Linear-response density cumulant theory for
excited electronic states

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Abstract

We present a linear-response formulation of
density cumulant theory (DCT) that provides
a balanced and accurate description of many
electronic states simultaneously. In the origi-
nal DCT formulation, only information about
a single electronic state (usually, the ground
state) is obtained. We discuss the derivation
of linear-response DCT, present its implemen-
tation for the ODC-12 method (LR-ODC-12),
and benchmark its performance for excitation
energies in small molecules (N2, CO, HCN,
HNC, C2H2, and H2CO), as well as challeng-
ing excited states in ethylene, butadiene, and
hexatriene. For small molecules, LR-ODC-12
shows smaller mean absolute errors in excita-
tion energies than equation-of-motion coupled
cluster theory with single and double excita-
tions (EOM-CCSD), relative to the reference
data from EOM-CCSDT. In a study of buta-
diene and hexatriene, LR-ODC-12 correctly de-
scribes the relative energies of the singly-excited
1^1B_u and the doubly-excited 2^1A_g states, in ex-
cellent agreement with highly accurate semi-stochastic heat-bath configuration interaction
results, while EOM-CCSD overestimates the
energy of the 2^1A_g state by almost 1 eV. Our
results demonstrate that linear-response DCT
is a promising theoretical approach for excited
states of molecules.

1 Introduction

Accurate simulation of excited electronic states
remains one of the major challenges in modern
electronic structure theory. Ab initio methods
for excited states can be divided into single-
reference and multi-reference categories, based
on their ability to treat static electron correla-
tion. Multi-reference methods[1–18] can correctly
describe static correlation in near-degenerate
valence orbitals and electronic states with
multiple-excitation character, but often lack ac-
curate treatment of important dynamic corre-
lation effects or become computationally very
costly when the number of strongly correlated
orbitals is large. Meanwhile, single-reference
methods[19–33] often provide a compromise be-
tween the computational cost and accuracy,
and can be used to reliably compute properties
of molecules in low-lying electronic states
near the equilibrium geometries. In these situ-
ations, single-reference equation-of-motion cou-
ped cluster theory (EOM-CC)[21–26] is usually
the method of choice, especially when high ac-
curacy is desired.

The EOM-CC methods yield size-intensive
excitation energies[28,29] and can be systemat-
ically improved by increasing the excitation
rank of the cluster operator in the exponential
parametrization of the wavefunction. Although
EOM-CC is usually formulated in the context
of a similarity-transformed Hamiltonian, its ex-
citation energies are equivalent to those ob-
tained from linear-response coupled cluster the-
ory (LR-CC). Both EOM-CC and LR-CC are based on non-Hermitian eigenvalue problems, which complicates the computation of molecular properties (e.g., transition dipoles) by requiring evaluation of left and right eigenvectors, and may result in an incorrect description of potential energy surfaces in the vicinity of conical intersections where complex excitation energies may be obtained.

Several Hermitian alternatives to EOM-CC and LR-CC have been proposed to avoid these problems, such as algebraic diagrammatic construction, unitary and variational LR-CC, similarity-constrained CC, and propagator-based LR-CC.

In this work, we present a linear-response formulation of density cumulant theory for excited electronic states. In density cumulant theory (DCT), the electronic energy is determined directly in terms of the one-particle reduced density matrix and the density cumulant, i.e. the fully connected part of the two-body reduced density matrix (2-RDM). In this regard, DCT is related to approaches based on the variational optimization or parametrization of the 2-RDM. On the other hand, DCT has a close relationship with wavefunction-based electronic structure theories, such as linearized, unitary, and variational coupled cluster theory.

In contrast to variational 2-RDM theory and traditional coupled cluster methods, DCT naturally combines size-extensivity and a Hermitian energy functional. In addition, the DCT electronic energy is fully optimized with respect to all of its parameters, which greatly simplifies computation of the first-order molecular properties. We have successfully applied DCT to a variety of chemical systems with different electronic structure effects (e.g., open-shell, symmetry-breaking, and multi-reference). One limitation of the original DCT formulation is the ability to describe only the lowest-energy state of a particular symmetry (usually, the ground state). By combining DCT with linear response theory, we remove this limitation, providing access to many electronic states simultaneously.

We begin with a brief overview of DCT (Section 2.1) and linear response theory (Section 2.2). In Section 2.3, we describe the derivation of the linear-response equations for the ODC-12 model (LR-ODC-12). In Section 2.4, we compare the LR-ODC-12 method with linear-response orbital-optimized linearized coupled cluster theory with double excitations (LR-OLCCD), which we derive by linearizing the LR-ODC-12 equations. We outline the computational details in Section 3. In Section 4, we demonstrate that the LR-ODC-12 excitation energies are size-intensive (Section 4.1), test the performance of LR-ODC-12 for the dissociation of H$_2$ (Section 4.2), benchmark its accuracy for vertical excitation energies of small molecules (Section 4.3), and apply LR-ODC-12 to challenging excited states in ethylene, butadiene, and hexatriene (Section 4.4). We present our conclusions in Section 5.

2 Theory

2.1 Overview of Density Cumulant Functional Theory

We begin with a brief overview of density cumulant theory (DCT) for a single electronic state. Our starting point is to express the electronic energy as a trace of the one- and antisymmetrized two-electron integrals ($h_{pq}^{rs}$ and $\bar{g}_{pq}^{rs}$) with the reduced one- and two-body density matrices ($\gamma_{pq}$ and $\gamma_{pq}^{rs}$):

$$E = h_{pq}^{rs} \gamma_{pq} + \frac{1}{4} g_{pq}^{rs} \gamma_{pq}^{rs}$$

where summation over the repeated indices is implied. In DCT, the two-body density matrix $\gamma_{rs}^{pq}$ is expanded in terms of its connected part, the two-body density cumulant ($\lambda_{rs}^{pq}$), and its disconnected part, which is given by an antisymmetrized product of one-body density matrices ($\gamma_q^p$ and $\gamma_{rs}^{pq}$):

$$\gamma_{rs}^{pq} = \langle \Psi | a_{rs}^{pq} | \Psi \rangle = \lambda_{rs}^{pq} + P_{(r/s)} \gamma_{r}^{p} \gamma_{s}^{q}$$

where $P_{(r/s)} v_{rs} = v_{rs} - v_{sr}$ denotes antisymmetrization and $\alpha_{rs}^{pq} = a_{r}^{p} a_{s}^{q} a_{r}^{s}$ is the two-body operator in second quantization. The one-body density matrix $\gamma_{q}^{p}$ is determined from its non-
linear relationship to the cumulant's partial trace,
\[ \gamma_q^p = \gamma_r^p \gamma_q^r - \lambda_{pr}^q \]  
(3)

