

Tensor Hypercontraction Equation-of-Motion Second-Order Approximate Coupled Cluster: Electronic Excitation Energies in $O(N^4)$ Time

Edward G. Hohenstein,^{†,‡} Sara I. L. Kokkila,^{†,‡} Robert M. Parrish,[¶] and Todd J. Martínez^{*,†,‡}

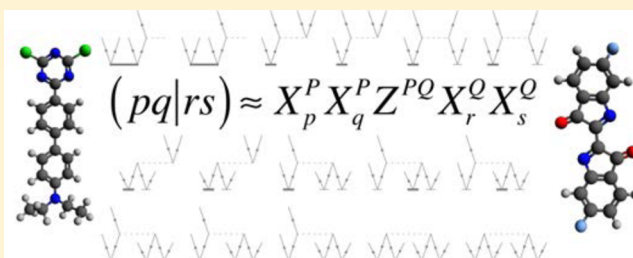
[†]Department of Chemistry and the PULSE Institute, Stanford University, Stanford, California 94305, United States

[‡]SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States

[¶]Center for Computational Molecular Science and Technology, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400, United States

Supporting Information

ABSTRACT: The tensor hypercontraction (THC) formalism is applied to equation-of-motion second-order approximate coupled cluster singles and doubles (EOM-CC2). The resulting method, THC-EOM-CC2, is shown to scale as $O(N^4)$, a reduction of one order from the formal $O(N^5)$ scaling of conventional EOM-CC2. Numerical tests for a variety of molecules show that errors of less than 0.02 eV are introduced into the excitation energies.



■ INTRODUCTION

Methods for obtaining electronic excited states that are both efficient and reliable are scarce in electronic structure theory. One method that provides a practical compromise between accuracy and efficiency is second-order approximate coupled cluster singles and doubles (CC2).¹ Excited states can be obtained from CC2 using either an equation-of-motion (EOM)^{2,3} or a coupled cluster response formalism.⁴ When only excitation energies are considered, as in the present work, both approaches are equivalent. For a discussion of the connection between CC response and EOM-CC, the reader is referred to ref 5. Although EOM-CC2 is not as accurate as the full EOM coupled cluster singles and doubles method (EOM-CCSD),⁶ it is robust against many of the issues that plague lower-scaling methods like configuration interaction singles (CIS) or time-dependent density functional theory (TDDFT), such as the overstabilization of charge-transfer states or the neglect of long-range dynamic electron correlation.⁷ A highly efficient implementation of CC2 excitation energies^{8,9} has been developed by introducing the density fitting (DF) approximation.^{10,11} Further improvements have been made through the use of orbital localization.^{12,13} DF has the advantage that its accuracy is independent of the molecular system; however, it cannot reduce the formal $O(N^5)$ scaling of CC2. Local approximations can help combat the scaling problem but are not effective for large conjugated molecules where the electronic orbitals are very delocalized.

Recently, we have developed the tensor hypercontraction (THC) approximation to the electron repulsion integrals (ERIs).^{14,15} The THC approximation reveals a hidden factorizable tensor structure of the ERIs that offers superior

flexibility for factorizing contractions involving the ERIs. Our application of THC to the wave function coefficients in correlated methods, such as CCSD, demonstrates that a similar factorizable tensor structure also exists in the double excitation amplitudes.¹⁶ Previously, we have applied THC to the CC2 method (THC-CC2), in the context of ground state correlation energies, demonstrating that an analytic factorization of the doubles amplitudes is possible with THC that allows the formal scaling of the method to be reduced from $O(N^5)$ to $O(N^4)$.¹⁷ In this work, we apply THC to excited states for the first time in the context of EOM-CC2 (THC-EOM-CC2). The factorization of the ground state doubles amplitudes can be leveraged in concert with an analogous factorization of the excited-state wave function coefficients to obtain a quartic-scaling method for determining excitation energies. We find that the introduction of the THC approximation introduces errors of less than 0.02 eV to the EOM-CC2 excitation energies.

■ THEORY

In this work, we will use the following notation: i, j, k, l , and m will be used to index occupied molecular orbitals, a, b, c, d , and e will be used to index virtual molecular orbitals, p, q, r , and s will index all molecular orbitals, A and B will index the density fitting auxiliary basis, and P and Q will index the THC auxiliary

Special Issue: Peter G. Wolynes Festschrift

Received: March 4, 2013

Revised: August 21, 2013

Published: August 21, 2013

index (here, grid points). We will adhere to a generalized Einstein summation convention, where summation over repeated indices appearing only on one side of an equation is implied.

In coupled cluster theory, the Schrödinger equation is written as¹⁸

$$\hat{H}e^{\hat{T}}|\Phi_0\rangle = Ee^{\hat{T}}|\Phi_0\rangle \quad (1)$$

where the excitation operator, \hat{T} , is given as

$$\hat{T} = t_i^a a_a^\dagger a_i + \frac{1}{4} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i + \dots \quad (2)$$

Left multiplication by $e^{-\hat{T}}$ and subsequent projection by the reference and excited determinants provides equations that define the ground state coupled cluster energy and amplitudes, respectively.

$$\langle \Phi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = E \quad (3)$$

$$\langle \Phi_i^a | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0 \quad (4)$$

$$\langle \Phi_{ij}^{ab} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0 \quad (5)$$

