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Direct calculation of excited-state electronic energies and two-electron reduced density matrices from the anti-Hermitian contracted Schrödinger equation

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Direct calculation of the ground-state two-electron reduced density matrix (2-RDM) and its energy has recently been achieved for many-electron atoms and molecules by solving the anti-Hermitian part of the contracted Schrödinger equation (ACSE) [D. A. Mazziotti, Phys. Rev. Lett. **97**, 143002 (2006)]. In this paper the ACSE method is extended to computing the 2-RDMs and energies of excited states without the many-electron wave function. The contracted Schrödinger equation (CSE) is an important ingredient for excited-state 2-RDM methods because it is a stationary-state condition for both ground and excited states. We develop the theoretical framework for the ACSE as a stationary-state condition through its connections to the CSE and the Schrödinger equation. As in previous ground-state calculations, the indeterminacy of the ACSE is removed by reconstructing its 3-RDM as a functional of its 2-RDM through a cumulant theory for RDMs [D. A. Mazziotti, Chem. Phys. Lett. **289**, 419 (1998)]. We calculate the initial 2-RDM from a multiconfiguration self-consistent-field calculation that includes multireference electron correlation, which can be especially important for excited states. The excited-state ACSE method is applied to computing absolute excited-state energies and vertical excitation energies of the molecules HF, H_2O, and N_2 as well as ground and excited potential-energy curves of HF. Comparisons are made to traditional multireference methods as well as full configuration interaction. Computed excited-state 2-RDMs nearly satisfy necessary *N*-representability conditions.

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I. INTRODUCTION

Knowledge of the two-electron reduced density matrix (2-RDM) of a given quantum-mechanical state determines its energy and fundamental electronic properties [1]. In the mid-1950s Joseph Mayer and others [2] considered the possibility of computing the ground-state 2-RDM without the many-electron wave function. Simple calculations showed that the two-electron density matrix must be constrained by nontrivial conditions to ensure that it can be produced from integration of an *N*-electron density matrix [3–5]. Coleman called these constraints *N-representability conditions* [4], and the search for such conditions became known as the *N*-representability problem [6–8]. After 50 years two complementary approaches to the direct calculation of the 2-RDM have emerged: (i) variational minimization of the ground-state energy as a functional of the 2-RDM [9–15] that is constrained by necessary *N*-representability conditions known as positivity conditions [1,5] and (ii) solution of the contracted Schrödinger equation [16–32] or its anti-Hermitian part [33–42] for the 2-RDM. These recent methods have focused largely on ground-state electronic energies and 2-RDMs. In the present paper we extend the latter class of methods for the direct calculation of excited-state energies and 2-RDMs.

Excited electronic states of atoms and molecules are critically important throughout physics and chemistry including the study of light-activated or nonadiabatic chemical reactions from fluorescence to photochemistry. Despite their fundamental importance, nonetheless, the calculation of excited states has received much less attention than the calculation of ground states. In part this is because excited states can be much more difficult to compute. Variationally, the excited states must be constrained to be orthogonal to the lower lying states. Moreover, excited states are generally much further from a mean-field solution than their ground-state counterparts. Multiple determinants often contribute significantly to the excited-state wave function in its zeroth order of perturbation theory, which is usually called *multireference correlation* [43,44]. Many ground-state methods, such as density functional theory and coupled cluster theory, use the response of the ground state to a weak time-dependent electric field to generate energy spectra [45,46]; a related response method has been developed for the variational 2-RDM method [47,48]. With these response methods, however, it can be difficult to extract the properties and 2-RDMs of the excited states. The solution of the Schrödinger equation in a finite basis set, known as full configuration interaction (FCI), produces both ground- and excited-state wave functions, but such solutions scale exponentially in computational cost with respect to the number *N* of electrons. Multireference methods, which build correlation upon more-than-one reference determinant, are probably the most effective techniques for excited states, especially for states with significant correlation [43]. Multireference configuration interaction with single-and-double excitations, however, can be rather costly while multireference second-order perturbation theory (MRPT2) may not be sufficiently accurate.

Integration (or contraction in a matrix formulation) of the density-matrix version of the Schrödinger equation over all electrons save two produces the *contracted Schrödinger equation* (CSE) [16–32]. The CSE was first obtained in a coordinate representation in 1976 by Cohen and Frishberg

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[49] and Nakatsuji [50]; the anti-Hermitian part of the CSE (or ACSE) was first examined by Harriman [51,52] in 1979. Neither the CSE nor the ACSE, however, can be solved for the 2-RDM because they both depend on higher-particle RDMs. In 1993 Colemenero *et al.* [16] recognized that the CSE could be solved if its higher-particle RDMs were expressed as functionals of the 2-RDM. One of the authors [22] in 1998 systematized the reconstruction of the higher RDMs from the 2-RDM by developing a cumulant theory for RDMs [22,23,25,26,28,53,54]. Applications of the CSE to computing ground-state energies and 2-RDMs of atoms and molecules were made by Colmenero and Valdemoro [18,32], Nakatsuji and Yasuda [19,20], and Mazziotti [21,30]. In 2006 ground-state energies and 2-RDMs of greater accuracy were obtained from solving the ACSE with cumulant reconstruction of the 3-RDM [33–42].

In this paper we extend the contracted Schrödinger methods to computing energies and 2-RDMs of excited states without the many-electron wave function. The CSE is an important ingredient for excited-state 2-RDM methods because it is a *stationary-state condition for both ground and excited states*. By Nakatsuji's theorem, if the RDMs in the CSE are N-representable, then for energetically nondegenerate states there is a one-to-one mapping between solutions of the Schrödinger equation and solutions of the CSE [21,50,52]. To treat excited states, we choose to solve the ACSE subset of the CSE which, although it does not appear to have a complete equivalent to Nakatsuji's theorem, has several advantages: (i) unlike the CSE, the ACSE depends upon only the 3-RDM [29,33,51] and (ii) with a first-order reconstruction of the 3-RDM by cumulant theory, it is accurate to one additional order of a renormalized perturbation theory than the CSE [29,33]. Because the ACSE does not depend upon a mean-field reference, it can be seeded with an initial 2-RDM from either a mean-field (Hartree-Fock) [33–37] or a correlated calculation [38,40,41]. In previous ground-state calculations on reactions with significant multireference correlation, such as the electrocyclic ring opening of bicyclobutane [40] and the hydrogenic sigmatropic shift in propene [41], the ACSE has been successfully initiated with 2-RDMs from multiconfiguration self-consistent-field (MCSCF) calculations whose wave functions are linear combinations of more than one determinant (or configuration). Because excited states are in general more likely to contain substantial multireference correlation than ground states, we seed the ACSE method for excited states with 2-RDMs from MCSCF calculations. After its theoretical development in Sec. II the excited-state ACSE method is applied in Sec. III to computing absolute excited-state energies and vertical excitation energies of the molecules hydrogen fluoride, water, and nitrogen as well as ground and excited potential-energy surfaces of hydrogen fluoride.