This allows us to determine the energy (1) from the two-body density cumulant and the spin-orbitals, thereby defining the DCT energy functional. The density cumulant is parametrized by choosing a specific Ansatz for the wavefunction \(|\Psi\rangle\) such that

\[ \lambda_{rs}^{pq} = \langle \Psi | a_{rs}^{pq} | \Psi \rangle_c \]  
(4)

where \(c\) indicates that only fully connected terms are included in the parametrization. Importantly, due to the connected nature of Eq. (4), DCT is both size-consistent and size-extensive for any parametrization of \(|\Psi\rangle\), and is exact in the limit of a complete parametrization (i.e., when \(|\Psi\rangle\) is expanded in the full Hilbert space). \[\text{Eq. (4)}\] can be considered as a set of \(n\)-representability conditions that constrain the resulting one- and two-body density matrices to (at least approximately) represent a physical \(n\)-electron wavefunction. To compute the DCT energy, the functional (1) is made stationary (at least approximately) through a unitary treatment of double excitations:

\[ |\Psi\rangle = e^{\hat{T}_1^{\dagger} - \hat{T}_1^{\dagger}} (1 + \hat{T}_2) |\Phi\rangle \]  
(5)

\[ \hat{T}_1 = t_1 \cdot a_1 = t'_a a_i^a \]  
(6)

\[ \hat{T}_2 = t_2 \cdot a_2 = \frac{1}{2} \lambda_{ab}^{ij} a_i^{ab} \]  
(7)

The exponential singles operator \(e^{\hat{T}_1^{\dagger} - \hat{T}_1^{\dagger}}\) has the effect of a unitary transformation of the spin-orbital basis and is incorporated in our ODC-12 implementation by optimizing the orbitals.\[\text{Eq. (5)}\] The \(t_1\) and \(t_2\) parameters are obtained from the stationarity conditions

\[ \frac{\partial E}{\partial t_1} = 0, \quad \frac{\partial E}{\partial t_2} = 0 \]  
(8)

and are used to compute the ODC-12 energy. Explicit equations for the stationarity conditions are given in Refs. 53 and 54. Although in ODC-12 the wavefunction parametrization is linear with respect to double excitations (Eq. (5)), the ODC-12 energy stationarity conditions are non-linear in \(t_2\) due to the non-linear relationship between the one-particle density matrix and the density cumulant (Eq. (3)).\[\text{Eq. (8)}\] results in the equations that define the linearized orbital-optimized coupled cluster doubles method (OLCCD). This method is equivalent to the orbital-optimized coupled electron pair approximation zero (OCEPA\(_0\)).

2.2 Linear Response Theory

We now briefly review linear response theory in the quasi-energy formulation.\[\text{Ref. 99}\] For a more detailed presentation, we refer the readers to Ref. 99. The quasi-energy of a system perturbed by a time-dependent interaction \(\hat{V} f(t)\) is defined as

\[ Q(t) = \langle \Psi(t) | \hat{H} + \hat{V} f(t) - i \frac{\partial}{\partial t} | \Psi(t) \rangle \]  
(9)

where \(\Psi(t)\) is the phase-isolated wavefunction, from which the usual Schrödinger wavefunction can be recovered as follows:

\[ \Phi_S(t) = e^{-i \int_0^t dt' Q(t')} | \Psi(t) \rangle \]  
(10)

Assuming that the perturbation is Hermitian and periodic, the time average of the quasi-energy over a period of oscillation, denoted as \(\{ Q(t) \}\), is variational with respect to the exact dynamic state.\[\text{Ref. 99}\] The time-dependence of the perturbation can be expressed as a Fourier expansion

\[ f(t) = \sum_\omega f(\omega) e^{-i \omega t} \]  
(11)

where the sum runs over frequencies of a common period, and Hermiticity demands that the negative frequencies are included as well to satisfy the condition \(f(-\omega) = f^*(\omega)\). The independent parameters \(u(\omega)\) defining the time-dependent wavefunction can be expressed in polynomial orders of \(f(t)\) as

\[ u(t) = u + \sum_\omega u(\omega) e^{-i \omega t} + \cdots \]  
(12)
where only the linear (first-order) contribution is relevant in the present work. The stationarity of the time-averaged quasi-energy implies the following relationship:

\[
0 = \frac{d}{df(\omega)} \left. \partial \{Q(t)\} \right|_{f=0} = \left. \frac{\partial^2 \{Q(t)\}}{\partial u^\dagger(\omega) \partial u(\omega)} \right|_{f=0} + \left. \frac{\partial^2 \{Q(t)\}}{\partial u^\dagger(\omega) \partial f(\omega)} \right|_{f=0} + \left. \frac{\partial^2 \{Q(t)\}}{\partial u(\omega) \partial f(\omega)} \right|_{f=0}
\]

which constitutes a linear equation for the first-order response of the system to the perturbation. When the frequency \(\omega\) is in resonance with an excitation energy of the system, Eq. (13) will result in an infinite first-order response \(\frac{\partial u(\omega)}{\partial f(\omega)}\). From Eq. (13), we find that these poles occur when the Hessian matrix of the quasi-energy with respect to the wavefunction parameters \(u(\omega)\) becomes singular. We can express this Hessian matrix in the form:

\[
\left. \frac{\partial^2 \{Q(t)\}}{\partial u^\dagger(\omega) \partial u(\omega)} \right|_{f=0} \equiv E - \omega M
\]

where \(E\) is the Hessian of the time-averaged electronic energy \(\langle \langle \Psi(t) | \hat{H} | \Psi(t) \rangle \rangle\) and \(\omega M\) is the Hessian of the time-derivative overlap \(\langle \langle \Psi(t) | i\Psi(t) \rangle \rangle\). The excitation energies of the system \(\omega_k\) can therefore be determined by solving the following generalized eigenvalue equation:

\[
Ez_k = \omega_k Mz_k
\]

where \(M\) serves as the metric matrix. Eq. (15) allows the determination of excitation energies for an arbitrary parametrization of \(|\Psi(t)\rangle\).

The generalized eigenvectors \(z_k\) can be used to compute transition properties for excited states. In particular, in the exact linear response theory, the transition strength of the perturbing interaction, \(|\langle \langle \Psi(t) | \hat{V} | \Psi(t) \rangle \rangle|^2\), is equal to the complex residue of the following quantity at \(\omega \to \omega_k\):

\[
\langle \langle \hat{V} | \hat{V} \rangle \rangle_{\omega} \equiv \mathbf{v}'^\dagger \left. \frac{\partial u(\omega)}{\partial f(\omega)} \right|_{f=0}
\]

This quantity is known as the linear response function and \(\mathbf{v}'\) is termed the property gradient vector, which is defined as follows:

\[
\mathbf{v}' \equiv \frac{\partial^2 \{Q(t)\}}{\partial u^\dagger(\omega) \partial f(\omega)} \bigg|_{f=0}
\]

Substituting Eqs. (14) and (17) into Eq. (13) and decomposing the quasi-energy Hessian as

\[
E - \omega M = (Z^\dagger)^{-1}(Z^\dagger M Z)(\Omega - \omega I)(Z)^{-1}
\]

where \(Z\) is the matrix of generalized eigenvectors for \(E\) and \(M\) and \(\Omega\) is the diagonal matrix of eigenvalues (Eq. (15)), we obtain the general formula for the transition strengths:

\[
\lim_{\omega \to \omega_k} \langle \langle \hat{V} | \hat{V} \rangle \rangle_{\omega} = \frac{|z_k^\dagger \mathbf{v}'|^2}{z_k^\dagger M z_k}
\]

In Section 2.3, we will use the quasi-energy formalism to derive equations for the linear-response ODC-12 method (LR-ODC-12).

