

Global solutions of restricted open-shell Hartree-Fock theory from semidefinite programming with applications to strongly correlated quantum systems

Srikant Veeraraghavan and David A. Mazziotti^{a)}

Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, Illinois 60637, USA

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We present a density matrix approach for computing global solutions of restricted open-shell Hartree-Fock theory, based on semidefinite programming (SDP), that gives upper and lower bounds on the Hartree-Fock energy of quantum systems. While wave function approaches to Hartree-Fock theory yield an upper bound to the Hartree-Fock energy, we derive a semidefinite relaxation of Hartree-Fock theory that yields a rigorous lower bound on the Hartree-Fock energy. We also develop an upper-bound algorithm in which Hartree-Fock theory is cast as a SDP with a nonconvex constraint on the rank of the matrix variable. Equality of the upper- and lower-bound energies guarantees that the computed solution is the globally optimal solution of Hartree-Fock theory. The work extends a previously presented method for closed-shell systems [S. Veeraraghavan and D. A. Mazziotti, *Phys. Rev. A* **89**, 010502(R) (2014)]. For strongly correlated systems the SDP approach provides an alternative to the locally optimized Hartree-Fock energies and densities with a certificate of global optimality. Applications are made to the potential energy curves of C₂, CN, Cr₂, and NO₂. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4868242>]

I. INTRODUCTION

The most widely used approach to obtain the ground-state Hartree-Fock (HF) energy and density matrix has been to solve the Euler-Lagrange equations associated with the minimization of the Hartree-Fock energy. In 1951 Roothaan^{1,2} and Hall³ proposed the first self-consistent-field (SCF) method to solve the Hartree-Fock equations. However, the method was soon discovered to converge only for well-behaved cases. Since then numerous algorithms have been proposed to modify the SCF method to improve its convergence properties, including level-shifting,^{4,5} damping,^{6,7} and direct inversion of the iterative subspace (DIIS).^{8,9} DIIS is currently the most popular SCF algorithm because of its computational efficiency in most cases. Nevertheless, it is not globally convergent, and in many cases it is known to fail even with a good initial guess. A method is globally convergent when it converges to a local minimum from any initial guess. Level-shifting is globally convergent for a large enough shift parameter,¹⁰ but its speed of convergence decreases as the shift parameter increases.

Since SCF methods do not ensure an energy decrease at each iteration, a potentially more natural approach to solving the Hartree-Fock problem is to minimize the Hartree-Fock energy directly as a function of the density matrix using gradient or Hessian-based methods. In 1956, McWeeny¹¹ proposed direct-minimization methods,^{12–18} but they have not yet found wide applicability either due to their slow convergence or prohibitive cost. Recently, a combination of the monotonic energy decrease property of direct-minimization

methods and the speed of SCF methods was achieved in the relaxed-constraints algorithms^{19,20} and trust-region methods^{21–23} which are both globally convergent and efficient. However, none of these methods can certify that the computed solution is the global minimum.

Convex minimization problems possess the attractive property that the existence of a local minimum implies that it is the global minimum. Semidefinite programs (SDP) are a class of convex optimization problems in which a linear function of a positive semidefinite matrix is optimized subject to linear constraints. For an N -electron system the minimization of the ground-state energy as a functional of the two-electron reduced density matrix (2-RDM) subject to N -representability constraints^{24–26} has been expressed as a SDP,^{24,27–30} and the resulting variational 2-RDM method^{24,26–37} in conjunction with large-scale SDP solvers^{34,38} has been applied to computing directly the 2-RDMs of strongly correlated systems including molecules like polyaromatic hydrocarbons³⁹ and firefly luciferin⁴⁰ as well as quantum dots,⁴¹ quantum phase transitions,⁴² and one- and two-dimensional spin models.^{37,43} We recently presented two SDP algorithms that yield upper and lower bounds on the ground-state energy from Hartree-Fock theory.^{8,4} Here we extend these algorithms to treat restricted open-shell Hartree-Fock (ROHF) theory. While wave function approaches to Hartree-Fock theory yield an upper bound to the Hartree-Fock energy, we derive a semidefinite relaxation of Hartree-Fock theory that yields a rigorous lower bound on the Hartree-Fock energy. In the lower-bound SDP algorithm the idempotency constraint on the one-electron density matrix is relaxed. We also develop an upper-bound algorithm in which Hartree-Fock theory is cast as a SDP with a nonconvex constraint on the rank of the matrix variable.

^{a)}Electronic mail: damaz@uchicago.edu

Whenever the upper and lower bounds are equal to each other, they provide a certificate of global optimality to the obtained solution.

