PHYSICAL REVIEW A **75**, 022505 (2007)

Anti-Hermitian part of the contracted Schrödinger equation for the direct calculation of two-electron reduced density matrices

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(Received 15 September 2006; published 8 February 2007)

A recent advance in the theory of the contracted Schrödinger equation (CSE), in which only the anti-Hermitian part of the equation is solved, permits the direct determination of ground-state two-electron reduced density matrices (2-RDM's) that yield 95%–100% of the correlation energy of atoms and molecules [D. A. Mazziotti, Phys. Rev. Lett. **97**, 143002 (2006)]. Here we discuss in detail the anti-Hermitian contracted Schrödinger equation (ACSE) and its comparison to the CSE with regard to cumulant reconstruction of RDM's, the role of Nakatsuji's theorem, and the structure of the wave function. The ACSE is also formulated in the Heisenberg representation and related to canonical diagonalization. The solution of the ACSE is illustrated with a variety of molecules including H_2O, CH_2, NH_4^+, HF, and N_2, and potential energy and dipole-moment surfaces are computed for boron hydride in a polarized double-ζ basis set. The computed 2-RDM's very closely satisfy known N-representability conditions.

DOI: 10.1103/PhysRevA.75.022505 PACS number(s): 31.10.+z, 31.25.−v

I. INTRODUCTION

Because electrons are indistinguishable with pairwise interactions, both energies and properties of electronic quantum systems can be computed by the contraction (or integration) of the many-electron density matrix onto the space of two electrons, known as the *two-electron reduced density matrix* (2-RDM) [1,2]. In 1951 Coleman considered at a conference at Chalk River whether the energy could be variationally optimized as a functional of only the 2-RDM rather than the N-electron wave function [1–3], and in 1955 Mayer proposed a 2-RDM approach to electronic structure calculations with an illustrative computation of a quantum gas [4]. Coleman [3], Mayer [4], Tredgold [5], Coulson [6], and others [7,8] soon realized, however, that a realistic variational calculation could not be performed without imposing nontrivial and at-the-time unknown constraints upon the 2-RDM to ensure that it is representable by an N-particle wave function. In a 1963 paper by Coleman these constraints became known as *N-representability conditions* [3]. Despite the challenge of N-representability, which for many years stymied 2-RDM calculations, two complementary approaches for the direct calculation of the 2-RDM have recently emerged: (i) the iterative solution of the contracted Schrödinger equation on the two-particle space [9–34] and (ii) the variational calculation of the ground-state energy as a 2-RDM functional constrained by N-representability conditions [33,35–56].

Contraction (or integration) of the N-electron Schrödinger equation onto the space of two particles yields the *contracted Schrödinger equation* (CSE) [9–34,57,58]. By itself the CSE cannot be directly solved for the 2-RDM because the equation depends upon not only the 2-RDM but also the 3- and 4-RDM's. In 1993 Colmenero and Valdemoro proposed removing the indeterminacy of the CSE by building (or reconstructing) the 3- and 4-RDM's as approximate functionals the 2-RDM [9–11]. Nakatsuji and Yasuda [13,14] and Mazziotti [15–17,19,23] employed Green's function theory and cumulant theory, respectively, to improve the 3- and 4-RDM reconstruction from the 2-RDM. Mazziotti [15] utilized early work by Rosina [59] to demonstrate that there is a one-to-one mapping between the ground-state 2-RDM and each of the higher RDM's, and Nakatsuji [15,58] showed that, if the RDM's are N-representable, there is a one-to-one mapping between the solutions of the CSE and the Schrödinger equation. Calculations with the CSE were performed on a variety of atoms and molecules [11,13,25,26] as well as spin systems [15–17,23].

The solution of the CSE provided the first direct calculation of the 2-RDM without the wave function, and it motivated the development of variational 2-RDM methods using positivity constraints. Despite its success the CSE method does have some limitations: (i) the reconstruction of the 3-RDM requires all second-order corrections to obtain an energy correct through second order [13,19], and (ii) the 2-RDM often must be adjusted during the solution to satisfy known N-representability conditions [25,31]. Recently, an approach to the CSE has been proposed and implemented which removes these limitations by solving only the anti-Hermitian part of the CSE [34].

In this paper we develop in detail a methodology for solving the *anti-Hermitian contracted Schrödinger equation* (ACSE). This includes reconstructing the 3-RDM in the ACSE from the 2-RDM by cumulant theory and developing a system of differential equations which uses infinitesimal unitary transformations to solve the ACSE for the 2-RDM. Three different reconstructions of the 3-RDM are implemented: the cumulant expansion in terms of the 2-RDM [15–17,19,23] as well as the corrected cumulant expansions of Nakatsuji and Yasuda [13] and Mazziotti [19,23]. In the ACSE each of these reconstructions includes all third-order and many high-order correlation contributions to the energy.

Using either the ACSE or CSE in lieu of the Schrödinger equation, it is shown in Sec. II E, imposes a *special structure on the N-particle wave function* [29,62]. The CSE (or ACSE) ansatz for the wave function consists of a series of two-body

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exponential (or unitary) transformations applied to a reference wave function. The use of two-body unitary transformations (and, hence, the structure of the ACSE wave function) in the solution of the ACSE keeps the 2-RDM N-representable to the accuracy of the 3-RDM reconstruction. From the one-to-one mapping between the CSE and Schrödinger equation, known as Nakatsuji's theorem [15,58], it follows that the CSE ansatz for the wave function is exact for all quantum systems with only pairwise interactions [29]. We discuss whether Nakatsuji's theorem can be extended to the ACSE.

In the final theoretical section the solution of the ACSE is formulated in the *Heisenberg representation*. In this representation the optimization of the ground-state energy and the ACSE occurs by two-body unitary transformations of the Hamiltonian with respect to an invariant reference wave function. Solution of the ACSE in the Heisenberg picture has connections with canonical diagonalization [63–67]. Two important limitations of the Heisenberg approach to the ACSE are that (i) the method produces a ground-state energy but not a 2-RDM from which other properties can be readily computed, and (ii) an operator formulation of the 3-RDM cumulant reconstruction can be implemented, but the second-order corrections of Nakatsuji and Yasuda [13] or Mazziotti [19] cannot be included without generating complicated Hamiltonians with many-particle interactions.

Application of the ACSE in the Schrödinger representation is made to a variety of molecules including H_2O, CH_2, NH_4^+, HF, and N_2 as well as the dissociation of BH in a polarized double-ζ basis set. For BH both potential energy and dipole-moment curves are computed with the ACSE and compared to several wave function methods. Correlation energies are obtained here within 2% of the full configuration interaction, and the computed 2-RDM's very closely satisfy important N-representability conditions.

II. ANTI-HERMITIAN CONTRACTED SCHRÖDINGER EQUATION

The anti-Hermitian contracted Schrödinger equation is derived from the contracted Schrödinger equation. Because the ACSE depends on both the 2- and 3-RDM's, cumulant reconstruction of the 3-RDM from the 2-RDM [16,17] is introduced in Sec. II B with corrections by Nakatsuji and Yasuda [13] and Mazziotti [19]. With the 3-RDM reconstruction an autonomous system of differential equations is derived for solving the ACSE for the ground-state energy and 2-RDM. In Sec. II D the N-particle wave function implicit in the 2-RDM from the solution of either the CSE or ACSE is shown to have a special structure. Finally, the ACSE is developed in the Heisenberg representation.