II. THEORY

After the Hermitian and anti-Hermitian parts of the CSE are obtained from the Schrödinger equation in Sec. II A, their properties as stationary-state conditions for both ground and excited states are discussed in Sec. II B. In Sec. II C we develop a system of differential equations to solve the ACSE for ground- and excited-state energies and 2-RDMs. The dependence of the ACSE and its differential equations on the 3-RDM is approximately removed through the cumulant reconstruction of the 3-RDM as a functional of the 2-RDM.

A. Hermitian and anti-Hermitian contracted Schrödinger equations

For a quantum N-electron system with Hamiltonian $\hat{H}$ the stationary-state energies E_n and wave functions Ψ_n can be computed from the time-independent Schrödinger equation

$$\hat{H}\Psi_n = E_n\Psi_n \tag{1}$$

or its density-matrix formulation

$$\hat{H}\,{}^{N}D_n = E_n\,{}^{N}D_n, \tag{2}$$

where the N-particle density matrix for the nth state is given by ${}^{N}D_n = \Psi_n\Psi_n^{*}$. The density-matrix Schrödinger equation can be divided into two separate Hermitian and anti-Hermitian equations:

$$\frac{1}{2}(\hat{H}\,{}^{N}D_n + {}^{N}D_n\hat{H}) = E_n\,{}^{N}D_n, \tag{3}$$

$$\frac{1}{2}(\hat{H}\,{}^{N}D_n - {}^{N}D_n\hat{H}) = 0. \tag{4}$$

Integration of Eqs. (2)–(4) over the spin and spatial coordinate of electrons 3 to N yields the CSE [16–32,49,50]

$$\int \hat{H}\,{}^{N}D_n d3 \ldots dN = E_n\,{}^{2}D_n \tag{5}$$

as well as the *Hermitian* contracted Schrödinger equation (HCSE) [24,51,55] and *anti-Hermitian* contracted Schrödinger equation (ACSE) [17,29,33–42,51,55] parts of the CSE:

$$\frac{1}{2}\int (\hat{H}\,{}^{N}D_n + {}^{N}D_n\hat{H}) d3 \ldots dN = E_n\,{}^{2}D_n, \tag{6}$$

$$\frac{1}{2}\int (\hat{H}\,{}^{N}D_n - {}^{N}D_n\hat{H}) d3 \ldots dN = 0. \tag{7}$$

By definition, the sum of the HCSE and the ACSE produces the CSE. If the Hamiltonian contains at most *pairwise* interactions, both the CSE and the HCSE depend on the 2-, 3-, and 4-RDMs, while the ACSE depends only on the 2- and 3-RDMs. Second-quantized formulations of the CSE and the ACSE as well as explicit spin-orbital expressions in terms of matrix elements of the reduced Hamiltonian and RDMs have been given elsewhere [1,17,21,29,33].

B. Stationary-state conditions for ground and excited states

The time-independent Schrödinger equation is the stationary-state condition for a nonrelativistic quantum-mechanical system. The density-matrix Hermitian and anti-

Hermitian Schrödinger equations in Eqs. (3) and (4) are important parts of the stationary-state condition. Taking the trace of both sides of the Hermitian Schrödinger equation yields the energy relation

$$E = \hat{\mathrm{Tr}}(\hat{H}\,{}^{N}D), \tag{8}$$

while multiplying the Hermitian Schrödinger equation by the Hamiltonian operator $\hat{H}$ before taking the trace yields the energy-squared expectation value

$$E^2 = \hat{\mathrm{Tr}}(\hat{H}^2\,{}^{N}D). \tag{9}$$

Assuming that the density-matrix is *pure* (that it can be expressed in terms of a single wave function where ${}^{N}D = |\Psi\rangle\langle\Psi|$), Eqs. (8) and (9) imply the energy dispersion relation $\langle\Phi|\Phi\rangle = 0$ with

$$|\Phi\rangle = (\hat{H} - E)|\Psi\rangle, \tag{10}$$

which is true if and only if the wave function $|\Psi\rangle$ satisfies the Schrödinger equation $|\Phi\rangle = 0$. Importantly, the anti-Hermitian Schrödinger equation can also be shown by a different mechanism to imply the Schrödinger equation. The anti-Hermitian Schrödinger equation with a pure-state density-matrix states that

$$\hat{H}|\Psi\rangle\langle\Psi| - |\Psi\rangle\langle\Psi|\hat{H} = 0. \tag{11}$$

If $|\Lambda\rangle = \hat{H}|\Psi\rangle$ and $|\Lambda\rangle \neq \alpha|\Psi\rangle$ where α is any real scalar constant, then $|\Lambda\rangle\langle\Psi|$ is non-Hermitian, which means that

$$|\Lambda\rangle\langle\Psi| - |\Psi\rangle\langle\Lambda| \neq 0, \tag{12}$$

and hence, satisfaction of the anti-Hermitian Schrödinger equation with a pure-state density matrix implies the Schrödinger equation. Therefore, either the Hermitian or the anti-Hermitian Schrödinger equations with a pure-state density matrix is equivalent to the Schrödinger equation in terms of its strength as a stationary-state condition.

A central question in treating excited states with 2-RDMs is the respective strengths of the CSE and ACSE as stationary-state conditions. Any subset or particle contraction of the N-electron Schrödinger equation will be a necessary stationary-state condition. In 1976, however, Nakatsuji proved that if the 2-, 3-, and 4-RDMs in the CSE are restricted to be pure N-representable (meaning that the RDMs correspond to a pure N-electron density matrix), then the RDMs satisfy the CSE if and only if they correspond to a wave function that satisfies the Schrödinger equation [21,50]. Whether in first [50] or second [21] quantization the proof follows from showing that the CSE implies the energy dispersion relation which, as shown above, is satisfied if and only if the Schrödinger equation is satisfied. Importantly, for quantum systems with pairwise interactions Nakatsuji's theorem shows that the CSE with appropriate N-representability conditions on the RDMs is a necessary and sufficient stationary-state condition for *both ground and excited states*.