### 2.3 Linear-Response ODC-12

In the ODC-12 method, the time-dependence of the electronic state is specified by the following parameters:

\[
\mathbf{u}(t) = \begin{pmatrix} t_1(t) \\ t_2(t) \\ t_1^*(t) \\ t_2^*(t) \end{pmatrix}
\]

The ODC-12 electronic Hessian can be written as:

\[
E = \begin{pmatrix} A_{11} & A_{12} & B_{11} & B_{12} \\ A_{21} & A_{22} & B_{21} & B_{22} \\ B_{11}^* & B_{12}^* & A_{11}^* & A_{12}^* \\ B_{21}^* & B_{22}^* & A_{21}^* & A_{22}^* \end{pmatrix}
\]

where the submatrices are defined in general as

\[
A_{nm} = \frac{\partial^2 E}{\partial t_n \partial t_m} \bigg|_{f=0}, \quad B_{nm} = \frac{\partial^2 E}{\partial t_n^\dagger \partial t_m^*} \bigg|_{f=0}
\]

These complex derivatives relate to the second derivatives of the electronic energy with respect to variations of the orbitals \((A_{11}, B_{11})\) and cumulant parameters \((A_{22}, B_{22})\). Similarly, the mixed second derivatives couple vari-
ations in the orbitals and cumulant parameters ($A_{12}, B_{12}$). The metric matrix $M$ has a block-diagonal structure, as a consequence of the linear parametrization of the wavefunction in Eq. (5):

$$
M = \begin{pmatrix}
S_{11} & 0 & 0 & 0 \\
0 & 1_2 & 0 & 0 \\
0 & 0 & -S_{11} & 0 \\
0 & 0 & 0 & -1_2
\end{pmatrix}
$$

(23)

where $1_2 = \langle \Phi|a_2^\dagger a_2|\Phi\rangle$ is an identity matrix over the space of unique two-body excitations and the orbital metric is defined as follows:

$$
\omega S_{11} = \left. \frac{\partial^2 \{ \langle \Psi(t)|i\dot{\Psi}(t)\rangle \} }{\partial t_1^2(\omega)\partial t_1(\omega)} \right|_{f=0}
$$

(24)

Equations for all blocks of $E,$ $M,$ and the property gradient vector $\nu'$ are shown explicitly in the Supporting Information. The computational cost of solving the LR-ODC-12 equations has $O(N^4)$ scaling (where $O$ and $V$ are the numbers of occupied and virtual orbitals, respectively), which is the same as the computational scaling of the single-state ODC-12 method. We note that, due to the Hermitian nature of the DCT energy functional [1], the ODC-12 energy Hessian $E$ is always symmetric. As a result, in the absence of instabilities (i.e., as long as the Hessian is positive semi-definite), the LR-ODC-12 excitation energies are guaranteed to have real values.

To illustrate the derivation of the LR-ODC-12 energy Hessian, let us consider the diagonal two-body block of $E.$ Expressing the energy [1] using the cumulant expansion [2] and differentiating with respect to $t_2,$ we obtain:

$$
A_{22} = \left. \frac{\partial^2 \{ \langle \Psi(t)|i\dot{\Psi}(t)\rangle \} }{\partial t_1^2(\omega)\partial t_2(\omega)} \right|_{f=0} = f_p^q \frac{\partial^2 \gamma_p^q}{\partial t_1^2\partial t_2} + \tilde{G}_{pr}^{qs} \frac{\partial^2 \gamma_r^s}{\partial t_1^2\partial t_2} + \frac{1}{4} \tilde{G}_{pq}^{rs} \frac{\partial^2 \lambda_p^q}{\partial t_1^2\partial t_2}
$$

(25)

where we have introduced the generalized Fock matrix $f_p^q \equiv h_p^q + \tilde{G}_{pr}^{qs} \gamma_r^s.$ The derivatives of the one-body density matrix can be expressed in terms of the derivatives of the density cumulant

$$
A_{22} = F_p^q \frac{\partial^2 \lambda_p^q}{\partial t_1^2\partial t_2} + G_{pr}^{qs} \frac{\partial^2 \lambda_r^s}{\partial t_1^2\partial t_2} + \frac{1}{4} \tilde{G}_{pq}^{rs} \frac{\partial^2 \lambda_p^q}{\partial t_1^2\partial t_2}
$$

(26)

where the intermediates $F_p^q$ and $G_{pr}^{qs}$ can be computed using a transformation of the one- and two-electron integrals to the natural spin-orbital basis (see appendix A for details). These cumulant derivatives are straightforward to evaluate from Eqs. (1) and (5) using either algebraic or diagrammatic techniques.

Next, we outline the derivation of the metric $M$ (see Supporting Information for more details). For the one-electron block of the metric, substituting Eq. (5) into Eq. (24) gives

$$
\omega S_{11} = \left. \frac{\partial^2 \{ \langle \Psi([\tilde{T}_1^\dagger(t), i\dot{\tilde{T}}_1(t)]|\Psi\rangle \} }{\partial t_1^2(\omega)\partial t_1(\omega)} \right|_{f=0}
$$

(27)

where we have assumed that we are working in the variational orbital basis so that $\tilde{T}_1(t)|f=0 = 0,$ and $\Psi = \Psi(t)|_{f=0}$ denotes the ground state wavefunction. Using the Fourier expansion of the $t_1(t)$ parameters (Eq. (12)), the gradients of the time derivatives can be evaluated as:

$$
\left. \frac{\partial \tilde{T}_1(t) }{\partial t_1(\omega)} \right|_{f=0} = +\omega a_1 e^{-i\omega t}
$$

(28)

$$
\left. \frac{\partial i\tilde{T}_1^\dagger(t) }{\partial t_1(\omega)} \right|_{f=0} = -\omega a_1^\dagger e^{+i\omega t}
$$

(29)

Substituting Eqs. (28) and (29) into Eq. (27) and evaluating the gradients of $\tilde{T}_1$ and $\tilde{T}_1^\dagger$ similarly gives the final working equation for the one-body metric:

$$
\omega(S_{11})_{ia,jb} = \omega \langle \Psi|[a_i^\dagger a_j^b]|\Psi\rangle = \omega (\delta_{ai}^b \delta_{ja}^b - \delta_{ai}^b \delta_{ja}^b)
$$

(30)

The metric contributions involving the second
derivatives with respect to $t_2$ have been determined using the linearized doubles parametrization of the wavefunction in Eq. (5). Since the ODC-12 energy is correct to the third order in perturbation theory, the $t_2$ contributions to the metric are also truncated at the third order. Using this approximation, we find that in LR-ODC-12 the $t_2$ second derivative contributions to the metric vanish. These results are in agreement with the expressions for the metric matrix elements in time-dependent unitary coupled-cluster doubles theory, which do not contain $t_2$ contributions up to the third order in perturbation theory. The mixed $t_1$-$t_2$ (orbital-cumulant) blocks of the metric are zero at any order of perturbation theory.

