Global Solutions of Hartree-Fock Theory and their Consequences for Strongly Correlated Quantum Systems

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We present a density matrix approach for computing global solutions of Hartree-Fock theory, based on semidefinite programming (SDP), that gives upper and lower bounds on the Hartree-Fock energy of quantum systems. Equality of the upper- and lower-bound energies guarantees that the computed solution is the globally optimal solution of Hartree-Fock theory. For strongly correlated systems the SDP approach provides an alternative to the locally optimized Hartree-Fock energies and densities from the standard solution of the Euler-Lagrange equations. Applications are made to the potential energy curves of the H\textsubscript{4} dimer and the N\textsubscript{2} molecule.

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In the 1950s Roothan\textsuperscript{1} developed the self-consistent-field approach to solving Hartree-Fock theory. In addition to providing some of the earliest electronic structure calculations of atoms and molecules, Roothan’s method with a variety of refinements to accelerate convergence\textsuperscript{2\textsuperscript{\textsuperscript{a}}\textsuperscript{9}} and to treat large systems \textsuperscript{3\textsuperscript{\textsuperscript{a}}\textsuperscript{\textsuperscript{b}}\textsuperscript{17}} has remained the standard approach to implementing Hartree-Fock theory for nearly 60 years. In this Letter we present a density matrix approach to Hartree-Fock theory, based on semidefinite programming (SDP) \textsuperscript{18\textsuperscript{\textsuperscript{\textsuperscript{a}}\textsuperscript{\textsuperscript{b}}\textsuperscript{20}}, that gives upper and lower bounds on the Hartree-Fock energy of atoms and molecules. For strongly correlated quantum systems this SDP approach provides an alternative to the locally optimized Hartree-Fock energies and densities from standard algorithms.

Two complementary semidefinite programming formulations of Hartree-Fock theory are derived that yield upper and lower bounds on the Hartree-Fock energy, respectively. When the upper- and lower-bound energies are equal, we have a guaranteed certificate that the computed solution is the global solution of Hartree-Fock theory. The computed energy is the global energy minimum, and the computed density is the electron density at that global minimum. We illustrate the methodology through applications to the dissociation curves of the H\textsubscript{4} dimer and the N\textsubscript{2} molecule.

In both examples, we compare SDP and DIIS algorithms that implement the restricted Hartree-Fock method in which the spin symmetry is conserved\textsuperscript{21}. At geometries away from equilibrium, the SDP Hartree-Fock method yields spatial-symmetry-broken Hartree-Fock energies that are lower than those from the standard DIIS Hartree-Fock method. When the electron correlation is significant, the standard DIIS Hartree-Fock method or other methods based on the solution of the Euler-Lagrange equations have difficulty selecting the global minimum from multiple local minima of different spatial symmetries. These solutions from SDP satisfy the standard Euler-Lagrange equations just like the higher-in-energy DIIS solutions.

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) \textsuperscript{22,\textsuperscript{23}}, we can understand the self-consistent-field method as iteratively checking extreme points of the set of one-electron RDMs (1-RDMs) for satisfaction of the Euler-Lagrange equations where each extreme point corresponds to a 1-RDM with a Slater determinant preimage\textsuperscript{24,\textsuperscript{26}}. The optimization of the Hartree-Fock energy over the set of extreme 1-RDMs (those with an N-electron Slater determinant as a preimage) 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)\textsuperscript{4,\textsuperscript{27}}:

\[
\begin{align*}
\text{minimize} & \quad E_{\text{HF}}(1D) \\
\text{subject to} & \quad \text{Tr}(1D) = N \\
& \quad 1D + 1Q = I
\end{align*}
\]

where \(E_{\text{HF}}\) is the following quadratic function of the 1-RDM:

\[
E_{\text{HF}}(1D) = \sum_{ij} r_{ij}^{1} 1D_{ij}^{1} + \sum_{ijkl} r_{ijkl}^{1} 1D_{ij}^{1} 2V_{ij}^{1} 1D_{kl}^{1}
\]

\[
1K_{ij} = \langle ij|\hat{h}|ij\rangle
\]

\[
2V_{ij} = \frac{1}{2}(\langle ij|kl\rangle - \langle ij|lk\rangle).
\]