Because the Hamiltonian is Hermitian, the Hermitian part of the CSE (HCSE) also implies the energy dispersion relation, which leads to a Nakatsuji-like theorem, and hence, for systems with pairwise interactions it is also a complete stationary-state condition for the N-representable RDMs. Because the Hermitian and anti-Hermitian parts of the Schrödinger equation are equivalent stationary-state conditions for a pure-state density matrix, one might conjecture that either the HCSE or the ACSE is equivalent to the CSE as a stationary-state condition for pure N-representable RDMs. Calculations with the Lipkin quasispin model, however, have shown that a wave function can be computed that satisfies the ACSE and yet does not exactly satisfy either the CSE, the HCSE, or the N-particle Schrödinger equation [33]. Nevertheless, the ACSE is theoretically an important subset of the CSE, and practically, the distinction between the ACSE and the CSE or HCSE may be unimportant. Calculations demonstrate that the computational error introduced from approximating the 3-RDM by 2-RDM cumulant reconstruction is generally larger than the error from approximating the stationarity of the Schrödinger equation by the ACSE.

The CSE is variationally equivalent to the stationarity of the energy of a quantum state with respect to all differential two-body transformations applied to the wave function. Consequently, the author has shown that a trial wave function $|\Psi\rangle$ formed by repeatedly applying differential two-body transformations to a reference wave function $|\Psi_0\rangle$ will minimize the energy if and only if it satisfies the CSE and the Schrödinger equation (Nakatsuji's theorem):

$$|\Psi\rangle = e^{\epsilon\hat{S}_m} \cdots e^{\epsilon\hat{S}_2} e^{\epsilon\hat{S}_1} |\Psi_0\rangle, \tag{13}$$

where $\hat{S}_m$ is the mth two-body operator and ϵ is a differentially small quantity [56]. If the reference wave function $|\Psi_0\rangle$ is chosen to have an energy below that of the first excited state with the same spin and spatial symmetry as the ground state, then the variational ansatz for the wave function in Eq. (13) is sufficiently flexible to converge to the exact ground-state wave function within a given finite-orbital basis set [56]. By constraining the $\hat{S}_m$ operators to be Hermitian, we can construct an analogous variational ansatz that implies the HCSE at its minimum. The ansatz for the wave function in Eq. (13) can also be refashioned to imply the ACSE at its variational minimum by restricting each of the two-body operators S_m to be anti-Hermitian. As is shown in the next section, this series of differential unitary transformations can be practically employed to solve the ACSE for both ground and excited states.

C. Solving the ACSE for ground and excited states

In this section, having established the ACSE as an important stationary-state condition, we develop a method for solving it for both ground and excited states. We consider a sequence of infinitesimal two-body unitary transformations of an initial wave function $\Psi(\lambda)$, which are ordered by a continuous timelike variable λ:

$$|\Psi(\lambda + \epsilon)\rangle = e^{\epsilon\hat{S}(\lambda)}|\Psi(\lambda)\rangle, \tag{14}$$

where $\hat{S}(\lambda)$ is an anti-Hermitian two-body operator. Although we develop the equations with the wave function, the final equations are exactly expressible in terms of ground- or excited-state 2- and 3-RDMs only; furthermore, the dependence on the 3-RDM is removed by its cumulant expansion in the next section.

After an infinitesimal transformation over the interval ϵ, the 2-RDM at $\lambda+\epsilon$ is

$$
{}^2D^{i,j}_{k,l}(\lambda+\epsilon) = \langle\Psi(\lambda)|e^{-\epsilon S(\lambda)}\,{}^2\hat{\Gamma}^{i,j}_{k,l}e^{\epsilon S(\lambda)}|\Psi(\lambda)\rangle = {}^2D^{i,j}_{k,l}(\lambda) + \epsilon\langle\Psi(\lambda)|[{}^2\hat{\Gamma}^{i,j}_{k,l},\hat{S}(\lambda)]|\Psi(\lambda)\rangle + O(\epsilon^2), \quad (15)
$$

or in the limit that $\epsilon\to 0$, [33–35,38]

$$
\frac{d\,{}^2D^{i,j}_{k,l}}{d\lambda} = \langle\Psi(\lambda)|[{}^2\hat{\Gamma}^{i,j}_{k,l},\hat{S}(\lambda)]|\Psi(\lambda)\rangle, \quad (16)
$$

where the operator ${}^2\hat{\Gamma}^{i,j}_{k,l}$ is the two-electron *reduced density operator* (2-RDO)

$$
{}^2\hat{\Gamma}^{i,j}_{k,l} = a^{\dagger}_i a^{\dagger}_j a_l a_k. \quad (17)
$$

If the differential equation for the 2-RDM in Eq. (16) is traced against the one- and two-electron reduced Hamiltonian matrices comprising the Hamiltonian operator [35], we obtain an analogous equation for the change in the energy with λ

$$
\frac{dE}{d\lambda} = \langle\Psi(\lambda)|[\hat{H},\hat{S}(\lambda)]|\Psi(\lambda)\rangle. \quad (18)
$$

To find a ground- or excited-state root of the ACSE from an initial guess for the RDMs, we select the two-body operator $\hat{S}(\lambda)$ to minimize the energy. Specifically, the operator $\hat{S}(\lambda)$ is expressible in terms of the matrix elements of the two-particle matrix ${}^2S(\lambda)$

$$
\hat{S}(\lambda) = \sum_{p,q,s,t} {}^2S^{p,q}_{s,t}(\lambda)\,{}^2\hat{\Gamma}^{p,q}_{s,t}. \quad (19)
$$

At each λ we select the elements of the two-particle matrix ${}^2S^{p,q}_{s,t}(\lambda)$ to minimize $dE/d\lambda$ along its gradient with respect to these matrix elements to produce

$$
{}^2S^{p,q}_{r,s}(\lambda) = \langle\Psi(\lambda)|[{}^2\hat{\Gamma}^{p,q}_{s,t},\hat{H}]|\Psi(\lambda)\rangle. \quad (20)
$$

Importantly, the left side of Eq. (20) is simply the residual of the ACSE. If the residual in the ACSE vanishes, the unitary transformations become the identity operator, and the energy and 2-RDM cease to change with λ. Hence, Eqs. (16), (18), and (20) collectively provide a system of differential equations [33–35,38] for evolving an initial 2-RDM to a final 2-RDM that solves the ACSE for either a ground or excited state.