2.4 Linear-Response OLCCCD

As we discussed in Section 2.1, the orbital-optimized linearized coupled cluster doubles method (OLCCD) can be considered as an approximation to the ODC-12 method where all of the non-linear $t_2$ terms are neglected in the stationarity conditions. Similarly, we can formulate the linear-response OLCCD method (LR-OLCCD) by linearizing the LR-ODC-12 equations. This simplifies the expressions for the electronic Hessian blocks that involve the second derivatives with respect to $t_2$. For example, for the $A_{22}$ block, we obtain:

$$A_{22} = (f_0)^q_p \frac{\partial^2 \lambda_{pq}}{\partial t_2 \partial t_2} - (f_0)^q_p \frac{\partial^2 \lambda_{pq}}{\partial t_1 \partial t_2} + \frac{1}{2} f_{pq} \frac{\partial^2 \rho_{pq}}{\partial t_2 \partial t_2}$$

(31)

where $(f_0)^q_p = h^q_p + \bar{g}^q_{pi}$ is the usual (mean-field) Fock operator. Comparing Eq. (31) with Eq. (26) from the LR-ODC-12 method, we observe that the former equation can be obtained from the latter by replacing the $F^q_p$ intermediates with the mean-field Fock matrix elements and ignoring the term that depends on $G^q_{pp}$. These simplifications arise from the fact that the $F^q_p$ and $G^q_{pp}$ intermediates contain high-order $t_2$ contributions that are not included in the linearized LR-OLCCD formulation (see appendix A and Ref. 53 for details). For the $B_{22}$ block, we find that all of the Hessian elements are zero. A complete set of working equations for LR-OLCCD is given in the Supporting Information.

3 Computational Details

The LR-ODC-12 and LR-OLCCD methods were implemented as a standalone Python program, which was interfaced with Psi4 to obtain the one- and two-electron integrals. To compute excitation energies, our implementation utilizes the multi-root Davidson algorithm, which solves the generalized eigenvalue problem by progressively growing an expansion space for the $n_{\text{root}}$ lowest generalized eigenvectors of the electronic Hessian and the metric matrix. A key feature of this algorithm is that it avoids storing the Hessian and metric matrices, significantly reducing the amount of memory required by the computations. Our implementation of the energy Hessian was validated by computing the static response function for a dipole perturbation (i.e., the dipole polarizability):

$$\langle \hat{V}; \hat{V} \rangle_0 = -v^f E^{-1} v$$

(32)

This quantity can be evaluated numerically as a derivative of the ground state energy

$$\langle \hat{V}; \hat{V} \rangle_0 = \left. \frac{d^2 E}{df^2} \right|_{f=0}$$

(33)

by perturbing the one-electron integrals $h^q_p \leftarrow h^q_p + f v^q_p$ with the integrals of the perturbing dipole operator ($v^f$), and solving the ODC-12 (or OLCCD) equations for different values of $f$. For the dipole polarizability of the water molecule along its $C_2$ symmetry axis, the values of $\langle \hat{V}; \hat{V} \rangle_0$ computed using Eqs. (32) and (33) matched to $10^{-9}$ a.u.

We used Q-CHEM 4.1 to obtain results from equation-of-motion coupled cluster theory with single and double excitations (EOM-CCSD) and EOM-CCSD with triple excitations in the EOM part [EOM-CC(2,3)]. The MRCC program was used to obtain results for equation-of-motion coupled cluster theory with up to full triple excitations (EOM-CCSDT). All electrons were correlated in all
Table 1: Ground-state energies (in $E_h$) and vertical excitation energies (in eV) for the four lowest-energy excited states of the CO molecule and noninteracting systems of CO with Ne atoms (CO + nNe, n = 1, 2, 3) computed using the ODC-12 and LR-ODC-12 methods (cc-pVDZ basis set). Also shown results for two noninteracting CO molecules (CO + CO). The noninteracting systems were separated from each other by 10000 Å and the C–O bond distance was set to 1.12547 Å. Results demonstrate size-intensivity of the LR-ODC-12 excitation energies.

| State | CO | CO + Ne | CO + 2Ne | CO + 3Ne | CO + CO |
|-------|----|---------|----------|----------|---------|
| $X^1\Sigma^+$ | -113.051282 | -241.730913 | -370.410543 | -499.090174 | -226.102565 |
| $^3\Pi$ | 6.48597 | 6.48597 | 6.48597 | 6.48597 | 6.48597 |
| $^3\Sigma^+$ | 8.41225 | 8.41225 | 8.41225 | 8.41225 | 8.41225 |
| $^1\Pi$ | 8.90866 | 8.90866 | 8.90866 | 8.90866 | 8.90866 |
| $^3\Delta$ | 9.33189 | 9.33189 | 9.33189 | 9.33189 | 9.33189 |

computations. We used tight convergence parameters in all ground-state ($10^{-8} E_h$) and excited-state computations ($10^{-5} E_h$). In Sections 4.2 and 4.3 the augmented aug-cc-pVTZ and d-aug-cc-pVTZ basis sets of Dunning and co-workers were employed. For alkenes (Section 4.4), the ANO-L-pVXZ (X = D, T) basis sets were used as in Ref. 111. To compute vertical excitation energies in Section 4.3 geometries of molecules were optimized using ODC-12 (for LR-ODC-12), OLCCD (for LR-OLCCD), or CCSD [for EOM-CCSD, EOM-CC(2,3), and EOM-CCSDT]. For the alkenes in Section 4.4 frozen-core MP2/cc-pVQZ geometries were used as in Refs. 111 and 112.

4 Results

4.1 Size-Intensivity of the LR-ODC-12 Energies

In Section 2.1 we mentioned that all DCT methods are by construction size-extensive, meaning that their electronic energies scale linearly with the number of electrons. In this section, we demonstrate that the LR-ODC-12 excitation energies are size-intensive, i.e. they satisfy the following property: $E(A^* + B) = E(A^*) + E(B)$, where A and B are two noninteracting fragments in their corresponding ground states and A* is the fragment A in an excited state. Table 1 shows the ODC-12 ground-state energies and the LR-ODC-12 excitation energies for the CO molecule and noninteracting systems composed of CO and the neon atoms separated by 10000 Å (CO + nNe, n = 1, 2, 3), as well as for two noninteracting CO molecules (CO + CO). The scaling of the ODC-12 energies with the number of electrons for the ground $X^1\Sigma^+$ electronic state is perfectly linear up to $10^{-8} E_h$, which is the convergence parameter used in our ODC-12 computations. Upon the addition of the noninteracting atoms and molecules, the excitation energies of the CO molecule remain constant up to the convergence threshold set in LR-ODC-12 ($10^{-6} eV$). These results provide numerical evidence that the LR-ODC-12 excitation energies are size-intensive.

