Molecule-optimized Basis Sets and Hamiltonians for Accelerated Electronic Structure Calculations of Atoms and Molecules

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Molecule-optimized basis sets, based on approximate natural orbitals, are developed for accelerating the convergence of quantum calculations with strongly correlated (multi-referenced) electrons. We use a low-cost approximate solution of the anti-Hermitian contracted Schrödinger equation (ACSE) for the one- and two-electron reduced density matrices (RDMs) to generate an approximate set of natural orbitals for strongly correlated quantum systems. The natural-orbital basis set is truncated to generate a molecule-optimized basis set whose rank matches that of a standard correlation-consistent basis set optimized for the atoms. We show that basis-set truncation by approximate natural orbitals can be viewed as a one-electron unitary transformation of the Hamiltonian operator and suggest an extension of approximate natural-orbital truncations through two-electron unitary transformations of the Hamiltonian operator, such as those employed in the solution of the ACSE. The molecule-optimized basis set from the ACSE improves the accuracy of the equivalent standard atom-optimized basis set at little additional computational cost. We illustrate the method with the potential energy curves of hydrogen fluoride and diatomic nitrogen. Relative to the hydrogen fluoride potential energy curve from the ACSE in a polarized triple-zeta basis set, the ACSE curve in a molecule-optimized basis set, equivalent in size to a polarized double-zeta basis, has a nonparallelity error of 0.0154 a.u. which is significantly better than the nonparallelity error of 0.0252 a.u. from the polarized double-zeta basis set.

Keywords: multi-reference electron correlation, natural orbitals, reduced density matrices, anti-Hermitian contracted Schrödinger equation, unitary transformations

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I. INTRODUCTION

While the basis sets describing atoms and molecules have been extensively studied and optimized\textsuperscript{12,24}, significant opportunities exist for the improvement of molecule-optimized basis sets and Hamiltonians for the acceleration of electronic structure computations, especially in the presence of strong electron correlation. Standard atomic-orbital basis sets are optimized only to minimize electronic energies of the constituent atoms rather than the total electronic energy of the molecules\textsuperscript{3}. While the concept of atoms forming molecules has a critical role throughout chemistry, such atom-centered basis sets do not capitalize on opportunities for greater efficiency arising from the nature of the bonding. Molecule-optimized basis sets and Hamiltonians accelerate correlation-energy calculations by minimizing the size (rank) of the orbital basis set in the description of the correlated Hamiltonian and wave function (or reduced density matrix). Such basis sets realize the intuitive idea that the optimal basis set for a molecule at a stretched geometry is different from the optimal basis set at the equilibrium geometry. Molecule-optimized orbitals, largely based on approximate natural orbitals\textsuperscript{25,26} or frozen natural orbitals\textsuperscript{27,28,29,30}, have been extensively studied in the context of perturbation methods about the Hartree-Fock reference wave function, but their study has been much more limited for strongly correlated molecular systems.

The aim of the present paper is to generate a molecule-optimized double-zeta basis set and Hamiltonian in which quantum chemistry calculations of strongly correlated systems can be performed. We (i) form the molecule-optimized double-zeta basis set and Hamiltonian from an approximate solution of the anti-Hermitian contracted Schrödinger equation (ACSE)\textsuperscript{27,28} in a higher (triplet-zeta) basis set and (ii) apply the molecule-optimized double-zeta basis set and Hamiltonian to solving the ACSE. The molecule-optimized double-zeta orbitals capture strong correlation, if present, because they are generated from an ACSE calculation starting with an initial multi-configuration self-consistent-field (MCSCF) two-electron reduced density matrix (2-RDM). In the theory section we present a general formulation for molecule-optimized basis sets and Hamiltonians in terms of unitary transformations of the Hamiltonian operator. Optimized orbitals can be viewed as one-electron unitary transformations of the Hamiltonian operator. Within this framework more general unitary transformations can potentially be explored. Illustrative applications are made to the potential energy curves of hydrogen fluoride and diatomic nitrogen. The ACSE-computed molecule-optimized basis sets significantly improve the nonparallelity errors in both curves. Although we specifically use the optimized basis orbitals and Hamiltonians in the ACSE, they can be more generally employed with any electronic structure method.
II. THEORY

Molecule-optimized orbitals are generally developed from approximate natural orbitals in section II A. The construction of a set of natural orbitals from the ACSE that are suitable for treating strongly correlated many-electron molecular systems is described in section II B. In section II C we recast the acceleration of convergence as a unitary transformation of the molecular Hamiltonian and suggest extensions of the approximate natural-orbital transformations.