Without additional N-representability conditions, the differential equations in Eqs. (16), (18), and (20) are indeterminate since they depend upon not only the 2-RDM but also the 3-RDM. This indeterminacy can be removed by reconstructing the 3-RDM as an functional of the 2-RDM by its *cumulant expansion* [22,23,25,26,28,54]

$$
{}^3D^{i,j,k}_{q,s,t} = {}^1D^i_q \wedge {}^1D^j_s \wedge {}^1D^k_t + 3\,{}^2\Delta^{i,j}_{q,s} \wedge {}^1D^k_t + {}^3\Delta^{i,j,k}_{q,s,t} \quad (21)
$$

where

$$
{}^2\Delta^{i,j}_{k,l} = {}^2D^{i,j}_{k,l} - {}^1D^i_k \wedge {}^1D^j_l, \quad (22)
$$

and the operator $\wedge$ denotes the antisymmetric tensor product known as the Grassmann wedge product [21,57]. As in Ref. [38], we approximate the cumulant 3-RDM as zero; calculations show that this approximation is sufficient when the 2-RDM is initialized from an MCSCF calculation. For *both ground and excited states* the first-order reconstruction of the 3-RDM in the solution of the ACSE yields 2-RDMs with all second-order as well as many higher-order correlation effects. Because the cumulant reconstruction of the 3-RDM is approximate, the resulting system of differential equations is evolved in λ until either (i) the energy or (ii) the least-squares norm of the ACSE increases.

Even though the unitary rotations are selected in Eq. (20) to minimize the energy, the system of differential equations in Eqs. (16), (18), and (20) is capable of producing energy and 2-RDM solutions of the ACSE for both ground and excited states. Because excited states correspond to local energy minima of the ACSE and the gradient in Eq. (20) leads to a *local* rather than global energy minimum, an excited-state solution can be readily obtained from a good guess for the initial 2-RDM. A guess will be good when it is closer to the minimum of the desired solution of the ACSE than to any other minimum. Such 2-RDM guesses can be generated from MCSCF calculations. Importantly, choosing an initial MCSCF 2-RDM directs the optimization of the ACSE to a desired excited state because it contains important multireference correlation effects that identify the state.

III. APPLICATIONS

After discussing some additional computational details, we apply the ACSE to computing excited-state energies of water, methylene, and nitrogen as well as their excitation energies. We also calculate potential energy curves of hydrogen fluoride for its $X\,{}^1\Sigma^+$, $B\,{}^1\Sigma^+$, ${}^1\Pi$, and ${}^1\Sigma^-$ states.

A. Computational details

For excited states we initiate the solution of the differential equations in Eqs. (16), (18), and (20) with 2-RDMs from a special MCSCF technique that is often called the complete-active-space self-consistent-field (CASSCF) method [43,44,58]. Computation of a CASSCF wave function and 2-RDM proceeds by the following four steps: (i) division of initial orbitals into four classes, frozen core orbitals that are always occupied and unchanged throughout the calculation, core orbitals that are always occupied, active orbitals that are partially occupied, and virtual orbitals that are completely unoccupied, (ii) diagonalization of the Hamiltonian in the space of the active orbitals, (iii) rotation of all orbitals by unitary transformations to lower the energy, and (iv) repetition of steps (ii) and (iii) until convergence. Therefore, the CASSCF procedure generates a wave function where the active orbitals are treated by a configuration interaction calculation while the inactive orbitals (frozen core, core, and virtual) are treated by a mean-field (Hartree-Fock) calculation. In CASSCF calculations the size of the active space is usually denoted by the notation $[X,Y]$, where X is

TABLE I. Accuracy of absolute energies for selected singlet states of water, methylene, and the nitrogen molecule. The results from the ACSE are compared with other multireference methods such as CASSCF, MRCI, MRCI+Q, and MRPT2, as well as the results from FCI.

			Energy error relative to FCI (mH)				
Molecule	State	FCI	CASSCF	MRPT2	MRCI	MRCI+Q	ACSE
H_2O	$1\,^1A_1$	−76.258208	162.75	12.93	3.92	−2.88	0.79
	$1\,^1B_1$	−75.984532	137.41	14.71	3.00	−3.21	1.92
	$1\,^1A_2$	−75.919727	158.97	12.81	4.41	−3.20	0.96
	$2\,^1A_1$	−75.895339	164.01	14.71	4.73	−8.77	2.67
	$1\,^1B_2$	−75.831492	168.87	13.55	5.79	−4.47	0.90
CH_2	$1\,^1A_1$	−39.032135	88.08	16.93	1.85	−1.59	0.33
	$1\,^1B_2$	−38.968737	92.81	11.38	2.22	−1.76	0.64
	$1\,^1A_2$	−38.821386	95.96	11.02	2.80	−1.72	−0.73
	$1\,^1B_1$	−38.748720	97.04	21.96	7.21	0.15	6.35
N_2	$^1\Sigma_g^+$	−109.276528	174.29	18.24	5.75	−2.42	5.05
	$^1\Pi_g$	−108.924305	193.19	10.43	6.97	−3.66	−5.08
	$^1\Sigma_u^-$	−108.896956	203.65	11.76	7.26	−4.52	−4.36
	$^1\Delta_u$	−108.882636	200.05	9.92	7.23	−4.07	−0.44
	$^1\Pi_u$	−108.776427	207.52	6.36	8.17	−4.94	8.51

the number of active electrons and Y is the number of active orbitals.