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 \(1D \succeq 0\) and \(1Q \succeq 0\), indicates that both the 1-particle RDM \(1D\) and the 1-hole
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 $E_{\text{HF}}$ in a higher dimensional (two-electron) matrix $2M \in \mathbb{R}_{+}^{r \times r}$. Rewriting $E_{\text{HF}}$ as a linear functional of $2M$

$$E(1D, 2M) = \text{Tr}(1K1D) + \text{Tr}(2V2M),$$

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

$$\begin{align*}
\text{minimize} & \quad E(1D, 2M) \\
\text{subject to} & \quad \text{Tr}(1D) = N \\
& \quad \text{Tr}(2M) \leq N \\
& \quad 1D + 1Q = I \\
& \quad \sum_{j=1}^{r} 2M_{ijk} = N^{-1}D_{k}^{i}.
\end{align*}$$

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.

The first set of constraints, yielding the upper bound, consists of a single rank constraint

$$\text{rank}(2M) = 1.$$ (13)

The $2M \in \mathbb{R}_{+}^{r \times r}$ matrix with its rank-one constraint and the contraction constraint in Eq. (12), we can show, is a tensor product of two identical 1-RDMs

$$2M^{ik}_{jl} = 1D^{i}_{k}1D^{j}_{l}.$$ (14)

It follows that the solution of the optimization program in Eqs. (12) with the rank constraint in Eq. (13) is equivalent to the solution of the RDM formulation of Hartree-Fock theory in Eqs. (1). We have mapped Hartree-Fock theory exactly onto a rank constrained semidefinite program (rc-SDP HF) [28]. The rank constrained semidefinite program is convex except for the rank restriction; 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.

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

$$\sum_{j=1}^{r} 2M_{ijk} = 1D_{k}^{i}$$

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. (12) with these additional constraints (lb-SDP) is an SDP relaxation of the reduced-density-matrix formulation of Hartree-Fock theory in Eqs. (1). 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.

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.

**FIG. 1.** Upper and lower bounds to the ground-state restricted Hartree-Fock energy from rc-SDP and lb-SDP, respectively, as well as the Hartree-Fock energy from DIIS are shown as functions of the distance between the $H_{2}$ monomers. The rc-SDP energy is certified by lb-SDP to be globally optimal for $R \leq 2$ Å and within 0.003 a.u. of the globally optimal solution for all $R$. In contrast, the DIIS solutions converge to local solutions for all separations $R \geq 2$ Å.
dissociation curves for singlet \((\text{H}_4)_2\) and \(\text{N}_2\) in the cc-pVDZ basis set \(\text{[29]}\). 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) \(\text{[30-32]}\) calculations. The rec-SDP and lb-SDP are solved using the SDP solver RRSDP \(\text{[20]}\). Since DIIS is the standard accelerator for SCF HF calculations, we compare rec-SDP HF results with DIIS results. Both rec-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 RRSDP imposes the semidefinite constraint on each matrix \(M\) through the factorization \(M = RR^T\). For rec-SDP HF, the rank-one constraint on \(2M\) is readily enforced by defining \(R\) to be a rectangular \(r \times 1\) matrix. Scaling of RRSDP \(\text{[20]}\) is determined by the \(RR^T\) matrix multiplication for the largest matrix block, which is the \(r^2 \times r^2\) matrix \(2M\) for both rec-SDP and lb-SDP. For rec-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 \(r^2\) after applying the bound on the maximum rank from Pataki \(\text{[33]}\) and Barvinok \(\text{[34]}\), and hence, the matrix multiplication scales approximately as \(r^5\).

\(\text{H}_4\) is known to be a multireferenced diradical system at square geometries \(\text{[35, 36]}\). Hence, molecules constructed from square \(\text{H}_4\)'s can be expected to be challenging systems for Hartree-Fock and correlation methods. Here we examine the dimer of square \(\text{H}_4\) molecules whose H-H bond lengths are 1.0 \(\text{Å}\). Figure 1 shows the upper and lower bounds to the ground-state restricted Hartree-Fock energy from rec-SDP and lb-SDP, respectively, as well as the restricted Hartree-Fock energy from DIIS as functions of the distance \(R\) between the \(\text{H}_4\) monomers. Because the lb-SDP curve is identical to the rec-SDP and DIIS curves for \(R \leq 2.0\) \(\text{Å}\) we have a certificate of global optimality for that part of the curve. Furthermore, since lb-SDP is never lower than rec-SDP by more than 0.003 a.u. after 2.0 \(\text{Å}\) the rest of the rec-SDP curve is equal to the globally optimal Hartree-Fock solution within that threshold. Its optimality is corroborated by the fact that the rec-SDP curve is size consistent, meaning that it is asymptotically equal to exactly twice the restricted Hartree-Fock energy of the singlet \(\text{H}_4\) monomer. The energy of the monomer is the same from both rec-SDP and DIIS and certified to be globally optimal within 0.001 a.u. by lb-SDP.