A. Anti-Hermitian part of the CSE

Contraction of the Schrödinger equation onto the space of two particles yields the contracted Schrödinger equation [9–34]

$$\langle\Psi|a_i^\dagger a_j^\dagger a_l a_k \hat{H}|\Psi\rangle = 2E\,{}^2D^{i,j}_{k,l}, \tag{1}$$

where the indices denote spin orbitals, $a_i^\dagger$ and a_i are the second-quantized creation and annihilation operators, the 2-RDM is

$${}^2D^{i,j}_{k,l} = \frac{1}{2}\langle\Psi|a_i^\dagger a_j^\dagger a_l a_k|\Psi\rangle, \tag{2}$$

and the Hamiltonian operator $\hat{H}$ for quantum systems with pairwise interactions is

$$\hat{H} = \sum_{p,s} {}^1K^p_s a_p^\dagger a_s + \sum_{p,q,s,t} {}^2V^{p,q}_{s,t} a_p^\dagger a_q^\dagger a_t a_s. \tag{3}$$

The reduced matrices ${}^1K$ and ${}^2V$ represent a partitioning of the Hamiltonian into one- and two-particle parts. By rearranging the second-quantized operators in Eq. (1) and using the second-quantized definitions of RDM's,

$${}^pD^{i,j,\ldots,m}_{q,s,\ldots,v} = \frac{1}{p!}\langle\Psi|a_i^\dagger a_j^\dagger \cdots a_m^\dagger a_v \cdots a_s a_q|\Psi\rangle, \tag{4}$$

we can express the CSE in terms of the 2-, 3-, and 4-RDM's [10,12,15,26].

The CSE can be written as a sum of Hermitian and anti-Hermitian parts:

$$\langle\Psi|\{a_i^\dagger a_j^\dagger a_l a_k,(\hat{H}-E)\}|\Psi\rangle + \langle\Psi|[a_i^\dagger a_j^\dagger a_l a_k,(\hat{H}-E)]|\Psi\rangle = 0, \tag{5}$$

where the brackets [and { denote the commutator and anticommutator, respectively. The CSE is satisfied if and only if both Hermitian and anti-Hermitian parts vanish. Therefore, the anti-Hermitian CSE, also known as the Brillouin condition [24,28], is

$$\langle\Psi|[a_i^\dagger a_j^\dagger a_l a_k,\hat{H}]|\Psi\rangle = 0. \tag{6}$$

The significance of this condition, as will be explained later in Eqs. (29)–(36), is that it enforces the stationarity of the energy with respect to a set of unitary transformations of the wave function. Rearranging the second-quantized operators and using the definition of the 2- and 3-RDM's, we can write the ACSE in terms of the 2- and 3-RDM's only:

$$\begin{aligned}
&\sum_s {}^1K^k_s\,{}^2D^{i,j}_{s,l} - \sum_s {}^1K^l_s\,{}^2D^{i,j}_{s,k} + \sum_p {}^1K^p_j\,{}^2D^{p,i}_{k,l} - \sum_p {}^1K^p_i\,{}^2D^{p,j}_{k,l}\\
&\quad + 6\sum_{p,s,t} {}^2V^{p,k}_{s,t}\,{}^3D^{i,j,p}_{s,t,l} - 6\sum_{p,s,t} {}^2V^{p,l}_{s,t}\,{}^3D^{i,j,p}_{s,t,k}\\
&\quad + 6\sum_{p,q,s} {}^2V^{p,q}_{s,j}\,{}^3D^{p,q,i}_{k,l,s} - 6\sum_{p,q,s} {}^2V^{p,q}_{s,i}\,{}^3D^{p,q,j}_{k,l,s} + 2\sum_{s,t} {}^2V^{k,l}_{s,t}\,{}^2D^{i,j}_{s,t}\\
&\quad + 2\sum_{p,q} {}^2V^{p,q}_{j,i}\,{}^2D^{p,q}_{k,l} = 0.
\end{aligned} \tag{7}$$

Explicit expressions for the CSE in terms of 2-, 3-, and 4-RDM's can be found in Refs. [11,12,15,26]. From these expressions it can be readily shown that the terms with the 4-RDM contribute only to the Hermitian part of the CSE and, hence, cancel upon evaluation of the ACSE. Furthermore, by a similar cancelation, the 3-RDM in the ACSE appears only in terms with the perturbative part ${}^2V$ of the Hamiltonian. After approximation of the 3-RDM in terms of the 2-RDM, as will be discussed in the next section, this difference is responsible for the improved accuracy of the ground-state energy and 2-RDM from solving the ACSE rather than the CSE.

B. Cumulant reconstruction of the 3-RDM

Because the ACSE depends upon both the 2- and 3-RDM's, the 3-RDM must be approximated as a functional of the 2-RDM. As with the CSE method, the 3-RDM can be reconstructed from the 2-RDM by its *cumulant expansion* [16,17,19,21–23,28]

$$ {}^3D^{i,j,k}_{q,s,t} = {}^1D^i_q \wedge {}^1D^j_s \wedge {}^1D^k_t + 3\,{}^2\Delta^{i,j}_{q,s} \wedge {}^1D^k_t + {}^3\Delta^{i,j,k}_{q,s,t}, \qquad (8) $$

where

$$ {}^2\Delta^{i,j}_{k,l} = {}^2D^{i,j}_{k,l} - {}^1D^i_k \wedge {}^1D^j_l \qquad (9) $$

and the operator $\wedge$ denotes the antisymmetric tensor product known as the Grassmann wedge product [15,60,61]. The wedge product of two matrices can be evaluated by summing the distinct products arising from all antisymmetric permutations of the upper and lower indices of the two matrices and dividing the result by the total number of distinct products—for example,

$$ {}^1D^i_k \wedge {}^1D^j_l = \frac{1}{2}\left({}^1D^i_k\,{}^1D^j_l - {}^1D^i_l\,{}^1D^j_k\right). \qquad (10) $$

The cumulant (or connected) part ${}^p\Delta$ of a p-RDM vanishes unless all p particles are statistically dependent. Hence, the cumulant RDM's scale linearly with the number N of particles in the system.

Neglecting the cumulant 3-RDM

$$ {}^3\Delta^{i,j,k}_{q,s,t} = 0 \qquad (11) $$

yields a first-order reconstruction of the 3-RDM from the 1- and 2-RDM's, which we call Valdemoro's (V) reconstruction [9]. Some important second-order contributions can be included by approximating the cumulant 3-RDM. Such approximations have been introduced by Nakatsuji and Yasuda [13] and Mazziotti [19,23], which we will denote as NY and M. The NY reconstruction for ${}^3\Delta$ is

$$ {}^3\Delta^{i,j,k}_{q,s,t} \approx \frac{1}{6}\sum_l s_l \hat{A}\left({}^2\Delta^{i,l}_{q,s}\,{}^2\Delta^{j,k}_{l,t}\right), \qquad (12) $$

where s_l equals 1 if l is occupied in the Hartree-Fock reference and -1 if l is not occupied and the operator $\hat{A}$ performs all distinct antisymmetric permutations of the indices excluding the summation index l. In a natural-orbital basis set the M reconstruction is

$$ n^{i,j,k}_{q,s,t}\,{}^3\Delta^{i,j,k}_{q,s,t} \approx -\frac{1}{6}\sum_l \hat{A}\left({}^2\Delta^{i,l}_{q,s}\,{}^2\Delta^{j,k}_{l,t}\right), \qquad (13) $$

where

$$ n^{i,j,k}_{q,s,t} = {}^1D^i_i + {}^1D^j_j + {}^1D^k_k + {}^1D^q_q + {}^1D^s_s + {}^1D^t_t - 3. \qquad (14) $$

Each of the reconstructions contains many contributions from higher orders of perturbation theory via the 1- and 2-RDM's and, thus, may be described as highly *renormalized*. The CSE requires a second-order correction of the 3-RDM functional to generate second-order 2-RDM's and energies, but the ACSE can produce second-order 2-RDM's and third-order energies from only a first-order reconstruction of the 3-RDM.