The ground state coupled cluster amplitudes parametrize a similarity transformation of the electronic Hamiltonian,

$$\bar{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}} \quad (6)$$

Truncating \hat{T} after double excitations (e.g., $\hat{T} = \hat{T}_1 + \hat{T}_2$) defines the coupled cluster singles and doubles method (CCSD).¹⁹ In the following, we use a normal-ordered form of \hat{H} ,

$$\hat{H} = E_0 + \hat{F} + \hat{V} = E_0 + f_{pq} \{a_p^\dagger a_q\} + \frac{1}{4} \langle pq || rs \rangle \{a_p^\dagger a_q^\dagger a_s a_r\} \quad (7)$$

where the braces denote that the operators are normal-ordered relative to the Fermi vacuum. The second-order approximate coupled-cluster method (CC2) is defined by introducing an additional approximation that \hat{T}_2 acts only on \hat{F} when doubly excited determinants appear in the bra.¹ That is, eqs 3 and 4 remain unchanged, but eq 5 becomes

$$\langle \Phi_{ij}^{ab} | e^{-\hat{T}_1} \hat{H} e^{\hat{T}_1} + e^{-\hat{T}_2} \hat{F} e^{\hat{T}_2} | \Phi_0 \rangle = 0. \quad (8)$$

The CC2 approximation dramatically simplifies the CCSD doubles amplitude equations.

In the spirit of configuration interaction (CI), we can introduce a linear excitation operator,³

$$\hat{R}^{(n)} = r_0 + r_i^a a_a^\dagger a_i + \frac{1}{4} r_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i + \dots \quad (9)$$

corresponding to an electronic state, n . In CC2, the \hat{R} operator will be truncated at the double excitation operators. Then, we can write a more general form of the coupled cluster Schrödinger equation:

$$\bar{H} \hat{R}^{(n)} |\Phi_0\rangle = E^{(n)} \hat{R}^{(n)} |\Phi_0\rangle \quad (10)$$

Solving this equation is equivalent to diagonalizing \bar{H} in a basis of Slater determinants, where the eigenvectors define the \hat{R} amplitudes and the corresponding eigenvalues are the total electronic energies. Alternatively, one could solve for the excitation energies, ω , directly by including only contributions where \hat{R} is connected to \hat{H} :³

$$(\bar{H} \hat{R}^{(n)} |\Phi_0\rangle)_c = \omega^{(n)} \hat{R}^{(n)} |\Phi_0\rangle \quad (11)$$

In EOM-CC, the only disconnected contributions to the right-hand eigenvalue problem with nonzero matrix elements are from the CC reference energy (i.e., $\langle \Phi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle$). The linear excitation operator, \hat{R} , used to generate the excited determinants can be truncated arbitrarily. The EOM-CCSD method is defined by truncating both \hat{T} and \hat{R} after double excitations. The CC2 approximation can be extended to EOM-CC2 by extending the restrictions imposed on \hat{T}_2 to construct an effective Hamiltonian.

$$\tilde{H}_{CC2} = \begin{bmatrix} 0 & \langle \Phi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_k^c \rangle & \langle \Phi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_{kl}^{cd} \rangle \\ 0 & \langle \Phi_i^a | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_k^c \rangle & \langle \Phi_i^a | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_{kl}^{cd} \rangle \\ 0 & \langle \Phi_{ij}^{ab} | e^{-\hat{T}_1} \hat{H} e^{\hat{T}_1} | \Phi_k^c \rangle & \langle \Phi_{ij}^{ab} | e^{-\hat{T}_2} \hat{F} e^{\hat{T}_2} | \Phi_{kl}^{cd} \rangle \end{bmatrix} \quad (12)$$

Provided that only connected contributions are included (eq 11), diagonalization of this Hamiltonian yields EOM-CC2 wave functions and excitation energies (and one vanishing eigenvalue corresponding to the ground state). Since \tilde{H}_{CC2} is non-symmetric, a full solution to the problem requires determining both left and right eigenvectors. However, when only the eigenvalues are required (as in the present work), it suffices to solve only one of these (left/right) eigenvalue problems. We choose to solve for the right-hand eigenvectors here. From this point forward, we will only consider the specific case of EOM-CC2.

Since we are only interested in obtaining a few of the eigenvalues of \tilde{H}_{CC2} , there is no need to explicitly construct the entire matrix defined in eq 12. In the following, we will solve for the EOM-CC2 excitation energies; therefore we only include contributions to matrix elements of \tilde{H}_{CC2} where \hat{H} and \hat{R} are connected, which we will denote as $\langle \Phi_I | \tilde{H}_{CC2} | \Phi_J \rangle_c$ where I and J index Slater determinants (a detailed derivation and definitions of matrix elements are provided in Supporting Information). Additionally, we will assume the use of canonical Hartree–Fock (HF) orbitals. However, the algorithm we present is easily extended to arbitrary orbitals provided that they are semicanonicalized and off-diagonal contributions from the Fock operator are included. To find a few of the lowest eigenvalues, an iterative algorithm can be used provided we are able to evaluate matrix-vector products of \tilde{H}_{CC2} with r_i^a and r_{ij}^{ab} (the amplitudes that parametrize the \hat{R} operator are the eigenvectors of \tilde{H}_{CC2}),

$$\omega r_i^a = \langle \Phi_i^a | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_k^c \rangle_c r_k^c + \langle \Phi_i^a | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_{kl}^{cd} \rangle_c r_{kl}^{cd} \quad (13)$$