To illustrate these algorithms, we apply them to computing the symmetry-broken spin-restricted Hartree-Fock potential energy curves for C_2 , CN, Cr_2 , and NO_2 . This problem is challenging because there are multiple local minima of different spatial symmetries on the potential energy surfaces. Traditional methods that solve the Euler-Lagrange equations often converge to minima higher in energy than the global minimum. In principle, Čížek-Paldus stability analysis can be applied to locate multiple solutions to the Euler-Lagrange equations, but it can be computationally expensive and it cannot determine whether a local solution is also a global solution. We find that the upper-bound SDP algorithm consistently converges to the lowest energy solutions and that the lower-bound SDP algorithm generates a tight lower bound. Neither the upper- or lower-bound SDP algorithm relies on the quality of the initial guess for the density matrix, and in all SDP calculations presented here the initial density matrix is equated to a matrix whose elements are formed by a random number generator. When the upper and lower bounds are equal, the SDP algorithms provide a certificate of global optimality for the Hartree-Fock solution. The energetically degenerate symmetry-broken solutions are important because they can be combined convexly into an ensemble density matrix that not only has the desired molecular symmetry but also yields a size-consistent energy. All of the Hartree-Fock solutions that we obtain using the SDP approach are restricted, i.e., $\langle S^2 \rangle$ has exactly the correct expectation value. In many strongly correlated cases, as shown in Sec. III, employing the symmetry-broken Hartree-Fock wave function as a reference in single-reference correlation methods like coupled cluster singles-doubles improves the correlated solution.

II. THEORY

A. Canonical Hartree-Fock theory

The quantity that we have been discussing as the density matrix can be more precisely called the one-particle reduced density matrix (1-RDM), which we denote as 1D . The Hartree-Fock problem for an N -electron system in an orthonormal basis of rank r is typically expressed as the following minimization problem over the set of Hermitian matrices (\mathbb{H}^r):

$$\underset{{}^1D \in \mathbb{H}^r}{\text{minimize}} \quad E_{\text{HF}}({}^1D), \quad (1)$$

$$\text{subject to } \text{Tr}({}^1D) = N, \quad (2)$$

$${}^1D^2 = {}^1D. \quad (3)$$

The self-consistent-field Hartree-Fock method for an N -electron system iteratively solves a system of Euler-Lagrange equations for a stationary point. The stationary point yields a ground-state Hartree-Fock energy and a set of N occupied orbitals. The computed Hartree-Fock energy is not guaranteed to be the global-energy minimum. From the perspective of reduced density matrices (RDMs),^{24,25} we can understand the

self-consistent-field method as iteratively checking extreme points of the set of 1-RDMs for satisfaction of the Euler-Lagrange equations where each extreme point corresponds to a 1-RDM with a Slater-determinant preimage.^{26,44,45} The set of extreme 1-RDMs (those with an N -electron Slater determinant as a preimage) can be characterized by the idempotency constraint in Eq. (3).

B. SDP Hartree-Fock theory

1. Convex relaxation

The optimization of the Hartree-Fock energy over the set of extreme 1-RDMs can be replaced without approximation by an optimization over the larger (and convex) set of N -representable 1-RDMs (those with any N -electron wave function as a preimage),^{10,46}

$$\underset{{}^1D, {}^1Q \in \mathbb{H}_+^r}{\text{minimize}} \quad E_{\text{HF}}({}^1D), \quad (4)$$

$$\text{subject to } \text{Tr}({}^1D) = N, \quad (5)$$

$${}^1D + {}^1Q = I, \quad (6)$$

where E_{HF} is the following quadratic function of the 1-RDM:

$$E_{\text{HF}}({}^1D) = \sum_{ij} {}^1K_j^i {}^1D_j^i + \sum_{ijkl} {}^1D_k^i {}^2V_{jl}^{ik} {}^1D_l^j, \quad (7)$$

$${}^1K_j^i = \langle i | \hat{h} | j \rangle, \quad (8)$$

$${}^2V_{jl}^{ik} = \frac{1}{2} (\langle ij | kl \rangle - \langle ij | lk \rangle). \quad (9)$$

The one-electron Hamiltonian operator \hat{h} contains the kinetic energy operator and electron-nuclei potential, $\langle ij | kl \rangle$ represents the electron-electron repulsion integrals, and the indices i, j, k , and l denote the orbitals in the one-electron basis set of rank r . The notation ${}^1D, {}^1Q \in \mathbb{H}_+^r$, equivalent to ${}^1D \geq 0$ and ${}^1Q \geq 0$, indicates that both the 1-particle RDM 1D and the 1-hole RDM 1Q are contained in the set of $r \times r$ Hermitian positive semidefinite matrices.

The reduced-density-matrix formulation of Hartree-Fock theory can be recast as a convex semidefinite program by embedding the quadratic product of 1-RDMs in E_{HF} in a higher dimensional (two-electron) matrix ${}^2M \in \mathbb{H}_+^{r^2}$. Rewriting E_{HF} as a linear functional of 2M ,

$$E({}^1D, {}^2M) = \text{Tr}({}^1K {}^1D) + \text{Tr}({}^2V {}^2M), \quad (10)$$

we can relax the non-convex Hartree-Fock optimization to a convex semidefinite program,

$$\underset{{}^1D, {}^1Q \in \mathbb{H}_+^r, {}^2M \in \mathbb{H}_+^{r^2}}{\text{minimize}} \quad E({}^1D, {}^2M), \quad (11)$$

$$\text{subject to } \text{Tr}({}^1D) = N, \quad (12)$$

$$\text{Tr}({}^2M) \leq N, \quad (13)$$

$${}^1D + {}^1Q = I, \quad (14)$$

$$\sum_{j=1}^r {}^2M_{jj}^{ik} = N {}^1D_k^i. \quad (15)$$

The solution of this SDP relaxation yields a lower bound to the Hartree-Fock energy. Because the constraints on the matrix 2M are minimal, this convex SDP formulation will typically yield energies that are significantly below the Hartree-Fock energy. To reproduce Hartree-Fock, further constraints on 2M are required.