C. Cumulant (or connected) structure of the ACSE

Cumulant theory offers a systematic approach to reconstructing the 3- and 4-RDM's from the 2-RDM, but it also provides insight into the structure of both the CSE and ACSE. We begin by defining the *connected* (or cumulant) part of the CSE (or ACSE) to be the part which scales linearly with N. Products of cumulant RDM's in the CSE (or ACSE) can scale linearly if and only if they share (or are connected by) the indices of one- or two-particle matrices ${}^1K$ and ${}^2V$ that scale linearly with N [2]. Consider, for example, the following term M^i_j in the 1,3-CSE:

$$ M^i_j = \sum_{i,j,k,l} {}^2\Delta^{i,p}_{r,s}\,{}^2V^{p,q}_{r,s}\,{}^1D^q_j, \qquad (15) $$

in which both the 1-RDM ${}^1D$ and the cumulant 2-RDM ${}^2\Delta$ share (or are connected by) the indices of ${}^2V^{p,q}_{r,s}$. To understand why this connected term scales linearly with N, we evaluate it in a basis set of localized orbitals for which each of the matrices, the potential, the 1-RDM, and the cumulant 2-RDM, is explicitly local. In such a basis set, because the 1-RDM and the cumulant 2-RDM share the indices of the potential, the term M^i_j will be nonzero if and only if the indices i and j refer to orbitals that are sufficiently close in coordinate space to couple through the potential. The required proximity of orbitals i and j causes the information in the matrix M (or the number of nonzero elements in a local basis set) to scale linearly rather than quadratically with N. In fact, the sharing of the summation indices by all terms in the product (its connectivity) is not only sufficient but necessary for the matrix M to scale linearly with N. Since the product of cumulant RDM's and potentials is invariant under unitary orbital transformations [30], this term is connected in any one-particle basis set. We can denote the sum of the connected terms in the CSE and Schrödinger equation contracted onto the 1-particle space (1,3-CSE) as

$$ {}^2C^{i,j}_{k,l} = \frac{1}{2}\langle\psi|a_i^\dagger a_j^\dagger a_l a_k(\hat{H}-E)|\psi\rangle_C \qquad (16) $$

and

$$ {}^1C^i_k = \langle\psi|a_i^\dagger a_k(\hat{H}-E)|\psi\rangle_C, \qquad (17) $$

respectively.

The CSE has the following structure in terms of its connected parts ${}^1C$ and ${}^2C$ and the 1- and 2-RDM's:

$$ E\,{}^2D^{i,j}_{k,l} + 2\,{}^1D^i_k \wedge {}^1C^j_l + {}^2C^{i,j}_{k,l} = E\,{}^2D^{i,j}_{k,l}. \qquad (18) $$

For any choice of the 2-RDM the first unconnected term on the left-hand side of the CSE precisely cancels with the right-hand side. This part of the CSE, therefore, does not contain any information about the 2-RDM, and the CSE is satisfied if and only if

$$ 2\,{}^1D^i_k \wedge {}^1C^j_l + {}^2C^{i,j}_{k,l} = 0. \qquad (19) $$

Similarly, the 1,3-CSE can be written in terms of its connected part ${}^2C$ and the 1-RDM as

$$ E\,{}^1D^i_k + {}^1C^i_k = E\,{}^1D^i_k \qquad (20) $$

or upon simplification

$$ {}^1C^i_k = 0. \tag{21} $$

The CSE and 1,3-CSE in Eqs. (19) and (21) are satisfied if and only if the connected 1,3-CSE and the connected CSE vanish:

$$ {}^1C^i_k = 0, \tag{22} $$

$$ {}^2C^{i,j}_{k,l} = 0. \tag{23} $$

The connected structure of the CSE has been explored by Yasuda [18] and Mazziotti [2] using Grassmann algebra, Kutzelnigg and Mukherjee [24] using a cumulant version of second-quantized operators, and Herbert and Harriman [27] using a diagrammatic technique.

The anti-Hermitian part of the CSE has the following structure in terms of the connected CSE parts:

$$ 2\,{}^1D^i_k \wedge ({}^1C^j_l - {}^1C^l_j) + {}^2C^{i,j}_{k,l} - {}^2C^{k,l}_{i,j} = 0, \tag{24} $$

where for notational convenience we assume that the 1-RDM and the matrices ${}^1C$ and ${}^2C$ are real. Similarly, the anti-Hermitian part of the 1,3-CSE, known as the 1,2-ACSE, can be written as

$$ {}^1C^j_l - {}^1C^l_j = 0. \tag{25} $$

The ACSE and 1,2-ACSE in Eqs. (24) and (25) are satisfied if and only if the anti-Hermitian parts of the connected 1,3-CSE and the connected CSE vanish:

$$ {}^1C^j_l - {}^1C^l_j = 0, \tag{26} $$

$$ {}^2C^{i,j}_{k,l} - {}^2C^{k,l}_{i,j} = 0. \tag{27} $$

Although evaluation of the matrices ${}^1C$ and ${}^2C$ requires the 3- and 4-RDM's, respectively, their anti-Hermitian parts can be evaluated with only the 2- and 3-RDM's, respectively, because terms involving the highest RDM's cancel.

D. Differential equations for solving the ACSE

A system of differential equations for solving the ACSE for the ground-state energy and its 2-RDM can be developed by examining a sequence of infinitesimal unitary transformations of an initial wave function $\Psi(0)$. We order the unitary transformations applied to the wave function $\Psi(0)$ by a continuous timelike variable λ. The initial wave function can be a Slater determinant from a Hartree-Fock calculation or a linear combination of Slater determinants from a correlated calculation. While we develop the equations with the wave function, the final equations will be expressible in terms of the 2-RDM only.

After an infinitesimal transformation over the interval ϵ the energy at $\lambda+\epsilon$ is

$$ \begin{aligned} E(\lambda+\epsilon) &= \langle \Psi(\lambda) | e^{-\epsilon S(\lambda)} \hat{H} e^{\epsilon S(\lambda)} | \Psi(\lambda) \rangle \\ &= E(\lambda) + \epsilon \langle \Psi(\lambda) | [\hat{H}, \hat{S}(\lambda)] | \Psi(\lambda) \rangle + O(\epsilon^2), \end{aligned} \tag{28} $$

where the unitary transformation is represented by the exponential of an anti-Hermitian operator $\hat{S}$. In the limit that $\epsilon \rightarrow 0$ this equation becomes

$$ \frac{dE}{d\lambda} = \langle \Psi(\lambda) | [\hat{H}, \hat{S}(\lambda)] | \Psi(\lambda) \rangle. \tag{29} $$

If the Hamiltonian is replaced with the two-particle reduced density operator, we obtain an analogous equation for the change in the 2-RDM with λ:

$$ \frac{d\,{}^2D^{i,j}_{k,l}}{d\lambda} = \langle \Psi(\lambda) | [a^\dagger_i a^\dagger_j a_l a_k, \hat{S}(\lambda)] | \Psi(\lambda) \rangle. \tag{30} $$

Restricting the operator $\hat{S}(\lambda)$ to contain no more than two-particle interactions means that variational degrees of freedom of $\hat{S}(\lambda)$ are representable by one- and two-particle matrices ${}^1S(\lambda)$ and ${}^2S(\lambda)$:

$$ \hat{S}(\lambda) = \sum_{p,s} {}^1S^p_s(\lambda) a^\dagger_p a_s + \sum_{p,q,s,t} {}^2S^{p,q}_{s,t}(\lambda) a^\dagger_p a^\dagger_q a_t a_s. \tag{31} $$