A second important computational detail is that we filter the two-body anti-Hermitian operator $\hat{S}(\lambda)$ governing the unitary transformations to exclude transitions that involve (i) only active orbitals or (ii) more than two virtual orbitals. As discussed elsewhere [38,40], the first exclusion prevents multireference effects in the 2-RDM from affecting the accuracy of the cumulant 3-RDM reconstruction in the ACSE. It is a reasonable approximation because after the active space is optimized in a CASSCF calculation, two-body rotations of the active orbitals account for a secondary correlation effect that is much smaller in magnitude than the correlation of the inactive spaces. The second exclusion eliminates terms that, while computationally expensive, are essentially unimportant for the accuracy of the final energies and 2-RDMs. With this second restriction the ACSE solution scales in floating-point operations as $(r_c+r_a)^2 r_v^4$, where r_c, r_a, and r_v are the numbers of core, active, and virtual orbitals, respectively. By contrast, both MRPT2 and multireference configuration interaction (MRCI) with single and double excitations have an exponential dependence on the size of the active space; even with further approximations in what is often described as a fully contracted theory the scalings of MRPT2 and MRCI with respect to the active space are r_a^8 and r_a^{10}, respectively.

B. Results

Excited-state energies and excitation energies

The ACSE method is applied to computing both singlet ground- and excited-state energies as well as excitation energies of H_2O, CH_2, and N_2. For water and the nitrogen molecule we employ the correlation-consistent polarized valence double-zeta (cc-pVDZ) basis set [59], supplemented with diffuse functions in the case of water; the geometries and additional details of the basis sets can be found in Ref. [60]. For methylene we treat the ground and excited states in the augmented cc-pVDZ basis set [61] at the experimental geometry of its $1\,^1A_1$ state for which $R_{CH}=1.107$ Å and $A_{HCH}=102.4°$ [62]. The energies from the ACSE are compared with those from the CASSCF method [58], MRPT2 [63], MRCI with single and double excitations, MRCI plus the Davidson correction (MRCI+Q) [64], and FCI. The CASSCF, MRPT2, and MRCI calculations were performed with the GAMESS electronic structure package [65], while the ACSE and FCI calculations were performed with the authors' codes. For the nitrogen, water, and methylene molecules the CASSCF, MRPT2, MRCI, and ACSE methods employ [10,8]-, [6,6]-, and [6,6]-active spaces, respectively.

The errors in the excited-state energies from the ACSE relative to FCI are compared in Table I with the errors from the multireference methods CASSCF, MRPT2, MRCI, and MRCI+Q. Among the excited-state energies for water the CASSCF, MRPT2, MRCI, MRCI+Q, and ACSE methods have maximum energy errors of 168.9, 14.7, 5.8, −8.8, and 2.7 millihartrees (mH) and minimum energy errors of 137.4, 12.8, 3.0, −2.9, and 0.8 mH. For this molecule the ACSE yields more accurate excited-state energies than the more traditional multireference methods based on perturbation theory or configuration interaction. For methylene the CASSCF, MRPT2, MRCI, MRCI+Q, and ACSE methods have maximum energy errors of 97.0, 22.0, 7.2, −1.8, and 6.4 mH and minimum energy errors of 88.1, 11.0, 1.9, 0.15, and 0.33 mH. While the MRCI+Q performs slightly better than the ACSE with respect to maximum and minimum errors when all four excited states are considered, for the lowest

TABLE II. Vertical excitation energies for selected singlet states of water, methylene, and the nitrogen molecule. The results from the ACSE are compared with other multireference methods such as CASSCF, MRCI, MRCI+Q, and MRPT2, as well as the results from FCI.

		Vertical excitation energy (mH)					
Molecule	State	FCI	CASSCF	MRPT2	MRCI	MRCI+Q	ACSE
H_2O	$1\ ^1B_1$	273.68	248.33	275.46	272.75	273.35	274.81
	$1\ ^1A_2$	338.48	334.70	338.37	338.97	338.17	338.65
	$2\ ^1A_1$	362.87	364.13	364.66	363.68	356.98	364.75
	$1\ ^1B_2$	426.72	432.83	427.34	428.58	425.13	426.82
CH_2	$1\ ^1B_2$	63.40	28.13	57.85	63.77	63.23	63.70
	$1\ ^1A_2$	210.75	218.63	204.84	211.70	210.62	209.68
	$1\ ^1B_1$	283.42	292.38	288.45	288.77	285.16	289.43
N_2	$^1\Pi_g$	352.22	371.13	344.41	353.44	350.98	342.09
	$^1\Sigma_u^-$	379.57	408.94	373.09	381.08	377.48	370.16
	$^1\Delta_u$	393.89	419.65	385.87	395.38	392.24	388.40
	$^1\Pi_u$	500.10	533.33	488.22	502.53	497.58	503.56

three states the ACSE outperforms all of the multireference methods including the MRCI+Q; furthermore, the computational cost of both MRCI and MRCI+Q is significantly more expensive than that of the ACSE. Finally, for the nitrogen molecule the CASSCF, MRPT2, MRCI, MRCI+Q, and ACSE methods have maximum energy errors of 207.5, 18.2, 8.2, −4.9, and 8.5 mH and minimum energy errors of 174.3, 6.4, 5.8, −2.4, and −0.4 mH. Interestingly, the maximum error for both the ACSE and the MRCI methods occurs for the $^1\Pi_u$ state, which in the FCI solution displays significant contributions from double excitations from the ground state in contrast to the other states that are dominated by single excitations [60]; the maximum error of 18.2 mH for MRPT2 occurs for the $^1\Sigma_g^+$ state.

As shown in Table II, the ACSE vertical excitation energies are greater in accuracy than those from CASSCF and similar in accuracy to those from MRPT2, MRCI, and MRCI+Q. The most accurate excitation energies from the ACSE are obtained for H_2O, where the maximum error relative to FCI is 1.9 mH for the $2\ ^1A_1$ state. For methylene, the errors in the vertical excitation energies for the $1\ ^1A_2$ and $1\ ^1B_2$ states, −1.1 and 0.3 mH, respectively, are more accurate than those from MRPT2, −5.1 and −5.6 mH, respectively. While the ACSE vertical excitation energy for the $2\ ^1B_1$ state is 6.0 mH above FCI, it is similar in accuracy to the 5.0 and 5.4 mH errors from MRPT2 and MRCI. For the nitrogen molecule, all post-CASSCF methods significantly improve upon the CASSCF excitation energies, and the MRCI methods yield the best agreement with FCI. The ACSE and MRPT2 methods yield excitation energies with similar accuracy, their maximum deviations relative to FCI being −10.1 mH and −11.9 mH, respectively.