A. Approximate natural orbitals

The “best” molecule-optimized molecular orbitals are the natural orbitals, the eigenfunctions of the 1-RDM. The optimality of the natural orbitals follows from a mathematical theorem derived by E. Schmidt in 1907. While finding the exact natural orbitals in a large standard atom-optimized basis set might require the same computational cost as solving the correlation problem in that large basis set, significant cost savings can be achieved by identifying an approximate set of natural orbitals and then solving the correlation problem in a truncated set of these orbitals.

Approximate natural orbitals can be obtained from a low-cost correlation-energy calculation and then employed after truncation in a higher cost correlation-energy calculation. Examples of the strategy from the literature include the early use of natural orbitals from perturbation theory,15,26–33,36–37,42 or iterative refinement,15,27 in configuration interaction and the recent use of natural orbitals from second-order many-body perturbation theory in coupled cluster calculations.45,48,49,51.

Most previous calculations differ from the general approach to the optimal natural orbitals adopted here in two respects: (1) they typically employ a truncation scheme for the natural orbitals based on a threshold for their occupations and (2) they usually determine approximate natural orbitals either from or for single-reference electron correlation methods. Taube and Bartlett45,47 have truncated their natural orbitals according to a pre-defined percentage, and Roos and co-workers44 have employed approximate natural orbitals in complete-active-space second-order perturbation theory.

In this work we generate molecule-optimized basis sets that use a truncation of the natural orbitals based on the rank of the orbitals (see also Ref.42 for a truncation by basis-set size). For example, the approximate natural orbitals are obtained from a low-cost method in a large standard atom-optimized basis set

\[ 1Dv_i = n_iv_i, \]

where \( 1D \) denotes the 1-RDM, \( n_i \) are the natural occupation numbers ordered from largest to smallest, and \( v_i \) are the eigenvectors whose components denote the expansion coefficients of the natural orbitals in terms of the initial molecular-orbital basis set. Then the set of natural orbitals \( \{v_i\} \) is truncated to share the rank \( M \) of the smaller standard atom-optimized basis set. In accordance with the Schmidt theorem, the largest \( M \) of the \( n_i \) are retained to generate the optimal set of \( M \) orbitals. The compact molecule-optimized basis set can then be employed in a higher cost method for more accurate and more efficient description of the molecule’s electron correlation.

Truncation by basis-set rank has a different philosophy from truncation by threshold. In truncation by threshold the aim of the calculation is to reproduce the accuracy of the larger basis set within a given tolerance (threshold), but in truncation by basis-set rank the aim of the calculation is to attain some of the accuracy of the larger basis set at the significantly reduced cost of a smaller basis set. For larger molecules where the computational cost of the larger basis set is prohibitive, the strategy of truncation by basis-set rank has important advantages because the basis-set rank can be chosen to remain within existing computational resources. Furthermore, the generation of molecule-optimized basis sets which mimic traditional atom-optimized basis sets share some advantages of atom-optimized basis sets such as correlation consistency and systematic extrapolation to the complete-basis-set limit.

Secondly, as discussed in section II B we aim to develop molecule-optimized molecular orbitals that can be employed in multi-reference calculations for the description of strongly correlated electrons. We generate approximate natural orbitals through a partial solution of the ACSE, starting with a 2-RDM from an MCSCF calculation. The resulting natural orbitals from the partial ACSE solution have a natural ordering with respect to correlation effects that inherently require multiple many-electron configurations in the reference wave function. Natural orbitals from single-reference theories typically do not reflect the multi-reference correlation in the wave functions of highly correlated atoms molecules. Furthermore, as shown in the results, canonical orbitals from MCSCF, ordered by their canonical energies, do not provide a suitable ordering for accelerating convergence with respect to basis-set size.

