

Coupled cluster-based methods for linear and nonlinear spectroscopies in different frequency regions

Andersen, Josefine Hvarregaard

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COUPLED CLUSTER-BASED METHODS FOR LINEAR AND NONLINEAR SPECTROSCOPIES IN DIFFERENT FREQUENCY REGIONS

COUPLED CLUSTER-BASED METHODS FOR LINEAR AND NONLINEAR SPECTROSCOPIES IN DIFFERENT FREQUENCY REGIONS

JOSEFINE HVARREGAARD ANDERSEN



May 2023

AUTHOR: Josefine Hvarregaard Andersen

SUPERVISOR: Prof. Sonia Coriani DTU Chemistry Technical University of Denmark

CO-SUPERVISOR: Prof. Klaus B. Møller DTU Chemistry Technical University of Denmark

ASSESSMENT COMMITTEE: Prof. Daniel Crawford Department of Chemistry Virginia Tech Prof. Patrick Norman Department of Theoretical Chemistry and Biology KTH Royal Institute of Technology Assoc. Prof. Jógvan Magnus Olsen

DTU Chemistry Technical University of Denmark

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Både lineære og ikke-lineære spektroskopier er blevet implementeret og anvendt. Størstedelen af arbejdet omhandler fænomenet cirkulær dikroisme (CD), dvs. den differentielle absorption af venstre– og højrecirkulært polariseret lys.

Den enkleste manifestation af CD er elektronisk cirkulær dikroisme (ECD). ECD er en lineær egenskab, der kun forekommer for chirale molekyler. I dette arbejde er implementeringen af ECD blevet anvendt til at undersøge elektroniske excitationer for en række små til mellemstore molekyler i både UV-Vis– og røntgenregionerne, hvor sidstnævnte også udforsker virkningen af spin–orbit kobling. I forbindelse med implementeringen af ECD er optisk rotation også blevet gjort tilgængelig sammen med dens komplekse formulering, hvorfra ECD-tværsnittet kan beregnes.

Magnetisk cirkulær dikroisme (MCD) og kernespin-induceret cirkulær dikroisme (NSCD) er de to ikke-lineære dikroismer, der behandles i dette arbejde. De er perturbationsinducerede egenskaber; MCD stammer fra det elektroniske systems interaktion med et eksternt magnetfelt, mens NSCD induceres af det magnetiske felt, der opstår fra kernernes spin.

Derudover er den såkaldte "core–valence separation and uncoupled valence singles"-tilnærmelse blevet udledt for beregning af røntgentofotonsabsorption (X2PA) og undersøgt for et sæt af små testmolekyler.

Arbejdet er baseret på coupled cluster (CC) metoden, inden for hvilken "coupled cluster singles and doubles" (CCSD) og "second-order coupled cluster singles and doubles" (CC2) modellerne er blevet anvendt. ECD, optisk rotation, og X2PA er blevet implementeret for CCSD i Q-Chem, mens CC2 blev anvendt i implementeringerne af MCD og NSCD i TURBOMOLE. En intern python-kode til prototypeimplementering af CC-baserede molekylære egenskaber, pyCCRSP, er blevet udvidet og anvendt i forbindelse med CCSD-arbejdet.

Linear and nonlinear spectroscopies have been implemented and applied. Most of the efforts revolve around the phenomenon of circular dichroism (CD), i.e., the differential absorption of left and right circularly polarized light.

The simplest manifestation of CD is electronic circular dichroism (ECD). ECD is a linear property only occurring for chiral molecules. In this work, it has been applied to a variety of small to medium-sized molecules, to investigate electronic excitations in the UV-Vis and X-ray regimes, the latter also exploring the effects of spin–orbit coupling in the latter. In relation to the implementation of ECD, optical rotation has also been made available along with its damped formulation from which the ECD cross section can be obtained.

Magnetic circular dichroism (MCD) and nuclear spin-induced circular dichroism (NSCD) are the two nonlinear dichroisms treated in this work. They are perturbation-induced dichroisms; MCD originates from the interaction of the electronic system with an external magnetic field, while NSCD is induced by the magnetic field arising from the spin of the nuclei.

Furthermore, the core–valence separation and uncoupled valence singles approximation has been derived for computing X-ray two-photon absorption (X2PA) and investigated for a set of small benchmark molecules.

The developments rely on the *ab initio* coupled cluster (CC) method within which the coupled cluster singles and doubles (CCSD) and the second-order coupled cluster singles and doubles (CC2) models have been applied. ECD, optical rotation, and X2PA have been implemented for CCSD in Q-Chem, while the CC2 framework was employed for the implementations of MCD and NSCD in TURBOMOLE. An in-house python code for prototyping implementations of CC-based molecular properties, pyCCRSP, has been extended and applied in connection with the CCSD work.

This thesis presents the work conducted at the Department of Chemistry, Technical University of Denmark, between December 2019 and May 2023. It has been handed in as partial fulfillment of the requirements for a Ph.D. degree within the field of theoretical chemistry. The Ph.D. studies took place under the supervision of Prof. Sonia Coriani and co-supervision of Prof. Klaus B. Møller.

Part of the work was carried out during two visits, totaling three months' duration, to Ruhr-Universität Bochum, Germany, hosted by Prof. Christof Hättig.

The work presented herein is the outcome of various collaborations with Prof. Hättig, with Dr. Petr Štěpánek from University of Oulu, Finland, and with Prof. Anna I. Krylov and Dr. Kaushik D. Nanda from University of Southern California, USA.

Kongens Lyngby, 31. May 2023

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Josefine H. Andersen

First and foremost I would like to thank my supervisor Prof. Sonia Coriani for her guidance, endless trust, and eternal optimism in my projects. Also, all of my travel activities were only possible thanks to her generosity, and those experiences have had enormous influence on the person and researcher I am today. My co-supervisor Prof. Klaus B. Møller is also acknowledged for his presence on the contract.

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Publications and manuscripts included in this thesis:

PUBLICATION I

"Probing molecular chirality of ground and electronically excited states in the UV–Vis and X-ray regimes: An EOM-CCSD study" Josefine H. Andersen, K. D. Nanda, A. I. Krylov, and S. Coriani *J. Chem. Theory Comput.* **2022**, 18 (3), 1748–1764

PUBLICATION II

"Cherry-picking resolvents: recovering the valence contribution in X-ray two-photon absorption within the core–valence-separated equation-ofmotion coupled-cluster response theory" Josefine H. Andersen, K. D. Nanda, A. I. Krylov, and S. Coriani

J. Chem. Theory Comput. **2022**, 18 (10), 6189–6202

MANUSCRIPT I

"An efficient protocol for computing MCD spectra in a broad frequency range combining resonant and damped CC2 quadratic response theory" Josefine H. Andersen, S. Coriani, and C. Hättig **2023** (*Submitted*)

MANUSCRIPT II

"Insights into localization, energy ordering, and substituent effect in excited states of azobenzenes from coupled cluster calculations of nuclear spin-induced circular dichroism" Josefine H. Andersen, C. Hättig, S. Coriani, and P. Štěpánek

2023 (Submitted)

Publications not included in this thesis:

"Linear response properties of solvated systems: a computational study" L. Goletto, S. Gómez, J. H. Andersen, H. Koch, and T. Giovannini *Phys. Chem. Chem. Phys.* **2022**, 24 (45), 27866–27878

"Software for the frontiers of quantum chemistry: An overview of developments in the Q-Chem 5 package" E. Epifanovski *et al. J. Chem. Phys.* **2021**, 155 (8), 084801

"eT 1.0: An open source electronic structure program with emphasis on coupled cluster and multilevel methods"

S. D. Folkestad, E. F. Kjønstad, R. H. Myhre, J. H. Andersen, A. Balbi, S. Coriani, T. Giovannini, L. Goletto, T. S. Haugland, A. Hutcheson, I. Høyvik, T. Moitra, A. C. Paul, M. Scavino, A. S. Skeidsvoll, Å. H. Tveten, and H. Koch

J. Chem. Phys. 2020, 152 (18), 184103

Manuscripts not included in this thesis:

"TURBOMOLE: Today and Tomorrow" Y. J. Franzke *et al. J. Chem. Theory Comput.* **2023** (*In review*)

"CCSD calculations of origin-independent dynamic polarizability density"

F. F. Summa, J. H. Andersen, S. Coriani, P. Lazzeretti, G. Monaco, S. P. A. Sauer, and R. Zanasi 2023 (*In preparation*)

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- 2PA Two-photon absorption
- CC Coupled cluster
- CC2 Second-order coupled cluster singles and doubles
- CD Circular dichroism
- CCSD Coupled cluster singles and doubles
- CVS-uS Core-valence separation and uncoupled valence singles
- ECD Electronic circular dichroism
- EOM Equation-of-motion
- fc-CVS Frozen-core core-valence separation
- HF Hartree-Fock
- LCP Left circularly polarized
- MCD Magnetic circular dichroism
- NSCD Nuclear spin-induced circular dichroism
- RCP Right circularly polarized
- RI Resolution-of-identity
- SOS Sum-over-states
- UV-Vis Ultraviolet-visible
- X2PA X-ray two-photon absorption

Part I

INTRODUCTORY MATTER

This part contains an introduction to the thesis (Chapter 1), a summary of relevant theoretical aspects (Chapter 2), and a description of the spectroscopies under investigation (Chapter 3). Elaborations upon the theoretical aspects and working equations for the properties of interest can be found in the respective manuscripts (Part II, Chapter 5).

INTRODUCTION

Technological and scientific advances arise from an increased understanding of how the world around us functions. This, in itself, argues the value of pursuing a both broad and deep understanding of the scientific principles governing our surroundings.

Chemistry as a natural science aims at understanding the macroscopic behaviour of matter in terms of the properties of the individual molecules. In its youth, chemistry was a purely experimental science. However, it reached a point of advancement where inconsistencies with the predictions of classical physics were observed. From the interplay of experiments and physics, quantum mechanics arose during the 20th century. In its description of nature at the atomic scale, quantum mechanics predicted that atoms and molecules take only discrete energies. This prediction provides the basis for understanding spectroscopic properties [1].

Molecular response properties are manifestations of the response of a molecule to electromagnetic fields. The interaction of matter with light as the perturbing field gives rise to the phenomena studied in molecular spectroscopy. Depending on the frequency of the light beam, different responses are probed. With a radiation in the ultraviolet–visible (UV-Vis) or X-ray regions of the spectrum, transitions of valence or core electrons, respectively, are induced. By evaluating the responses of the atoms and molecules based on the laws of quantum mechanics, it is possible to gain insight into the electronic transitions that are convoluted in bands of varying resolution in an experimental spectrum.

The experimental endeavours of scientists continue to increase our abilities to probe highly sophisticated phenomena on the atomic level. This focus on properties of individual molecules and atoms brings about an emerging necessity for the development of robust theoretical models to aid in the interpretation and analysis of the results obtained from such advanced experiments.

This is where quantum chemistry enters the equation. While the exact formulation of quantum mechanics is unfeasible for application to molecular systems, quantum chemistry is, in principle, the application of the laws of quantum mechanics by a collection of approximations. These approximations make the theoretical description and investigation of experimental observables possible.