C. Excited-state potential energy curves

The potential energy curves for the $X\ ^1\Sigma^+$ ground state of hydrogen fluoride and its $B\ ^1\Sigma^+$, $^1\Pi$, and $^1\Sigma^-$ excited states were computed by the ACSE as well as the CASSCF, MRPT2, MRCI, MRCI+Q, and FCI methods in the cc-pVDZ basis set [59]. For all computational methods except FCI we employed a [6,6]-active space including the occupied σ, π_x, and π_y orbitals and their corresponding antibonding orbitals. The CASSCF for the $B\ ^1\Sigma^+$ state was performed with an averaging of the $B\ ^1\Sigma^+$ and $X\ ^1\Sigma^+$ states with weights of 0.95 and 0.05. The post-CASSCF and FCI calculations correlated all ten electrons. The CASSCF, MRCI, and MRPT2 results were computed with the electronic structure package GAMESS [65], while the FCI calculations were performed with the package PSI 3.3 [66].

The ground and lowest singlet excited states of hydrogen fluoride from the ACSE are shown as a function of internuclear distance in Fig. 1. Both the $X\ ^1\Sigma^+$ ground state and the $^1\Pi$ excited state dissociate into ground-state atomic fragments, and hence, they become degenerate at long bond lengths. In contrast, the $B\ ^1\Sigma^+$ excited state dissociates into H^+ and $F^-(^1S)$ ionic fragments, and the higher-in-energy $^1\Sigma^-$ state dissociates into $H^-(^1S)$ and $F^+(^1S)$ fragments. While both of the $B\ ^1\Sigma^+$ and $^1\Sigma^-$ excited states have bound vibrational states with a potential-energy minimum around 2 Å, the $^1\Pi$ is purely repulsive. The potential-energy curves from the CASSCF, MRPT2, MRCI, and MRCI+Q methods, not shown here, are qualitatively similar to the ACSE results.

The accuracy of the electronic energies from the ACSE for the $X\ ^1\Sigma^+$ ground state and the $B\ ^1\Sigma^+$, $^1\Pi$, and $^1\Sigma^-$ excited states of hydrogen fluoride are shown at selected bond lengths in Table III. The errors in the energies from the ACSE, relative to the FCI energies, are compared to the errors from other multireference methods such as CASSCF, MRPT2, MRCI, and MRCI+Q. The ACSE results for the $X\ ^1\Sigma^+$ ground state have been reported previously [38]. For the $B\ ^1\Sigma^+$ excited state the CASSCF, MRPT2, MRCI, MRCI+Q, and ACSE methods have maximum absolute errors of 154.4, 9.7, 2.5, 7.9, and 1.3 mH; for the $^1\Pi$ excited state these methods have maximum absolute errors of 149.3,

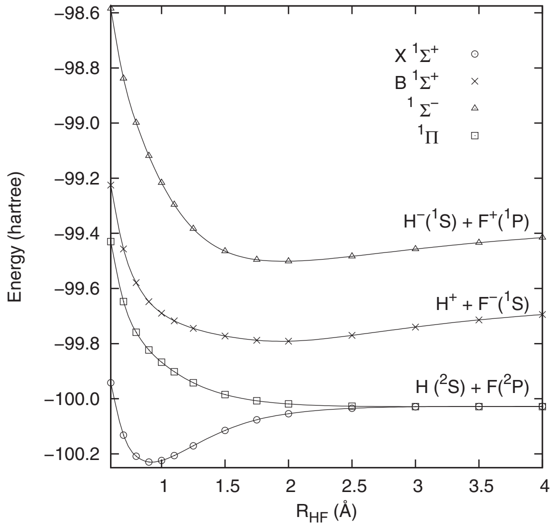

FIG. 1. Ground and lowest singlet excited states of hydrogen fluoride from the ACSE are shown as a function of internuclear distance.

12.6, 2.3, 2.1, and 1.0 mH, and finally, for the $^1\Sigma^-$ excited state these methods have maximum absolute errors of 135.0, 12.7, 3.6, 1.0, and 1.0 mH. For the excited states $B\ ^1\Sigma^+$, $^1\Pi$, and $^1\Sigma^-$ the ACSE significantly improves the nonparallelity errors [67] of 10.7, 12.9, and 12.4 from CASSCF to 2.54, 0.83, and 1.11 mH, which are similar in accuracy to those from MRPT2, MRCI, and MRCI+Q. Finally, vertical excitation energies relative to the ground state from the ACSE as well as the CASSCF, MRPT2, MRCI, MRCI+Q, and FCI methods are given in Table IV for $R_{\mathrm{HF}}=0.9$ Å and 1.75 Å. The CASSCF consistently predicts excitation energies that are 10–30 mH larger than those from FCI because the dynamic correlation has an important role of lowering the energies of the excited states relative to the ground state. The ACSE yields excitation energies that are within a few millihartrees of those from FCI, which is similar to the accuracy from MRCI and MRCI+Q.

The ground- and excited-state 2-RDMs, produced by the ACSE, maintain the N-representability of the 2-RDM within the accuracy of the 3-RDM reconstruction. Necessary N-representability constraints, known as two-positivity conditions [5,10,55], require keeping the eigenvalues of three

TABLE III. Accuracy of the electronic energies for the $X\ ^1\Sigma^+$ ground state and the $B\ ^1\Sigma^+$, $^1\Pi$, and $^1\Sigma^-$ excited states of hydrogen fluoride are shown at selected bond lengths. The errors in the energies from the ACSE, relative to the FCI energies, are compared to the errors from other multireference methods such as CASSCF, MRPT2, MRCI, and MRCI+Q.