B. ACSE natural orbitals

Solution of the anti-Hermitian contracted Schrödinger equation (ACSE)67–69, the anti-Hermitian part of the contracted Schrödinger equation (CSE)36,54, for the 2-RDM and its energy can be tuned for single-reference or multi-reference electron correlation through the choice of the initial 2-RDM. The 2-RDM can be chosen from an initial mean-field (Hartree-Fock) or a correlated calculation such as a multi-configuration self consistent field (MC-SCF) calculation.67,68. The ACSE method is applicable to both ground and excited states as well as arbitrary spin states.45. It has been applied to studying multi-reference
correlation in excited states and conical intersections in the photoexcitation of *gauche*-1,3-butadiene to form bicyclobutane, the tautomerization of vinyl alcohol to acetyldialdehyde, and the reaction of firefly luciferin for bioluminescence.

In a finite basis set the contracted Schrödinger equation (CSE) as well as its anti-Hermitian part (ACSE) can be expressed in second quantization as

\[\langle \Psi_n | a_i^\dagger a_j^\dagger a_l^\dagger a_k^\dagger \hat{H} | \Psi_n \rangle = E_n \sum_{k,l}^2 D_{k,l}^{i,j} \]  

(2)

and

\[\frac{1}{2} \langle \Psi_n | [a_i^\dagger a_j^\dagger a_l^\dagger a_k^\dagger, \hat{H}] | \Psi_n \rangle = 0,\]

(3)

where each index \(i, j, k,\) and \(l\) denotes a one-electron spin orbital that is a product of a spatial orbital and a spin function \(\sigma\) equal to either \(\alpha\) (+1/2) or \(\beta\) (-1/2) and the elements of the 2-RDM

\[2 D_{k,l}^{i,j} = \langle \Psi_n | a_i^\dagger a_j^\dagger a_l^\dagger a_k^\dagger | \Psi_n \rangle\]

(4)

follow from the expectation value of the 2-RDO with respect to \(|\Psi_n\rangle\). In second quantization the creation operator \(a_i^\dagger\) generates an electron in the \(i\)^{th} spin orbital while the annihilation operator \(a_i\) destroys an electron in the \(K\) \^{th} spin orbital. For a quantum many-electron system the Hamiltonian is expressible as

\[\hat{H} = \sum_{p,s}^{1} K_{p,s}^0 a_p^\dagger a_s + \sum_{p,q,s,t}^{2} V_{s,t}^{p,q} a_p^\dagger a_q^\dagger a_s a_t\]

(5)

where the one- and two-electron reduced Hamiltonian matrices \(K\) and \(V\) contain the one- and two-electron integrals respectively. By rearranging the creation and annihilation operators according to the anti-commutation relations for fermions, we can write the CSE in terms of the elements of the 2-, 3-, and 4-RDMs and the ACSE in terms of the elements of the 2- and 3-RDMs. Explicit expressions for these contracted equations in terms of the spin-orbital elements of the reduced Hamiltonians and RDMs are given elsewhere.

The ACSE can be solved by propagating the following initial-valued differential equation as a function of the parameter \(\lambda\) which serves as an imaginary time:

\[\frac{d^2 D_{k,l}^{i,j}}{d\lambda^2} = \langle \Psi(\lambda) | [\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l^\dagger \hat{a}_k^\dagger, \hat{S}(\lambda)] | \Psi(\lambda) \rangle\]

(6)

where the two-body operator \(\hat{S}\)

\[\hat{S}(\lambda) = \sum_{p,q,s,t}^{2} S_{s,t}^{p,q}(\lambda) a_p^\dagger a_q^\dagger a_s a_t\]

(7)

depends upon a two particle reduced matrix \(^2S\) equal to the residual of the ACSE

\[2 S_{s,t}^{p,q}(\lambda) = \langle \Psi(\lambda) | [\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s, \hat{H}] | \Psi(\lambda) \rangle\]

(8)

where \(\hat{H}\) is the Hamiltonian operator. The dependence of the above equations on the three-electron reduced density matrix (3-RDM) is removed by reconstructing the 3-RDM as a cumulant functional of the lower 1-and 2-RDMs. The 2-RDM is propagated until either the energy or the residual the ACSE ceases to decrease.