4.2 H₂ Dissociation

One of the desirable properties of an electronic structure method is exactness for two-electron systems. While the ODC-12 method is not exact for two-electron systems, it has been shown to provide a very good description of the ground-state H₂ dissociation curve, with errors of $\sim 1$ kcal mol$^{-1}$ with respect to full configuration interaction (FCI) near the dissociation limit. Here, we investigate the performance of LR-ODC-12 for the excited states of H₂. Figure 1a shows the errors in vertical excitation energies for six lowest-lying electronic states as a function of the H–H distance, relative to FCI. The FCI energies were computed using the EOM-CCSD method, which is exact for two-electron systems. At the equilibrium geometry ($r_e = 0.742$ Å) the errors in excitation

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Figure 1: Errors in vertical excitation energies (eV) for six lowest-lying electronic states of H$_2$ computed using LR-ODC-12 (1a) and LR-OLCCD (1b) as a function of the H–H bond length, relative to full configuration interaction. All methods employed the d-aug-cc-pvtz basis set. In each figure, the inset shows the same plot for a larger range of errors.

energies for all states do not exceed 0.02 eV. Between 0.6 and 1.45 Å ($r \approx 2r_e$), the LR-ODC-12 excitation energies remain in good agreement with FCI, with errors less than 0.1 eV for all states. In this range, the largest error is observed for the $3\Sigma_u^+$ state. For $r \geq 1.5$ Å, the error in the $1\Sigma_g^+$ excited state energy rapidly increases from 0.10 eV (at 1.5 Å) to 2.13 eV (at 2.35 Å), while for other states the errors increase much more slowly. Analysis of the FCI wavefunction for the $1\Sigma_g^+$ state shows a significant contribution from the $(1\sigma_g)^2 \rightarrow (1\sigma_u)^2$ double excitation already at $r = 1.55$ Å. This contribution becomes dominant for $r \geq 1.75$ Å. Thus, the large LR-ODC-12 errors observed for the $1\Sigma_g^+$ state are likely due to the increasingly large double-excitation character of this electronic state at long H–H bond distances. The second largest error near the dissociation is observed for the $3\Sigma_u^+$ state (0.43 eV). For other electronic states, smaller errors of $\sim 0.25$ eV are observed near the dissociation.

The importance of the non-linear terms in the LR-ODC-12 equations can be investigated by comparing the LR-ODC-12 and LR-OLCCD results. Figure 1b shows the errors in the LR-OLCCD vertical excitation energies as a function of the H–H bond length. Although near the equilibrium geometry the performance of LR-OLCCD and LR-ODC-12 is similar, the LR-OLCCD errors increase much faster with increasing H–H distance compared to LR-ODC-12. At $r = 1.3$ Å, the LR-OLCCD error for the $3\Sigma_u^+$ state (0.4 eV) is almost six times larger than the corresponding error from LR-ODC-12 (0.07 eV). For $r \geq 1.35$ Å, the LR-OLCCD errors for all excitation energies show very steep increase in magnitude, ranging from 1.5 to 4.7 eV already at $r = 1.75$ Å. We were unable to converge the LR-OLCCD equations for $r \geq 1.80$ Å. Overall, our results demonstrate that the non-linear terms in LR-ODC-12 significantly improve the description of the excited states at long H–H distances where the electron correlation effects are stronger.

4.3 Benchmark: Small Molecules

Here, we benchmark the performance of LR-ODC-12 for vertical excitation energies in several small molecules: N$_2$, CO, HCN, HNC, C$_2$H$_2$, and H$_2$CO. Tables 2 and 3 show the errors in excitation energies computed using EOM-CCSD, LR-OLCCD, and LR-ODC-12 for the singlet and triplet excited states, respectively, relative to the results from EOM-CCSDT. To measure the performance of each method, we computed the mean absolute errors ($\Delta_{\text{MAE}}$) and the standard deviations from the
Table 2: Errors in vertical excitation energies (eV) for singlet states computed using LR-OLCCD, LR-ODC-12, and EOM-CCSD, relative to EOM-CCSDT (aug-cc-pVTZ basis set). All electrons were correlated in all computations. Also shown are mean absolute errors ($\Delta_{\text{MAE}}$), standard deviations ($\Delta_{\text{STD}}$), and maximum absolute errors ($\Delta_{\text{MAX}}$) computed for each method.

|          | $\Delta_{\text{EOM-CCSD}}$ | $\Delta_{\text{LR-OLCCD}}$ | $\Delta_{\text{LR-ODC-12}}$ | $\Delta_{\text{EOM-CCSDT}}$ |
|----------|-----------------------------|-----------------------------|-----------------------------|-------------------------------|
| $N_2$    | 0.18                        | 0.08                        | 0.20                        | 9.29                          |
| $1\Pi_g$ |                             |                             |                             |                               |
| $1\Sigma_u^-$ | 0.23                      | 0.15                        | 0.09                        | 9.84                          |
| $1\Delta_u$ | 0.26                      | 0.14                        | 0.10                        | 10.26                         |
| CO       | 0.16                        | 0.09                        | 0.17                        | 8.46                          |
| $1\Sigma^-$ | 0.19                      | -0.10                       | -0.01                       | 9.89                          |
| $1\Delta$ | 0.19                        | -0.22                       | -0.05                       | 10.03                         |
| HCN      | 0.16                        | 0.05                        | 0.00                        | 8.25                          |
| $1\Sigma^-$ | 0.17                      | 0.04                        | 0.01                        | 8.61                          |
| $1\Pi$   | 0.17                        | 0.05                        | 0.20                        | 9.12                          |
| HNC      | 0.15                        | -0.01                       | 0.10                        | 8.13                          |
| $1\Sigma^+$ | 0.24                      | 0.05                        | 0.12                        | 8.46                          |
| $1\Sigma^-$ | 0.15                      | -0.09                       | 0.04                        | 8.67                          |
| $1\Delta$ | 0.15                        | -0.18                       | -0.03                       | 8.84                          |
| C$_2$H$_2$ | 0.12                        | 0.06                        | 0.02                        | 7.11                          |
| $1\Sigma_u^-$ | 0.10                      | 0.07                        | 0.03                        | 7.45                          |
| $1\Delta_u$ | 0.10                      | -0.07                       | 0.02                        | 3.95                          |
| H$_2$CO  | 0.10                        | -0.08                       | 0.08                        | 0.08                          |

Figure 2: Mean absolute deviations ($\Delta_{\text{MAE}}$) and standard deviations from the mean signed error ($\Delta_{\text{STD}}$) for vertical excitation energies (Tables 2 and 3) computed using LR-OLCCD, LR-ODC-12, and EOM-CCSD, relative to EOM-CCSDT (aug-cc-pVTZ basis set). The $\Delta_{\text{MAE}}$ value is represented as a height of each colored box, while the $\Delta_{\text{STD}}$ value is depicted as a radius of the black vertical bar.