			$E_{\mathrm{approx}}-E_{\mathrm{FCI}}$ (mH)				
State	R (Å)	FCI (H)	CASSCF	MRPT2	MRCI	MRCI+Q	ACSE
$X\ ^1\Sigma^+$	1.0	−100.22472	120.45	10.87	1.40	−0.98	0.38
	1.5	−100.11564	120.66	9.27	1.28	−1.23	0.49
	2.0	−100.05103	120.57	8.30	1.21	−1.27	−3.38
	2.5	−100.03317	120.42	8.11	1.18	−1.28	−1.59
	3.0	−100.02964	120.38	8.09	1.18	−1.28	0.36
	4.0	−100.02883	120.33	8.08	1.18	−1.28	0.94
$B\ ^1\Sigma^+$	1.0	−99.68844	143.76	7.99	2.02	−6.70	−1.26
	1.5	−99.77376	145.96	8.17	2.05	−7.86	1.28
	2.0	−99.79165	150.85	8.30	2.26	−4.82	0.32
	2.5	−99.76967	154.42	9.24	2.47	−5.02	−0.62
	3.0	−99.73895	154.17	9.69	2.45	−5.43	−0.94
	4.0	−99.69338	153.40	9.52	2.38	−5.20	−1.12
$^1\Pi$	1.0	−99.86846	149.29	12.63	2.34	−2.05	0.97
	1.5	−99.98535	140.26	11.50	1.88	−1.96	0.45
	2.0	−100.01910	137.10	11.21	1.75	−1.84	0.14
	2.5	−100.02730	136.63	11.04	1.74	−1.66	0.16
	3.0	−100.02873	136.50	11.06	1.74	−1.59	0.19
	4.0	−100.02882	136.40	11.06	1.73	−1.57	0.19
$^1\Sigma^-$	1.0	−99.21774	135.02	12.61	3.57	−1.02	1.03
	1.5	−99.46495	130.65	12.71	3.30	−0.88	0.06
	2.0	−99.50106	125.49	11.27	2.98	−0.73	−0.08
	2.5	−99.48333	123.37	10.61	2.89	−0.68	−0.06
	3.0	−99.45717	122.77	10.43	2.87	−0.67	−0.06
	4.0	−99.41538	122.61	10.37	2.86	−0.67	−0.08

TABLE IV. Vertical excitation energies relative to the ground state from the ACSE as well as the CASSCF, MRPT2, MRCI, MRCI+Q, and FCI methods are given for $R_{\mathrm{HF}}=0.9$ and 1.75 Å. The CASSCF consistently predicts excitation energies that are 10–30 mH larger than those from FCI because the dynamic correlation has an important role of lowering the energies of the excited states relative to the ground state. The ACSE, with an accuracy similar to MRCI and MRCI+Q, yields excitation energies that are within a few millihartrees of those from FCI.

		Vertical excitation energy (mH)					
R (Å)	State	FCI	CASSCF	MRPT2	MRCI	MRCI+Q	ACSE
0.9	$^1\Pi$	405.94	434.58	407.72	406.87	404.87	406.53
	$B\ ^1\Sigma^+$	583.29	603.56	580.45	583.79	577.93	582.10
	$^1\Sigma^-$	1110.01	1121.83	1110.37	1111.89	1109.94	1111.09
1.75	$^1\Pi$	67.45	84.7	70.31	68.00	66.79	68.96
	$B\ ^1\Sigma^+$	285.92	312.76	285.32	286.77	281.35	288.47
	$^1\Sigma^-$	579.38	586.25	582.68	581.25	579.85	580.60

different forms of the 2-RDM, known as the ^2D, ^2Q, and ^2G matrices, non-negative; these three matrices correspond to the probability distributions for two particles, one particle and one hole, and two holes, respectively. While the two-positivity conditions are not sufficient N-representability constraints as seen computationally in calculations by Mazziotti [1,9,10], as well as Nakata *et al.* [11,12], they are an important set of necessary constraints whose near satisfaction by 2-RDM solutions of the ACSE offers an effective measure of N-representability, particularly because the two-positivity conditions are not enforced in the solution of the ACSE [33]. For the ground and excited states of hydrogen fluoride at both 1 Å and 2 Å, Table V provides the lowest eigenvalues of these matrices, normalized to $N(N-1)$, $(r-N)(r-N-1)$, and $N(r-N+1)$, respectively, where r is the rank of the spin-orbital basis set. The most negative eigenvalues are three-to-five orders of magnitude smaller than the largest positive eigenvalues, which are on the order of unity save for the largest eigenvalue of ^2G that is on the order of N. Furthermore, for each state of hydrogen fluoride at either bond distance the expectation value of the N-electron spin operator $\hat{S}^2$, computed with respect to the ACSE 2-RDM, equals zero.

TABLE V. For the ground and excited states of hydrogen fluoride at both 1 and 2 Å the table provides the lowest eigenvalues of the ^2D, ^2Q, and ^2G matrices, normalized to $N(N-1)$, $(r-N)(r-N-1)$, and $N(r-N+1)$, respectively, where r is the rank of the spin-orbital basis set. A necessary set of N-representability constraints, known as the two-positivity conditions, requires these matrices to be positive semidefinite (that is, have nonnegative eigenvalues). The most negative eigenvalues are three-to-five orders of magnitude smaller than the largest positive eigenvalues, which are on the order of unity save for the largest eigenvalue of ^2G that is on the order of N. The number in square brackets denotes the power of 10.

		Lowest eigenvalues		
R (Å)	State	^2D	^2Q	^2G
1.0	$X\ ^1\Sigma^+$	−1.14[−4]	−2.16[−5]	−1.10[−4]
	$B\ ^1\Sigma^+$	−2.32[−3]	−2.97[−4]	−3.50[−3]
	$^1\Pi$	−1.39[−3]	−8.01[−5]	−7.98[−4]
	$^1\Sigma^-$	−1.35[−3]	−1.36[−4]	−2.28[−3]
2.0	$X\ ^1\Sigma^+$	−3.05[−3]	−5.64[−4]	−4.18[−3]
	$B\ ^1\Sigma^+$	−1.42[−3]	−1.52[−5]	−8.45[−4]
	$^1\Pi$	−1.11[−3]	−9.09[−5]	−7.71[−4]
	$^1\Sigma^-$	−1.41[−3]	−1.39[−4]	−2.19[−3]

IV. DISCUSSION AND CONCLUSIONS

The contracted Schrödinger equation (CSE) is a stationary-state condition for both ground and excited states of many-electron atoms and molecules. If the RDMs in the CSE are pure N-representable, then by Nakatsuji's theorem there is a one-to-one mapping between the RDM solutions of the CSE and the wave-function solutions of the N-electron Schrödinger equation. Consequently, for the set of N-representable 2-, 3-, and 4-RDMs the CSE is a *complete stationary-state condition* that is fully equivalent to the N-particle Schrödinger equation. The correspondence between solutions of the CSE and those of the Schrödinger equation for many-electron atoms and molecules reveals a fundamental reduction in the complexity of the N-particle Hilbert space for particles with at most pairwise interactions. For such systems the wave functions in the N-particle Hilbert space are at most functionals of the N-representable 4-RDM; by an extended Rosina's theorem, for each energetically nondegenerate state there is a one-to-one mapping between its 4-RDM and its wave function [21,24]. Therefore, the CSE has a central role in the development of 2-RDM methods for excited states. Despite the explicitness of Nakatsuji's theorem in stating that the CSE is a stationary-state condition for both ground and excited states, recent solutions of either the CSE or its anti-Hermitian part (ACSE) have focused on the calculation of the ground-state 2-RDM. In the present paper the solution of the ACSE has been theoretically and practically extended to the direct computation of excited-state energies and 2-RDMs.