Because the ACSE can treat multi-reference correlation, it can serve as a general platform for creating an approximate set of natural orbitals. The 1-RDM is obtained from the 2-RDM by contraction

\[1 D_k = \frac{1}{N-1} \sum_j^2 D_{k,j}^{i,i}\]

(9)

and the natural orbitals and their occupations are readily obtained from Eq. (11). A family of approximate orbitals can be systematically generated from the ACSE by evolving the 2-RDM over a short length in the parameter \(\lambda\). By choosing the distance in \(\lambda\) to be a small fraction of the total distance \(\lambda^*\) required for the solution of the ACSE, we can obtain an approximate set of natural orbitals at low computational cost. The evolution over the short distance in \(\lambda\) can be performed in a large standard atom-centered basis set. From the 1-RDM obtained, a truncated set of natural orbitals sharing the rank \(M\) of the smaller standard atom-centered basis set can be employed for solving the ACSE to convergence. Hence, through the choice of the evolution distance in \(\lambda\) we are able to generate both low-cost and higher cost methods for electron correlation directly within a common ACSE framework.

For convenience, we diagonalize only the virtual virtual block of the 1-RDM to obtain natural orbitals in terms of the virtual MCSCF orbitals; in this manner, we can truncate these approximate natural orbitals without changing the original MCSCF 1-RDM at \(\lambda = 0\). These approximate natural orbitals are similar in spirit to those created from the Hartree-Fock virtual virtual block of the 1-RDM in single-reference methods, which have been called frozen natural orbitals. Importantly, because the approximate natural orbitals obtained from the ACSE are molecule optimized, they incorporate important features of the molecule’s electron density and chemical bonding that are not present in the standard atom-centered basis sets of the same size (or rank).

C. Molecule-optimized Hamiltonians

The generation of molecule-optimized basis sets through the use of natural orbitals and Schmidt’s theorem can also be viewed as a unitary transformation of the Hamiltonian in the original larger basis set \(\hat{H}_0\) to produce a more compact Hamiltonian \(\hat{H}_1\) whose non-negligible elements can be captured in a smaller basis set

\[\hat{H}_1 = e^{-\hat{S}_1} \hat{H}_0 e^{\hat{S}_1},\]

(10)

where \(\hat{S}_1\) is a one-body anti-Hermitian operator

\[\hat{S}_1 = \sum_{p,s}^1 S_{p,s}^0 a_p^\dagger a_s.\]

(11)
Similar anti-Hermitian operators arise in the unitary transformations underlying contracted Schrödinger theory, including the solution of the ACSE. In the ACSE we employ unitary transformations from not only one-body anti-Hermitian operators but also such transformations from two-body anti-Hermitian operators, which are critical to capturing important many-body correlation effects.

The molecule-optimized Hamiltonian from a one-body unitary transformation can be generalized to a molecule-optimized Hamiltonian from a two-body unitary transformation

$$H_2 = e^{-\hat{S}_2}H_0 e^{\hat{S}_2},$$

where $\hat{S}_2$ is a two-body anti-Hermitian operator. As in the previous case, the two-body transformation produces a more compact Hamiltonian $H_2$ whose non-negligible elements can be captured in a smaller basis set. Because the two-body unitary transformations contain the one-body unitary transformations, the set of potential Hamiltonian operators $\{H_2\}$ is larger than a set of potential Hamiltonian operators $\{H_1\}$. Consequently, the two-body transformations generalize the set of molecule-optimized Hamiltonians obtainable from approximate natural orbitals.

Unlike the one-body transformations, the two-body transformations generate three-body Hamiltonians whose expectation values depend upon the three-electron RDM (3-RDM). As in contracted Schrödinger theory, however, these three-body Hamiltonians can be readily approximated as two-body Hamiltonians through cumulant reconstruction of the three-electron reduced density operators. While these extensions of the natural-orbital transformations are not pursued in the present work, the ACSE theory in the previous section provides a useful framework for (i) approximating suitable $\hat{S}_2$ operators and (ii) recasting the Hamiltonians $H_2$ as two-body operators through cumulant reconstruction. Recently, related two-body transformations of the Hamiltonian with cumulant reconstruction have been employed in the context of an explicit r12 theory.

III. APPLICATIONS

After brief discussion of the computational methodology, we apply the molecule-optimized basis sets described in the previous section to generating potential energy curves from hydrogen fluoride and diatomic nitrogen.