$$\omega r_{ij}^{ab} = \langle \Phi_{ij}^{ab} | e^{-\hat{T}_1} \hat{H} e^{\hat{T}_1} | \Phi_k^c \rangle_c r_k^c + \langle \Phi_{ij}^{ab} | e^{-\hat{T}_2} \hat{F} e^{\hat{T}_2} | \Phi_{kl}^{cd} \rangle_c r_{kl}^{cd} \quad (14)$$

where ω is the eigenvalue (in this case, excitation energy). It should be noted that while r_0 can contribute to the excited state eigenvectors, it is decoupled from r_i^a and r_{ij}^{ab} and, therefore, is not needed to determine the eigenvalue. Further simplifications are possible once it is recognized that the doubles–doubles block of \tilde{H}_{CC2} is diagonal,

$$\langle \Phi_{ij}^{ab} | \hat{F} | \Phi_{kl}^{cd} \rangle_c = \delta_{ac} \delta_{bd} \delta_{ik} \delta_{jl} (\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j) \quad (15)$$

Note that $e^{-\hat{T}_2} \hat{F} e^{\hat{T}_2}$ can be written as a series of nested commutators via the Baker–Campbell–Hausdorff expansion:

$$e^{-\hat{T}_2} \hat{F} e^{\hat{T}_2} = \hat{F} + [\hat{F}, \hat{T}_2] + \frac{1}{2} [[\hat{F}, \hat{T}_2], \hat{T}_2] + \dots \quad (16)$$

This allows r_{ij}^{ab} to be written in terms of r_i^a , ω , and \tilde{H}_{CC2} :

$$r_{ij}^{ab} = \frac{\langle \Phi_{ij}^{ab} | e^{-\hat{T}_1} \hat{H} e^{\hat{T}_1} | \Phi_k^c \rangle r_k^c}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b + \omega} \quad (17)$$

As a result, we can cast the diagonalization of \tilde{H}_{CC2} into a nonlinear eigenvalue problem where r_i^a and ω are the only undetermined quantities.⁸

$$\omega r_i^a = \langle \Phi_i^a | e^{-\hat{T}_1} \hat{H} e^{\hat{T}_1} | \Phi_k^c \rangle r_k^c + \frac{\langle \Phi_i^a | e^{-\hat{T}_1} \hat{H} e^{\hat{T}_1} | \Phi_m^e \rangle r_m^e}{\epsilon_k + \epsilon_l - \epsilon_c - \epsilon_d + \omega} \quad (18)$$

The complications that arise from this nonlinearity are preferable to the alternative, so we will pursue a factorization of the amplitude equations that does not require r_{ij}^{ab} to be explicitly constructed.

To improve the efficiency of EOM-CC2, we will approximate the electron repulsion integrals. First, we will apply the density fitting (DF) (or resolution of the identity) approximation.^{10,11} Here, we take the electron repulsion integrals,

$$(\mu\nu|\rho\sigma) = \iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_\mu(\mathbf{r}_1) \phi_\nu(\mathbf{r}_1) r_{12}^{-1} \phi_\rho(\mathbf{r}_2) \phi_\sigma(\mathbf{r}_2) \quad (19)$$

and fit the highly redundant orbital products (pseudodensities) with an auxiliary one-particle basis:

$$\phi_\mu(\mathbf{r}_1) \phi_\nu(\mathbf{r}_1) \approx c_{\mu\nu}^A \chi_A(\mathbf{r}_1) \quad (20)$$

This allows the electron repulsion integrals to be approximated as

$$(\mu\nu|\rho\sigma) \approx c_{\mu\nu}^A (A|B) c_{\rho\sigma}^B \quad (21)$$

In practice, the DF approximation has been found to be very reliable and can improve the efficiency of many methods. However, despite its successes, DF does not allow exchange-like contractions to be factorized. To overcome this problem, we have introduced the tensor hypercontraction (THC) approximation to the electron repulsion integrals.¹⁴

$$(\mu\nu|\rho\sigma) \approx X_\mu^P X_\nu^P Z^{PQ} X_\rho^Q X_\sigma^Q \quad (22)$$

The THC approximation unpins the bra and ket indices of the integral, allowing a great amount of flexibility for factorizing the expressions that arise in electronic structure methods. One way of determining the X and Z factor matrices is using the grid-based least-squares THC (LS-THC) method. In this case, we define some grid and let the X factors become collocation matrices of grid points and basis functions,

$$X_\mu^P = \phi_\mu(\vec{r}_P) \quad (23)$$

Once the X factors are defined, the core Z matrix is determined through a least-squares minimization:¹⁵

$$\min_Z \|(\mu\nu|\rho\sigma) - X_\mu^P X_\nu^P Z^{PQ} X_\rho^Q X_\sigma^Q\|_F^2 \quad (24)$$

where the subscript F denotes a Frobenius norm. In the minimization, we will use the density fitting approximation to represent the electron repulsion integrals. This allows the THC factorization to be formed with $O(N^4)$ effort. In the context of

EOM-CC2, we perform the LS-THC factorization in the molecular orbital (MO) basis,

$$(pq|rs) \approx X_p^P X_q^P Z^{PQ} X_r^Q X_s^Q \quad (25)$$

where these indices run over all active orbitals. Recently, we have presented an implementation of CC2 that exploits the flexibility afforded by the THC approximation to achieve quartic scaling. Structurally, the contractions that arise in eqs 13 and 14 are identical to those found in the CC2 amplitude equations. Therefore, the factorization presented in our previous work can be leveraged in the context of EOM-CC2 with minor modification.¹⁷