The methods embodied in quantum chemistry aim at approximately solving the electronic Schrödinger equation and thereby provide a description of the electronic structure of a molecule and its properties. The diverse quantum chemical methods offer different levels of theory in terms of accuracy of the predictions and the computational cost of a calculation. It is thus necessary for a computational chemist to take into account both computational limitations and theoretical requirements before carrying out a quantum chemical calculation. The nature of the problem at hand, the property of interest, the computational resources available, and the level of accuracy required must all be carefully considered when deciding on a theoretical model. Obtaining a good compromise between accuracy and computational cost is, and will probably always be, at the center of the work devoted to the development and implementation of quantum chemical methods for molecular properties.

A theory that over the last few decades has received increased attention and become widely employed is coupled cluster (CC) [2–5]. It is a wavefunction-based theory which efficiently includes electron correlation in the description of the wavefunction. It shows great robustness and high accuracy for computing ground states for both closed– and open-shell systems. Furthermore, the CC approximations constitute a hierarchy of models with a systematic increase in accuracy.

Different theoretical methods for simulating spectroscopies are available to CC. The frameworks offered by coupled cluster response theory [6, 7] and equation-of-motion coupled cluster (EOM-CC) [8–11] are reliable, accurate, and popular. Over the last few decades, a vast portfolio of spectroscopies that can be treated via these methods has been developed and is expanding still [12]. Spanning properties in both the linear and nonlinear regimes and across different frequency regions of the probing light, the methods are now routinely applied and found useful in the interpretation of spectroscopic measurements.

The work presented herein concerns the development of further additions to the portfolio of spectroscopies described at the CC level of theory. It extends the lists of both linear and nonlinear spectroscopies, employing response theory as well as EOM-CC.

This thesis is article-based and the chapters are therefore formulated in brevity. In the remainder of Part I, Chapter 2 touches upon the theoretical background of the CC model, response theory, and EOM-CC as frameworks for calculating molecular response properties, and Chapter 3 describes the spectroscopic properties of interest. Part II is initiated by a synopsis in Chapter 4 introducing the different projects that constitute the Ph.D. studies of the author. The articles are provided in full in Chapter 5 and some unpublished content is presented in Chapter 6. The thesis is rounded off with a conclusion and outlook in Chapter 7. Quantum chemistry is born from the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi = H\Psi \tag{1}$$

and the immense problem the equation represents. Its complexity makes it impossible to solve for any practical purposes, and approximations must be introduced to enable the treatment of molecules.

The first fundamental steps towards an applicable theoretical model are to divide the Schrödinger equation into time-dependent and independent parts, and then introduce the Born–Oppenheimer approximation to the time-independent equation for a further simplification. In this way, the time-independent electronic Schrödinger equation is obtained

 $H\psi = E\psi \tag{2}$

where *H* is the electronic Hamiltonian, *E* is the energy of the system, and ψ is the electronic wavefunction. In the Born–Oppenheimer approximation the nuclei are "fixed" and their presence is experienced by the electrons as a static external potential in the form of the electron–nuclear attraction while the nuclear–nuclear repulsion energy is a constant and independent of the position of the electrons. Solving Eq. (2) is the problem of interest in electronic structure theory. Unfortunately, even the electronic Schrödinger equation cannot be solved (analytically) for more than one electron, and more approximations are necessary. The various electronic structure models offer different approaches to tackle this problem, targeting different aspects of describing the electronic structure of atoms and molecules.

The simplest wavefunction model is the Hartree-Fock (HF) model. In the HF approximation, the electrons are considered as independent particles each of them moving in an average electrostatic field of the static nuclei and the charge distribution of the remaining electrons in the system. In this way, HF reduces the electronic Schrödinger equation from a many-body to a one-electron problem where the wavefunction is described by a single Slater determinant.

By approximating the electron–electron interactions as one-electron interactions with an average field, the HF model neglects what is known as electron correlation. From this fact, the correlation energy of an electronic system is defined as the difference between the exact energy and the HF energy of that system [13]

$$E_{corr} = E_{exact} - E_{\rm HF} . \tag{3}$$

 E_{corr} comprises the two types of electron correlation: dynamical and static correlation. The former describes the correlated electronic motion induced by the instantaneous interactions between the electrons, while the latter is present in systems with near-degenerate configurations. It is the aim of higher-level electronic structure methods to recover the correlation lost in the HF approximation. While HF alone does not provide a good approximation for studying properties, it serves as a convenient starting point for more accurate wavefunction-based models.

One of the most successful models for including dynamical correlation in the description of the wavefunction is CC; a method often employing a HF determinant as the reference state.

2.1 THE COUPLED CLUSTER ANSATZ AND APPROXIMATIONS

Coupled cluster is an *ab initio* method providing a correlated description of the electronic structure of a system. The CC wavefunction is typically expressed as the exponential of a cluster operator operating on a HF reference state [13, 14]

$$|\mathrm{CC}\rangle = e^T |\mathrm{HF}\rangle$$
 . (4)

The cluster operator, *T*, is a sum of excitation operators τ_{μ} weighted by their amplitudes t_{μ}

$$T = \sum_{\mu} t_{\mu} \tau_{\mu} \tag{5}$$

where μ indicates the excitation level. The CC Schrödinger equation is then constructed by inserting the CC wavefunction into the electronic Schrödinger equation

$$He^{T} |\mathrm{HF}\rangle = E_{0} e^{T} |\mathrm{HF}\rangle . \tag{6}$$

Here, E_0 is the optimized CC ground state energy. The expansion of the exponential is nonlinear in the cluster amplitudes, and the wavefunction must be solved in a nonvariational manner. This is carried out by projecting the CC Schrödinger equation onto the reference state and excitation projection manifold, { $\langle HF |, \langle \mu | \rangle$, giving rise to the CC equations

$$\langle \mathbf{HF} | \mathbf{H}\mathbf{e}^T | \mathbf{HF} \rangle = E_0 \tag{7}$$

$$\langle \mu | \bar{H} | \mathrm{HF} \rangle = 0 \tag{8}$$

where we have introduced the similarity-transformed Hamiltonian $\bar{H} = e^{-T}He^{T}$ and

$$\langle \mu | = \langle \mathrm{HF} | \, \tau_{\mu}^{\dagger} \, . \tag{9}$$

Eq. (7) is often referred to as the CC energy equation and Eq. (8) as the CC amplitude equations.

Solving Eqs. (7) and (8) with an untruncated cluster operator quickly becomes an unfeasible problem. The different levels of truncation of the cluster operator constitute a hierarchy of approximate CC models in which a systematic increase in accuracy is achieved by moving up the hierarchy

$$CCS < CC2 < CCSD < CC3 < CCSDT < \cdots$$
 (10)

The "S" indicates that single excitations are included in the excitation manifold, "D" refers to doubles, and "T" to triples. The intermediate CCn models can be viewed as approximations to the models one step above in the hierarchy, with the value of n indicating which excitation level has been approximated. Increasing the accuracy by moving up the hierarchy does, however, come with a steep increase in computational cost which scales exponentially with system size.

In this thesis, two CC models are employed: coupled cluster singles and doubles (CCSD), which is the most widely used CC model, and the intermediate second-order coupled cluster singles and doubles model (CC2).

2.1.1 CCSD

Coupled cluster singles and doubles is an approximate CC method constructed by truncating the cluster operator after double excitations [15]. The CCSD wavefunction then reads

$$CCSD = e^{T_1 + T_2} |HF\rangle . \tag{11}$$

In the CCSD projected equations, the projection space is restricted to all singly and doubly excited determinants as well as the reference, $\{\langle HF |, \langle \mu_1 |, \langle \mu_2 |\}$, shaping the CCSD equations [13, 15]

$$\langle \mathrm{HF}|\tilde{H}(1+T_2+\frac{1}{2}T_1^2)|\mathrm{HF}\rangle = E_{\mathrm{CCSD}} \tag{12}$$

$$\langle \mu_1 | \tilde{H} + [\tilde{H}, T_2] | \text{HF} \rangle = 0 \tag{13}$$

$$\langle \mu_2 | \tilde{H} + [\tilde{H}, T_2] + \frac{1}{2} [[\tilde{H}, T_2], T_2] | \text{HF} \rangle = 0.$$
 (14)

 \tilde{H} is the T_1 -transformed Hamiltonian, $\tilde{H} = e^{-T_1} H e^{T_1}$.

CCSD efficiently sums higher-order correlation effects as the expansion of the exponential includes both (disconnected) triple and quadruple excitations.

2.1.2 CC2

In between CCS and CCSD in the hierarchy lies the second-order coupled cluster singles and doubles model. It is formed by introducing an approximation to the CCSD doubles amplitude equations (Eq. (14)) by truncating the doubles at the lowest non-vanishing order in the fluctuation potential [16]. The singles amplitude equations remain unchanged compared with CCSD. The CC2 doubles equations then take the form

$$\langle \mu_2 | \tilde{H} + [F, T_2] | \text{HF} \rangle = 0 \tag{15}$$

where *F* is the Fock operator [16]. By comparing Eq. (15) with Eq. (14) it is evident that the CC2 equations form a subset of the CCSD equations.

2.2 MOLECULAR PROPERTIES WITH COUPLED CLUSTER

There are two main approaches to describing molecular properties within CC theory: response theory and equation-of-motion coupled cluster.

2.2.1 *Response Theory*

In response theory, time-dependence is reintroduced into the electronic Schrödinger equation in order to determine the time development of the electronic wavefunction in the presence of a time-dependent perturbation

$$H|0\rangle = i\frac{\partial}{\partial t}|0\rangle . \tag{16}$$

The electronic Hamiltonian now contains a time-independent part as well as a time-dependent perturbation

$$H = H_0 + V(t)$$
 . (17)

Response theory offers a convenient framework for treating the molecular responses to such perturbations by providing a formalism for deriving response functions, from which an observable can be described. From the perturbation expansion of the expectation value of an operator V_0 [7, 12]

$$\langle V_0 \rangle(t) = \langle \langle V_0 \rangle \rangle + \sum_x \epsilon_x \langle \langle V_0; V_x \rangle \rangle_{\omega_x} e^{-i\omega_x t} + \frac{1}{2!} \sum_{x,y} \epsilon_x \epsilon_y \langle \langle V_0; V_x, V_y \rangle \rangle_{\omega_x, \omega_y} e^{-i(\omega_x + \omega_y)t} + \frac{1}{3!} \sum_{x,y,z} \epsilon_x \epsilon_y \epsilon_z \langle \langle V_0; V_x, V_y, V_z \rangle \rangle_{\omega_x, \omega_y, \omega_z} e^{-i(\omega_x + \omega_y + \omega_z)t} + \cdots$$

$$(18)$$

we define the response functions as the expansion coefficients. The terms included in Eq. (18) are referred to as the zero-order, linear, quadratic, and cubic response functions, respectively. They describe the response of the expectation value to different orders in the perturbation strengths and do not depend on the representation of the wavefunction.