For all separations of the dimer larger than 2.0 \(\text{Å}\) the DIIS method converges to a local solution with \(\text{D}_{4h}\) symmetry while the rec-SDP method converges to the global \(\text{C}_{2v}\) solution. At \(R = 5.0\) \(\text{Å}\) the DIIS energy of the dimer is more than 0.2 a.u. (125 kcal/mol or the energy of a chemical bond) higher than the size consistent energy of the global Hartree-Fock solution. If the DIIS algorithm is seeded with an rec-SDP solution, it converges directly to that solution, showing that like the local DIIS solutions the rec-SDP solutions also satisfy the restricted Euler-Lagrange equations. In principle, even from a poor initial guess, the \(\text{C}_{2v}\) solution can also be obtained from DIIS from a repeated application of stability analysis involving the potentially expensive construction of the Hessian matrix \(\text{[27, 53]}\). Unlike the SDP methods, however, the DIIS with stability analysis cannot determine whether a local solution is the global solution. Both the DIIS and the rec-SDP restricted Hartree-Fock methods generate solutions with \(\langle S^2 \rangle = 0\) for all \(R\) while the unrestricted Hartree-Fock method produces a solution with \(\langle S^2 \rangle = 2\) for \(R > 2.25\) \(\text{Å}\).

An accurate description of a stretched triple bond in \(\text{N}_2\) is a challenging electronic structure problem \(\text{[29]}\). Figure 2 shows the ground-state restricted Hartree-Fock energies from rec-SDP and DIIS and the lower bound from lb-SDP are shown as functions of the N-N internuclear distance \(R\). When the energies from rec-SDP and lb-SDP agree, the solution from rec-SDP is guaranteed to be the global solution of Hartree-Fock theory. At stretched geometries the DIIS locates a \(\text{D}_{4h}\) solution while rec-SDP locates an energetically lower pair of \(\text{C}_{2v}\) solutions. By 4.1 \(\text{Å}\) the \(\text{D}_{4h}\) and \(\text{C}_{2v}\) solutions differ by 0.375 a.u. (235 kcal/mol). The \(\text{C}_{2v}\) solutions can be considered excited states in the Hartree-Fock model since they analytically continue to excited-state solutions at equilibrium geometries (not shown); however, because the two iso-energetic \(\text{C}_{2v}\) Hartree-Fock solutions are also the global minimum at stretched geometries, they provide insight into the correlated ground-state solution of the Schrödinger equation.

![FIG. 2. The ground-state restricted Hartree-Fock energies from rec-SDP and DIIS and the lower bound from lb-SDP are shown as functions of the N-N internuclear distance R. When the energies from rec-SDP and lb-SDP agree, the solution from rec-SDP is guaranteed to be the global solution of Hartree-Fock theory. At stretched geometries the DIIS locates a D_{4h} solution while rec-SDP locates an energetically lower pair of C_{2v} solutions. By 4.1 Å the D_{4h} and C_{2v} solutions differ by 0.375 a.u. (235 kcal/mol). The C_{2v} solutions can be considered excited states in the Hartree-Fock model since they analytically continue to excited-state solutions at equilibrium geometries (not shown); however, because the two iso-energetic C_{2v} Hartree-Fock solutions are also the global minimum at stretched geometries, they provide insight into the correlated ground-state solution of the Schrödinger equation.](image-url)
optimal curve although we do not have a formal mathematical guarantee. As in the \((H_2)_2\) example, after 1.5 Å the DIIS potential energy curve smoothly diverges from the rc-SDP global solution to a local solution. At 4.1 Å the rc-SDP energy per N atom is −54.118 a.u. which is 0.187 a.u. lower than the energy per N atom from DIIS and 0.270 a.u. higher than the energy of a single nitrogen in its quadruplet state from the restricted open-shell Hartree-Fock method.