In order to efficiently implement EOM-CC2, we must find a simple way of treating r_{ij}^{ab} that does not involve constructing the full fourth-order tensor.^{20,21} This is done in CC2 for t_{ij}^{ab} by defining modified collocation matrices.

$$\tau_i^P = X_i^P + t_i^a X_a^P \quad (26)$$

$$\tau_a^P = X_a^P - t_i^a X_i^P \quad (27)$$

Next, a Laplace transformation of $1/(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j)$ is introduced to remove the orbital energy denominator, and it is approximated by numerical quadrature (here, we use ν to index the quadrature points).^{22,23}

$$\frac{1}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} = - \int_0^\infty e^{-[\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j]t} dt \approx -\alpha_i^\nu \alpha_j^\nu \alpha_a^\nu \alpha_b^\nu \quad (28)$$

Finally, we have a simple expression for t_{ij}^{ab} that we can substitute wherever it appears in the CC2 amplitude equations (and in EOM-CC2).

$$t_{ij}^{ab} = -\alpha_i^\nu \alpha_j^\nu \alpha_a^\nu \alpha_b^\nu \tau_i^P \tau_a^P Z^{PQ} \tau_j^Q \tau_b^Q \quad (29)$$

Matters become slightly more complicated for r_{ij}^{ab} , because the appearance of a single commutator involving \hat{R} breaks some of the symmetries that exist in t_{ij}^{ab} . Nevertheless, we will use an analogous strategy and bury the contractions with r_i^a into two new intermediates.

$$\rho_i^P = r_i^a X_a^P \quad (30)$$

$$\rho_a^P = -r_i^a X_i^P \quad (31)$$

Additionally, we define the Laplace transformation of the shifted orbital energy denominator with w indexing the quadrature points.²⁴

$$\begin{aligned} \frac{1}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b + \omega} &= - \int_0^\infty e^{-[\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j - \omega]t} dt \\ &\approx -\beta_i^w \beta_j^w \beta_a^w \beta_b^w \end{aligned} \quad (32)$$

Now, we are left with a familiar, albeit more complicated, expression for r_{ij}^{ab} .

$$\begin{aligned} r_{ij}^{ab} &= -\beta_i^w \beta_j^w \beta_a^w \beta_b^w [\rho_i^P \tau_a^P Z^{PQ} \tau_j^Q \tau_b^Q + \tau_i^P \rho_a^P Z^{PQ} \tau_j^Q \tau_b^Q \\ &\quad + \tau_i^P \tau_a^P Z^{PQ} \rho_j^Q \tau_b^Q + \tau_i^P \tau_a^P Z^{PQ} \tau_j^Q \rho_b^Q] \end{aligned} \quad (33)$$

This THC factorization of r_{ij}^{ab} , as well as the factorization of the amplitude equations we have previously developed for CC2, can be combined to implement quartic scaling THC-EOM-

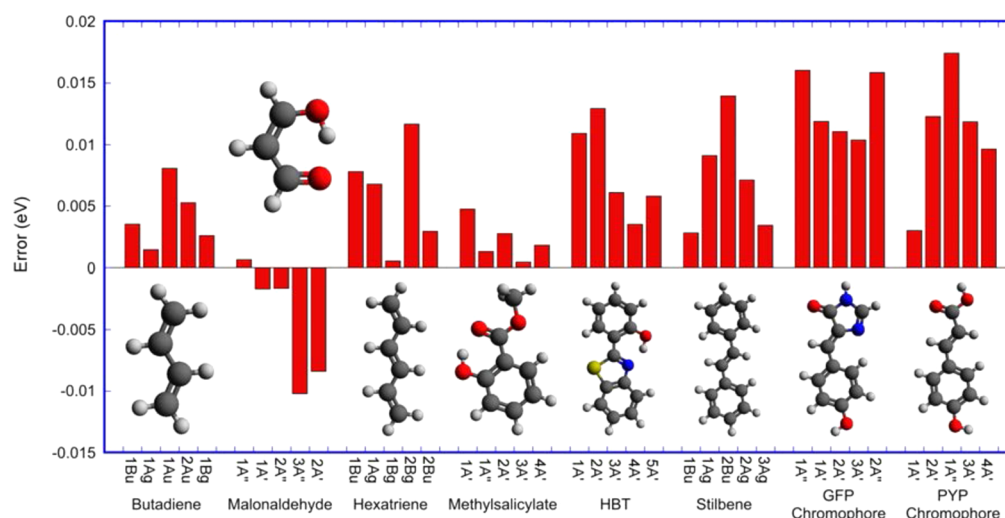


Figure 1. Error in electronvolts of THC-EOM-CC2/cc-pVDZ relative to canonical EOM-CC2/cc-pVDZ excitation energies for a variety of small molecules.