In the quasi-energy formulation, the response functions are then identified as the derivatives of the quasi-energy with respect to the perturbation strengths. In the nonvariational CC theory, the quasi-energy is used in its non-Hermitian form, i.e., the quasi-energy Lagrangian is employed [7]. CC response functions are then equivalently obtained as perturbation-derivatives of this Lagrangian. The CC quasi-energy Lagrangian has the form [7]

$$\mathcal{L} = \operatorname{Re}\left\{\langle \operatorname{HF}|H|\operatorname{CC}(t)\rangle + \sum_{\mu} \bar{t}_{\mu} \langle \bar{\mu}(t)|H - i\frac{\partial}{\partial t}|\operatorname{CC}(t)\rangle\right\}_{T}$$
(19)

with the Hamiltonian of Eq. (17) and

$$|\mathbf{CC}(t)\rangle = e^{T(t)} |\mathbf{HF}\rangle , \quad \langle \bar{\mu}(t) | = \langle \mu | e^{-T(t)} .$$
⁽²⁰⁾

The Lagrangian has variational properties with respect to the zeroorder (ground state) amplitudes and Lagrange multipliers. The CC amplitude equations are obtained from the stationary conditions for the zero-order multipliers, and the zero-order multipliers are determined from the stationary conditions for the zero-order amplitudes.

This formulation of CC response theory is applicable to all standard CC models by introducing the appropriate truncations of the cluster operator and excitation projection manifold. Meanwhile, the Lagrangian must be explicitly modified for the intermediate CC*n* models to accommodate the artificial truncation of the amplitude equations. Nevertheless, the modified CC*n* quasi-energy Lagrangians fulfill the same variational properties as does the regular one, and response functions can thus be derived also for the CC*n* models [16–19].

Dispersive observables are described directly from the response functions. Meanwhile, information on resonant states of a system can be obtained from their poles and residues. Considering, for example, the sum-over-states (SOS) representation of the (exact) linear response function with general operators *A* and *B* and associated optical frequency ω_B [20]

$$\langle\!\langle A;B\rangle\!\rangle_{\omega_{B}} = \sum_{k} \frac{\langle 0|A|k\rangle \langle k|B|0\rangle}{\omega_{B} - \omega_{k}} - \sum_{k} \frac{\langle 0|B|k\rangle \langle k|A|0\rangle}{\omega_{B} + \omega_{k}}$$
(21)

it is seen that the poles of the linear response function correspond to excitation energies, that is, when the optical frequency ω_B equals ω_k . The excitation energies may be determined from the eigenvalues of the

CC Jacobian, **A** [12]. Due to its non-Hermiticity, there are right and left eigenvalue equations

$$\mathbf{A}R_k = \omega_k R_k \quad \text{and} \quad L_k \mathbf{A} = \omega_k L_k \tag{22}$$

where ω_k is the excitation energy of excited state k and R_k and L_k are its associated eigenvectors that are orthogonal, but not each other's adjoint. From the residues of the linear response function,

$$\lim_{\omega_B \to \omega_k} (\omega_B - \omega_k) \left\langle\!\left\langle A; B \right\rangle\!\right\rangle_{\omega_B} , \quad \lim_{\omega_B \to -\omega_k} (\omega_B + \omega_k) \left\langle\!\left\langle A; B \right\rangle\!\right\rangle_{\omega_B}$$
(23)

the transition strength of an excitation may be determined. Other, nonlinear, transition properties can be obtained from the residues of the higher-order response functions [12, 21].

With response theory it is thus possible to calculate excited state properties without an explicit excited state wavefunction.

The transition strengths from standard response theory, however, are infinitely narrow absorption peaks, reflecting the infinite lifetime of the excited states when determined from the poles of the response functions. In reality, excited states have finite lifetimes.

Such finite lifetimes can be introduced by the application of a damping term making the response functions resonance-convergent. Different approaches exist [22–26], all sharing the fundamental action of imposing a finite lifetime by introducing an empirical damping parameter.

In damped response theory, the damping occurs in terms of a complex excitation energy which is introduced directly into the response functions by the substitution $\omega_k \rightarrow \omega_k - i\gamma$ [25]. By this substitution, the SOS formulation of the damped linear response function becomes [12]

$$\overline{\langle\langle A;B\rangle\rangle}_{\omega_{B}} = \sum_{k} \frac{\langle 0|A|k\rangle \langle k|B|0\rangle}{\omega_{B} - (\omega_{k} - i\gamma)} - \sum_{k} \frac{\langle 0|B|k\rangle \langle k|A|0\rangle}{\omega_{B} + (\omega_{k} - i\gamma)^{*}}$$
(24)

$$=\sum_{k}\frac{\langle 0|A|k\rangle \langle k|B|0\rangle}{(\omega_{B}+i\gamma)-\omega_{k}}-\sum_{k}\frac{\langle 0|B|k\rangle \langle k|A|0\rangle}{(\omega_{B}+i\gamma)+\omega_{k}}.$$
(25)

In Eq. (25), the damping term $i\gamma$ is associated with the optical frequency instead of the excitation energy. Thus, the damped response functions are effectively constructed by introducing a complex optical frequency according to

$$\omega_B \to \omega_B + i\gamma$$
 . (26)

The advantage of damped response theory is that it allows the calculation of absorption and dispersion spectra without explicitly solving for the excited states (Eq. (22)) and calculating their transition moments. Instead, a spectrum is obtained directly from the real (imaginary operator combination) or imaginary (real operator combination) component of the damped response function with a line-shape function superimposed by construction [25].

2.2.2 Equation-of-Motion Coupled Cluster

The equation-of-motion coupled cluster formalism offers an alternative to response theory for calculating molecular response properties. In EOM-CC theory, no time-dependence is introduced. Instead, CC theory is directly extended to describe excited states by applying a linear excitation operator to a pre-optimized CC ground state, thus creating an excited state wavefunction [8]. Due to the non-Hermitian nature of CC and, thus, EOM-CC theory, there exists both right and left EOM states [27]

$$|k\rangle = \mathcal{R}_k |\mathrm{CC}\rangle$$
, $\langle k| = \langle \mathrm{CC} | \mathcal{L}_k$ (27)

which are biorthogonal and can be normalized to the condition $\langle i|j \rangle = \delta_{ij}$. The EOM operators \mathcal{R}_k and \mathcal{L}_k are linear combinations of excitation operators with associated amplitudes

$$\mathcal{R}_k = \sum_{\mu} r_{\mu}^k \tau_{\mu} , \qquad \mathcal{L}_k = \sum_{\mu} l_{\mu}^k \tau_{\mu}^{\dagger} .$$
(28)

The excited states and their energies are the eigenfunctions and values of the energy-shifted (normal-ordered) Hamiltonian, and are thus obtained by solving the EOM eigenvalue equations [27]

$$H_N |k\rangle = \omega_k |k\rangle$$
, $\langle k| H_N = \omega_k \langle k|$ (29)

with $H_N = H - E_0$. The solution with zero eigenvalue corresponds to the CC ground state.

The EOM-CC formalism takes an expectation value approach and calculates the transition moments of an observable as the matrix elements of the operator between states i and j

$$\langle A \rangle = \langle i | A | j \rangle . \tag{30}$$

EOM-CC response functions are then constructed by inserting the eigenstates, their energies, and the transition matrix elements into the SOS expressions of the response functions derived for exact theory [28].

To summarize the two approaches, response theory derives approximate response functions from a CC quasi-energy Lagrangian, while EOM-CC inserts approximate states into the exact functions. For excitation energies, identical results are obtained from the two methods, while other molecular properties differ. All properties derived from the quasienergy formalism are size-intensive or extensive [12]. This is not the case for EOM-CC [29, 30]. In practice, however, the differences between the two are most often insignificant.

Spectroscopic observables arise from the interaction of light and matter. The light beam is typically linearly polarized light, and its frequency determines what kind of properties will be observed, i. e., whether it will be dispersive properties or properties related to electronic transitions. The latter process occurs when the radiation is resonant with electronic transitions in the system under investigation.

The effect of the light–matter interactions is often measured by investigating the light that passes through the sample, i. e., the absorption of the incoming light, the rotation of the plane of polarization of the incoming light, or the differential absorption of the left (LCP) and right circularly polarized (RCP) components. In the following sections, the spectroscopies of interest to this thesis are recapitulated.

3.1 OPTICAL ROTATION AND ELECTRONIC CIRCULAR DICHROISM

Optical rotatory dispersion and electronic circular dichroism (ECD) spectroscopy can be viewed as chiral variants of conventional refractive index measurements and absorption spectroscopy. They arise from the interaction of chiral matter with both the electric and magnetic fields of the radiation [31]. ECD is an absorptive property occurring in regions of electronic excitations, while optical rotatory dispersion is a dispersive property, often measured in transparent regions [32]. Optical rotation and ECD only occur for chiral species since these types of light–matter interactions require the distribution of the electric charge to possess a "handedness" [33].

The optical rotatory effect is measured as the rotation of the plane of polarization of the incoming light beam. If measured over a range of (transparent) frequencies, the optical rotatory effect is investigated as a dispersion curve. If the experiment is carried out at a single wavelength, the property manifests in a single angle of rotation which is a characteristic quantity simply called the optical rotation. This angle can be expressed as a molar property which will be a constant for a particular chiral system, and it can thus be applied as a measure for characterization [32].

Meanwhile, ECD is a spectroscopic technique that measures the difference in absorption of the LCP and RCP components of the light beam. The effect arises from the fact that chiral species absorb the two components to different extents. The bands measured in CD spectroscopy can take both positive and negative values due to its differential nature. The signs of the dichroic bands will depend on the absolute configuration of the sample. Thus, two mirror-image isomers will have exactly mirrored ECD spectra.

Theoretically, optical rotation can be calculated from the electric dipolemagnetic dipole ("length gauge") and linear momentum-magnetic dipole ("velocity gauge") linear response functions

$$\langle\!\langle \mu; m \rangle\!\rangle_{\omega}$$
, $\langle\!\langle p; m \rangle\!\rangle_{\omega}$ (31)

and ECD from their residues or as the real (length gauge) or imaginary (velocity gauge) component of the damped equivalents [34, 35].

3.2 MAGNETIC CIRCULAR DICHROISM

Magnetic circular dichroism (MCD) is a magneto-optic technique measuring the same quantity as in ECD. However, the origin of MCD and ECD are different; it is not a requirement for MCD that the molecular structure is chiral [33].

In MCD spectroscopy, CD is induced by placing the sample in an external magnetic field with a component parallel to the propagation of the light beam [33]. The MCD then arises from the magnetic perturbation of the electronic states involved in the transitions induced by the absorption of the incoming light. It is thus a universal absorption property for all matter.

The mathematical expression for MCD is traditionally divided into three terms, each term conveniently describing the physical contributions to the observed spectrum. They are denoted the MCD A, B, and C terms [33].

The presence of the external magnetic field induces Zeeman splitting of degenerate states. This effect is contained in the A term. Ground state degeneracy gives rise to the C term. It is temperature-dependent due to the population difference in the degenerate ground states. Finally, the B term describes the effect of the magnetic perturbation also on non-degenerate states. The states experience field-induced mixing, the extent of which is inversely proportional to the energy splitting between states [33].