Figure 2: Mean absolute deviations ($\Delta_{\text{MAE}}$) and standard deviations from the mean signed error ($\Delta_{\text{STD}}$) for vertical excitation energies (Tables 2 and 3) computed using LR-OLCCD, LR-ODC-12, and EOM-CCSD, relative to EOM-CCSDT (aug-cc-pVTZ basis set). The $\Delta_{\text{MAE}}$ value is represented as a height of each colored box, while the $\Delta_{\text{STD}}$ value is depicted as a radius of the black vertical bar.

For the singlet electronic states (Table 2), the excitation energies computed using LR-ODC-12 are in better agreement with EOM-CCSDT than those obtained from EOM-CCSD, on average. This is evidenced by $\Delta_{\text{MAE}}$, which is smaller for LR-ODC-12 compared to EOM-CCSD by a factor of two ($\Delta_{\text{MAE}} = 0.08$ and 0.17 eV, respectively). The LR-ODC-12 errors exceed 0.10 eV for only four states, with a maximum error $\Delta_{\text{MAX}} = 0.20$ eV. EOM-CCSD has a minimum error of 0.10 eV, shows errors greater than 0.10 eV for 14 states, and has $\Delta_{\text{MAX}} = 0.26$ eV. EOM-CCSD shows a somewhat smaller $\Delta_{\text{STD}}$ compared to that of LR-ODC-12 ($\Delta_{\text{STD}} = 0.05$ and 0.08 eV, respectively).

For the triplet states (Table 3), LR-ODC-12 is again superior to EOM-CCSD, on average, with $\Delta_{\text{MAE}} = 0.06$ and 0.11 eV for the two methods, respectively. LR-ODC-12 has errors larger than 0.10 eV for five states with $\Delta_{\text{MAX}}$. 
Table 3: Errors in vertical excitation energies (eV) for triplet states computed using LR-OLCCD, LR-ODC-12, and EOM-CCSD, relative to EOM-CCSDT (aug-cc-pVTZ basis set). All electrons were correlated in all computations. Also shown are mean absolute errors (\(\Delta_{\text{MAE}}\)), standard deviations (\(\Delta_{\text{STD}}\)), and maximum absolute errors (\(\Delta_{\text{MAX}}\)) computed for each method.

|          | \(\Delta_{\text{EOM-CCSD}}\) | \(\Delta_{\text{LR-OLCCD}}\) | \(\Delta_{\text{LR-ODC-12}}\) | \(\Delta_{\text{EOM-CCSDT}}\) |
|----------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| \(N_2\) | \(3\Sigma^+_u\)              | 0.11                          | 0.04                          | -0.02                         | 7.63                          |
|          | \(3\Pi_g\)                   | 0.15                          | 0.06                          | 0.11                          | 8.00                          |
|          | \(3\Delta_u\)                | 0.17                          | 0.08                          | 0.03                          | 8.82                          |
|          | \(3\Sigma^-_u\)              | 0.28                          | 0.03                          | 0.01                          | 9.63                          |
|          | \(3\Pi_u\)                   | 0.14                          | -0.01                         | 0.10                          | 11.18                         |
| \(\text{CO}\) | \(3\Pi\)                  | 0.12                          | 0.06                          | 0.08                          | 6.27                          |
|          | \(3\Sigma^+\)                | 0.05                          | -0.03                         | -0.03                         | 8.38                          |
|          | \(3\Delta\)                   | 0.11                          | -0.07                         | -0.03                         | 9.21                          |
|          | \(3\Sigma^-\)                | 0.19                          | -0.18                         | -0.06                         | 9.72a                         |
| \(\text{HCN}\) | \(3\Sigma^+\)              | 0.05                          | -0.04                         | -0.10                         | 6.40                          |
|          | \(3\Delta\)                   | 0.13                          | -0.02                         | -0.06                         | 7.40                          |
|          | \(3\Pi\)                      | 0.10                          | 0.08                          | 0.06                          | 8.01                          |
|          | \(3\Sigma^-\)                | 0.16                          | -0.10                         | -0.05                         | 8.15a                         |
| \(\text{HNC}\) | \(3\Pi\)                  | 0.09                          | 0.00                          | 0.03                          | 6.06                          |
|          | \(3\Sigma^+\)                | 0.04                          | -0.09                         | -0.11                         | 7.20                          |
|          | \(3\Delta\)                   | 0.10                          | -0.14                         | -0.11                         | 8.02                          |
|          | \(3\Sigma^+\)                | 0.22                          | -0.05                         | 0.04                          | 8.38                          |
|          | \(3\Sigma^-\)                | 0.15                          | -0.02                         | 0.11                          | 8.56a                         |
| \(\text{C}_2\text{H}_2\) | \(3\Sigma^+_u\)           | 0.01                          | -0.02                         | -0.08                         | 5.52                          |
|          | \(3\Delta_u\)                | 0.08                          | -0.02                         | -0.05                         | 6.41                          |
|          | \(3\Sigma^-_u\)              | 0.10                          | -0.03                         | -0.05                         | 7.10a                         |
| \(\text{H}_2\text{CO}\) | \(3\Sigma^-\)              | 0.04                          | -0.02                         | 0.01                          | 3.56                          |
|          | \(3\Delta\)                   | 0.10                          | -0.06                         | -0.14                         | 6.06                          |

\(\Delta_{\text{MAE}}\) \(\Delta_{\text{STD}}\) \(\Delta_{\text{MAX}}\) \n0.11 0.05 0.06  
0.06 0.07 0.07  
0.28 0.18 0.14

\(a\) For CO, HCN, HNC, and \(\text{C}_2\text{H}_2\), the \(3\Sigma^- (3\Sigma^-_u)\) excitation energies were obtained from EOM-CC(2,3), which energies were shifted to reproduce the EOM-CCSDT energy for the \(1\Sigma^- (1\Sigma^-_u)\) state.

\(= 0.14\) eV, whereas EOM-CCSD exceeds \(0.10\) eV error for 12 states and shows \(\Delta_{\text{MAX}} = 0.28\) eV. For linear molecules, EOM-CCSD exhibits consistently poor results for the \(3\Sigma^-\) electronic states, while the performance of LR-ODC-12 for different electronic states is similar. Notably, all EOM-CCSD excitation energies overestimate the EOM-CCSDT values, while the LR-ODC-12 energies are centered around the reference energies, suggesting that LR-ODC-12 provides a more balanced description of the ground and excited states.