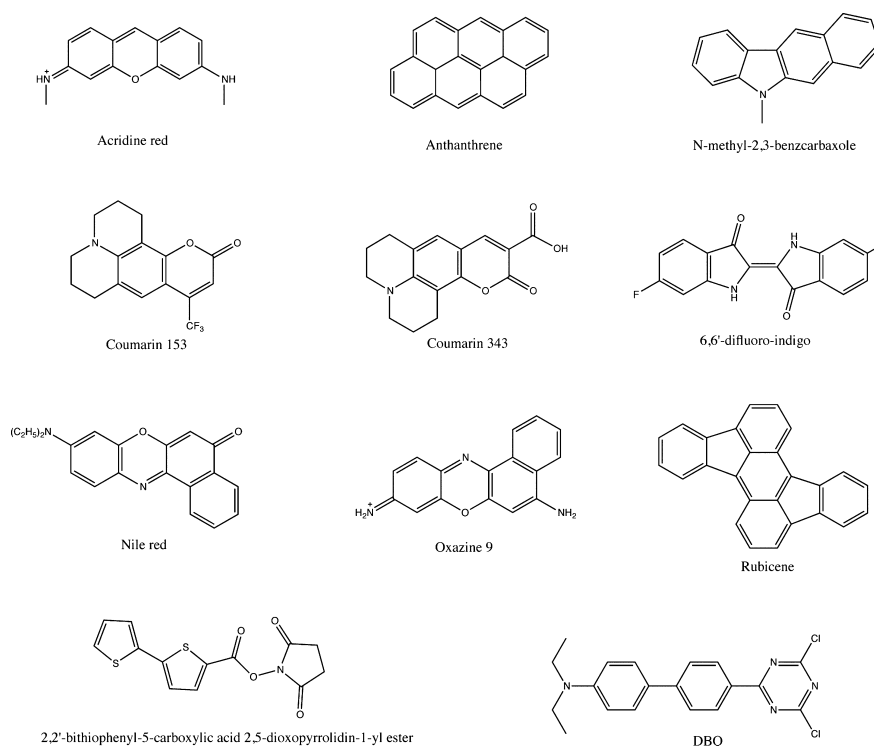


Figure 2. Molecules used to test the accuracy of THC-EOM-CC2; the numerical results are shown in Figures 3 and 4.

CC2. At first glance, it appears that each THC-EOM-CC2 iteration will be four times more expensive than a ground state THC-CC2 iteration. However, if terms are grouped carefully, each THC-EOM-CC2 iteration is only two times more expensive. A detailed outline of our THC-EOM-CC2 algorithm is provided in Supporting Information.

■ RESULTS

The THC-EOM-CC2 method has been implemented in a development version of the PSI4 electronic structure program.²⁵ To test the accuracy of the THC approximation in this context, canonical EOM-CC2 and density-fitted EOM-CC2 computations were performed with PSI4 and TURBOMOLE,²⁶ respectively. For EOM-CC2 computations, canonical

HF references were used; DF-HF references were used with DF-EOM-CC2. Dunning’s cc-pVDZ basis sets were used for all computations.²⁷ This is the minimal basis set size normally used for treating excited states with CC2. The ultimate success of THC-EOM-CC2 will involve extending the underlying THC approximation to larger basis sets, including those augmented with diffuse functions. This will be pursued in future work. The cc-pVTZ-JKFIT auxiliary basis set was used for DF-HF references.²⁸ In correlated computations, the aug-cc-pVTZ-RI (Figure 1) and cc-pVDZ-RI (Figures 3, 4, and 5) auxiliary basis sets were used.²⁹ The radial discrete variable representation grids used in the LS-THC approximation are described in ref 30. The grids are constructed from the aug-cc-pVTZ-RI basis (Figures 1 and 5) or the aug-cc-pVTZ-JKFIT basis (Figures 3

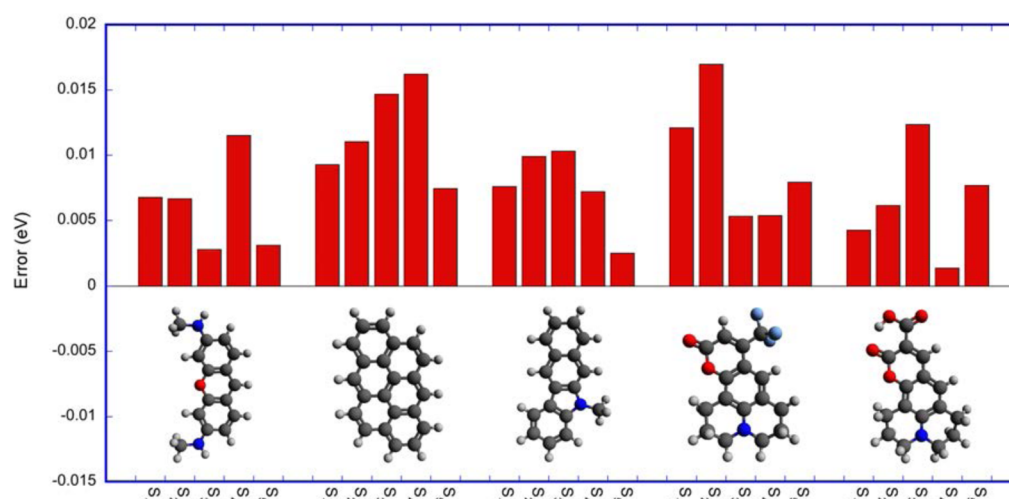


Figure 3. Error in electronvolts of THC-EOM-CC2/cc-pVDZ relative to DF-EOM-CC2/cc-pVDZ excitation energies. States are given adiabatic labels according to the ordering predicted by DF-EOM-CC2.