2. Upper-bound SDP algorithm

Two separate sets of additional conditions on the matrix 2M that yield upper and lower bounds on the Hartree-Fock energy, respectively, will be considered. The first set of constraints, yielding the upper bound, consists of a single rank constraint,

$$\text{rank}({}^2M) = 1. \quad (16)$$

The ${}^2M \in \mathbb{H}_+^{r^2}$ matrix with its rank-one constraint and the contraction constraint in Eq. (15), we can show, is a tensor product of two identical 1-RDMs,

$${}^2M_{jl}^{ik} = {}^1D_k^i {}^1D_l^j. \quad (17)$$

It follows that the solution of the optimization program in Eqs. (11)–(15) with the rank constraint in Eq. (16) is equivalent to the solution of the RDM formulation of Hartree-Fock theory in Eqs. (4)–(9). We have mapped Hartree-Fock theory exactly onto a rank-constrained semidefinite program (rc-SDP HF).⁴⁷ The rank-constrained semidefinite program is convex except for the rank constraint; the nonconvexity of the Hartree-Fock energy functional in the RDM formulation has been transferred to the rank restriction in the SDP formulation. Because of the rank constraint, the solution of rc-SDP HF is not necessarily a global solution, meaning that the solution can be a local minimum in the Hartree-Fock energy and hence, an upper bound on the global energy minimum. Unlike traditional formulations of Hartree-Fock theory, however, rc-SDP HF optimizes the 1-RDM over the convex set of N -representable 1-RDMs, and in practice, we find that this difference makes it much more robust than traditional formulations in locating the global solution.

3. Lower-bound SDP algorithm

The second set of conditions, yielding a lower bound, consists of four constraints including

$$\sum_{j=1}^r {}^2M_{jk}^{ij} = {}^1D_k^i \quad (18)$$

and three additional constraints from permuting the indices i and j and/or j and k symmetrically. These convex conditions are a relaxation of the idempotency of the 1-RDM. They are necessary but not sufficient for the idempotency of the 1-RDM at the Hartree-Fock solution, and hence, optimization of

the SDP program in Eqs. (11)–(15) with these additional constraints (lb-SDP) is a SDP relaxation of the reduced-density-matrix formulation of Hartree-Fock theory in Eqs. (4)–(9). The lb-SDP method yields a *lower bound on the energy* from the global Hartree-Fock solution. In practice, this lower bound is found to be quite tight, and in some cases it agrees exactly with the global Hartree-Fock solution. If lb-SDP produces a 1-RDM solution that is idempotent, then that solution is the global Hartree-Fock solution. Furthermore, when the upper and lower bounds from rc-SDP and lb-SDP agree, we have a guaranteed certificate that these computed bounds correspond to the global energy minimum of Hartree-Fock theory.

4. Closed- and open-shell spin restriction

We have formulated rc-SDP HF and lb-SDP in the spin-orbital basis set. To perform RHF and ROHF calculations in a spatial-orbital basis set, one needs to take into account the spin structure of the Hamiltonian and density matrices. For any RHF or ROHF calculation on an N -electron system, 1D , 2M , 1K , and 2V will have the following block structures:

$${}^1D = \begin{bmatrix} {}^1D_\alpha & 0 \\ 0 & {}^1D_\beta \end{bmatrix} \quad {}^2M = \begin{bmatrix} {}^2M_{\alpha\alpha} & {}^2M_{\alpha\beta} \\ {}^2M_{\alpha\beta}^t & {}^2M_{\beta\beta} \end{bmatrix}, \quad (19)$$

$${}^1K = \begin{bmatrix} {}^1K_\alpha & 0 \\ 0 & {}^1K_\alpha \end{bmatrix} \quad {}^2V = \begin{bmatrix} {}^2V_{\alpha\alpha} & {}^2V_{\alpha\beta} \\ {}^2V_{\alpha\beta} & {}^2V_{\alpha\alpha} \end{bmatrix}. \quad (20)$$

For RHF the two 1D blocks and the four blocks of 2M are identical. Therefore, the only necessary modifications in rc-SDP HF and lb-SDP are replacing N by $N/2$, r by $r/2$, and rewriting E as follows:

$$E({}^1D_\alpha, {}^2M_{\alpha\beta}) = 2 \text{Tr}({}^1K_\alpha {}^1D_\alpha) + \text{Tr}({}^2V {}^2M_{\alpha\beta}), \quad (21)$$

$${}^2V = 2({}^2V_{\alpha\alpha} + {}^2V_{\alpha\beta}), \quad (22)$$

$${}^2V_{ji}^{ik} = 2(\langle ij|kl\rangle - \langle ij|lk\rangle). \quad (23)$$

For ROHF the α and β blocks of 1D are not identical but (assuming $N_\alpha > N_\beta$) because the spatial orbitals of paired electrons are required to be the same, the row space of ${}^1D_\beta$ is a subset of the row space of ${}^1D_\alpha$. In order to enforce this relation, 1D is divided into closed-shell and open-shell blocks which are ${}^1D_c = {}^1D_\beta$ and ${}^1D_o = {}^1D_\alpha - {}^1D_\beta$, respectively. With these blocks E and SDP ROHF can be rewritten as follows:

$$E({}^1D_c, {}^1D_o, {}^2M) = 2 \text{Tr}({}^1K_\alpha {}^1D_c) + \text{Tr}({}^1K_\alpha {}^1D_o) + \text{Tr}({}^2V {}^2M) \quad (24)$$

$$\begin{aligned}
& \text{minimize} && E(^1D_c, ^1D_o, ^2M) \\
& ^1D_c, ^1D_o, ^1Q \in \mathbb{H}_+^r, ^2M \in \mathbb{H}_+^{r^2} \\
& \text{subject to} && \text{Tr}(^1D_c) = N_\beta \\
& && \text{Tr}(^1D_o) = N_\alpha - N_\beta \\
& && ^1D_c + ^1D_o + ^1Q = I \\
& && \sum_{j=1}^r {}^2M_{j\alpha j\alpha}^{i\alpha k\alpha} = N_\alpha ({}^1D_{c_k}^i + {}^1D_{o_k}^i) \\
& && \sum_{j=1}^r {}^2M_{j\beta j\beta}^{i\beta k\beta} = N_\beta {}^1D_{c_k}^i \\
& && \sum_{j=1}^r {}^2M_{j\beta j\beta}^{i\alpha k\alpha} = N_\beta ({}^1D_{c_k}^i + {}^1D_{o_k}^i) \\
& && \sum_{j=1}^r {}^2M_{j\alpha j\alpha}^{i\beta k\beta} = N_\alpha {}^1D_{c_k}^i.
\end{aligned}$$

For rc-SDP ROHF, the only additional constraint is on the rank, as in the spin-orbital formulation

$$\text{rank}(^2M) = 1. \quad (25)$$

For lb-SDP, the set of four constraints described earlier in Eq. (18) have to be enforced for all the four blocks of M as follows:

$$\sum_{j=1}^r {}^2M_{j\alpha k\alpha}^{i\alpha j\alpha} = ({}^1D_{c_k}^i + {}^1D_{o_k}^i), \quad (26)$$

$$\sum_{j=1}^r {}^2M_{j\beta k\beta}^{i\beta j\beta} = {}^1D_{c_k}^i, \quad (27)$$

$$\sum_{j=1}^r {}^2M_{j\beta k\beta}^{i\alpha j\alpha} = {}^1D_{c_k}^i, \quad (28)$$

$$\sum_{j=1}^r {}^2M_{j\alpha k\alpha}^{i\beta j\beta} = {}^1D_{c_k}^i. \quad (29)$$

Although formally there are 16 constraints in all, 6 of them are redundant due to the Hermiticity of M resulting in 10 linearly independent constraints.

III. APPLICATIONS

To illustrate the rc-SDP and lb-SDP methods, we apply them to computing the dissociation curves for C_2 , CN, Cr_2 , and NO_2 .

A. Methodology

The GAMESS electronic structure package is used to perform self-consistent-field Hartree-Fock calculations (SCF HF with DIIS) and coupled cluster singles doubles (CCSD)^{48–50} calculations. The rc-SDP and lb-SDP are solved using the SDP solver RRS_{DP}.³⁴ Since DIIS is the standard accelerator for SCF HF calculations, we compare rc-SDP HF results with DIIS results. Both rc-SDP HF and DIIS methods

are performed without enforcing a specific spatial symmetry. The DIIS solution at the internuclear distance R' where R' is differentially larger than the distance R is obtained by using the DIIS solution at R as an initial guess.

The SDP solver RRS_{DP} imposes the semidefinite constraint on each matrix M through the factorization $M = RR^T$. For rc-SDP HF, the rank-one constraint on 2M is readily enforced by defining R to be a rectangular $r \times 1$ matrix. Scaling of RRS_{DP}³⁴ is determined by the RR^T matrix multiplication for the largest matrix block, which is 2M for both rc-SDP and lb-SDP. For rc-SDP the rank of 2M is one, and hence, the matrix multiplication scales approximately as r^4 . For lb-SDP the rank of 2M scales as r after applying the bound on the maximum rank from Pataki⁵¹ and Barvinok,⁵² and hence, the matrix multiplication scales approximately as r^5 .

B. C_2 stretch

Because the C_2 molecule has many low-lying excited states, it is a significantly multireferenced system even at equilibrium, which makes it a challenging system for both Hartree-Fock and correlation energy calculations.⁵³ Figure 1 shows various RHF energy curves and the lower bound in the 6-31G* basis set as a function of the C–C bond distance. The D_{4h} and D_{2h} curves,⁵⁴ generated by seeding the scan of the potential energy surface at two different values of R were obtained using DIIS. The rc-SDP curve corresponds to D_{4h} for $R < 1.1$ Å, C_s for 1.1 Å $< R < 1.2$ Å, D_{2h} for 1.2 Å $< R < 2$ Å, and to C_i for $R > 2$ Å. The rc-SDP curve bifurcates from the D_{4h} curve and joins the D_{2h} curve without ever being non-differentiable. For $R < 1.5$ Å and $R > 2.9$ Å the lb-SDP solution is lower than the rc-SDP solution by less than 0.005 a.u. thereby certifying it to be the global minimum within that threshold. For the intermediate region, rc-SDP