For all internuclear distances larger than 1.6 Å the DIIS method converges to a local solution with \(D_{4h}\) symmetry while the rc-SDP method converges to the global \(C_{2v}\) solution. We can interpret the \(N_2\) solution from rc-SDP as an ensemble mean-field density matrix with \(D_{4h}\) symmetry, composed of two iso-energetic \(C_{2v}\) Slater determinants. As in the previous example, the rc-SDP solutions were additionally verified to be HF minima by showing that as initial guesses for the DIIS algorithm they satisfy the Euler-Lagrange equation. In principle, the \(C_{2v}\) determinants from rc-SDP can be computed with DIIS in combination with Hessian-based stability analysis; unlike the SDP approach, however, stability analysis cannot determine whether a local solution is also a global solution \([37, 38]\). Unlike the unrestricted Hartree-Fock solution, where \(\langle S^2 \rangle = 3\) after \(R = 2.0\) Å, the rc-SDP and lb-SDP solutions have \(\langle S^2 \rangle\) identically equal to zero for all \(R\).

![Figure 3](image-url)

**FIG. 3.** The potential energy curve of \(N_2\) from CCSD performed with the rc-SDP restricted Hartree-Fock reference wave function is compared with the potential energy curve from CCSD performed with the standard DIIS restricted Hartree-Fock reference wave function. The unphysical nature of the CCSD curve, well documented in the literature, has been attributed to missing electron correlation. As the bond is stretched, while CCSD with the \(D_{4h}\) reference from DIIS rises rapidly and then diverges, CCSD with the \(C_{2v}\) reference from rc-SDP yields a physically realistic dissociation curve.

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 \([30, 32]\) and parametric RDM methods \([40]\). Figure 3 explores the effect of using the global \(C_{2v}\) solution rather than the \(D_{4h}\) solution as the reference wave function in CCSD. The treatment of \(N_2\) by CCSD has been widely documented in the literature where the unphysical behavior of the \(N_2\) curve from CCSD has been attributed to the absence of \(T_2\) and \(T_4\) excitation amplitudes \([29, 41]\). The results in Fig. 3, however, show that in the dissociation limit, while CCSD with the \(D_{4h}\) reference rises rapidly and then diverges, CCSD with the \(C_{2v}\) reference yields a physically realistic dissociation curve.

State-of-the-art calculations on the \(H_4\) dimer \([35, 36, 42]\) and the \(N_2\) molecule \([43]\) require an explicit treatment of multiple determinants in the reference wavefunction, known as multireference correlation. The presented global-minimum Hartree-Fock theory can be useful in identifying the determinants in the \(H_4\) dimer and the \(N_2\) molecule that contribute most significantly to the strong electron correlation. Symmetry-broken determinants, for example, can be employed as an \(N\)-electron basis in a symmetry-restoring configuration interaction.

The SDP-based Hartree-Fock algorithms have also been applied to \(Cr_2\), \(CN\), and \(NO_2\) \([44]\) where there are many local solutions, especially in the case of \(Cr_2\). In these and other larger systems with symmetry breaking, alternatives to the local solution of the Hartree-Fock equations become essential to identifying the global solution. Because stability analysis only distinguishes local minima from saddle points \([37, 38]\), it becomes less useful in the presence of multiple local solutions as can occur in larger strongly correlated molecular systems and materials.

We have presented an RDM formulation of Hartree-Fock theory, based on semidefinite programming, 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 can converge to stationary points of Hartree-Fock theory with potentially non-global energies and densities. The SDP-based restricted Hartree-Fock method is directly extendable to a restricted open-shell Hartree-Fock method and an unrestricted Hartree-Fock method, which will be presented elsewhere.