A. Computational methodology

The initial MCSCF 2-RDM is computed with the wave function from an MCSCF calculation in the GAMESS package for electronic structure. The ACSE calculations are performed with the code developed by one of the authors in Refs. 4,75–77. Approximate sets of natural orbitals are generated from ACSE calculations in the correlation-consistent polarized valence triple-zeta (TZ) basis sets. Unless stated otherwise, the 2-RDM is evolved from $\lambda = 0.0$ to $\lambda = 0.01$. This evolution is a small fraction of the total evolution in $\lambda$ from 0.0 to $\lambda^*$ required for satisfying the ACSE method’s convergence criteria. As shown in previous work, convergence typically occurs at a value $\lambda^*$ between 1 and 10. The resulting natural orbitals are then truncated based on orbital occupations to produce a molecule-optimized basis set whose rank $M$ equals that of the standard correlation-consistent polarized valence double-zeta (DZ) basis set. The ACSE is then evolved in this molecule-optimized basis set until convergence.

B. Hydrogen fluoride

![FIG. 1. The potential energy curve in the molecule-optimized basis set from the ACSE with $\lambda$ equal to 0.01 (TZ/DZ[0.01]) is compared to those from solving the ACSE in the standard correlation consistent basis sets, DZ and TZ, the nonstandard DZ basis set derived from the energy-ordered orbitals of MCSCF in the TZ basis set (TZ/DZ[MCSCF]) as well as the molecule-optimized basis set with $\lambda$ evolved its full distance $\lambda^*$ to convergence (TZ/DZ[full]). Relative to TZ, the nonparallelity error (NPE) of 0.0154 a.u. from TZ/DZ[0.01] is significantly better than the error of 0.0292 a.u. from DZ or the error of 0.02411 a.u. from TZ/DZ[MCSCF].](image)
TABLE I: Table 1: Relative to TZ, the table reports the energy errors from the ACSE from the standard atom-optimized basis set DZ as well as a series of molecule-optimized basis sets for \( \lambda \) equal to 0.01, 0.05, 0.10, and \( \lambda^* \) where \( \lambda^* \) represents the full \( \lambda \) trajectory to convergence. The results show the error relative to TZ continues to decrease as the approximate set of natural orbitals is improved through longer \( \lambda \) evolutions. The molecule-optimized basis set from \( \lambda \) equal to 0.01 (TZ/DZ[0.01]) offers an improvement in accuracy at a computational cost that is not significantly different from that of the standard DZ calculation.

| Bond Distance (Å) | Energy (a.u.) | Energy Errors (a.u.) |
|------------------|---------------|----------------------|
|                  | TZ            | DZ                   | TZ/DZ[0.01]   | TZ/DZ[0.05]   | TZ/DZ[0.10]   | TZ/DZ[full]  |
| 0.8              | -100.328456   | 0.119026             | 0.084854      | 0.077534      | 0.065513      | 0.049063     |
| 1.0              | -100.341785   | 0.116656             | 0.083603      | 0.074740      | 0.063675      | 0.047857     |
| 1.2              | -100.298315   | 0.114687             | 0.086913      | 0.075308      | 0.060738      | 0.046282     |
| 1.4              | -100.248797   | 0.112944             | 0.085235      | 0.079852      | 0.059025      | 0.044952     |
| 1.8              | -100.175789   | 0.107404             | 0.078613      | 0.072371      | 0.061938      | 0.041952     |
| 2.2              | -100.144837   | 0.103344             | 0.075038      | 0.069548      | 0.058482      | 0.036774     |
| 2.8              | -100.132043   | 0.101452             | 0.072117      | 0.066604      | 0.055794      | 0.037054     |
| 3.4              | -100.130323   | 0.101302             | 0.071648      | 0.066151      | 0.055370      | 0.036750     |

the energy-ordered orbitals of MCSCF in the TZ basis set (TZ/DZ[MCSCF]), as well as the molecule-optimized basis set with \( \lambda = 0.01 \) has a rank equal to that of the polarized basis set TZ, it improves the energies from DZ by 20% relative to the TZ basis set. Furthermore, it has a nonparallelity error (NPE) of 0.0154 a.u. relative to TZ which is significantly better than the error of 0.0252 a.u. from DZ or the error of 0.02411 a.u. from TZ/DZ[MCSCF]. The NPE is defined as the difference between the maximum and minimum errors in the potential energy curve. The NPE of the molecule-optimized basis set with \( \lambda = \infty \) at 0.0136 a.u. is not much different from that of the basis set with \( \lambda = 0.01 \).