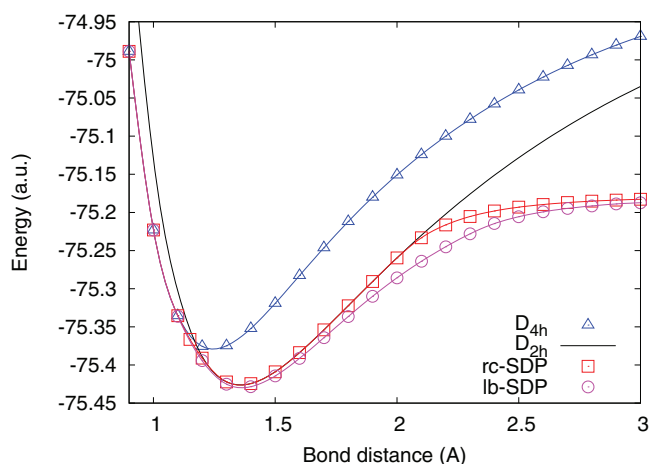


FIG. 1. The ground-state restricted Hartree-Fock energies from rc-SDP and DIIS and the lower bound from lb-SDP are shown as functions of the C–C internuclear distance R . When the energies from rc-SDP and lb-SDP agree, the solution from rc-SDP is guaranteed to be the global solution of Hartree-Fock theory. While DIIS locates a D_{4h} and a D_{2h} solution depending on the initial guess used, rc-SDP locates the energetically lowest solution which has a different symmetry for different internuclear distances. Although the rc-SDP solution has C_i symmetry for $R > 2$ Å it has a qualitatively correct shape for dissociation. By 3 Å the D_{2h} and C_i solutions differ by 0.148 a.u. (92.8 kcal/mol).

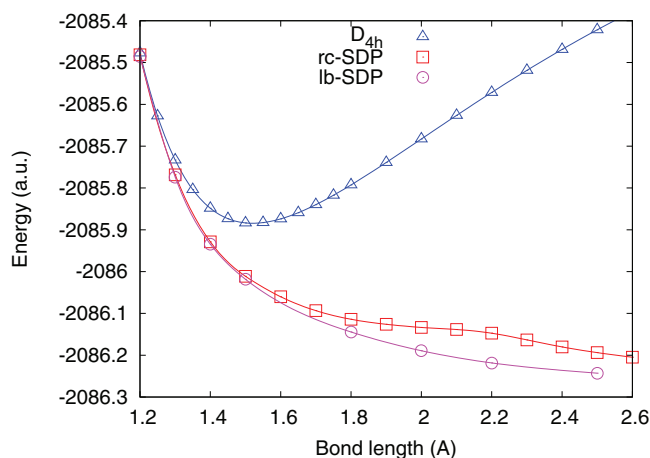


FIG. 2. The Hartree-Fock energies from rc-SDP and DIIS and the lower bound from lb-SDP are shown as functions of the Cr–Cr internuclear distance R . DIIS obtains a D_{4h} solution on seeding from smaller values of R to larger ones. While for $R > 1.2$ Å (shown) the rc-SDP solution has C_2 symmetry, for $R < 1.2$ Å (not shown) it smoothly joins the D_{4h} curve of DIIS. Even in the equilibrium region, for $R = 1.5$ Å the D_{4h} energy is 0.127 a.u. (80 kcal/mol) higher than the C_2 energy which is certified by lb-SDP to be globally optimal within 0.008 a.u. By 2.5 Å the energy difference increases to 0.772 a.u. (485 kcal/mol) where the C_2 solution is globally optimal within 0.05 a.u.

likely continues to give the globally optimal curve although we do not have a formal mathematical guarantee.

C. Cr_2 stretch

Cr_2 is known to be an extremely challenging molecule to describe correctly by *ab initio* electronic structure theory.^{55–63} Figure 2 shows the HF energy in the valence triple-zeta (TZV)⁶⁴ basis set as a function of the Cr–Cr distance. The large number of HF solutions that are energetically close to each other, shown in Fig. 3, provides a novel characterization of the substantial multireference correlation in Cr_2 . The number of energetically close HF solutions is comparable in the STO-6G basis, indicating that this feature is not significantly dependent upon the basis set. The solution found by DIIS has D_{4h} symmetry for all R whereas the solution found by rc-SDP has D_{4h} symmetry for $R < 1.2$ Å and C_2 symmetry for $R > 1.2$ Å. Although the rc-SDP solution is symmetry-broken for $R > 1.2$ Å, it is globally optimal within the bound provided by lb-SDP. Further verification of the rc-SDP solutions being HF minima is provided by the fact that DIIS is able to obtain them when they are employed as initial guesses.