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[1] C. C. J. Roothaan, Rev. Mod. Phys. 23, 69 (1951).
[2] V. R. Saunders and I. H. Hillier, Int. J. Quantum Chem. 7, 699 (1973).
[3] P. Pulay, Chem. Phys. Lett. 73, 393 (1980).
[4] E. Cancés, Mathematical Models and Methods for Ab Initio Quantum Chemistry, 1st ed., edited by M. De Franceschi and C. L. Bris (Springer, New York, 2000) Chap. 2.
[5] L. Thogersen, J. Olsen, D. Yeager, P. Jorgensen, P. Salek, and T. Helgaker, J. Chem. Phys. 121, 16 (2004).
[6] J. B. Francisco, J. M. Martinez, and L. Martinez, J. Chem. Phys. 121, 10863 (2004).
[7] A. J. Garza and G. E. Scuseria, J. Chem. Phys. 137, 064110 (2012).
[8] R. McWeeny, Proc. R. Soc. Lon. Ser-A 235, 496 (1956).
[9] X.-P. Li, R. W. Nunes, and D. Vanderbilt, Phys. Rev. B 47, 10891 (1993).
[10] E. Schwegler and M. Challacombe, J. Chem. Phys. 105, 2726 (1996).
[11] W. Yang, Phys. Rev. B 56, 9294 (1997).
[12] J. M. Millam and G. E. Scuseria, J. Chem. Phys. 106, 5569 (1997).
[13] A. H. R. Palser and D. E. Manolopoulos, Phys. Rev. B 58, 12704 (1998).
[14] S. Goedecker, Rev. Mod. Phys. 71, 1055 (1999).
[15] D. A. Mazziotti, J. Chem. Phys. 115, 8305 (2001).
[16] A. M. Niklasson, Phys. Rev. B 68, 233104 (2003).
[17] J. Kussmann, M. Beer, and C. Ochsenfeld, Wiley Interdisciplinary Reviews: Computational Molecular Science 1, 335 (2009).
[18] L. Vandenberghe and S. Boyd, SIAM Review 38, 49 (1996).
[19] S. Burer and R. D. Monteiro, Math. Program., Ser. A 103, 427 (2005).
[20] D. A. Mazziotti, Phys. Rev. Lett. 93, 213001 (2004).
[21] F. Jensen, Introduction to Computational Chemistry, 2nd ed. (Wiley, New York, 2007).
[22] D. A. Mazziotti, ed., Reduced-Density-Matrix Mechanics: With Application to Many-electron Atoms and Molecules, Advances in Chemical Physics, Vol. 134 (Wiley, New York, 2007).
[23] A. J. Coleman and V. I. Yukalov, Reduced Density Matrices: Coulson’s Challenge (Springer-Verlag, New York, 2000).
[24] A. J. Coleman, Rev. Mod. Phys. 35, 668 (1963).
[25] J. E. Harriman, Phys. Rev. A 17, 1249 (1978).
[26] D. A. Mazziotti, Phys. Rev. Lett. 108, 263002 (2012).
[27] E. H. Lieb, Phys. Rev. Lett. 46, 457 (1981).
[28] J. Dattorro, Convex Optimization and Euclidean Distance Geometry (Meboo, Palo Alto, 2013) Chap. 4, pp. 308–333.
[29] T. H. Dunning, Jr., J. Chem. Phys. 90, 1007 (1989).
[30] G. D. Purvis III and R. J. Bartlett, J. Chem. Phys. 76, 1910 (1982).
[31] R. J. Bartlett and M. Musial, Rev. Mod. Phys. 79, 291 (2007).
[32] P. Piecuch, S. A. Kucharski, K. Kowalski, and M. Musial, Comp. Phys. Comm. 149, 71 (2002).
[33] G. Fataki, Math. Oper. Res. 23, 339 (1998).
[34] A. Barvinok, Discrete Comput. Geom. 13, 189 (1995).
[35] J. P. Finley, R. K. Chaudhuri, and K. F. Freed, J. Chem. Phys. 103, 4990 (1995).
[36] A. M. Sand and D. A. Mazzotti, Comp. Theor. Chem. 1003, 44 (2013).
[37] J. Čížek and J. Paldus, J. Chem. Phys. 47, 3976 (1967).
[38] R. Seeger and J. A. Pople, J. Chem. Phys. 66, 3045 (1977).
[39] P. Piecuch, S. A. Kucharski, and K. Kowalski, Chem. Phys. Lett. 344, 176 (2001).
[40] D. A. Mazziotti, Phys. Rev. Lett. 101, 253002 (2008); Phys. Rev. A 81, 062515 (2010).
[41] W. D. Laidig, P. Saxe, and R. J. Bartlett, J. Chem. Phys. 86, 887 (1987).
[42] M. Nakata, M. Ehara, and H. Nakatsuji, J. Chem. Phys. 116, 5432 (2002).
[43] D. A. Mazziotti, Phys. Rev. A 76, 052502 (2007).
[44] S. Veeraraghavan and D. A. Mazziotti, J. Chem. Phys. (submitted).