Comparing LR-ODC-12 with LR-OLCCD, we see that both methods show very similar results for the triplet states (\(\Delta_{\text{MAE}} = 0.06\) and \(0.05\) eV, respectively), with noticeable differences observed only for the \(3\Sigma^-\) states. For the singlet electronic states, LR-OLCCD shows a somewhat larger \(\Delta_{\text{MAE}} = 0.09\) eV and \(\Delta_{\text{STD}} = 0.11\) eV compared to LR-ODC-12 (\(\Delta_{\text{MAE}} = 0.08\) eV and \(\Delta_{\text{STD}} = 0.08\) eV). In this case, significant differences are observed for the \(1\Pi\) states of \(N_2\) and HCN, \(1\Sigma^-\) of HNC, and \(1\Delta\) of CO and HNC, indicating that the non-linear terms
Table 4: Ground-state total energies ($E_h$) and vertical excitation energies (eV) computed using LR-OLCCD, LR-ODC-12, and EOM-CCSD for the low-lying electronic states of ethylene ($C_2H_4$), butadiene ($C_4H_6$), and hexatriene ($C_6H_8$). Computations employed the ANO-L-pVDZ (for $C_4H_6$ and $C_6H_8$) and ANO-L-pVTZ (for $C_2H_4$) basis sets and the MP2/cc-pVQZ optimized geometries. For LR-OLCCD and LR-ODC-12, oscillator strengths of the allowed transitions are given in parentheses. All electrons were correlated in all computations.

| Molecule | State  | EOM-CCSD | LR-OLCCD | LR-ODC-12 | SHCI \(^a\) |
|----------|--------|----------|----------|-----------|----------|
| $C_2H_4$ | $1^1A_g$ | -78.441518 | -78.455352 | -78.450874 | -78.4381 |
|          | $1^3B_{1u}$ | 4.46 | 4.66 | 4.52 | 4.59 |
|          | $1^1B_{1u}$ | 8.14 | 8.20 (1.8) | 8.13 (1.9) | 8.05 |
| $C_4H_6$ | $1^1A_g$ | -155.546920 | -155.568356 | -155.559882 | -155.5582 |
|          | $1^3B_u$ | 3.20 | 3.58 | 3.43 | 3.37 |
|          | $1^1B_u$ | 6.53 | 6.76 (4.2) | 6.67 (4.4) | 6.45 |
|          | $2^1A_g$ | 7.28 | 7.14 | 6.81 | 6.58 |
| $C_6H_8$ | $1^1A_g$ | -232.737880 | -232.771738 | -232.758675 | -232.7567 |
|          | $1^3B_u$ | 2.64 | 3.01 | 2.83 | 2.77 |
|          | $1^1B_u$ | 5.60 | 5.89 (6.5) | 5.74 (8.1) | 5.59 |
|          | $2^1A_g$ | 6.55 | 4.21 | 5.73 | 5.58 |

\(^a\) Also shown are the energies from the semistochastic heat-bath CI (SHCI) method, extrapolated to the full CI limit. The 1s orbitals of carbon atoms were not included in the SHCI correlation treatment. The SHCI computations used the same basis sets and optimized geometries as those used for LR-OLCCD, LR-ODC-12, and EOM-CCSD.

4.4 Ethylene, Butadiene, and Hexatriene

Finally, we apply the LR-ODC-12 method to challenging excited states of ethylene ($C_2H_4$), butadiene ($C_4H_6$), and hexatriene ($C_6H_8$). A reliable description of these electronic states requires an accurate treatment of electron correlation.\(^{111,112,114-128}\) All three molecules feature a dipole-allowed $1^1B_u$ (or $1^3B_{1u}$) state that is well described as a $\pi - \pi^*$ excitation, but requires a very accurate description of dynamic correlation between the $\sigma$ and $\pi$ electrons. In butadiene and hexatriene, the $1^3B_u$ state is near-degenerate with a dipole-forbidden $2^1A_g$ state that has a substantial double-excitation character, requiring the description of static correlation in the $\pi$ and $\pi^*$ orbitals.\(^{122,123}\) For this reason, the relative energies and ordering of the $1^3B_u$ and $2^1A_g$ states are very sensitive to various levels of theory. For example, single-reference methods truncated to single and double excitations describe the $1^3B_u$ state more accurately than the $2^1A_g$ state, while multi-reference methods are more reliable for the $2^1A_g$ state, missing important dynamic correlation for the $1^3B_u$ state. Very recently, Chien et al.\(^{113}\) reported accurate vertical excitation energies for the low-lying states of ethylene, butadiene, and hexatriene computed using semistochastic heat-bath configuration interaction (SHCI) extrapolated to the full CI limit. In this section, we will use the SHCI results to benchmark the accuracy of the LR-ODC-12 method.

Table 4 reports the ground-state total energies and vertical excitation energies of ethylene, butadiene, and hexatriene computed using the EOM-CCSD, LR-OLCCD, and LR-ODC-12 methods, along with the SHCI results from Ref.\(^{113}\) We refer to the $B_{1u}$ states of $C_2H_4$ as $B_u$ for brevity. All methods employed the same optimized geometries and basis sets (see Table 4 for details). We note that in the SHCI
computations the 1s orbitals of carbon atoms were not included in the correlation treatment, while in other methods all electrons were correlated. To estimate the effect of the frozen-core approximation on the SHCI vertical excitation energies, we compared the excitation energies computed using the all-electron and frozen-core EOM-CCSD methods. The errors due to the frozen core did not exceed 0.01 eV.

All excitation energies decrease as the number of double bonds in a molecule increases. For butadiene and hexatriene, the $|1\text{B}_u; 2\text{A}_g\rangle$ excitation energies computed using the SHCI method are (6.45; 6.58) and (5.59; 5.58) eV, respectively, indicating that the two states are nearly degenerate for the longer polyene. This feature is not reproduced by the EOM-CCSD method, which predicts the $|1\text{B}_u\rangle$ state energies in close agreement with SHCI, but significantly overestimates the energies for the doubly-excited $|2\text{A}_g\rangle$ state. As a result, the EOM-CCSD method overestimates the energy spacing between the $|1\text{B}_u\rangle$ and $|2\text{A}_g\rangle$ states by $\sim 0.6$ eV and 1.0 eV for butadiene and hexatriene, respectively.

The LR-ODC-12 method, by contrast, correctly describes the relative energies and ordering of the $|1\text{B}_u\rangle$ and $|2\text{A}_g\rangle$ states. The energy spacing between these states computed using LR-ODC-12 is 0.14 and $-0.01$ eV for butadiene and hexatriene, respectively, in an excellent agreement with the SHCI results (0.13 and $-0.01$ eV). For the singlet excited states, the LR-ODC-12 method consistently overestimates the excitation energies by $\sim 0.1 - 0.2$ eV, relative to SHCI. For the $|1\text{B}_u\rangle$ state, the LR-ODC-12 errors are smaller in magnitude ($\sim 0.06$ eV).

Importantly, these results suggest that the LR-ODC-12 method provides a balanced description of the excited states with different electronic structure effects, as illustrated by its consistent performance for the $|1\text{B}_u\rangle$, $|1\text{B}_a\rangle$, and $|2\text{A}_g\rangle$ states in ethylene, butadiene, and hexatriene.