The MCD A and B terms can be calculated from the residues of the electric dipole–dipole–magnetic dipole quadratic response function

$$\langle\!\langle \mu; \mu, m \rangle\!\rangle_{\omega,0}$$
 (32)

or as the real component of the corresponding damped response function [36].

3.3 NUCLEAR SPIN-INDUCED CIRCULAR DICHROISM

Nuclear spin-induced circular dichroism (NSCD) can be viewed as a localized analogue of the classical MCD, with the nuclear magnetization acting as the source of the magnetic field. NSCD is manifested in the same quantity as the previously discussed CDs but requires the sample to possess a macroscopic nuclear spin polarization parallel to the light beam [37, 38]. The phenomenon involves optical excitations and local hyperfine interactions within the molecule, and the method is therefore expected to exhibit nucleus-specific features [37, 39].

By replacing the magnetic dipole operator in Eq. 32 with the hyperfine interaction operator of nucleus K, h_K^{hf} , the NSCD observable may also be obtained from the residues of the quadratic response function [40, 41]

$$\langle\!\langle \mu; \mu, h_K^{\rm ht} \rangle\!\rangle_{\omega,0}$$
 (33)

or from the real component of the damped counterpart.

3.4 X-RAY TWO-PHOTON ABSORPTION

The absorption phenomenon is not limited to a single photon: multiphoton processes such as two-photon absorption (2PA) can also occur. In 2PA, one electron is excited from an initial to a final state via an (artificial) intermediate state by the simultaneous absorption of two photons with frequencies summing to an excitation energy. Due to this intermediate state, different selection rules apply to 2PA compared to regular onephoton absorption [42].

In X-ray 2PA (X2PA), the final state of the system is a core-excited state [43]. In the work presented herein, the two absorbed photons are degenerate and thus have frequencies corresponding to half the value of a core-excitation energy. Such energies will typically lie within the extreme-UV (XUV) or soft X-ray regimes.

In response theory, the 2PA cross section observable is described by the cubic response function, but the 2PA transition matrix elements may be calculated from the single residue of the electric dipole–dipole–dipole quadratic response function [44, 45]

$$\langle\!\langle \mu; \mu^a, \mu^b \rangle\!\rangle_{\omega_a, \omega_b}$$
 (34)

or from the damped cubic response function

$$\langle\!\langle \mu; \mu^a, \mu^b, \mu^c \rangle\!\rangle_{\omega_a, \omega_b, \omega_c} . \tag{35}$$

Part II

WORK

On the following pages, a synopsis of the work constituting this thesis is provided (Chapter 4), followed by the publications and manuscripts (Chapter 5). Afterwards, some elaboration upon the work on X-ray two-photon absorption is reported (Chapter 6). The thesis ultimately ends with a conclusion and outlook (Chapter 7).



4.1 OPTICAL ROTATION AND ELECTRONIC CIRCULAR DICHROISM

Optical rotation and ECD have been implemented in Q-Chem within the EOM-CCSD approach in collaboration with Prof. A.I. Krylov and Dr. K.D. Nanda.

Publication I (pp. 21) employs the new feature to calculate ECD spectra in the UV-Vis and X-ray regimes for molecules in their ground and excited states. Furthermore, the published work includes a proof-ofprinciple calculation using the damped linear response approach to obtain an ECD spectrum from an interpolation of cross section points. Those results were produced with pyCCRSP, but the functionality is also available in Q-Chem.

The implementation of optical rotation was carried out in close connection to that of ECD but is unpublished.

4.2 X-RAY TWO-PHOTON ABSORPTION

Another collaboration with Prof. Krylov and Dr. Nanda concerned twophoton absorption in the X-ray regime, and the outcome is presented in Publication II (pp. 39). In this contribution to the Q-Chem package, the so-called core–valence separation and uncoupled valence singles (CVS-uS) approach is derived and implemented for computing EOM-CCSD X2PA spectra. The frozen-core core–valence separation (fc-CVS) scheme [46] is used to reach core excitations and subsequently the CVSuS approximate treatment is applied to the response space.

For initial prototyping and debugging, X2PA and the different levels of approximation were implemented and tested in pyCCRSP. To document the working equations as implemented in the python code, the derivation of the CVS-uS approximation in an alternative notation is reported in Section 6.1.
4.3 MAGNETIC CIRCULAR DICHROISM

The project on MCD was carried out in TURBOMOLE employing the resolution-of-identity (RI-) CC2 model [17] combined with response theory in a collaboration with Prof. C. Hättig. It concerns two developments: the implementation of the MCD A term for explicit excited states and a generalization of the quadratic response function to the damped formulation with complex frequencies. The addition of the A term to the program makes it possible to investigate the MCD of molecules with degenerate excited states.

The combination of the efforts in resonant and damped response theory resulted in a protocol for calculating the MCD spectra of relatively large molecules in a broad frequency range. In this protocol, the spectrum is calculated by explicit solution of the excited states in the lowenergy region with well-separated states, while higher-energy excitations are covered by the damped approach which can be applied at any given frequency.

The work is documented in Manuscript I (pp. 55) by application to a showcase example for which also the relative performance of the resonant and damped approaches and the damped and regular quadratic response functions was assessed by recording the timings of sample calculations.

4.4 NUCLEAR SPIN-INDUCED CIRCULAR DICHROISM

Another project in TURBOMOLE was carried out in collaboration with Dr. P. Štěpánek and Prof. Hättig. Based on a pre-existing implementation of the MCD \mathcal{B} term, the computation of NSCD at the RI-CC2 level of theory was facilitated by a generalization of the code.

In Manuscript II (pp. 91), the NSCD of three derivates of azobenzene is investigated with the aim of uncovering correlations between the localization of the excited states, the character of the substituents, and the strength of the NSCD signal.

PUBLICATIONS AND MANUSCRIPTS

5.1 PUBLICATION I

"Probing molecular chirality of ground and electronically excited states in the UV–Vis and X-ray regimes: An EOM-CCSD study" Josefine H. Andersen, K. D. Nanda, A. I. Krylov, and S. Coriani *J. Chem. Theory Comput.* **2022**, 18 (3), 1748–1764

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Article

Probing Molecular Chirality of Ground and Electronically Excited States in the UV-vis and X-ray Regimes: An EOM-CCSD Study

Josefine H. Andersen, Kaushik D. Nanda, Anna I. Krylov, and Sonia Coriani*

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| ACCESS | III Metrics & More | 🔲 🕅 Article Re | ecommendations | Supporting Information |
| ABSTRACT: We electronic circulat frequency ranges at and doubles level | present several strategie r dichroism (CD) spectra t the equation-of-motion cou of theory. CD spectra of | s for computing across different pled-cluster singles both ground and | EO. | M-CCSD (.S) |

frequency ranges at the equation-of-motion coupled-cluster singles and doubles level of theory. CD spectra of both ground and electronically excited states are discussed. For selected cases, the approach is compared with coupled-cluster linear response results as well as time-dependent density functional theory. The extension of the theory to include the effect of spin—orbit coupling is presented and illustrated by calculations of X-ray CD spectra at the *L*-edge.

1. INTRODUCTION

An object is chiral if its mirror images cannot be brought into coincidence by rotation. In molecules, chirality typically arises either due to the presence of chiral centers, i.e., asymmetrically substituted tetrahedral centers, or due to the handedness of a helical structure (axial chirality), which makes clockwise and counterclockwise structures nonsuperimposable. The isomers with nonsuperimposable mirror structures are called enantiomers, whereas those that are nonsuperimposable and are not mirror images are named diastereomers.¹

Chirality is a common and important molecular property with broad consequences. On a molecular level, many biological objects, such as sugars, amino acids, and secondary structures of proteins and nucleic acids, are chiral. Thus, chirality makes living beings enantio-sensitive. This is critically important for the pharmaceutical and food industry because different enantiomers have drastically different biological effects: e.g., left-handed sugars taste bitter; different enantiomers of the same drug may have different pharmacological effects, the thalidomide tragedy² being a never-fading reminder. Any prospective new drug based on a chiral structure must have clearly assigned absolute configuration.

Also fascinating, life is homochiral—in living organisms, chiral biological molecules exist almost exclusively as single enantiomers. For example, all naturally occurring chiral amino acids are left-handed and all naturally occurring sugars are right-handed. The origin of the homochirality in life remains an unsolved mystery: when synthesized in the lab, left- and right-handed molecules of a compound most often form a racemic mixture, implying that primordial processes in Nature must have been driven by a directing (chiral) template.³

Opposite enantiomers have practically the same energy spectrum; hence, they cannot be distinguished by simple

absorption of linearly polarized light. A pseudoscalar effect is needed, such as the differential interaction with the left or right circularly polarized components of linearly polarized light. Differential transmission results in oppositely signed rotation of the plane of polarization, which is exploited in optical rotation (OR) measurements. Even more powerful is the technique of measuring the differential absorption of the two circularly polarized components, which is the basis of circular dichroism spectroscopies.⁴ In electronic circular dichroism (ECD),^{4,5} the probing light activates electronic transitions in the sample, most typically in the UV-visible frequency region, where valence excitations occur. X-ray radiation can also be used, in principle, to probe chirality via excitations of core electrons. In vibrational circular dichroism (VCD),^{1,4,6} infrared light is used to probe dichroism effects in vibrational transitions of the enantiomers in their ground states. An emerging chiral rotational spectroscopy exploits dichroism effects using microwave (MW-CD) radiation.^{7–9} Chirality can also be probed by transitions to the continuum, as done in photoelectron circular dichroism. $^{10,11}\,$

ECD - XCD

The key step in contemporary use of spectroscopy for chiral discrimination is the simulation of the spectra for an *a priori* chosen absolute configuration of the chiral species.^{12,13} Indeed, experimental measurements of optical activity alone are not sufficient to establish the absolute configuration, since there is

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no direct correspondence between the enantiomer's configuration and the measured sign of the chiroptical property. However, if the simulated spectrum of the chosen configuration matches the sign pattern of the measured spectrum, one can conclude that the experimental sample contains the same enantiomer as in the simulation, $^{5,12-1.4}_{5,12-1.4}$ provided, of course, that the computational method is reliable.