At each λ we select the elements of the one- and two-particle matrices, ${}^1S^p_s(\lambda)$ and ${}^2S^{p,q}_{s,t}(\lambda)$, to minimize the energy along its gradient with respect to these matrix elements:

$$ {}^1S^p_s(\lambda) = -\frac{1}{\epsilon} \frac{\partial E(\lambda+\epsilon)}{\partial({}^1S^p_s(\lambda))}, \tag{32} $$

$$ {}^2S^{p,q}_{r,s}(\lambda) = -\frac{1}{\epsilon} \frac{\partial E(\lambda+\epsilon)}{\partial({}^2S^{p,q}_{s,t}(\lambda))}. \tag{33} $$

If the two-particle matrix ${}^2S(\lambda)$ is restricted to scale linearly with N, then

$$ {}^2S^{p,q}_{r,s}(\lambda) = -\left[\frac{1}{\epsilon} \frac{\partial E(\lambda+\epsilon)}{\partial({}^2S^{p,q}_{s,t}(\lambda))} \right]_C \tag{34} $$

or

$$ {}^1S^p_s(\lambda) = \langle \Psi(\lambda) | [a^\dagger_p a_s, \hat{H}] | \Psi(\lambda) \rangle, \tag{35} $$

$$ {}^2S^{p,q}_{s,t}(\lambda) = \langle \Psi(\lambda) | [a^\dagger_p a^\dagger_q a_t a_s, \hat{H}] | \Psi(\lambda) \rangle_C, \tag{36} $$

where the subscript C on the right side of Eqs. (34) and (36), as in the previous section, indicates the connected part of the equation. The restriction of ${}^2S(\lambda)$ is accomplished by selecting only the connected parts of the energy gradient. Equations (29)–(36) can be evaluated with only the 2- and 3-RDM's where the right sides of Eqs. (35) and (36) are the residuals of the 1,2-ACSE and the connected ACSE and the right side of Eq. (30) is the residual of the ACSE with $\hat{H}$ replaced by the anti-Hermitian $\hat{S}(\lambda)$. The differential equations produce energy and 2-RDM trajectories in λ that minimize the energy until the ACSE is satisfied. In practice, since the reconstruction of the 3-RDM is approximate, trajectories in λ are continued until either (i) the energy or (ii) the least-squares error of the ACSE or the 1,3-CSE increases rather than decreases. Because the error of the 1,3-CSE usually increases before either the energy or the error of the ACSE, the algorithm in principle solves both the ACSE and the 1,3-CSE for the 2-RDM.

E. Structure of the wave function

For a quantum system with only pairwise interactions the solution of the CSE (or ACSE) rather than the N-particle Schrödinger equation implies a special structure for the N-particle wave function [29,62]. Consider the unnormalized trial N-particle wave functions from a series of infinitesimal exponential transformations,

$$|\Psi(\lambda+\epsilon)\rangle = \exp[\epsilon\hat{S}(\lambda)]|\Psi(\lambda)\rangle, \tag{37}$$

where the $\hat{S}(\lambda)$ operator has only two-particle interactions

$$\hat{S}(\lambda) = \sum_{p,q,s,t} {}^2S^{p,q}_{s,t}(\lambda) a^{\dagger}_p a^{\dagger}_q a_t a_s, \tag{38}$$

but the two-particle reduced matrix ${}^2S$ is completely general (not necessarily Hermitian or anti-Hermitian). At $\lambda=0$ the trial wave function $\Psi(0)$ can be assumed to be a Slater determinant of N orbitals. At each value of λ the elements of the two-particle reduced matrix ${}^2S$ are selected to minimize the energy along its gradient with respect to ${}^2S$. This produces a trajectory of trial energies $E(\lambda)$ which, by the variational principle, is nonincreasing. We can extend this trajectory until the wave function at a final $\lambda(=\lambda_f)$ equals the wave function at $\lambda(=\lambda_f+\epsilon)$ and the variational improvement in the energy terminates.

At $|\Psi(\lambda_f+\epsilon)\rangle$ the *normalized* expression for the energy is

$$E(\lambda_f+\epsilon)\langle\Psi(\lambda_f+\epsilon)|\Psi(\lambda_f+\epsilon)\rangle = \langle\Psi(\lambda_f+\epsilon)|\hat{H}|\Psi(\lambda_f+\epsilon)\rangle. \tag{39}$$

If we assume that the wave function is real, differentiating Eq. (39) with respect to the elements of the two-particle reduced matrix ${}^2S(\lambda_f)$, dividing by ϵ, and taking the limit to the energy minimum ${}^2S(\lambda_f)\to 0$ yields

$$\lim_{{}^2S(\lambda_f)\to 0}\left\langle \frac{1}{\epsilon}\frac{\partial\Psi(\lambda_f+\epsilon)}{\partial({}^2S^{p,q}_{s,t}(\lambda_f))}\middle|\hat{H}-E(\lambda_f+\epsilon)\middle|\Psi(\lambda_f+\epsilon)\right\rangle = 0. \tag{40}$$

Because

$$\lim_{{}^2S(\lambda_f)\to 0}\frac{1}{\epsilon}\frac{\partial\Psi(\lambda_f+\epsilon)}{\partial({}^2S^{p,q}_{s,t}(\lambda_f))} = a^{\dagger}_p a^{\dagger}_q a_t a_s, \tag{41}$$

evaluation of the derivative and limit in Eq. (40) yields

$$\langle\Psi(\lambda_f)|a^{\dagger}_p a^{\dagger}_q a_t a_s[\hat{H}-E(\lambda_f)]|\Psi(\lambda_f)\rangle = 0. \tag{42}$$

Equation (42) is the CSE in Eq. (1), and hence, for the trial wave function $|\Psi(\lambda)\rangle$ the variational minimization conditions in Eq. (40) are equivalent to the CSE.

Is the trial wave function defined by a *series of two-body exponential transformations* in Eq. (37) an exact variational ansatz for any quantum system with two-body interactions? The answer is "yes." For quantum systems with only pairwise interactions an N-particle wave function satisfies the CSE if and only if it satisfies the Schrödinger equation [15,58]. Therefore, as shown in Ref. [29], the trial wave function $|\Psi(\lambda_f)\rangle$ satisfies not only the CSE but also the N-particle Schrödinger equation, and by the variational principle it must be the exact ground-state wave function [29].

If the $\hat{S}(\lambda)$ is restricted to be anti-Hermitian as in differential equations of the previous section, then

$$\lim_{{}^2S(\lambda_f)\to 0}\frac{1}{\epsilon}\frac{\partial\Psi(\lambda_f+\epsilon)}{\partial({}^2S^{p,q}_{s,t}(\lambda_f))} = a^{\dagger}_p a^{\dagger}_q a_t a_s - a^{\dagger}_s a^{\dagger}_t a_q a_p, \tag{43}$$

and Eq. (40) simplifies to

$$\langle\Psi(\lambda_f)|a^{\dagger}_p a^{\dagger}_q a_t a_s - a^{\dagger}_s a^{\dagger}_t a_q a_p[\hat{H}-E(\lambda_f)]|\Psi(\lambda_f)\rangle = 0. \tag{44}$$

If we assume that the wave function is real and use Hermiticity, Eq. (44) becomes

$$\langle\Psi(\lambda_f)|[a^{\dagger}_p a^{\dagger}_q a_t a_s,\hat{H}]|\Psi(\lambda_f)\rangle = 0, \tag{45}$$

which is the ACSE in Eq. (6). Hence, the variational minimization conditions in Eq. (40) are equivalent to the ACSE for the trial wave function $|\Psi(\lambda)\rangle$. The equivalence establishes a deep connection between the class of variational wave functions obtainable by two-body *unitary* transformations [unitary when $\hat{S}(\lambda)$ is restricted to be anti-Hermitian] and the solution of the ACSE. Variational minimization of the energy by a series of two-body unitary transformations always leads to a solution of the ACSE. In the previous section we utilized this connection in designing a system of differential equations for solving the ACSE approximately where the two-body unitary transformations help to preserve the N-representability of the 2-RDM to the level of accuracy present in the 3-RDM reconstruction.

