a semidefinite program is feasible in both its primal and dual formulations if and only if it is a global extremum.

The variational 2-RDM method, therefore, has the special property that for a given Hamiltonian and set of *N*-representability conditions its approximate energy and 2-RDM are unique. In contrast, the Rayleigh−Ritz variational method for a wave function with nonlinear parameters cannot in general determine whether a local minimum is a global minimum. Moreover, techniques that solve a system of nonlinear equations such as the coupled-cluster method may have a family of mathematical solutions. For carbon monoxide at equilibrium and stretched geometries the 2-RDM method yields a unique ground-state energy and 2-RDM independent of the initial guess for the 2-RDM, which may be the Hartree−Fock 2-RDM, the 2-RDM from a nearby internuclear separation, or even a matrix of random numbers.

The variational 2-RDM method with 2-positivity yields accurate potential energy surfaces for carbon monoxide in both weak and strong electric fields regardless of the orientation of the field. For a field oriented in the negative *z* direction, coupled cluster methods such as CCSD and CR-CCSD(T) also provide a good potential energy surface, but for a strong field oriented in the positive *z* direction, these methods fail to describe the qualitative features of the correct surface. Properties such as the dipole moment may also be computed by the 2-RDM method. The 2-RDM dipole moments at both equilibrium and stretched molecular geometries are more accurate than those obtained with truncated configuration interaction with single and double excitations and even competitive with the computationally much more expensive truncated configuration interaction through quadruple excitations. Further improvements in the accuracy of 2-RDM potential energy surfaces will be explored in future work by imposing additional *N*-representability conditions, such as full or partial 3-positivity conditions.[6,8,11,19]

Potential energy surfaces provide the landscape for chemical reactions from spectroscopic constants and geometries to quantum dynamics and kinetics. In experiments, the properties of potential energy surfaces are probed by studying the interactions of radiation with atoms and molecules, and in quantum control theory, molecular processes from population transfer to dissociation are controlled by tailoring laser pulses. We demonstrate in this paper that the variational 2-RDM method is capable of describing changes in a potential energy surface from the interaction of a molecule with an electric field. One- and two-electron properties such as the dipole moment may also be computed. In future work, we plan to use the 2-RDM method within optimal control calculations that adjust for the effect of an electric field on a molecule's electronic structure.[37−39]

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