The appeal of this strategy has stimulated the development of reliable computational methods to simulate ORD, ECD, and VCD spectra. Time-dependent density functional theory approaches (TDDFT) are undoubtedly playing the leading role in this endeavor,^{5,12} but the need for alternative, wave function-based methods has been highlighted on many occasions—at the very least, to provide a reliable benchmark against which the validity and accuracy of TDDFT can be checked.^{15–19}

Equation-of-motion coupled-cluster theory (EOM-CC)^{20–23} and the closely related coupled-cluster response theory (CC-RSP)^{18,24,25} are popular and robust theoretical frameworks for simulating spectroscopy. The portfolio of spectroscopies that can be treated using EOM-CC/CC-RSP methods is vast and expanding. Spanning linear and nonlinear regimes, as well as different frequency ranges of probing radiation, it comprises UV-vis one- and two-photon absorption^{26–28} and dichroism,²⁹ magnetic circular dichroism,^{30,31} X-ray absorption,³² dichroism³³ and photoemission,^{32,34} resonant inelastic X-ray scattering,^{33,35,36} and many more. The non-Hermitian (bivariational) nature of the underlying formalism has initially posed some complications (compared to Hermitian variational methods) for modeling natural optical activity, but solutions have been proposed for dealing with issues such as gaugeinvariance and gauge-origin dependency.^{37,38}

In this work, we focus on EOM-CC theory, specifically, the EOM-CC model with singles and doubles (EOM-CCSD),²⁰ as the theoretical framework for computing electronic circular dichroism spectra. We consider the calculation of ECD both in the UV–vis and in the X-ray frequency regimes. The latter requires using specific techniques to treat the core-level transitions—for that purpose, we employ our frozen-core core–valence-separated (fc-CVS) EOM-CC approach.³² In addition to the ECD of molecules in their ground states, we also simulate excited-state circular dichroism, i.e., the ECD spectra of electronically excited species, needed for the simulation of time-resolved/pump–probe experiments employing circular dichroism as the probe.^{39–43} So far, theoretical studies of excited-state ECD have been limited to the TDDFT^{43,44} and algebraic diagrammatic construction (ADC) levels of theory.⁴⁵

Although the fundamental equations for simulating ECD using EOM-CCSD have been known for decades, only CC-RSP appears to have been used, ^{16,17,46-49} maybe because of a fear of the "lack of size-intensivity" of the EOM-CCSD transition moments.^{50,51} However, whether this trait of the theory has any serious practical consequences in calculations of ECD spectra has not been explored; we consider this issue here by comparing EOM-CCSD with CC-RSP results. An advantage of EOM-CC over CC-RSP is that EOM-CC does not require solving additional response equations (for the excited-state multipliers) and performing additional matrix transformations, thus resulting in a computationally slightly less expensive approach. As computing the extra response amplitudes in the CC-RSP approach can become tricky, especially in the high-energy regime, the EOM-CC approach is

less prone to divergences. Furthermore, the EOM-CC approach avoids the spurious poles originating from the *T*-amplitude response, which plague the transition and excited-state properties computed with the CC-RSP approach.⁵²

The paper is organized as follows. In the theory section, we recapitulate the general definitions of the ECD spectroscopic parameters and observables and then discuss strategies for computing them within EOM-CCSD and CCSD-RSP. This encompasses both the calculation of "stick spectra" (i.e., excitation energies and ECD rotatory strengths) and the direct calculation of the ECD cross sections via damped response theory. We then present illustrative results for ECD of ground and excited states of methyloxirane, norcamphor, and binol. We also discuss the exemplary X-ray CD results for methyloxirane and L-alanine at the K-edge and chloroethanol at the *L*-edge of chlorine, with and without the inclusion of spin–orbit splitting. Concluding remarks are given at the end.

2. THEORY

2.1. Definitions. For isotropic samples, CD spectra are typically obtained by calculating the rotatory strengths R_{nf} for the electronic transitions $n \rightarrow f$ (n = 0 for the ground state). In the length gauge (labeled lg), these are defined as the scalar products (Rosenfeld equation)

$$R_{nf}^{lg} = \sum_{\alpha = x, y, z} \Im \langle n | \hat{\mu}_{\alpha} | f \rangle \langle f | \hat{m}_{\alpha} | n \rangle$$
$$= \frac{1}{2} \sum_{\alpha = x, y, z} \Im \langle n | \hat{\mu}_{\alpha} | f \rangle \langle f | \hat{L}_{\alpha} | n \rangle$$
(1)

where \Im stands for the imaginary part, and $\hat{\mu}_{\alpha}$ and \hat{m}_{α} are the Cartesian components of the electric dipole and magnetic dipole operators, respectively. In atomic units (a.u.), $\hat{\mu} = -\hat{r}$ and $\hat{m} = -\frac{1}{2}\hat{L}$, where \hat{r} is the position operator, $\hat{L} = \hat{r} \times \hat{p} = -i\hat{r} \times \hat{\nabla}$ is the orbital angular momentum, and $\hat{p} = -i\hat{\nabla}$ is the linear momentum. By exploiting Ehrenfest's off-diagonal hypervirial relationship (in a.u.)^{15,53,54}

$$i\langle n|\hat{\boldsymbol{p}}|f\rangle = \langle n|[\hat{\boldsymbol{r}},H]|f\rangle = \omega_{fn}\langle n|\hat{\boldsymbol{r}}|f\rangle$$
(2)

where $\omega_{fn} = (E_f - E_n)$ is the energy difference between the two states, one obtains the rotatory strength in the velocity gauge (abbreviated vg)

$$\begin{split} R_{nf}^{\text{vg}} &= \frac{1}{\omega_{fn}} \sum_{\alpha = x, y, z} \Re\langle n | \hat{p}_{\alpha} | f \rangle \langle f | \hat{m}_{\alpha} | n \rangle \\ &= -\frac{1}{2\omega_{fn}} \sum_{\alpha = x, y, z} \Re\langle n | \hat{p}_{\alpha} | f \rangle \langle f | \hat{L}_{\alpha} | n \rangle \end{split}$$
(3)

where \mathfrak{R} indicates the real part.

The dipole oscillator strength f of one-photon absorption (OPA) can also be expressed in different gauges—length, velocity, and mixed (mx):⁵⁵

$$f^{\rm lg} = \frac{2\omega_{fn}}{3} \sum_{\alpha} \langle n|\hat{\mu}_{\alpha}|f\rangle \langle f|\hat{\mu}_{\alpha}|n\rangle \tag{4}$$

$$f^{\rm vg} = \frac{2}{3\omega_{fn}} \sum_{\alpha} \langle n|\hat{p}_{\alpha}|f\rangle \langle f|\hat{p}_{\alpha}|n\rangle$$
(5)

$$f^{\rm mx} = \frac{2i}{3} \sum_{\alpha} \langle n | \hat{\mu}_{\alpha} | f \rangle \langle f | \hat{f}_{\alpha} | n \rangle \tag{6}$$

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2.2. EOM-CC Theory for Valence and Core-Level States. The (ground-state) coupled-cluster wave function ($\Psi_{\rm CC}$) is given in terms of the exponential of the cluster operator \hat{T} acting on the reference (usually, Hartree–Fock) Slater determinant Φ_0 :⁵⁶

$$|\Psi_{\rm CC}\rangle \equiv |\Psi_0\rangle = e^{\tilde{T}}|\Phi_0\rangle \tag{7}$$

At the CCSD level, the second-quantization form of \hat{T} reads

$$\hat{T} = \hat{T}_{1} + \hat{T}_{2}; \qquad \hat{T}_{1} = \sum_{ia} t_{i}^{a} \hat{a}_{a}^{\dagger} \hat{a}_{i}; \qquad \hat{T}_{2} = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} \hat{a}_{a}^{\dagger} \hat{a}_{b}^{\dagger} \hat{a}_{j} \hat{a}_{i}$$
(8)

where t_a^a and t_{ij}^{ab} are cluster amplitudes associated with singles and doubles excitations, and \hat{a}_{i} , \hat{a}_{a}^{\dagger} are (electron) annihilation and creation operators, respectively. We adopt the standard notation, where indices i, j, k, \cdots refer to occupied, a, b, c, \cdots to virtual, and p, q, r, \cdots to general molecular spin–orbitals; the separation between the occupied and virtual orbital spaces is determined by the choice of the reference determinant Φ_0 . The cluster amplitudes satisfy the CC equations

$$\left\langle \Phi_{\nu} | \overline{H} | \Phi_{0} \right\rangle = 0 \tag{9}$$

where, for CCSD, Φ_{ν} spans the singles and doubles excitation manifold. $\bar{H} = e^{-\bar{T}}\hat{H}e^{\bar{T}}$ is the similarity-transformed Hamiltonian.

The EOM-CCSD target state *n* is expressed using the (right) EOM operator $\hat{\mathcal{R}}^n$ acting on the CCSD wave function as follows:

$$|\Psi_n\rangle = \hat{\mathcal{R}}^n \Psi_{\rm CC} = \hat{\mathcal{R}}^n e^{\hat{T}} |\Phi_0\rangle \tag{10}$$

The type of target states determines the choice of $\hat{\mathcal{R}}$. $\hat{\mathcal{R}}$ accesses a specific sector of the Fock space defined by the set of target determinants, relative to the reference determinant. Within EOM-CCSD for excitation energies (EOM-EE-CCSD), $\hat{\mathcal{R}}^n$ accesses the reference and valence singly and doubly excited configurations:

$$\hat{\mathcal{R}} = r_0 + \sum_{ia} r_i^a \hat{a}_a^{\dagger} \hat{a}_i + \frac{1}{4} \sum_{ijab} r_{ij}^{ab} \hat{a}_a^{\dagger} \hat{a}_b^{\dagger} \hat{a}_j \hat{a}_i$$
(11)

where r_0 , r_i^a , and r_{ij}^{ab} are the EOM-EE-CCSD amplitudes satisfying the following eigenvalue equation:

 $\wedge n$

 $\wedge n$

$$\bar{H}\mathcal{R}^{''}|\Phi_0\rangle = E_n \mathcal{R}^{''}|\Phi_0\rangle \tag{12}$$

The state with $r_0 = 1$ and $r_i^a = r_{ij}^{ab} = 0 \ \forall \{i,j,a,b\}$ is the reference CCSD state (n = 0, usually, but not always, the ground state), and the rest (n > 0) are EOM-CC target states (e.g., valence excited states). In a similar fashion, target core-excited states can be computed from the EOM-CCSD eigenvalue equation by restricting the EOM-CCSD operator to only access the core-excited configurations.^{32,57} In the here-adopted core-valence-separated EOM-EE-CCSD approach with frozen-core approximation (fc-CVS-EOM-EE-CCSD),³² this corresponds to

$$\hat{\mathcal{R}} = \sum_{Ia} r_{I}^{a} \hat{a}_{a}^{\dagger} \hat{a}_{I} + \frac{1}{2} \sum_{Ijab} r_{Ij}^{ab} \hat{a}_{a}^{\dagger} \hat{a}_{b}^{\dagger} \hat{a}_{j} \hat{a}_{I} + \frac{1}{4} \sum_{IJab} r_{IJ}^{ab} \hat{a}_{a}^{\dagger} \hat{a}_{b}^{\dagger} \hat{a}_{J} \hat{a}_{I}$$
(13)

where capital labels *I* and *J* denote core orbitals. In contrast to the CVS scheme employed by Coriani and Koch,⁵⁷ in the fc-CVS-EOM-EE-CCSD approach of Vidal et al.,³² the core

orbitals are frozen (uncorrelated) in the ground-state calculation.