Is the trial wave function defined by *a series of two-body unitary transformations* in Eq. (37) an exact variational ansatz for any quantum system with two-body interactions? A sufficient condition for the answer to be "yes" would be that the ACSE like the CSE implies the N-particle Schrödinger equation. Nakatsuji's proof for the CSE also applies to the Hermitian part of the CSE [15] but not necessarily to the anti-Hermitian part of the CSE. Unpublished calculations indicate that the two-body unitary transformations provide a highly accurate but not exact variational ansatz [68]. In practical molecular calculations, however, the accuracy of the ACSE appears to be limited by the approximate reconstruction of the 3-RDM rather than any approximation in the two-body unitary transformations.

F. Heisenberg representation of the ACSE

The solution of the ACSE can also be formulated in the Heisenberg representation where the Hamiltonian rather than the wave function changes. In Sec. II D the ACSE is solved via a system of differential equations that change the 2-RDM (or wave function) along a timelike variable λ that orders a series of infinitesimal unitary transformations. Rather than evolving the 2-RDM (or wave function) as in Eqs. (29) and (30), we can define unitary transformations to evolve the Hamiltonian operator

$$\hat{H}(\lambda+\epsilon) = e^{-\epsilon S(\lambda)}\hat{H}(\lambda)e^{\epsilon S(\lambda)} = \hat{H}(\lambda) + \epsilon[\hat{H},\hat{S}(\lambda)] + O(\epsilon^2), \tag{46}$$

where the initial operator $\hat{H}(0)$ is the Hamiltonian whose ground-state wave function is to be calculated. In the limit that $\epsilon \to 0$ this equation becomes

$$\frac{dH}{d\lambda} = [\hat{H}(\lambda),\hat{S}(\lambda)]. \tag{47}$$

The energy as a function of λ is computed in the Heisenberg representation by taking the expectation value of the λ-dependent Hamiltonian with respect to the initial, invariant wave function $\Psi(0)$:

$$E(\lambda) = \langle\Psi(0)|\hat{H}(\lambda)|\Psi(0)\rangle, \tag{48}$$

where the initial wave function can be an uncorrelated Slater determinant or a correlated linear combination of Slater determinants. The ground-state energy of the initial Hamiltonian $\hat{H}(0)$ can be computed by selecting $\hat{S}(\lambda)$ at each λ to minimize the energy. At the energy minimum the initial wave function $\Psi(0)$ is an eigenfunction of $H(\lambda_f)$ with an energy equal to the ground-state energy of the original Hamiltonian $H(0)$.

The satisfaction of the Heisenberg formulation of the ACSE at λ_f,

$$\langle\Psi(0)|[a^\dagger_p a^\dagger_q a_t a_s, \hat{H}(\lambda_f)]|\Psi(0)\rangle = 0, \tag{49}$$

is equivalent to the stationarity of the energy with respect to all unitary transformations where the anti-Hermitian operators $\hat{S}(\lambda)$ are restricted to two-body interactions as in Eq. (31). Even with this restriction on $\hat{S}(\lambda)$ and an initial Hamiltonian $H(0)$ with at most two-body interactions, however, the change $dH(0)/d\lambda$ contains two- and three-body interactions. Nevertheless, the Hamiltonian can be restricted to two-body interactions for all λ by approximating the three-body interactions in each change of the Hamiltonian operator by two-body interactions. Two possibilities for the approximation are (i) to neglect the three-body terms and (ii) to approximate the three-body terms by an operator version of the 3-RDM cumulant expansion in Sec. II B. The latter approximation permits a solution to the Heisenberg ACSE that is similar to the solution of the ACSE in Sec. II D.

The cumulant approximation of the three-body interactions can be readily expressed in second quantization. A p-body interaction in this notation is the sum of products of p creation operators with p annihilation operators. Each product of three creation and three annihilation operators, known as a three-particle reduced density operator (3-RDO),

$${}^3\hat{D}^{i,j,k}_{q,s,t} = \frac{1}{6}a^\dagger_i a^\dagger_j a^\dagger_k a_t a_s a_q, \tag{50}$$

has the following cumulant expansion [16,17,19,21–23,28]:

$${}^3\hat{D}^{i,j,k}_{q,s,t} \approx {}^1\hat{D}^i_q \wedge {}^1D^j_s \wedge {}^1D^k_t + 3\,{}^2\hat{\Delta}^{i,j}_{q,s} \wedge {}^1D^k_t, \tag{51}$$

where the 1-RDO is

$${}^1\hat{D}^i_k = a^\dagger_i a_k, \tag{52}$$

the 2-RDO is

$${}^2\hat{D}^{i,j}_{k,l} = \frac{1}{2}a^\dagger_i a^\dagger_j a_l a_k, \tag{53}$$

and the cumulant (or connected) 2-RDO is

$${}^2\hat{\Delta}^{i,j}_{k,l} = {}^2\hat{D}^{i,j}_{k,l} - {}^1D^i_k \wedge {}^1\hat{D}^j_l. \tag{54}$$

The expectation value of the approximate 3-RDO in Eq. (51) yields the 3-RDM cumulant expansion in Eq. (8) with the cumulant 3-RDM neglected. In the Heisenberg representation this approximation produces Hamiltonians with only two-body interactions at all values of λ. The solution of the Heisenberg ACSE with this approximation is similar to using Valdemoro's 3-RDM reconstruction in the solution of the ACSE in Sec. II D.

The Heisenberg ACSE method can be completed by choosing the one- and two-particle matrices ${}^1S(\lambda)$ and ${}^2S(\lambda)$ in Eq. (31) for $\hat{S}(\lambda)$. These matrices can be selected in a variety of ways including the minimization at each λ of either (i) the energy or (ii) the error in the Heisenberg ACSE until a variational minimum is achieved at λ_f. As in Sec. II D we suggest that these matrices be chosen to minimize the energy along its gradient with respect to these matrices:

$${}^1S^p_s(\lambda) = \langle\Psi(0)|[a^\dagger_p a_s, \hat{H}(\lambda)]|\Psi(0)\rangle, \tag{55}$$

$${}^2S^{p,q}_{s,t}(\lambda) = \langle\Psi(0)|[a^\dagger_p a^\dagger_q a_t a_s, \hat{H}(\lambda)]|\Psi(0)\rangle_C, \tag{56}$$

where the subscript C on the right side of Eq. (56) indicates the connected part of the equation. Importantly, Eqs. (55) and (56) differ from Eqs. (35) and (36) by (i) containing a λ-dependent Hamiltonian and (ii) evaluating expectation values with respect to the initial wave function $\Psi(0)$. The right sides of Eqs. (55) and (56) are the residuals of the 1,2-ACSE and the connected ACSE evaluated with respect to the wave function $\Psi(0)$. If the Hamiltonian $\hat{H}(\lambda)$ contains no more than two-particle interactions, these equations involve both the 2-RDM and 3-RDM where the 3-RDM can be approximated as a 2-RDM functional by the cumulant expansion in Eq. (8). Integrating Eq. (47) with these equations evolves the Hamiltonian until at λ_f the Heisenberg ACSE vanishes.