Table 1 reports the energy errors from the ACSE relative to TZ from the standard atom-optimized basis set DZ as well as a series of molecule-optimized basis sets for \( \lambda \) equal to 0.01, 0.05, 0.10, and \( \lambda^* \) where \( \lambda^* \) represents the full \( \lambda \) trajectory to convergence. The results show the error relative to TZ continues to decrease as the approximate set of natural orbitals is improved through longer \( \lambda \) evolutions. Qualitatively, the space spanned by the \( M \) most occupied natural orbitals improves the energy with increasing \( \lambda \) because it better represents the part of the one-electron Hilbert space that describes the electron density of the molecule. This increasing accuracy, however, comes at the price of increasing computational cost. The molecule-optimized basis set from \( \lambda \) equal to 0.01 (TZ/DZ[0.01]) offers an improvement in accuracy at a computational cost that is not significantly different from that of the standard DZ calculation. In this case, the TZ/DZ[0.01] calculation is more than an order of magnitude faster than the TZ calculation.

C. Diatomic nitrogen

Breaking the triple bond of diatomic nitrogen provides a challenging problem for single-reference methods and a benchmark problem for multi-reference methods. Here we generate the potential energy curve for the nitrogen dissociation from the ACSE in the molecule-optimized basis set with \( \lambda \) equal to 0.01. The shape of this potential energy curve is compared to the shapes of those from the standard DZ and TZ basis sets in Fig. 2a. The curves DZ and TZ/DZ[0.01] in Fig. 2a are shifted by \(-0.115426\) and \(-0.094708\) a.u. respectively to agree with the energy from TZ at 1.1 Å. Even though the molecule-optimized basis set has the same computational cost as the DZ basis set, it significantly improves the nonparallelity error relative to TZ from 0.115 a.u. (DZ) to 0.024 a.u. The curve from the molecule-optimized basis set (TZ/DZ[0.01]) better approximates both the curvature about equilibrium and the dissociation energy relative to TZ.

Figure 2b shows the energy errors from DZ and the molecule-optimized basis set TZ/DZ[0.01] relative to TZ. In terms of absolute energies, TZ/DZ[0.01] improves the energies from DZ at bond lengths in the vicinity of the equilibrium geometry; however, for bond lengths greater than 1.6 Å the molecule-optimized basis set yields energies that are higher than those from the standard correlation-consistent DZ basis set. This result can be understood from recalling that the standard basis sets are optimized to minimize atomic energies in the configuration interaction singles-doubles method. Upon dissociation the nitrogen molecule breaks up into two nitrogen atoms, and hence, the standard basis set is highly optimized in this region of the potential energy surface. Examining the errors in the cc-pVDZ basis set relative to the cc-pVTZ basis set, however, reveals that the errors at short bond lengths are significantly larger than the errors at longer bond lengths. This discrepancy in accuracy contributes to a large nonparallelity error. The molecule-optimized basis set significantly decreases this error by improving the energies in the equilibrium region while sacrificing the accuracy of energies in the dissociation region. The basis set that is optimized for the molecule provides a more balanced description of the molecule’s electron correlation throughout the potential energy surface.
FIG. 2. For the dissociation of diatomic nitrogen with the ACSE the figure compares the shape of the potential energy curve in the molecule-optimized basis set with $\lambda$ equal to 0.01 (TZ/DZ[0.01]) to the shapes of potential curves from the standard DZ and TZ basis sets. The curves DZ and TZ/DZ[0.01] in part (a) are shifted by $-0.115426$ and $-0.094708$ a.u. respectively to agree with the energy from TZ at 1.1 Å. Relative to TZ, the TZ/DZ[0.01] curve better approximates both the curvature about equilibrium and the dissociation energy than DZ; it significantly improves the nonparallelity error of 0.115 a.u. of DZ to 0.024 a.u. Part (b) shows the energy errors from DZ and TZ/DZ[0.01] relative to TZ.