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Within the non-Hermitian EOM-CC theory, the left and right eigenfunctions of \overline{H} are not complex conjugates of each other. The left eigenfunctions are obtained from the left EOM-CC eigenvalue equation

$$\langle \Phi_0 | \hat{\mathcal{L}}^n \overline{H} = \langle \Phi_0 | \hat{\mathcal{L}}^n E_n \tag{14}$$

where $\hat{\mathcal{L}}^n$ is the left EOM-CC operator. The left EOM-EE-CCSD and fc-CVS-EOM-EE-CCSD (de-excitation) operators are defined according to

$$\hat{\mathcal{L}} = l_0 + \sum_{ia} l_i^a \hat{a}_i^{\dagger} \hat{a}_a + \frac{1}{4} \sum_{ijab} l_{ij}^{ab} \hat{a}_i^{\dagger} \hat{a}_j^{\dagger} \hat{a}_b \hat{a}_a$$
(15)

and

$$\hat{\mathcal{L}} = \sum_{Ia} l_{I}^{a} \hat{a}_{I}^{\dagger} \hat{a}_{a} + \frac{1}{2} \sum_{Ijab} l_{Ij}^{ab} \hat{a}_{I}^{\dagger} \hat{a}_{j}^{\dagger} \hat{a}_{b} \hat{a}_{a} + \frac{1}{4} \sum_{IJab} l_{IJ}^{ab} \hat{a}_{I}^{\dagger} \hat{a}_{J}^{\dagger} \hat{a}_{b} \hat{a}_{a}$$
(16)

respectively. In the context of the left ground-state reference, $\hat{\mathcal{L}}$ is historically referred to as 1 + $\hat{\Lambda}$ according to

$$\langle \tilde{\Psi}_n | = \langle \Phi_0 | (1 + \hat{\Lambda}) e^{-\hat{T}}; \qquad \hat{\Lambda} = \sum_{\mu \neq \Phi_0} \lambda_\mu \hat{\tau}_\mu^\dagger$$
(17)

Note that $l_0 = 1$ for the reference (n = 0) CCSD state and $l_0 = 0$ for the EOM-CC states. In the literature, the ground-state left amplitudes are also often denoted as $\overline{t_{\mu}}$ to highlight that they are Lagrangian multipliers of the right amplitudes $t_{\mu}^{2.5}$

The EOM-CC left and right eigenvectors can be normalized to form a biorthonormal set, such that $\langle \hat{\mathcal{L}}^n | \hat{\mathcal{R}}^m \rangle = \delta_{nm}$, where δ_{nm} is the Kronecker delta.

2.3. EOM-CCSD Rotatory Strengths: Density-Based Implementation. Within the non-Hermitian CC theory, the right $(\langle \hat{O}^{fn} \rangle)$ and left $(\langle \hat{O}^{nf} \rangle)$ transition moments between different states are not equal; here, \hat{O} is a general operator. As a result, the expressions for the rotatory strengths (as those for the oscillator strengths) are explicitly symmetrized with respect to complex conjugation (denoted by *)

$$R_{nf}^{lg} = \frac{1}{2} \sum_{\alpha} \left\{ \frac{1}{2} (\langle \hat{r}_{\alpha}^{nf} \rangle \langle \hat{L}_{\alpha}^{fn} \rangle + \langle \hat{L}_{x}^{nf} \rangle^{*} \langle \hat{r}_{\alpha}^{fn} \rangle^{*}) \right\}$$
$$= \frac{1}{4} \sum_{\alpha} \left\{ \langle \hat{r}_{\alpha}^{nf} \rangle \langle \hat{L}_{\alpha}^{fn} \rangle - \langle \hat{L}_{\alpha}^{nf} \rangle \langle \hat{r}_{\alpha}^{fn} \rangle \right\}$$
(18)

$$R_{nf}^{\text{vg}} = -\frac{1}{4\omega_{nf}} \sum_{\alpha} \left\{ \langle \hat{p}_{\alpha}^{nf} \rangle \langle \hat{L}_{\alpha}^{fn} \rangle + \langle \hat{L}_{\alpha}^{nf} \rangle \langle \hat{p}_{\alpha}^{fn} \rangle \right\}$$
(19)

The right and left transition moments can be computed as

$$\langle \hat{O}^{fn} \rangle = \langle \Phi_0 \hat{\mathcal{L}}^f e^{-\hat{T}} | \hat{O} | e^{\hat{T}} \hat{\mathcal{R}}^n \Phi_0 \rangle = \sum_{pq} \gamma_{pq}^{f \leftarrow n} O_{pq}$$
(20)

$$\langle \hat{O}^{nf} \rangle = \langle \Phi_0 \hat{\mathcal{L}}^n e^{-\hat{T}} | \hat{O} | e^{\hat{T}} \hat{\mathcal{R}}^f \Phi_0 \rangle = \sum_{pq} \gamma_{pq}^{n \leftarrow f} O_{pq}$$
(21)

where $\gamma^{f \leftarrow n}$ and $\gamma^{n \leftarrow f}$ are the right and left reduced transition one-particle density matrices (1PDMs), respectively; O_{pq} is the matrix representation of the operator in the MO basis (i.e., property integrals). The programmable expressions for the

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transition 1PDMs between different EOM-CCSD target states used in this study are presented in the Appendix and also reported elsewhere. 20,32

2.4. EOM-CCSD Rotatory Strengths: Alternative Implementation. Within CC-RSP theory, the transition moments are often expressed as contractions of fundamental CC building blocks^{24,25}

$$\langle \hat{O}^{f0} \rangle_{\rm rsp} = \sum_{\mu} l^f_{\mu} \xi^O_{\mu} \tag{22}$$

$$\langle \hat{O}^{0f} \rangle_{\rm rsp} = \sum_{\mu} \eta_{\mu}^{O, \rm rsp} r_{\mu}^{f} + \sum_{\mu} \bar{M}_{\mu}^{f}(\omega_{f}) \xi_{\mu}^{O}$$
(23)

$$\langle \hat{O}^{kj} \rangle_{\rm rsp} = \sum_{\mu\nu} l^k_{\mu} A^{O,\rm rsp}_{\mu\nu} r^j_{\nu} + \sum_{\mu} \bar{N}^{kj}_{\mu} (\omega_k, \, \omega_j) \xi^O_{\mu} \tag{24}$$

where

$$\xi^{O}_{\mu} = \langle \Phi_{\mu} | e^{-\hat{T}} \hat{O} e^{\hat{T}} | \Phi_{0} \rangle \tag{25}$$

$$A_{\mu\nu}^{O,\mathrm{rsp}} = \langle \Phi_{\mu} | [e^{-\hat{T}} \hat{O} e^{\hat{T}}, \, \hat{\tau}_{\nu}] | \Phi_0 \rangle \tag{26}$$

$$\eta_{\mu}^{O,\mathrm{rsp}} = \langle \Phi_0 | [e^{-\hat{T}} O e^{\hat{T}}, \hat{\tau}_{\mu}] | \Phi_0 \rangle + \sum_{\lambda} \overline{t}_{\lambda} A_{\lambda\mu}^{O,\mathrm{rsp}}$$
(27)

Above, $\overline{M}_{\mu}^{f}(\omega_{f})$ and $\overline{N}_{\mu}^{kj}(\omega_{k}\omega_{\mu})$ are excited-state Lagrangian multipliers.²⁵ Greek indices refer to the excitation levels (here either singles or doubles) and $\hat{\tau}_{\mu}$ is the corresponding excitation operator. Note the superscripts *f* and *k* to distinguish between the excited state amplitudes r_{μ} and l_{μ} .

Analogous expressions can be written for the EOM-CCSD transition moments 35,50,58

$$\langle \hat{O}^{f0} \rangle = \sum_{\mu} l^{f}_{\mu} \xi^{O}_{\mu}$$
(28)

$$\langle \hat{O}^{0f} \rangle = \sum_{\mu} \eta^{O}_{\mu} r^{f}_{\mu}$$
⁽²⁹⁾

$$\langle \hat{O}^{kj} \rangle = \sum_{\mu\nu} l^k_{\mu} A^O_{\mu\nu} r^j_{\nu} - (\sum_{\rho} \overline{t}_{\rho} \xi^O_{\rho}) \delta_{kj} - (\sum_{\rho} l^k_{\rho} \xi^O_{\rho}) (\sum_{\rho} \overline{t}_{\rho} r^j_{\rho})$$
(30)

where the EOM-CCSD building blocks are³⁵

$$\eta^{O}_{\mu} = \langle \Phi_{0} | e^{-\hat{T}} \hat{O} e^{\hat{T}} | \Phi_{\mu} \rangle + \sum_{\lambda} \overline{t}_{\lambda} \langle \Phi_{\lambda} | e^{-\hat{T}} \hat{O} e^{\hat{T}} | \Phi_{\mu} \rangle - \langle \hat{O} \rangle_{\rm CC} \overline{t}_{\mu} \quad (31)$$

$$= \langle \Phi_0 | e^{-\hat{T}} \hat{O} e^{\hat{T}} | \Phi_{\mu} \rangle + \sum_{\lambda} \overline{t}_{\lambda} A^O_{\lambda \mu}$$
(32)

$$A^{O}_{\lambda\mu} = \langle \Phi_{\lambda} | e^{-\hat{T}} \hat{O} e^{\hat{T}} | \Phi_{\mu} \rangle - \delta_{\lambda\mu} \langle \Phi_{0} | e^{-\hat{T}} \hat{O} e^{\hat{T}} | \Phi_{0} \rangle$$
(33)

and $\left(\sum_{\rho} \overline{t}_{\rho} r_{\rho}^{j}\right) = -r_{0}^{j}$.

Simple manipulations connect the CC response and the EOM building blocks³⁵

$$\eta^{O}_{\mu} = \eta^{O, \text{rsp}}_{\mu} + \sum_{\mu > \nu} \overline{t}_{\mu} \langle \Phi_{\mu} | \hat{\tau}_{\nu} e^{-\hat{T}} \hat{O} e^{\hat{T}} | \Phi_{0} \rangle - \left(\sum_{\rho} \overline{t}_{\rho} \xi^{O}_{\rho} \right) \overline{t}_{\mu}$$
(34)

$$A^{O}_{\lambda\mu} = A^{O,\mathrm{rsp}}_{\lambda\mu} + \langle \Phi_{\mu} | \hat{\tau}_{\nu} e^{-\hat{T}} \hat{O} e^{\hat{T}} | \Phi_0 \rangle (1 - \delta_{\mu\nu})$$
(35)

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2.5. EOM-CCSD ECD Spectra from the Damped Optical Rotation Tensor. CD spectra can also be obtained directly from the absorbing component of the electric dipole– magnetic dipole optical rotation tensor, $G'_{\alpha\beta}(g)$,¹

$$\Delta \epsilon \propto -\frac{1}{3} \omega \mu_0 l N G'_{\alpha \alpha}(g) \tag{36}$$

Within damped linear response theory, ^{33,35,49,59-63} the latter corresponds, in the length gauge, to

$$G_{\alpha\beta}^{\prime,\mathrm{lg}}(-\omega,\,\omega) \propto \Re\langle\langle \hat{m}_{\alpha};\,\hat{\mu}_{\alpha}\rangle\rangle_{\omega+i\gamma}$$
 (37)

and to

$$G_{\alpha\beta}^{\prime,\mathrm{vg}}(g) \propto \omega^{-1} \Im\langle\langle \hat{m}_{\alpha}; \, \hat{p}_{\alpha} \, \rangle\rangle_{\omega+i\gamma}$$
(38)

in the velocity gauge; γ is the damping term, which can be regarded as a common inverse lifetime of all excited states. Note that the computation of the ECD spectrum from the absorptive component of the complex optical rotation tensor does not require the use of the modified velocity gauge,³⁷ since the imaginary part of the static correction term is trivially zero.⁴⁹

The general sum-over-states expression of a complex linear response function (in a.u.) is 61

$$\begin{split} \langle \langle \hat{O}_{1}; \ \hat{O}_{2} \rangle \rangle_{\omega+i\gamma} &= -\sum_{k>0} \left\{ \frac{\langle \hat{O}_{1}^{bk} \rangle \langle \hat{O}_{2}^{k0} \rangle}{E_{k} - E_{0} - \omega - i\gamma} \right. \\ &+ \frac{\langle \hat{O}_{2}^{0k} \rangle \langle \hat{O}_{1}^{k0} \rangle}{E_{k} - E_{0} + \omega + i\gamma} \end{split}$$
(39)

In our present implementation, we adopted an asymmetric form for the CC damped rotation tensor.^{25,49,64} In the vector–matrix notation of Section 2.4, this reads

$$\langle\langle \hat{X}; \, \hat{x} \rangle\rangle_{\omega+i\gamma} = \frac{1}{2} \hat{C}^{\pm\omega} \{ \overline{t}^{\,x} (\omega + i\gamma) \xi^{X} + \eta^{X} t^{x} (\omega + i\gamma) \}$$

$$\tag{40}$$

where the permutator $\hat{C}^{\pm \omega}$ only acts on the real frequency ω .