Neither the CSE nor the ACSE can be solved for the 2-RDM without additional information because they also depend upon the 3-RDM and/or 4-RDM. The indeterminacy of these equations, however, can be removed by reconstructing the higher RDMs as functionals of the lowers RDMs via cumulant theory for RDMs [22,23,25,26,28,54]. The ACSE is an important subset of the CSE. While the ACSE is not necessarily a complete stationary-state condition for *N*-representable RDMs, it has two practical advantages: (i) the ACSE, unlike the CSE, only depends on the 3-RDM and (ii) setting the cumulant 3-RDM to zero within the ACSE is correct to one additional order of renormalized perturbation theory than it is within the CSE. Solution of the ACSE for *both ground and excited states* can be accomplished through the system of differential equations in Eqs. (16), (18), and (20) that evolve an initial 2-RDM by a sequence of differential unitary transformations, which minimize the energy until convergence to a final 2-RDM.

Two important issues that arise in the extension to excited states are: (i) because excited states are generally more multireferenced than ground states (meaning that they depend on more than one determinant at zeroth order of perturbation theory), the initial 2-RDM must be chosen to reflect the multiple determinants in the zeroth-order wave function, and (ii) the initial 2-RDM must be chosen to be sufficiently close to the given excited state to converge to the desired solution of the ACSE. We select initial 2-RDMs from MCSCF calculations which, in all computations performed, satisfy both criteria (i) and (ii). In practice, these two issues are interrelated. The MCSCF calculation captures the important zeroth-order multireference correlation and then the projection of this correlation in the 2-RDM acts as a strong state-identifying signature for directing the ACSE solution to the correct energy and 2-RDM. While most solutions of the CSE for the 2-RDM have focused on the ground states of quantum systems, there have been a few CSE studies of excited states. In 1998 Mazziotti [21] extended the solution of the CSE to excited states in the context of the Lipkin model, and in 2000 Nakata *et al.* [27] solved the CSE for open-shell systems as well as some atomic and molecular excited states. The latter work, however, differs from the present molecular study in that (i) the initial 2-RDM guesses were computed by the Hartree-Fock method whose single-determinant wave function limits the treatment of excited states with significant multireference correlation and (ii) the computed excited states were mainly ground states of different spin symmetries. Other notable differences include choices of: (iii) the contracted equation (CSE versus ACSE), (iv) the optimization algorithm, and (v) the basis-set size.

In this paper the ACSE method has been applied to computing the ground- and excited-state energies of H_2O, CH_2, and N_2 at their equilibrium geometries as well as the ground- and excited-state potential energy curves of hydrogen fluoride. By introducing significant dynamic correlation in the inactive spaces, the ACSE substantially lowers the energy from CASSCF. Furthermore, because the cumulant reconstruction of the ACSE includes third-order and many higher-order correlation effects in the energy, the computed absolute energies are generally much closer to FCI than second-order multireference perturbation theory (MRPT2). The results from the ACSE are similar to those from multireference configuration interaction calculations, which are computationally more expensive. The potential energy curves of the $B\ {}^1\Sigma^+$, ${}^1\Pi$, and ${}^1\Sigma^-$ excited states of hydrogen fluoride also show that the ACSE accurately predicts the excited-state energies at both equilibrium and nonequilibrium geometries. The computed 2-RDMs at all geometries are also nearly *N*-representable.

The computation of both ground and excited states by the ACSE has applicability to a broad range of problems in quantum many-particle chemistry and physics. Contracted Schrödinger theory has an important connection to another general class of many-body methods, known as flow equations or continuous unitary transformations [68], that were developed in the early 1990s by Glazek and Wilson [69] and Weniger [70]. The flow equations remove correlation from the Hamiltonian by a series of unitary transformations before application of perturbative or renormalization-group methods. The key stationary equation in the flow equations is equivalent to the ACSE in the Heisenberg representation [33]. The ACSE method, however, has important differences including: (i) the ACSE is solved in the Schrödinger representation in contrast to the Heisenberg representation, (ii) because of (i), the fundamental variable of the ACSE is the 2-RDM while the basic variable of the flow equations is an effective Hamiltonian, (iii) in the ACSE the $\hat{S}$ operators for the unitary transformations are chosen to minimize the ground-state energy, while in the flow equations the unitary transformations are often designed to precondition the Hamiltonian for a range of energies, and (iv) in the ACSE the approximation of 3-body operators or density matrices is performed by cumulant expansions, but in the flow equations the treatment of three-body operators is often either more specific to a given problem or more approximate (i.e., neglect of the three-body operators). These connections may be harnessed to extend or improve both the ACSE and the flow equations. Specifically, the cumulant expansion of reduced density matrices or operators, developed in the context of the contracted Schrödinger theory, have been useful for improving the accuracy of the flow equations in certain applications such as electronic structure [71–73].

Improved knowledge of the excited-state energies and properties of many-electron atoms and molecules has important applications throughout chemistry and physics. Many excited-state methods produce excited-state energies by the response of the ground state to a weak electric field without calculation of the excited-state wave functions or properties. Contracted Schrödinger theory provides an important theoretical framework for the calculation of an excited-state 2-RDM and its energy without explicit computation of the many-electron wave function. In this paper the solution of the anti-Hermitian part of the CSE (ACSE) has been extended to treat both ground and excited states with illustrative applications. As shown in recent ground-state calculations of the electrocyclic rearrangement of bicyclobutane [40] and the sigmatropic shift in propene [41], the direct ACSE calculation of 2-RDMs for both ground and excited states has the ability to provide new insight into strong multireference correlation of quantum many-electron systems in chemistry and physics.

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