IV. DISCUSSION AND CONCLUSIONS

Molecule-optimized basis sets have been presented for accelerating the convergence of electron correlation calculations. As in previous work, the definition of the molecule-optimized basis set depends upon the generation of an approximate set of natural orbitals. Significant computational acceleration can be achieved because the natural orbitals provide the optimal one-electron basis set for the convergence of the many-electron wave function (or two-electron reduced density matrix). In contrast to most previous work, the molecule-optimized basis sets (1) are defined by truncation of the natural orbitals to a fixed rank that equals the rank of a standard correlation-consistent polarized basis set and (2) are optimized by a low-cost multi-reference calculation that can capture important contributions from strong electron correlation in their definition. With regard to (2), the present work does have important connections to the early refinement of the natural orbitals through iterative configuration interaction and the recent truncation of natural orbitals in both configuration interaction calculations and second-order complete-active-space perturbation theory.

While the approach is quite general, here we study the generation of molecule-optimized basis sets from the solution of the ACSE. By evolving the ACSE in a large standard atom-centered basis set for a short distance in the imaginary time-like parameter $\lambda$, we can generate an approximate 1-RDM whose eigenfunctions provide approximate natural orbitals. Selection of a smaller set of natural orbitals based on the occupation numbers generates a molecule-optimized basis set. We can choose the rank of this new basis set equal to that of a smaller standard atom-optimized basis set which can then be employed to solve the ACSE until convergence. In this fashion we can generate systematic sets of molecule-optimized basis sets that significantly accelerate the solution of multi-reference methods like the ACSE. These basis sets incorporate important features of chemical bonding and correlation of the molecule that are not present in the standard atom-optimized basis sets. Importantly, these molecule-optimized orbitals can be employed to accelerate any multi-reference quantum chemistry method.

Illustrative applications of the ACSE molecule-optimized basis sets to the potential energy curves of hydrogen fluoride and diatomic nitrogen show significant improvements in the nonparallelity errors. For diatomic nitrogen a molecule-optimized double-zeta-like basis set yields a nonparallelity error of 0.024 a.u., relative to the TZ basis set, which significantly improves upon the 0.115 a.u. error in the DZ basis set. For hydrogen fluoride the nonparallelity errors from the ACSE’s approximate natural orbitals ordered by occupation numbers are much better than those from the MCSCF’s canonical orbitals ordered by orbital energies. Significantly, the correlation of the active space with the inactive space, as performed with the approximate solution of the ACSE, is critical to generating a suitable set of natural orbitals.

While the improvement in absolute energies is not as substantial as the improvement in the nonparallelity errors, the present results provide a foundation for future work that may further improve these results. In section II C we show that basis-set truncation by approximate natural orbitals can be viewed as a one-electron unitary transformation of the Hamiltonian operator and suggest an extension of approximate natural-orbital truncations through two-electron unitary transformations of the Hamiltonian operator, similar to those employed in the ACSE method. In future work we plan to study larger...
molecules in larger basis sets, a variety of approaches for computing approximate sets of natural orbitals, extrapolations of molecule-optimized basis sets to the complete-basis-set limit, and extensions of natural-orbital truncations through two-electron unitary transformations of the Hamiltonian operator.

The acceleration of the ACSE method for multi-reference correlation can be applied to extending recent applications of the ACSE to the study of ground- and excited-state chemical reactions including conical intersections in vinyl alcohol, gauche-1,3-butadiene, and firefly luciferin. Often improvements in nonparallelity errors rather than absolute errors are more important for the accurate prediction of reaction and excitation energies and other energy differences studied in the above examples. The present work can also be applied to correlation methods that use natural orbitals as their basic variables such as natural-orbital functional theory, geminal functional theory, the precursors of the projected quasi-variational theory, and the natural-orbital solution of the contracted Schrödinger equation. The exploitation of molecule-optimized orbitals and Hamiltonians in electronic structure calculations has the potential for decreasing computational cost while maintaining computational accuracy.

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Anti-Hermitian
Contracted
Schrödinger Equation

\[ \langle \Psi_n | \hat{a}_i \hat{a}^\dagger \hat{a}_j \hat{a}^\dagger H | \Psi_n \rangle = 0 \]

FIG. 3. Table of Contents Figure