Note that, in Q-Chem's notation from refs 65 and 66, $t^x(\omega + i\gamma)$ and $\overline{t}^x(\omega + i\gamma)$ correspond to the response vectors $X^x(\omega + i\gamma)$ and $\tilde{X}^x(\omega + i\gamma)$ with the response intermediates η^x and ξ^x given by

$$\langle \eta^{x} | \Phi_{\rho} \rangle = \langle \tilde{D}^{x} | \Phi_{\rho} \rangle - \langle \tilde{D}^{x} | \Phi_{0} \rangle \langle \hat{\Lambda} | \Phi_{\rho} \rangle \tag{41}$$

and

$$\langle \Phi_{\rho} | \xi^x \rangle = \langle \Phi_{\rho} | D^x \rangle \tag{42}$$

Here, $(\tilde{D}^{x}|\Phi_{\rho}) = \langle \Phi_{0}(1 + \hat{\Lambda})|e^{-\hat{T}}\hat{x}e^{\hat{T}}|\Phi_{\rho}\rangle$ and $\langle \Phi_{\rho}|D^{x}\rangle = \langle \Phi_{\rho}|e^{-\hat{T}}\hat{x}e^{\hat{T}}|\Phi_{0}\rangle$ (see eqs 31 and 25).

Equation 40 requires the solution of the damped linear equations for the right response amplitudes, $t^{x}(\omega + i\gamma)$, and the left response multipliers $\overline{t}^{x}(\omega + i\gamma)$ of the same operator x

$$[\mathbf{A} - (\omega + i\gamma)\mathbf{1}]t^{x}(\omega + i\gamma) = -\xi^{x}$$
(43)

$$\overline{t}^{x}(\omega + i\gamma)[\mathbf{A} + (\omega + i\gamma)\mathbf{1}] = -\eta^{x}$$
(44)

where **A** is a sub-block of the similarity-transformed Hamiltonian matrix, often referred to as the CC Jacobian



Figure 1. Structures of molecules considered in this work: (a) *R*-methyloxirane, (b) 1*R*-norcamphor, (c) S_a -binol, (d) R_a -binol, (e) L-alanine, and (f) L-chloroethanol. Atom labeling is given when relevant for the discussion of the results.



Figure 2. (*R*)-Methyloxirane. EOM-CCSD (left) and CCSD-RSP (right) basis-set study of ground-state transition properties. ECD (top) and OPA (bottom) spectra in length (solid line) and velocity (dashed line) gauges. Lorentzian broadening with HWHM = 0.124 eV. Note that all spectra are based on 8 transitions except the RSP/dT one, which only includes 5 states.

$$\bar{H}_{\mu\nu} = \begin{pmatrix} E_{\rm CC} & \eta_{\nu} \\ \Omega_{\mu} & A_{\mu\nu} \end{pmatrix}$$
(45)

Note that, in contrast to the case of CC linear response, the EOM equations for the response multipliers are decoupled from those for the response amplitudes.³⁵ The damped response equations (eqs 43–44) can be solved iteratively using damped variants of standard procedures^{35,49,63} such as the Direct Inversion in the Iterative Subspace (DIIS) or generalized Davidson.

3. COMPUTATIONAL DETAILS

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We implemented the above expressions for the calculation of the electronic circular dichroism within the EOM-CCSD approach in Q-Chem.^{67,68} The theory is applicable for valence excitations (EOM-EE-CCSD) as well as core excitations (fc-CVS-EOM-EE-CCSD^{32,69}) of both ground and excited states. py-CCRSP⁷⁰ was used for code profiling and testing as well as for the damped-response calculations. To illustrate the methodology, we computed various CD spectra for the following systems (shown in Figure 1): (*R*)-methyloxirane, (1*R*)-norcamphor, S_a - and R_a -binol, L-alanine, and L-chloroethanol.

(R)-Methyloxirane has previously been used as a model system to computationally investigate excited-state CD (ES-ECD) at the TDDFT level of theory by Rizzo and Vahtras.⁴⁴ We use the same geometry as in ref 44. We investigated basisset effects by employing various correlation-consistent basis sets^{71–73} with different augmentation and polarization levels, as well as Pople's 6-311++G^{**} set. The EOM-CCSD results were compared to LR-CCSD results obtained with Dalton.⁷⁴ ES-ECD spectra were computed with the d-aug-cc-pVDZ and d-aug-cc-pVTZ basis sets.

For consistency, we used the ground-state geometry of (1R)norcamphor optimized at the DFT/CAM-B3LYP/aug-ccpVTZ level from ref 45. Ground-state and S_1 excited-state absorption and CD spectra were simulated using the d-aug-cc-pVDZ basis set.

For binol, we considered two structures, namely the S_0 structure of the S_a -isomer from ref 43 and the S_0 structure of the R_a -isomer of ref 45 (including a symmetrized variant). Calculations with the former structure were carried out using the 6-31G* basis set, as was done in ref 43 at the TDDFT level. The 20 lowest excitations in each irrep (*A* and *B* irreps of C_s point group) were computed. The ES-ECD was calculated for the L_a , L_b , and B_b states in each irrep. In the case of the (symmetrized) R_a -isomer, we used the cc-pVDZ basis set, as was done in ref 45 at the ADC(2) and TDDFT levels, and computed the GS-ECD arising from the 20 lowest excitations in each irrep, as well as the ES-ECD of the L_a , L_b , and B_b states. For calculations in the C_1 group, we used a single-precision implementation of CCSD and EOM-CCSD equations.⁷⁵

In the X-ray regime (XCD), we considered, once again, methyloxirane, employing the same geometry for the *R*-isomer as above, as well as a MP2/cc-pVTZ geometry from ref 76. We considered different basis sets, namely, augmented Dunning basis sets as well as standard and uncontracted variants of Pople's 6-311++G** set, which are well-suited for calculations of XAS spectra.⁷⁷ The core-excited states of the carbon *K*-edge were computed using the fc-CVS-EOMEE-CCSD scheme in Q-Chem. The linear response results were obtained with the CVS-CCSD scheme in Dalton.^{57,74,78}

The XCD of L-alanine was investigated with the d-aug-ccpVDZ basis set. We computed the *K*-edges of carbon, nitrogen, and oxygen for the neutral and zwitterionic forms of the amino acid. Coordinates for the neutral form were taken from ref 76; the zwitterion structure was obtained from neutron diffraction experiment in ref 79.

Finally, inspired by ref 80, we considered the chlorine *L*-edge of chloroethanol. XAS and XCD spectra with and without



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Figure 3. (R)-Methyloxirane. Absorption (bottom panel) and CD (upper panel) spectra for S_{00} , S_{11} and S_2 . EOM-CCSD and TDDFT/CAM-B3LYP (20 states in both cases) with the d-aug-cc-pVDZ basis set. Dashed line is velocity gauge. Experimental spectra (dotted line) were digitized from ref 82. Lorentzian broadening with HWHM = 0.124 eV.

spin–orbit coupling (SOC) were computed with the 6- $311(2+,+)G^{**}$ basis, specifically uncontracted to describe the 2p orbitals of the Cl atom.⁶⁹

Unless otherwise specified, the gauge origin was located at the center of charge, which is the default setup in Q-Chem. RSP-CCSD and TDDFT/CAM-B3LYP results used for comparison were obtained using Dalton.^{74,78} Most spectra discussed in the following section were obtained by Lorentzian broadening of the computed stick spectra (excitation energies, oscillator and rotatory strengths), and are reported as decadic molar extinction coefficient for OPA and as extinction coefficient anisotropy for the CD.

4. RESULTS AND DISCUSSION

4.1. UV-vis ECD Spectra. *4.1.1. Methyloxirane.* Methyloxirane (also known as propylene oxide or 1, 2-epoxypropane) is a popular test case for calculations of optical activity in both the UV-vis and X-ray regimes. This chiral organic molecule is small enough for high-level *ab initio* calculations and is also manageable for experimental absorption and circular dichroism studies available in the gas phase.^{81,82}

We investigated the basis-set dependence of the groundstate OPA and ECD obtained from the EOM-CCSD and CCSD-RSP calculations. The resulting spectra are shown in Figure 2. See Table S1 for the underlying raw data.

We observe good agreement between the EOM-CCSD rotatory and oscillator strengths obtained from the length and the velocity formulations for all basis sets considered here. The maximum absolute difference between the EOM rotatory strength in the two gauges is 0.004 au for the Pople basis set, 0.003 au for aug-cc-pVDZ and d-aug-cc-pVDZ, and 0.002 au for aug-cc-pVTZ and d-aug-cc-pVTZ. Increasing the basis-set size does not seem to affect this difference, at least not within the sequence of the bases investigated here. However, the quality of the basis moderately affects the peak positions and intensities, although the overall sign pattern is the same for all basis sets. The EOM-CCSD and RSP-CCSD results are nearly identical; the only noticeable difference seen for the d-aug-cc-pVTZ case is due to the smaller number of roots computed in the case of RSP-CCSD.

Next, we examined the performance of EOM-CCSD for calculation of ES-ECD, using the d-aug-cc-pVDZ and d-aug-ccpVTZ sets, see Tables S2 and S3 in the SI, where transitions from the ground state and from the first 8 excited states up to the twentieth excited state were considered. We immediately note larger differences between the two gauges, now up to 0.09 au in absolute values of the rotatory strength for d-aug-ccpVDZ and 0.04 au for d-aug-cc-pVTZ. In a few instances, a negative value of the velocity-gauge oscillator strength is obtained. The 6 \rightarrow 7 transition is also accompanied by a change in sign and magnitude of the rotatory strengths (see Tables S2 and S3). It is important to note, however, that these transitions fall significantly below 0.2 eV (IR-NIR region), which means that numerical instability, resulting from the corresponding small denominators of the order of 0.009 hartree in the vg expressions for oscillator and rotatory strengths, cannot be discounted.