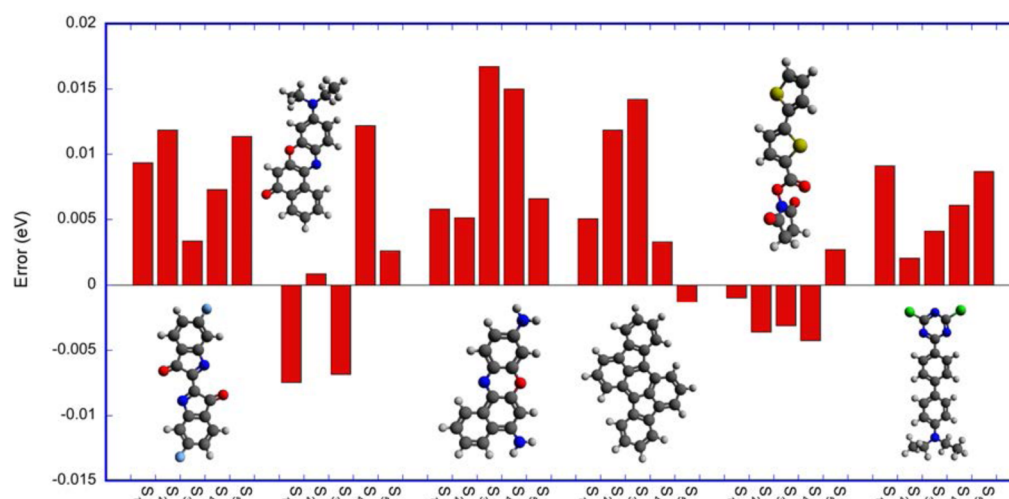


Figure 4. Error in electronvolts of THC-EOM-CC2/cc-pVDZ relative to DF-EOM-CC2/cc-pVDZ excitation energies. States are given adiabatic labels according to the ordering predicted by DF-EOM-CC2.

and 4) and up to ninth-order Lebedev–Laikov quadratures.³¹ Molecular geometries for the molecules shown in Figure 1 were optimized at the B3LYP/6-31G** level of theory; geometries for the molecules in Figure 2 were taken from refs 32–34. Geometries of stilbene (Figure 5) were optimized at the DF-EOM-CC2/cc-pVDZ level of theory with TURBOMOLE²⁶ with a constraint placed on the torsion angle formed by the carbon atoms across the ethylenic bond (C–C=C–C).

In Figure 1, the accuracy of THC-EOM-CC2 excitation energies (from the ground electronic state) is assessed relative to canonical EOM-CC2 for eight small molecules. A large auxiliary DF basis (aug-cc-pVTZ-RI) is used so that most of the error is due to the THC approximation. The errors are reported as $\Delta E_{\text{EOM-CC2}} - \Delta E_{\text{THC-EOM-CC2}}$. Among these molecules, there is a slight tendency for underestimation of the excitation energies by THC-EOM-CC2. However, the THC-EOM-CC2 excitation energies are always within 0.02 eV of the EOM-CC2 predictions, which is acceptable accuracy for most practical applications (and well within the intrinsic errors of EOM-CC2). These errors include contributions from both the DF approximation to the two-electron integrals and the THC approximation to the DF integrals. In Figures 3 and 4, THC-

EOM-CC2 excitation energies are compared with DF-EOM-CC2 for slightly larger molecules. This comparison isolates the error due to the THC approximation. The THC error in excitation energies is again always less than 0.02 eV. Furthermore, there is no visible tendency for these errors to increase with increasing molecular size. Many of the larger molecules in Figures 3 and 4 are highly conjugated, which could be problematic for methods involving orbital localization. Thus, these comparisons also highlight the fact that the approximations in THC do not depend explicitly on localization and therefore do not degrade in cases involving highly delocalized orbitals.

The results for THC-EOM-CC2 presented thus far focus on the accuracy of the excitation energies. In order to achieve $O(N^4)$ scaling, it is necessary in practice to also carry out the ground state CC2 calculations using the THC approximation (and this was done in the results presented above). In many applications, the excited state potential energy surface will be of interest. In this case, the errors from the THC-CC2 calculation of the ground state and the subsequent THC-EOM-CC2 calculation of the excitation energy will both be important. We choose stilbene as an example for the accuracy of THC-EOM-

CC2 in calculations of excited state surfaces. The photoinduced isomerization of *trans*-stilbene has been used as a paradigm for reaction rate theories, and the torsional barrier height has been of considerable interest in this context.³⁵ The S_1 excited state potential energy curve for torsion in stilbene is shown in Figure 5. The THC-EOM-CC2 calculations follow the DF-EOM-CC2

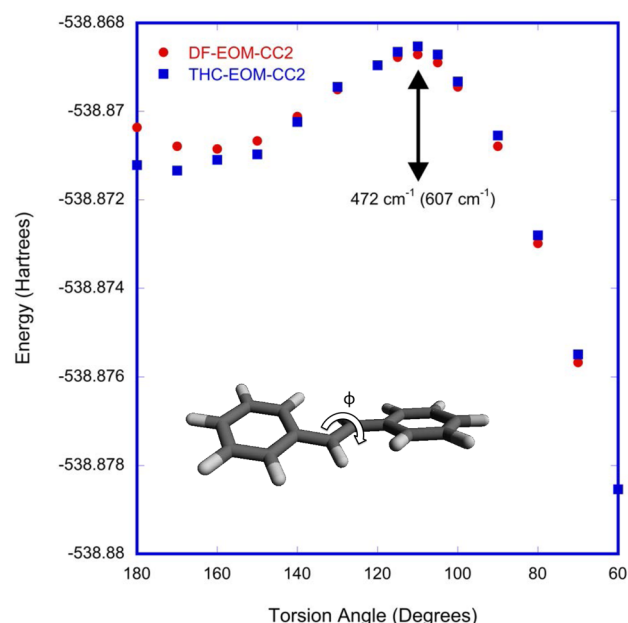


Figure 5. First excited electronic state of stilbene computed with DF-EOM-CC2/cc-pVDZ and THC-EOM-CC2/cc-pVDZ for fixed torsion angles. Geometries were relaxed on S_1 with DF-EOM-CC2/cc-pVDZ under the constraint that the torsion angle remained fixed. The barrier to rotation is given in wavenumbers as computed by DF-EOM-CC2 and THC-EOM-CC2 (in parentheses).

results quite closely, with slight differences in the region of the *trans* S_1 minimum. The torsional barrier is somewhat (~ 100 cm^{-1}) larger with THC-EOM-CC2 compared with DF-EOM-CC2.