Comparing to LR-OLCCCD shows that including the non-linear terms in LR-ODC-12 is crucial for the description of excited states with double-excitation character. While for the $|1\text{B}_u\rangle$ and $|1\text{B}_a\rangle$ states the LR-OLCCCD errors exceed the LR-ODC-12 errors by $\sim 0.15$ eV, for the doubly-excited $|2\text{A}_g\rangle$ state the LR-OLCCCD errors are much bigger: 0.56 and $-1.37$ eV for butadiene and hexatriene, respectively.

5 Conclusions

We have presented a new approach for excited electronic states based on the linear-response formulation of density cumulant theory (DCT). The resulting linear-response DCT model (LR-DCT) has the same computational scaling as the original (single-state) DCT formulation but can accurately predict energies and properties for many electronic states, simultaneously. We have described the general formulation of LR-DCT, derived equations for the linear-response ODC-12 method (LR-ODC-12), and presented its implementation. In LR-ODC-12, excited-state energies are obtained by solving the generalized eigenvalue equation that involves a symmetric Hessian matrix. This simplifies the computation of the excited-state properties (such as transition dipoles) and ensures that the excitation energies have real values, provided that the Hessian is positive semi-definite. In addition, the LR-ODC-12 excitation energies are size-intensive, which we have verified numerically for a system of noninteracting fragments.

Our preliminary results demonstrate that LR-ODC-12 yields very accurate excitation energies for a variety of excited states with different electronic structure effects. For a set of small molecules ($\text{N}_2$, CO, HCN, HNC, C$_2$H$_2$, and H$_2$CO), LR-ODC-12 outperforms equation-of-motion coupled cluster theory with single and double excitations (EOM-CCSD), with mean absolute errors in excitation energies of less than 0.1 eV, relative to reference data. Importantly, both LR-ODC-12 and EOM-CCSD have the same computational scaling. In a study of ethylene, butadiene, and hexatriene, we have compared the performance of LR-ODC-12 and EOM-CCSD with the results from highly-accurate semistochastic heat-bath configuration interaction (SHCI). For butadiene and hexatriene, LR-ODC-12 provides a balanced description of the singly-excited $|1\text{B}_u\rangle$ and the doubly-excited $|2\text{A}_g\rangle$ states, predicting that
the two states become nearly-degenerate in hexatriene, in excellent agreement with SHCI. By contrast, EOM-CCSD drastically overestimates the energy of the $2^1\text{A}_g$ state, resulting in a $\sim 1$ eV error in the energy gap between these states of hexatriene.

Overall, our results demonstrate that linear-response density cumulant theory is a promising theoretical approach for spectroscopic properties of molecules and encourage its further development. Several research directions are worth exploring. One of them is the efficient implementation of LR-ODC-12 and its applications to chemical systems with challenging electronic states. Two classes of systems that are particularly worth exploring are open-shell molecules and transition metal complexes. Another direction is to extend LR-DCT to simulations of other spectroscopic properties, such as photoelectron or X-ray absorption spectra. In this regard, applying LR-DCT to the computation of optical rotation properties is of particular interest as it is expected to avoid gauge invariance problems due to the variational nature of the DCT orbitals. We plan to explore these directions in the future.

A Derivatives of the One-Body Density Matrix in Density Cumulant Theory

Repeated differentiation of the one-body n-representability condition (Eq. (3)) gives the following formulas for the first and second derivatives of the cumulant partial trace:

$$\frac{\partial \lambda_{qr}^{\nu'}}{\partial y} = \gamma_q^p \frac{\partial \gamma_q^s}{\partial y} + \frac{\partial \gamma_q^s}{\partial y} \gamma_q^p - \frac{\partial \gamma_q^p}{\partial y} \gamma_q^s \quad (34)$$

$$\frac{\partial^2 \lambda_{qr}^{\nu'}}{\partial x \partial y} = \gamma_q^p \frac{\partial \gamma_q^s}{\partial x \partial y} + \frac{\partial \gamma_q^p}{\partial x \partial y} \gamma_q^s - \frac{\partial \gamma_q^p}{\partial y} \gamma_q^s \frac{\partial \gamma_q^p}{\partial x} \quad (35)$$

Transforming to the natural spin-orbital basis (NSO, denoted by prime indices) where the one-body density matrix is diagonal, the first and second derivatives of the one-body density matrix can be determined from the cumulant derivatives as follows:

$$\frac{\partial \gamma_{qr}^{\nu'}}{\partial y} = \theta_{\nu'\nu} \frac{\partial \lambda_{qr}^{\nu'}}{\partial y} \quad (36)$$

$$\frac{\partial^2 \gamma_{qr}^{\nu'}}{\partial x \partial y} = \theta_{\nu'\nu} \frac{\partial^2 \lambda_{qr}^{\nu'}}{\partial x \partial y} - \delta_{\nu'\nu} \frac{\partial \lambda_{qr}^{\nu'}}{\partial x} \frac{\partial \lambda_{qr}^{\nu'}}{\partial y} \quad (37)$$

Here, we have defined the following matrix:

$$\theta_{\nu'\nu} \equiv \begin{cases} (\gamma_{\nu'} + \gamma_{\nu} - 1)^{-1} & \text{if } \nu' \in \text{occ or vir} \\ 0 & \text{otherwise} \end{cases} \quad (38)$$

where $\gamma_{\nu'}$ denotes an eigenvalue of the one-body density matrix (i.e., an occupation number). The natural spin-orbital $\nu'$ is considered occupied if $\gamma_{\nu'} > 0.5$.

Eqs. (36) and (37) can be used to derive expressions for the two-body energy Hessian in Eq. (26). Simplifying the resulting equations allows us to determine the intermediates defined in Eq. (26). In the NSO basis, these intermediates are given by

$$F_{\nu'\nu}^{\nu'} \equiv \theta_{\nu'\nu} F_{\nu'\nu}^{\nu'} \quad (39)$$

$$G_{\nu'\nu'}' (\gamma_{\nu'\nu'}') \equiv \theta_{\nu'\nu} \theta_{\nu'\nu'}' (\gamma_{\nu'\nu'}') - F_{\nu'\nu}^{\nu'} \delta_{\nu'\nu} - F_{\nu'\nu'}^{\nu'} \delta_{\nu'\nu} \quad (40)$$

These quantities are computed in the NSO basis and back-transformed to the original spin-orbital basis using the eigenvectors of the one-particle density matrix (see Ref. 53 for more details).

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Supporting Information Available

The following files are available free of charge. Formulas for the energy Hessian (E), the metric matrix (M), and the property gradient vector (v′) for the LR-ODC-12 and LR-OLCCD methods are included in the Supporting Information.

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Linear-response density cumulant theory (LR-DCT) accurately describes challenging excited states in polyenes: hexatriene (C₆H₈)

| Method   | 1'Bᵤ eV | 2'Aᵥ eV |
|----------|---------|---------|
| EOM-CCSD | 5.60    | 6.55    |
| LR-DCT   | 5.74    | 5.73    |
| Reference| 5.59    | 5.58    |