Changes in Hartree-Fock energies and densities can impact correlation energy calculations in two ways: (1) any change in the Hartree-Fock energy changes the correlation energy by its very definition and (2) any change in the Hartree-Fock density (or the Hilbert space spanned by the molecular orbitals) changes the reference wave function employed in many-electron correlation methods including coupled cluster^{48–50} and parametric RDM methods.^{65,66} In this and other examples considered, rc-SDP helps to identify symmetry-broken Hartree-Fock solutions that often generate improved CCSD solutions. While rc-SDP may identify

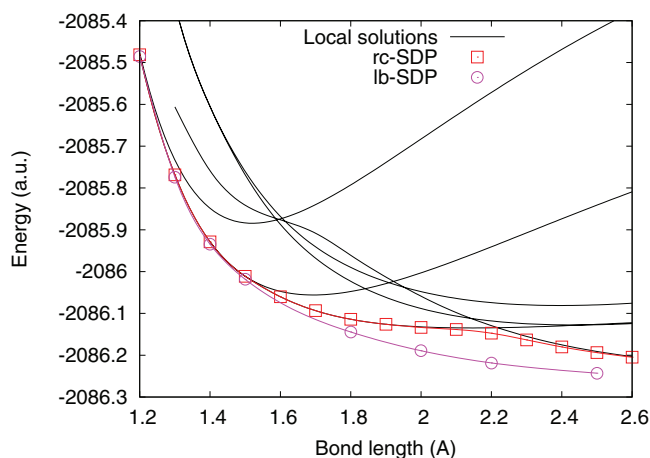


FIG. 3. All the local Hartree-Fock solutions found are shown in order to provide a visual depiction of the substantial multireference correlation that exists in Cr_2 and the concomitant difficulty in obtaining global Hartree-Fock solutions.

a piecewise smooth potential energy surface, each piece can be analytically continued to generate a smooth Hartree-Fock surface from which a smooth CCSD surface can be computed. Cr_2 is known to be extremely challenging for single-reference methods like coupled cluster theories.⁶⁷ Figure 4 explores the effect of using the global symmetry-broken C_2 solution rather than the local D_{4h} solution as the reference wave function in CCSD. The results in Fig. 4 show that much of the failure noted in the literature can be attributed to the D_{4h} reference wave function rather than CCSD. While CCSD with the D_{4h} reference diverges beyond 1.7 Å, CCSD with the C_2 reference at least yields a physically realistic dissociation curve for the ground state.

D. CN stretch

The CN radical is of astrophysical interest due its presence in the interstellar medium.⁶⁸ Although its low-lying

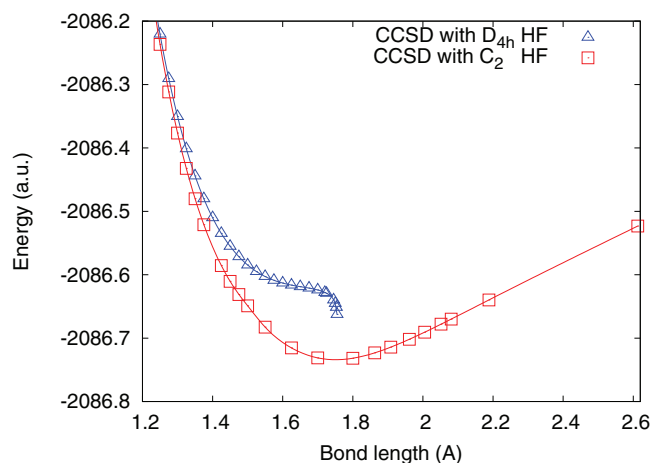


FIG. 4. The potential energy curves of Cr_2 from CCSD with the D_{4h} and C_2 Hartree-Fock wave functions are compared. The CCSD method applied with the D_{4h} reference yields an unphysical curve. In contrast, CCSD with the C_2 reference yields a physically realistic dissociation curve. Consequently, the energy divergence from CCSD can be attributed to the D_{4h} reference wave function.

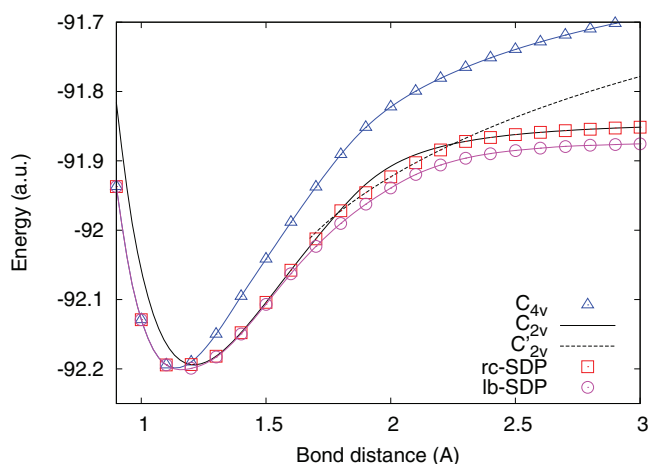


FIG. 5. The Hartree-Fock energies from rc-SDP and DIIS and the lower bound from lb-SDP are shown as functions of the C–N internuclear distance. In spite of there being multiple solutions, rc-SDP successfully obtains the lowest energy solution for all internuclear distances. By 3 Å the difference between the C_{4v} and C_{2v} solutions is 0.156 a.u. (98 kcal/mol).