The use of a series of unitary transformations to remove correlation (or precondition) Hamiltonians in quantum field theory before the use of perturbative or renormalization-group methods was independently studied in the early 1990s by Glazek and Wilson [63] and Weniger [64]. These methods, called the flow equations [65], continuous unitary transformations, or canonical diagonalization [66], differ from the ACSE in (i) their truncation of the three-body interactions and (ii) their selection of the $\hat{S}$ operators for the unitary transformations. Canonical diagonalization has recently been applied to molecular electronic structure by White [66] and Yanai and Chan [67]. In the calculating the change of the Hamiltonian Yanai and Chan [67] apply the 3-RDM cumulant expansion [16,17,19,21–23,28] from the CSE literature [9–34] to approximate the three-body interactions, although

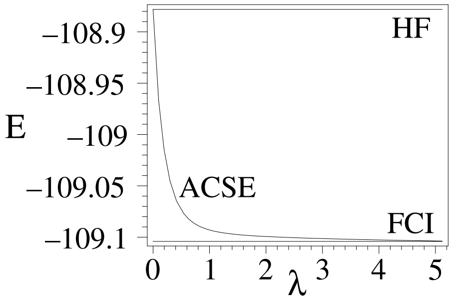

FIG. 1. For N_2 the ACSE energy converges to 0.3 mH above the FCI energy.

they select the unitary transformations by a different strategy from the one suggested for the Heisenberg ACSE.

The Heisenberg ACSE method (or the canonical diagonalization method) differs from the solution of the ACSE in Sec. II D in two significant respects: (i) the Heisenberg ACSE (or canonical diagonalization) does not produce a 2-RDM, and (ii) the second-order corrections to the 3-RDM of Nakatsuji and Yasuda and Mazziotti cannot be included in the 3-RDO approximation without producing complicated many-body interactions in the Hamiltonian for $\lambda > 0$. Knowledge of the 2-RDM is very useful for obtaining properties other than the ground-state energy as well as checking the *N*-representability of the solution. In the Heisenberg representation the loss of *N*-representability becomes hidden in the approximation to the transformed Hamiltonian. Furthermore, as shown in the applications, the second-order correction of the 3-RDM significantly improves the accuracy of energies and properties when the initial 2-RDM is determined from a Hartree-Fock calculation.

III. APPLICATIONS

In this section we examine the accuracy of the ACSE method in the Schrödinger representation with calculations on a variety of molecules. The energy and 2-RDM of the ACSE are optimized by integrating the equations in Eqs. (29)–(36) with an extrapolated Euler's method. At $\lambda = 0$ the energy and 2-RDM are initialized to their values from a Hartree-Fock (mean-field) calculation. The evolution of the energy and the 2-RDM with λ continues until (i) the energy or (ii) the least-squares error of either the ACSE or the 1,3-CSE ceases to decrease. In most molecular calculations the error of the 1,3-CSE increases before either the energy or the error of the ACSE and, hence, provides the stopping criterion. Figure 1 displays the energy as a function of λ for N_2 in a valence double-ζ basis set where the 3-RDM in Eqs. (29)–(36) is reconstructed with the M functional. The ACSE recovers 99.9% of the correlation energy by converging to 0.3 millihartree above the full-configuration-interaction (FCI) energy.

For ten molecules Table I presents the errors in the singlet ground-state correlation energies from the ACSE with the V, NY, and M 3-RDM reconstructions and the CSE with NY 3-RDM reconstruction, as well as several wave function methods, including Hartree-Fock (HF), second-order many-body perturbation theory (MP2), coupled-cluster singles-doubles (CCSD), and FCI. Calculations are performed at equilibrium geometries [69] in a valence double-ζ basis set [70], electron integrals are computed with GAMESS [71], and except for lithium the occupation numbers of core orbitals are set to unity (frozen). The ACSE methods are not variational, but the V reconstruction of the 3-RDM consistently yields a lower bound. Supplementing the V reconstruction with either the NY or M cumulant 3-RDM greatly improves

TABLE I. The ground-state energies from the ACSE with V, NY, and M 3-RDM reconstructions are compared with the energies from the CSE with NY 3-RDM reconstruction as well as several wave function methods, including Hartree-Fock (HF), second-order many-body perturbation theory (MP2), coupled-cluster singles-doubles (CCSD), and full configuration interaction (FCI), for molecules in valence double-ζ basis sets.

		Energy error (mhartree)						
		Wave function methods			CSE methods			
	FCI				CSE[a]	ACSE		
System	Energy (H)	HF	MP2	CCSD	NY	V	NY	M
BeH_2	−15.800201	39.962	11.818	0.419	3.796	−2.409	0.034	−0.194
CH_2	−38.945153	85.557	23.454	1.753		−1.785	−0.433	0.162
H_2O	−76.141146	132.000	7.964	1.658	5.940	−3.172	1.199	0.988
NH_3	−56.303459	127.751	14.654	1.773	7.665	−2.835	1.052	0.942
NH_4^+	−56.655413	127.682	16.937	1.503		−2.803	−0.147	−0.217
CH_4	−40.299343	113.886	21.153	1.564	8.541	−2.287	0.336	0.180
HF	−100.145846	123.952	3.669	1.592	31.880	−0.825	2.137	2.064
Li_2	−14.895376	27.310	11.582	0.034		−2.065	−0.282	−0.107
N_2	−109.104089	225.950	−2.310	8.311	34.118	−12.640	−0.297	0.321
HCN	−93.054260	225.025	6.607	8.735		−16.736	3.439	4.287

[a] The CSE energies are obtained from Ref. [26].

TABLE II. The 2-RDM's from solving the ACSE very nearly satisfy known *N*-representability conditions which require the eigenvalues of three forms of the 2-RDM matrix, known as ^2D, ^2Q, and ^2G, to be non-negative. In general, the NY and M reconstructions of the 3-RDM decrease the absolute value of the maximum negative eigenvalue by an order of magnitude.

		Lowest eigenvalue of 2-RDM matrices		
System	Method	^2D	^2Q	^2G
HF	V	−1.89[−4]	−1.53[−4]	−3.33[−4]
	NY	−1.05[−7]	+8.77[−6]	−3.46[−8]
	M	−4.57[−6]	+1.94[−5]	−3.61[−6]
CH_2	V	−1.57[−3]	−6.61[−4]	−9.27[−4]
	NY	−2.60[−4]	+1.07[−4]	−1.55[−4]
	M	−4.48[−4]	−5.13[−5]	−3.06[−4]

the energy of each molecule with a two-orders-of-magnitude improvement being observed for the triple-bonded N_2. For each of the singlet states computed the expectation of the total electron spin operator $\hat{S}^2$ with respect to the 2-RDM is zero. As shown in Table I, the ACSE with NY or M reconstruction produces 98%–100.5% of the correlation energy which significantly improves upon the 71%–96% recovered by the CSE with NY or M reconstruction [25]. The difference between the ACSE and the MP2 energies highlights that each of the ACSE methods contains all second- and third-order as well as higher-order correlation effects. Except for HF and Li_2 the energies of the ACSE with NY or M reconstruction are more accurate than those of the CCSD method.

Solutions of the CSE for the 2-RDM often require that the 2-RDM be adjusted at each iteration to satisfy important *N*-representability conditions in a process called *purification* [25,31]. The solution of the ACSE, however, naturally maintains the *N*-representability of the 2-RDM within the accuracy of the 3-RDM reconstruction. Necessary *N*-representability conditions require keeping the eigenvalues of three different forms of the 2-RDM, known as the ^2D, ^2Q, and ^2G matrices, non-negative [45]. The ^2D, ^2Q, and ^2G matrices restrict the probability distributions for two particles, two holes (where a hole is the absence of a particle), and one particle and one hole to be non-negative. For HF and CH_2, Table II shows the lowest eigenvalues of these matrices, normalized to $N(N-1)$, $(r-N)(r-N-1)$, and $N(r-N+1)$ where r is the rank of the spin-orbital basis set. The largest negative eigenvalue for each of these matrices is three to eight orders of magnitude smaller than the largest positive eigenvalue which is near unity. The NY and M 3-RDM reconstructions decrease the absolute value of the most negative eigenvalue from the V reconstruction by one and two orders of magnitude for CH_2 and HF, respectively. Similar results are obtained for the other molecules in Table I.