CONCLUSIONS

We have presented an extension of our quartic-scaling CC2 method to molecular excited states. Our formulation of EOM-CC2 uses the THC approximation to the two-electron integrals and Laplace transformation of orbital energy denominators to avoid the explicit formation of doubles amplitudes, which allows for a quartic-scaling factorization of THC-EOM-CC2. Preliminary tests show that excitation energies can be obtained from THC-EOM-CC2 with errors of less than 0.02 eV using a grid-based formulation of the LS-THC approximation. More importantly, THC-EOM-CC2 exhibits the same formal scaling as more approximate methods such as CIS or TDDFT. There is great potential in THC-EOM-CC2 to be able to study excited states in large molecules as well as to rapidly compute excitation energies in smaller molecules. It should be possible to combine some of the techniques used in THC-EOM-CC2 with our previous work on THC-CCSD¹⁶ to obtain a quartic-scaling THC-EOM-CCSD method. Beyond that, it should also be possible to extend these ideas to EOM-CC methods with an approximate treatment of triple excitations. The complication in the case of EOM-CCSD is, of course, the fact that the r_{ij}^{ab} amplitudes cannot be factored analytically as they can in CC2.

Additionally, the inclusion of triple excitations would likely lead to at least a quintic-scaling algorithm. Regardless, the extension of the THC approximation to more complete EOM-CC methods should be pursued.

ASSOCIATED CONTENT

Supporting Information

Details of the basis sets and grids used, a more detailed derivation of the EOM-CC2 equations we use, and detailed equations suitable for computer implementation of THC-EOM-CC2 are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: toddjmartinez@gmail.com.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (Grant No. OCI-1047577) and by the Department of Defense (Office of the Assistant Secretary of Defense for Research and Engineering) through a National Security Science and Engineering Faculty Fellowship. R.M.P. is a DOE Computational Science Graduate Fellow (Grant DE-FG02-97ER25308).

REFERENCES

- (1) Christiansen, O.; Koch, H.; Jørgensen, P. The 2nd-Order Approximate Coupled-Cluster Singles and Doubles Model CC2. *Chem. Phys. Lett.* **1995**, *243*, 409–418.
- (2) Geertsens, J.; Rittby, M.; Bartlett, R. J. The Equation-of-Motion Coupled-Cluster Method: Excitation Energies of Be and CO. *Chem. Phys. Lett.* **1989**, *164*, 57–62.
- (3) Shavitt, I.; Bartlett, R. J. *Many-Body Methods in Chemistry and Physics: MBPT and Coupled-Cluster Theory*; Cambridge University Press: Cambridge, U.K., 2009.
- (4) Koch, H.; Jørgensen, P. Coupled Cluster Response Functions. *J. Chem. Phys.* **1990**, *93*, 3333–3344.
- (5) Snegov, K.; Christiansen, O. Excited State Coupled Cluster Methods. *WIREs Comput. Mol. Sci.* **2012**, *2*, 566–584.
- (6) Stanton, J. F.; Bartlett, R. J. The Equation of Motion Coupled-Cluster Method. A Systematic Biorthogonal Approach to Molecular Excitation Energies, Transition Probabilities, and Excited State Properties. *J. Chem. Phys.* **1993**, *98*, 7029–7039.
- (7) Plötnner, J.; Tozer, D. J.; Dreuw, A. Dependence of Excited State Potential Energy Surfaces on the Spatial Overlap of the Kohn–Sham Orbitals and the Amount of Nonlocal Hartree–Fock Exchange in Time-Dependent Density Functional Theory. *J. Chem. Theory Comput.* **2010**, *6*, 2315–2324.
- (8) Hättig, C.; Weigend, F. CC2 Excitation Energy Calculations on Large Molecules Using the Resolution of the Identity Approximation. *J. Chem. Phys.* **2000**, *113*, 5154–5161.
- (9) Hättig, C.; Köhn, A. Transition Moments and Excited-State First-Order Properties in the Coupled-Cluster Model CC2 Using the Resolution-of-the-Identity Approximation. *J. Chem. Phys.* **2002**, *117*, 6939–6951.
- (10) Vahtras, O.; Almlöf, J.; Feyereisen, M. W. Integral Approximations for LCAO-SCF Calculations. *Chem. Phys. Lett.* **1993**, *213*, 514–518.
- (11) Feyereisen, M. W.; Fitzgerald, G.; Komornicki, A. Use of Approximate Integrals in Ab Initio Theory. An Application in MP2 Energy Calculations. *Chem. Phys. Lett.* **1993**, *208*, 359–363.
- (12) Kats, D.; Korona, T.; Schütz, M. Local CC2 Electronic Excitation Energies for Large Molecules with Density Fitting. *J. Chem. Phys.* **2006**, *125*, No. 104106.