excited states⁶⁹ enhance its utility as an optical probe^{70,71} for studying various properties, they also make it a multireferenced system. Figure 5 shows various HF energy curves and the lower bound in the cc-pVDZ basis⁷² plotted as a function of the C–N internuclear distance R . The C_{4v} , C_{2v} , and C'_{2v} curves were obtained using DIIS. The rc-SDP curve corresponds to C_{4v} for $R < 1.2$ Å and to C_{2v} for all other values of R . The rc-SDP method manages to obtain the lowest curve among three different Hartree-Fock curves for all values of R . As is evident from the figure, the ground-state Hartree-Fock curve is a piecewise defined function of the three Hartree-Fock curves with there being three points of non-smoothness where the curves intersect at $R = 1.2, 1.8,$ and 2.25 Å. If DIIS is given the Hückel guess, it converges to different curves in different regions which are not always the lowest solutions for those regions. If DIIS is used to generate the curve from left to right with the solution for a smaller bond distance being the guess for a larger bond distance, only the C_{4v} curve is obtained. Consistent generation of the C_{4v} curve might be the reason why the C_{2v} and C'_{2v} curves have not been previously reported.⁷³ The fact that the lb-SDP curve is never lower than rc-SDP by more than 0.006 a.u. for $R \leq 1.6$ Å provides a certificate of global optimality for those rc-SDP points within that threshold. After 1.6 Å rc-SDP likely continues to give the globally optimal curve although we do not have a formal mathematical guarantee. This is corroborated by the fact that the rc-SDP (and C_{2v}) curve is size consistent, meaning that it is asymptotically equal to exactly the sum of Hartree-Fock energies of doublet N and singlet C. The energy of doublet N and singlet C is the same from both rc-SDP and DIIS and certified by lb-SDP to be globally optimal within 0.002 a.u. and 0.0004 a.u., respectively.

It is also worth noting that rc-SDP (and the C_{2v} curve) does not dissociate CN into quadruplet N and triplet C in spite of them being lower in energy than doublet N and singlet C, respectively. This is not due to convergence to a local minimum but instead is due to the inability of “restricted” orbitals in ROHF (and RHF) to dissociate a molecule into fragments

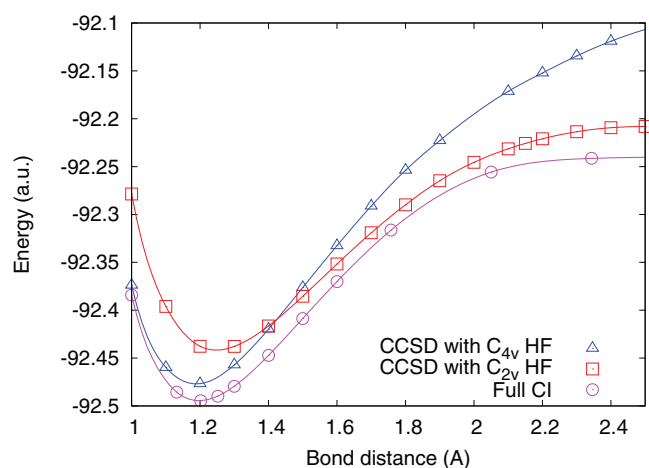


FIG. 6. The potential energy curves of CN from CCSD with the C_{4v} and C_{2v} Hartree-Fock references are shown as functions of the C–N internuclear distance. Like the C_{4v} and C_{2v} Hartree-Fock solutions, the C_{4v} and C_{2v} CCSD solutions provide good descriptions at equilibrium and dissociation, respectively.

which have spatially separated electron pairs. This is a consequence of using the same spatial orbital to describe electron pairs. Since (doublet) CN has one unpaired electron, ROHF can describe its dissociation into fragments which have a total of one unpaired electron at most which is why it dissociates CN into doublet N and singlet C.

Figure 6 shows the CCSD curves obtained using the C_{4v} and C_{2v} Hartree-Fock solutions of which the latter was identified using rc-SDP. As is evident from the figure, although the CCSD with the C_{4v} reference curve is lower in energy for $R \leq 1.4$ Å, it rises rapidly after that point as it dissociates into charged species. The CCSD with the C_{2v} reference curve is lower in energy after 1.4 Å and gives a qualitatively correct representation of dissociation into neutral species. It is also worth noting that the C_{4v} and C_{2v} Hartree-Fock curves cross at 1.2 Å, which is before the corresponding CCSD curves cross.

E. NO₂ bend

The NO₂ radical is known to have a complicated, extensively studied photochemistry.⁷⁴ It has a conical intersection between the ground and first excited states.^{75,76}

Figure 7 shows various HF energy curves (C_{2v} symmetry) and the lower bound in the cc-pVDZ basis⁷² plotted as a function of the O–N–O angle (θ) for a symmetric configuration with a N–O bond length of 1.197 Å. Despite the existence of multiple HF minima which are energetically close, rc-SDP obtains the lowest minimum for all bond angles. For $\theta \leq 70^\circ$, $\theta \geq 135^\circ$ lb-SDP certifies the C_{2v} curve from both DIIS and rc-SDP to be globally optimal. Furthermore, since lb-SDP is never lower than rc-SDP by more than 0.01 a.u., the entire rc-SDP curve is globally optimal within that threshold. Although the rc-SDP curve for $85^\circ \leq \theta \leq 120^\circ$ corresponds to a saddle point on the complete NO₂ potential energy surface (as a function of the two bond lengths in addition to the bond angle) it is indeed the global minimum (within 0.01 a.u.) for the fixed values of N–O bond lengths used in the calculation.