The energy of the BH molecule as a function of internuclear separation is given in Table III where the energy is computed by the ACSE with V, NY, and M reconstructions, coupled-cluster with single and double excitations (CCSD) and a perturbative correction for triple excitations [CCSD(T)], and full configuration interaction (FCI). Calculations are performed in a correlation consistent polarized valence double-ζ (cc-pVDZ) basis set with the core orbital of boron frozen. Although the ACSE with V reconstruction yields energies at least 10 mhartree below the FCI at all geometries, it is more than twice as accurate as MP2. The NY and M corrections improve the ACSE energies by at least an order of magnitude. Between $R=1$ Å and $R=1.8$ Å the maxi-

TABLE III. The energy of the BH molecule as a function of internuclear separation is presented in a correlation consistent polarized valence double-ζ (cc-pVDZ) basis set with the core orbital of boron frozen from each of the following methods: ACSE with V, NY, and M reconstructions, coupled-cluster with single and double excitations (CCSD) and a perturbative correction for triple excitations [CCSD(T)], and full configuration interaction (FCI). Between $R=1$ Å and $R=1.8$ Å the maximum energy errors of CCSD, CCSD(T), and the ACSE with NY reconstruction are 2.68, 0.66, and 0.65 mhartree, respectively.

		Energy error (mH)						
		Wave function methods				Anti-Hermitian CSE methods		
R	FCI energy (hartree)	HF	MP2	CCSD	CCSD(T)	V	M	NY
0.850	−25.091663	86.182	27.966	1.658	0.457	−11.869	1.743	−0.727
0.900	−25.130088	86.388	28.013	1.667	0.457	−11.455	1.633	−0.686
1.000	−25.179459	87.069	28.216	1.699	0.461	−11.172	1.442	−0.644
1.100	−25.204337	88.074	28.567	1.748	0.468	−11.396	1.191	−0.487
1.200	−25.214144	89.340	28.688	1.811	0.477	−11.520	1.089	−0.431
1.256	−25.215324	90.138	29.414	1.853	0.483	−11.650	1.034	−0.361
1.300	−25.214580	90.674	29.590	1.761	0.360	−11.877	0.868	−0.468
1.400	−25.209739	92.430	30.525	1.990	0.508	−12.149	0.940	−0.311
1.600	−25.191851	96.162	32.640	2.267	0.566	−14.456	1.087	−0.374
1.800	−25.170969	100.680	35.520	2.679	0.655	−16.380	1.590	−0.512
2.000	−25.151292	106.219	39.264	3.250	0.754	−20.457	2.903	−1.612
2.200	−25.134391	112.973	43.922	3.990	0.815	−26.337	5.470	−4.797

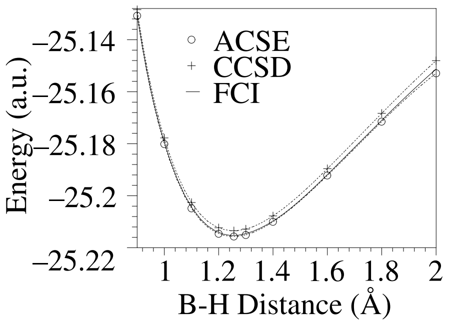

FIG. 2. The potential energy curve of BH from the ACSE with NY reconstruction is compared with the curves from CCSD and FCI. In the equilibrium region the ACSE energies are an order of magnitude more accurate than those from CCSD. Calculations are performed in a correlation consistent polarized valence double-ζ (cc-pVDZ) basis set with the core orbital of boron frozen.

mum energy errors of CCSD, CCSD(T), and the ACSE with NY reconstruction are 2.68, 0.66, and 0.65 mhartree, respectively. Figure 2 compares the potential energy surfaces from the ACSE(NY) with CCSD and FCI. In the equilibrium region the ACSE energies are an order of magnitude more accurate than those from CCSD.

Dipole moments and 1-RDM's for BH at equilibrium and stretched geometries are examined in Table IV from calculations with Hartree-Fock (HF), coupled-cluster with single and double excitations (CCSD), the ACSE with second-order NY reconstruction, and full configuration interaction (FCI). In comparison to FCI the dipole moments from both the ACSE and CCSD are at least an order of magnitude more accurate than the mean-field moments from Hartree-Fock calculations. Before the equilibrium geometry $R=1.256$ the dipole moments from the ACSE are more accurate by as much as an order of magnitude than those from CCSD while after equilibrium the dipole moments from CCSD are more accurate. The ACSE dipole moment is an upper bound to the FCI dipole moment at all computed geometries (theoretically, it can be an upper or lower bound); the CCSD dipole moment is also an upper bound except at $R=2.2$ Å. Figure 3 shows the dipole-moment surface for BH as a function of the internuclear distance R for HF, CCSD, the ACSE with NY reconstruction, and FCI. All three approximate methods predict the change in sign of the dipole moment between $R=1.6$ Å and $R=1.8$ Å, but both the CCSD and the ACSE surfaces deviate significantly at long bond lengths from the Hartree-Fock surface which remains linear. The ACSE dipole moment at $R=1.256$ Å of 0.477 283 a.u. is consistent with the experimental value of 0.500 ± 0.083 a.u.

The accuracy of the 1-RDM's at different BH bond lengths is also shown in Table IV for the HF, CCSD, and ACSE(NY) methods. The error in the 1-RDM is measured by the l_2 norm of the error matrix formed from the difference of the FCI and approximate 1-RDM's where the l_2 norm of a matrix is defined as the absolute value of the eigenvalue with the largest magnitude. For evaluating the size of the 1-RDM errors, we also report the l_2 norm of each FCI 1-RDM which,

TABLE IV. Dipole moments and 1-RDM's for BH at equilibrium and stretched geometries are examined from calculations with the ACSE with second-order NY reconstruction, Hartree-Fock (HF), coupled-cluster with single and double excitations (CCSD), and full configuration interaction (FCI). In comparison to FCI the dipole moments from both the ACSE and CCSD are at least an order of magnitude more accurate than the mean-field moments from HF. The error in the 1-RDM is measured by the l_2 norm of the error matrix formed from the difference of the FCI and approximate 1-RDM's where the l_2 norm of a matrix is defined as the absolute value of the eigenvalue with the largest magnitude. The errors in the ACSE 1-RDM's are three orders of magnitude smaller than the largest eigenvalues of the FCI 1-RDM. Calculations are performed in a correlation consistent polarized valence double-ζ (cc-pVDZ) basis set with the core orbital of boron frozen. [−1] denotes $\times10^{-1}$.