- (13) Kats, D.; Schütz, M. A Multistate Local Coupled Cluster CC2 Response Method Based on the Laplace Transform. *J. Chem. Phys.* **2009**, *131*, No. 124117.
- (14) Hohenstein, E. G.; Parrish, R. M.; Martínez, T. J. Tensor Hypercontraction Density Fitting. I. Quartic Scaling Second- and Third-Order Møller-Plesset Perturbation Theory. *J. Chem. Phys.* **2012**, *137*, No. 044103.
- (15) Parrish, R. M.; Hohenstein, E. G.; Martínez, T. J.; Sherrill, C. D. Tensor Hypercontraction. II. Least-Squares Renormalization. *J. Chem. Phys.* **2012**, *137*, No. 224106.
- (16) Hohenstein, E. G.; Parrish, R. M.; Sherrill, C. D.; Martínez, T. J. Tensor Hypercontraction. III. Least-Squares Tensor Hypercontraction for the Determination of Correlated Wavefunctions. *J. Chem. Phys.* **2012**, *137*, No. 221101.
- (17) Hohenstein, E. G.; Kokkila, S. I. L.; Parrish, R. M.; Martínez, T. J. Quartic Scaling Second-Order Approximate Coupled Cluster Singles and Doubles via Tensor Hypercontraction: THC-CC2. *J. Chem. Phys.* **2013**, *138*, No. 124111.
- (18) Čížek, J. On the Correlation Problem in Atomic and Molecular Systems. Calculation of Wavefunction Components in Ursell-Type Expansion Using Quantum-Field Theoretical Methods. *J. Chem. Phys.* **1966**, *45*, 4256–4266.
- (19) Purvis, G. D.; Bartlett, R. J. A Full Coupled-Cluster Singles and Doubles Model: The Inclusion of Disconnected Triples. *J. Chem. Phys.* **1982**, *76*, 1910–1918.
- (20) Christiansen, O.; Koch, H.; Jørgensen, P.; Helgaker, T. Integral Direct Calculation of CC2 Excitation Energies: Singlet Excited States of Benzene. *Chem. Phys. Lett.* **1996**, *263*, 530–539.
- (21) Koch, H.; de Merás, A. S.; Helgaker, T.; Christiansen, O. The Integral-Direct Coupled Cluster Singles and Doubles Model. *J. Chem. Phys.* **1996**, *104*, 4157–4165.
- (22) Almlöf, J. Elimination of Energy Denominators in Møller-Plesset Perturbation-Theory by a Laplace Transform Approach. *Chem. Phys. Lett.* **1991**, *181*, 319–320.
- (23) Braess, D.; Hackbusch, W. Approximation of $1/x$ by Exponential Sums in $[1, \infty)$. *IMA J. Numer. Anal.* **2005**, *25*, 685–697.
- (24) This transformation of the shifted orbital energy denominator is not applicable for $\omega \geq 2(\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}})$. In practice, this is not too limiting, since, only the lowest few excited states are usually sought.
- (25) Turney, J. M.; et al. PSI4: An Open-Source Ab Initio Electronic Structure Program. *WIREs Comput. Mol. Sci.* **2012**, *2*, 556–565.
- (26) TURBOMOLE V6.4 2012, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007; available from <http://www.turbomole.com>.
- (27) Dunning, T. H. Gaussian Basis Sets for Use in Correlated Molecular Calculations. I. The Atoms Boron Through Neon and Hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007–1023.
- (28) Weigend, F. A Fully Direct RI-HF Algorithm: Implementation, Optimised Auxiliary Basis Sets, Demonstration of Accuracy and Efficiency. *Phys. Chem. Chem. Phys.* **2002**, *4*, 4285–4291.
- (29) Weigend, F.; Köhn, A.; Hättig, C. Efficient Use of the Correlation Consistent Basis Sets in Resolution of the Identity MP2 Calculations. *J. Chem. Phys.* **2002**, *116*, 3175–3183.
- (30) Parrish, R. M.; Hohenstein, E. G.; Sherrill, C. D.; Martínez, T. J. Discrete Variable Representation in Electronic Structure Theory: Quadrature Grids for Least-Squares Tensor Hypercontraction. *J. Chem. Phys.* **2013**, *138*, No. 194107.
- (31) Lebedev, V. I.; Laikov, D. N. A Quadrature Formula for the Sphere of the 131st Algebraic Order of Accuracy. *Dokl. Math.* **1999**, *59*, 477–481.
- (32) Goerigk, L.; Moellmann, J.; Grimme, S. Computation of Accurate Excitation Energies for Large Organic Molecules with Double-Hybrid Density Functionals. *Phys. Chem. Chem. Phys.* **2009**, *11*, 4611–4620.
- (33) Goerigk, L.; Grimme, S. Assessment of TD-DFT Methods and of Various Spin Scaled CIS(D) and CC2 Versions for the Treatment of Low-Lying Valence Excitations of Large Organic Dyes. *J. Chem. Phys.* **2010**, *132*, No. 184103.
- (34) Sánchez-de Armas, R.; San Miguel, M. A.; Oviedo, J.; Sanz, J. F. Coumarin Derivatives for Dye Sensitized Solar Cells: a TD-DFT Study. *Phys. Chem. Chem. Phys.* **2012**, *14*, 225–233.
- (35) Leitner, D. M.; Levine, B.; Quenneville, J.; Martinez, T. J.; Wolynes, P. G. Quantum Energy Flow and *trans*-Stilbene Photoisomerization: An Example of a Non-RRKM Reaction. *J. Phys. Chem. A* **2003**, *107*, 10706–10716.