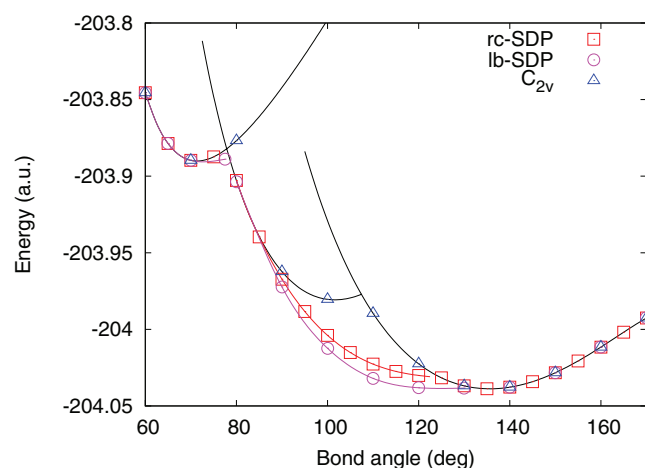


FIG. 7. The Hartree-Fock energies from rc-SDP and DIIS (all of which correspond to C_{2v} symmetry) and the lower bound from lb-SDP are shown as functions of the ONO angle. Despite there being multiple C_{2v} solutions, rc-SDP always finds the energetically lowest solution. Furthermore, lb-SDP certifies global optimality for the solutions $<70^\circ$ and $>135^\circ$.

IV. DISCUSSION

A RDM formulation of Hartree-Fock theory, based on semidefinite programming, has been presented that yields upper and lower bounds on the Hartree-Fock solution. When these bounds are equal, they provide a certificate guaranteeing the globally optimal Hartree-Fock solution. As electrons become more strongly correlated, methods for Hartree-Fock based on the self-consistent-field approach like DIIS converge to stationary points of Hartree-Fock theory with potentially non-global energies and densities. In most instances we have been able to certify global optimality for known solutions of Hartree-Fock theory for the first time. Although there are methods to determine whether the obtained stationary point is a local minimum, maximum, or saddle point,^{77,78} our approach is unique in that it certifies global optimality.

Semidefinite relaxation of Hartree-Fock theory, which we derived in Sec. II B 3, yields a rigorous lower bound on the Hartree-Fock energy. In contrast, wave function approaches to Hartree-Fock theory, such as the traditional optimization of a Slater determinant, yield upper bounds on the Hartree-Fock energy. Minimization of the electronic energy with respect to the orbitals of a Slater determinant generates a local stationary point which may or may not be the global minimum. Higher derivatives, such as those found in stability analysis, can be employed to search for additional local minima, each of which provides an upper bound on the energy of the global minimum. While not previously developed, the lower-bound approach enables us in many cases to certify that a solution is the global minimum of Hartree-Fock theory. If the 1-RDM obtained by the lower-bound SDP algorithm is idempotent, then the 1-RDM and its associated energy represent the global solution to the Hartree-Fock calculation. Furthermore, even if the 1-RDM is not idempotent, agreement of the lower-bound energy with the upper-bound energy from either a traditional wave function-based Hartree-Fock calculation or a SDP-based upper-bound calculation guarantees that the computed energy is the global minimum. As shown in

Sec. II, an upper bound to the Hartree-Fock energy can be computed through a rank-constrained SDP in which a non-convex rank constraint is added to the optimization. Importantly, this upper-bound formulation shows that Hartree-Fock theory is convex except for the presence of the rank constraint.

Symmetry breaking and restoration can be employed to capture correlation effects at a lower computational cost.⁷⁹ Recently, they have been employed in variational quasi-particle theory⁸⁰ to compute the ground-state energies from an antisymmetrized geminal power wave function⁸¹ at an r^4 computational cost where r is the number of orbitals. In the presence of strong electron correlation the lowest energy solutions of Hartree-Fock theory can be spatially symmetry broken. We employ the SDP methods to distinguish the global solution from multiple local solutions of different spatial symmetries. The symmetry breaking generates multiple wave functions at the global minimum that are energetically degenerate. In the present case symmetry restoration can be accomplished by two methods. First, the full molecular symmetry can be reestablished by taking the ensemble of the energetically degenerate symmetry-broken solutions. The ensemble nature of the ground-state density matrix is a consequence of pursuing a mean-field description of the strongly correlated system. Second, a linear combination of the symmetry-broken solutions can be taken to generate a wave function by a non-orthogonal configuration interaction.^{82,83} In the second approach the degenerate Hartree-Fock solutions become entangled to form a pure density matrix composed of a single correlated wave function. While in the present work we pursue the first approach, the second approach provides insight into how the different symmetry-broken solutions of Hartree-Fock theory contribute information to the correlated ground-state wave function.

Direct computation of the 2-RDM has been previously accomplished by minimizing the energy as a functional of the 2-RDM subject to N -representability conditions.^{24,26–37} Constrained optimization is performed by SDP. Although we have taken a different path in the derivation of the SDP algorithms for Hartree-Fock theory, they can be viewed within variational 2-RDM theory as the addition of further constraints on the 2-RDM to ensure that it represents the mean-field (or Hartree-Fock) limit. The upper-bound algorithm requires a nonconvex rank constraint, and the lower-bound algorithm requires relaxed idempotency conditions. As described above, the combination of the upper-bound and lower-bound SDP algorithms provides a mechanism for certifying the global minimum of Hartree-Fock theory. We have shown that global solutions are useful for seeding either wave function or reduced density matrix methods for describing strongly correlated quantum systems. The SDP-based restricted closed- and open-shell Hartree-Fock method, described here, is directly extendable to an unrestricted Hartree-Fock method, which will be presented elsewhere.

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