	Dipole moment (μ)				1-RDM (^1D)			
		$\mu_{\text{app}}-\mu_{\text{FCI}}$				$\lVert{}^1D_{\text{app}}-{}^1D_{\text{FCI}}\rVert$		
R	μ_{FCI}	HF	CCSD	ACSE(NY)	$\lVert{}^1D_{\text{FCI}}\rVert$	HF	CCSD	ACSE(NY)
0.850	0.825666	1.69[−1]	1.04[−2]	7.44[−4]	0.984340	8.12[−2]	5.98[−3]	1.46[−3]
0.900	0.794993	1.70[−1]	1.04[−2]	1.58[−3]	0.983927	8.08[−2]	5.85[−3]	1.54[−3]
1.000	0.720643	1.70[−1]	1.04[−2]	3.18[−3]	0.982882	8.00[−2]	5.61[−3]	1.76[−3]
1.100	0.631052	1.70[−1]	1.04[−2]	5.83[−3]	0.981514	7.94[−2]	5.38[−3]	2.17[−3]
1.200	0.466767	1.66[−1]	1.06[−2]	8.33[−3]	0.979764	7.89[−2]	5.16[−3]	2.48[−3]
1.256	0.528658	1.62[−1]	1.08[−2]	1.05[−2]	0.978592	7.87[−2]	5.05[−3]	2.80[−3]
1.300	0.416314	1.59[−1]	1.09[−2]	1.20[−2]	0.977560	7.86[−2]	4.98[−3]	2.99[−3]
1.400	0.297367	1.48[−1]	1.14[−2]	1.56[−2]	0.974804	7.83[−2]	4.83[−3]	3.43[−3]
1.600	0.055419	1.05[−1]	1.22[−2]	2.19[−2]	0.967260	7.81[−2]	4.78[−3]	4.18[−3]
1.800	−0.163620	2.04[−2]	1.17[−2]	2.58[−2]	0.957048	7.98[−2]	5.50[−3]	4.72[−3]
2.000	−0.329482	−1.19[−1]	7.83[−3]	1.44[−2]	0.947106	9.34[−2]	7.73[−3]	2.98[−3]
2.200	−0.423725	−3.22[−1]	−4.06[−4]	3.96[−3]	0.941649	1.25[−1]	1.15[−2]	7.14[−3]

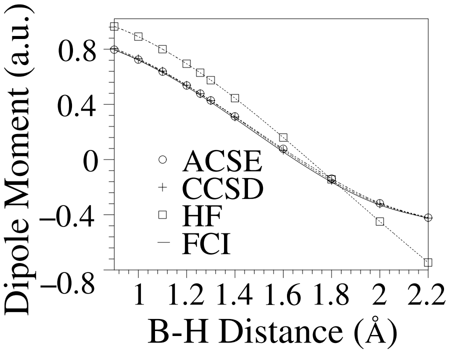

FIG. 3. The dipole-moment surface for BH is shown as a function of the internuclear distance R for HF, CCSD, the ACSE with NY reconstruction, and FCI. All three approximate methods predict the change in sign of the dipole moment between $R=1.6$ Å and $R=1.8$ Å, but both the CCSD and ACSE surfaces deviate significantly at long bond lengths from the Hartree-Fock surface which remains linear. Calculations are performed in a correlation consistent polarized valence double-ζ (cc-pVDZ) basis set with the core orbital of boron frozen.

in general, is approximately unity. The errors in the ACSE 1-RDM's are three orders of magnitude smaller than the largest FCI eigenvalues and two orders of magnitude smaller than the errors in the HF 1-RDM's. At all computed geometries the 1-RDM errors from the ACSE(NY) are smaller than the 1-RDM errors from CCSD with the greatest difference occurring at short bond lengths.

IV. DISCUSSION AND CONCLUSIONS

The ACSE significantly enhances the accuracy of the CSE method for the direct determination of the ground-state 2-RDM and its energy without the many-electron wave function. The ACSE is solved by propagating a system of initial-value differential equations whose solution optimizes the 2-RDM with a series of infinitesimal unitary transformations. Unlike the CSE, the ACSE translates the first-order reconstruction of the 3-RDM (V) [9,16,17] into molecular energies that contain all third-order and many higher-order correlation effects. The accuracy and N-representability of the energies and 2-RDM's can be further enhanced with the second-order reconstructions of Nakatsuji-Yasuda [13] and Mazziotti [19]. The ACSE with these second-order reconstructions produces energies that are competitive with the best wave function methods of comparable computational efficiency.

The solution of the CSE (or ACSE) rather than the Schrödinger equation implies a special structure for the N-particle wave function. Every N-particle wave function solution of the CSE (or ACSE) can be written as a product of *two-body* exponential (or unitary) transformations applied to any reference wave function such as a Slater determinant. To the degree that the reconstruction of the 3-RDM and the N-representability of the 2-RDM remain sufficiently accurate, the structure of the ACSE wave function is present in the differential equations for solving the ACSE in Sec. II D even though only the 2-RDM is explicitly computed. Because there is a one-to-one mapping between the solutions of the CSE and Schrödinger equation for any quantum system with only pairwise interactions (Nakatsuji's theorem) [15,58], it follows that the wave function ansatz from the CSE is sufficiently flexible to include the ground-state wave functions for all such systems. Does the more restrictive wave function ansatz from the ACSE also include all of these wave functions? We have shown that the ACSE ansatz is sufficiently flexible if Nakatsuji's theorem is extendable to the ACSE. Even though preliminary results indicate that Nakatsuji's theorem is not extendable [68], in practice the ability of two-body unitary transformations to reach the exact ground-state wave function may be unimportant because in the solution of the ACSE any error from this limitation appears to be small relative to the error from 3-RDM reconstruction.

The solution of the ACSE has also been formulated in the Heisenberg representation with connections made to canonical diagonalization. Because the unitary transformations are applied to the Hamiltonian in the Heisenberg representation, the Heisenberg ACSE contains a variable Hamiltonian and a fixed wave function. The ACSE method, implemented in this paper, differs significantly from its Heisenberg formulation in that (i) the ACSE in the Schrödinger representation can produce both an energy and a 2-RDM and (ii) the reconstruction of the 3-RDM can include second-order corrections by Nakatsuji and Yasuda [13,14] and Mazziotti [19,23]. Calculation of the 2-RDM is important for not only computing properties but also checking the N-representability of the ACSE solution, and the second-order reconstruction functionals for the 3-RDM are important for obtaining highly accurate energies and 2-RDM's. Canonical diagonalization [63–67] can be interpreted as a solution of the ACSE in the Heisenberg representation. The ACSE method further differs from canonical diagonalization plus cumulant theory in the choice of the unitary transformations. The solution of the ACSE also has connections to the effective Hamiltonian and unitary coupled-cluster methods [72,73] in which single unitary transformations are applied to the Hamiltonian and the wave function respectively.

The direct determination of the 2-RDM by the ACSE has an important relationship with the variational calculation of the 2-RDM [33,35–56]. A 2-RDM that is representable by an ensemble of N-particle states is said to be *ensemble* N-representable while a 2-RDM that is representable by a single N-particle state is said to be *pure* N-representable. The variational method, within the accuracy of the N-representability conditions, constrains the 2-RDM to be ensemble N-representable while the ACSE, within the accuracy of 3-RDM reconstruction, constrains the 2-RDM to be pure N-representable. The ACSE and variational methods, therefore, may be viewed as implementing complementary approaches, based on pure and ensemble N-representability perspectives, respectively, for the direct calculation of the 2-RDM.

Future research will (i) optimize the present implementation of the ACSE and (ii) explore the use of different initial 2-RDM's to initiate the solution of the ACSE. In an optimized form, the ACSE scales in floating-point operations as r^6 and in memory as r^4 where r is the number of spatial orbitals. While the calculations in this paper employ an initial 2-RDM from the Hartree-Fock method, the ACSE method permits the selection of any initial 2-RDM, including a 2-RDM from a multireference self-consistent-field calculation. With this flexibility the ACSE method can be adapted to treat strong multireference correlation effects that are often important at nonequilibrium geometries. Building upon the CSE, the ACSE yields 95%–100% of the correlation energy and accurate 2-RDM's. Both the accuracy and the *N*-representability of the 2-RDM's are controlled by the reconstruction without any additional purification. The ACSE in conjunction with the variational 2-RDM method opens a new frontier for the accurate calculation of many-electron quantum mechanics.

ACKNOWLEDGMENTS

The author expresses his appreciation to Dudley Herschbach, Herschel Rabitz, John Coleman, and Alexander Mazziotti for their support and encouragement. The author thanks the NSF, the Henry-Camille Dreyfus Foundation, the Alfred P. Sloan Foundation, and the David-Lucile Packard Foundation for their support.

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