The simulated absorption and CD spectra of the ground state (S_0) and the first two excited states $(S_1 \text{ and } S_2)$ obtained using the d-aug-cc-pVDZ set are shown in Figure 3, along with the results of TDDFT/CAM-B3LYP/d-aug-cc-pVDZ calculations (the d-aug-cc-pVTZ results are reported in SI, see Figure S2). The experimental spectra for the ground state taken from ref 82 are also shown. The CAM-B3LYP excitation energies are slightly lower than the CCSD ones for all three cases; otherwise, the spectra are qualitatively rather similar. No energy shift was applied. We refer to Tables S4 and S5 for the CAM-B3LYP excitation energies and strengths the corresponding spectra were obtained from. The S_0 spectra agree reasonably well with the available experimental results for Rmethyloxirane, at least up to 8 eV. Above 8 eV, both computational methods yield a much more intense negative peak than in the experiment, in line with previous findings.¹⁵ Adding Rydberg-type functions to the basis set partly redistributes the intensity over several electronic transitions, yet the third band remains more intense than observed experimentally (see Figure S1 in the SI). Note that the first ionization energy is 10.13 eV (EOM-IP-CCSD/d-aug-ccpVDZ).

Concluding this section, Figure 4 shows proof-of-principle illustration of our damped-response implementation of the ECD cross section. The trace of the real component of the

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Figure 4. (*R*)-Methyloxirane. EOM-CCSD/aug-cc-pVDZ groundstate ECD spectra obtained from a Lorentzian broadening (HWHM = 0.005 a.u.) of the rotatory strengths (dashed gray line, labelled ECD) and from the damped response function (red grid points and red cubic fit line, labelled CPP) in length gauge.

optical rotation tensor in the length gauge was computed at the frequency grid points indicated by the red X marks and then splined to yield the cross section. The spectrum is practically identical to the one obtained from a Lorentzian broadening of individual rotatory strengths from standard EOM-CCSD theory.

4.1.2. Norcamphor. Moving on to a larger organic molecule, we considered the bicyclic ketone (1R)-norcamphor (a.k.a., 2-norbornanone), which has also been investigated in previous theoretical^{19,45,83} and experimental⁸³ gas-phase studies. The ground-state ECD spectra (see right panel of Figure 5) from EOM-CCSD and TDDFT/CAM-B3LYP are rather similar in peak positions, intensities, and sign patterns



Figure 5. (1*R*)-Norcamphor. S_1 excited-state (ES) and ground-state (GS) ECD (upper panels) and absorption (bottom panels) spectra from EOM-CCSD (this work, 20 states), TDDFT/CAM-B3LYP (this work, 15 states), and ADC(3) (ref 45, 10 states) using the d-aug-cc-pVDZ basis. Dashed lines correspond to velocity gauge. The corresponding EOM-CCSD and TDDFT/CAM-B3LYP OPA and ESA spectra are shown in the two bottom panels. Experimental spectra (dotted line) from ref 83. Lorentzian broadening, HWHM = 0.124 eV.

up to 7.7 eV. Above 7.7 eV, CAM-B3LYP yields a strong negative band, whereas CCSD has a weaker positive peak, followed by a more intense negative one at around 8 eV. The corresponding ADC(3) spectrum of ref 45, also shown in Figure 5, is blue-shifted and has a negative peak centered at around 7.8 eV. Most electronic transitions have been previously assigned ns and np characters.⁸³ When Rydbergtype functions are included, the intensities are redistributed but the overall spectrum remains the same, see Figure S3 and Table S8. The experimental absorption spectrum of the ground state⁸³ also presents a very weak band centered just above 4 eV, previously assigned to an $n\pi^*$ excitation, with a very small positive rotatory strength. We obtain this band at 4.32 eV, with a tiny positive rotatory strength in length gauge and negative strength in velocity gauge. The same behavior was observed at the ADC(3) level. The CAM-B3LYP rotatory strength of the weak $n\pi^*$ is positive in both gauges.

The shapes of the ECD spectra of the lowest electronic excited state are again similar for all three methods up to 3.5 eV, with an overall blue shift of the ADC(3) spectrum. We note here that we recomputed the CAM-B3LYP ES-ECD spectrum and obtained intensity twice as large as the one reported by Scott et al.⁴⁵ Above 3.5 eV, the three methods clearly differ, also because a different number of final states were computed with the three methods (i.e., only 10 states were reported in the ADC(3) study). CAM-B3LYP yields an additional strong negative band and CCSD yields a weaker positive one, reflecting the differences observed in the ground-state spectrum. The raw data of Figure 5 are given in Tables S6 and S7 in the SI.

4.1.3. Binol. Binol (1,1'-bis-2-naphthol) is an axially chiral compound composed of two naphthol moieties connected by a single bond. The two atropoisomers are labeled either R_a/S_a or P/M. Here, we considered two structures: the ground-state optimized structure (S_0) of the S_a enantiomer taken from ref 43, where the dihedral angle between the two moieties is $\sim 90^{\circ}$ ("orthogonal" conformation) and the S_0 of the R_a enantiomer taken from the recent computational study at the ADC level of theory,⁴⁵ which is a DFT/CAM-B3LYP/cc-pVTZ optimized structure. A symmetrized version of the latter was also employed for computational efficiency, after validating that the two structures yield equivalent results. The steady-state and time-resolved ECD spectra of binol have been measured by Hache and co-workers in different solvents.^{39,43,84} Niezborala and Hache report the steady-state spectrum of R-binol in ethanol, whereas the one of S-binol in cyclohexane was reported by Schmid et al.43

Electronic transitions in binol are often labeled using the Platt nomenclature relative to the 2-naphthol precursor. The first two bright transitions are called L_a and L_b , where L_a is the more intense one (HOMO \rightarrow LUMO character). The relative ordering of the L_a and L_b transitions is method dependent. At the EOM-CCSD/6-31G(d) level, the lowest excited state of isolated 2-naphthol is L_b at 4.45 eV ($f^{lg} = 0.02$), whereas the second, at 5.39 eV ($f^{lg} = 0.06$), is L_a . They are followed by a third state at 6.28 eV ($f^{lg} = 0.04$). An intense B state (according to Platt's notation) comes as fourth at 6.60 eV ($f^{lg} = 1.29$). With the cc-pVDZ basis, we obtain the excited states at 4.40 eV ($f^{lg} = 0.02$); 5.26 eV ($f^{lg} = 0.047$); 6.19 eV ($f^{lg} = 0.033$); 6.49 eV ($f^{lg} = 1.21$). At the TDDFT level, the ordering of the two states is reversed, with L_a dropping below L_b .

This different ordering carries over to binol. Exciton pairs are obtained from the combination of the L_a and L_b states of

the two naphthol moieties. The lowest EOM-CCSD exciton pair comprises the two states, respectively at 4.42 eV ($f^{lg} = 0.052$) and 4.44 eV ($f^{lg} = 0.012$) in the 6-31G(d) basis, which are labeled L_b -1 (of B symmetry) and L_b -2 (of A symmetry). The states of the second exciton pair, of L_a character, are at 5.29 eV ($f^{lg} = 0.20$, L_a -1, B symmetry) and 5.33 eV ($f^{lg} = 0.012$, L_a -2, A symmetry). At the TDDFT/CAM-B3LYP level, the first exciton pair corresponds to L_a -1 (4.44 eV, $f^{lg} = 0.14$) and L_a -2 (4.48 eV, $f^{lg} = 0.02$); the second pair is L_b -1 (4.86 eV; $f^{lg} = 1.0 \times 10^{-4}$). We summarize in Table 1 our results for energies, oscillator strengths, and

| Table 1. | First H | Four Exc | ited S | States | of Binol | Acco | rding | to |
|----------|---------|----------|--------|---------|----------|-------|------------|------|
| CCSD a | nd CA | M-B3LY | P (Ro | otatory | Strengtl | ns in | 10^{-40} | cgs) |

| | E (eV) | f | State/ Sym | Label | $R^{ m lg}$ | R^{vg} |
|-----------------------------|--------|------|---------------|-------------------|-------------|-------------------|
| S _a -binol/6-310 | G(d) | | | | | |
| CCSD | 4.42 | 0.05 | 1/B | L_b -1 | 20.44 | 7.26 |
| | 4.44 | 0.01 | 1/A | L_b -2 | -37.52 | -20.21 |
| | 5.29 | 0.20 | 2/B | L_a -1 | -0.86 | 1.32 |
| | 5.33 | 0.01 | 2/A | L_a -2 | -25.95 | -17.39 |
| CAM-B3LYP | 4.44 | 0.14 | 1/B | L_a -1 | 33.91 | 31.46 |
| | 4.48 | 0.02 | 1/A | L_a -2 | -80.89 | -73.08 |
| | 4.86 | 0.10 | 2/B | L_b -1 | 4.11 | 2.83 |
| | 4.86 | 0.00 | 2/A | L_b -2 | -0.835 | -1.06 |
| R _a -binol/cc-pV | /DZ | | | | | |
| CCSD | 4.42 | 0.06 | 1/B | L_b-1 | -16.93 | -5.01 |
| | 4.44 | 0.01 | 1/A | L_b-2 | 37.49 | 21.55 |
| | 5.22 | 0.18 | 2/B | L_a-1 | 3.43 | 0.33 |
| | 5.26 | 0.01 | 2/A | L _a -2 | 18.69 | 12.63 |
| CAM-B3LYP | 4.42 | 0.15 | 1/B | L_a-1 | -23.27 | -25.03 |
| | 4.47 | 0.02 | 1/A | L_a-2 | 66.62 | 71.98 |
| | 4.85 | 0.09 | 2/B | L_b-1 | -1.05 | -2.05 |
| | 4.86 | 0.00 | 2/A | L_b-2 | 0.43 | 0.31 |

rotatory strengths of the L_a and L_b states of the R_a and S_a structures considered here, using EOM-CCSD and CAM-B3LYP and two different basis sets.

Thus, in comparing the ES-ECD of the excited states of binol for the two methods, one should keep in mind that the character of the first excited state is different at the EOM-CCSD and CAM-B3LYP levels.

Figure 6 shows the EOM-CCSD GS- and ES-ECD spectra of S_a -binol, together with the experimental data from ref 43 (measured in cyclohexane). The ES-ECD were computed for all four lowest excitations in Table 1, plus the 5A and 5B (B_b -1 and B_b -2) states. Raw data are given in Tables S9, S10, and S11. Table S12 contains natural transition orbitals (NTOs) and transition properties of the four lowest GS transitions. The corresponding data for the R_a conformation are given in SI, see Tables S14–S16.

The EOM-CCSD GS-ECD spectra of binol agree well with the experimental results of refs 84 (R_a) and 43 (S_a), despite the neglect of solvent effects. Curiously, the split band at 6 eV in the experimental spectrum of R_a (reproduced by the calculations) is absent in the experimental spectrum of S_a . Both CAM-B3LYP (this work, as well as ref 43) and ADC(2) (ref 45) also agree with the experimental data.

Turning our attention to the ES-ECD spectra, the first general observation is that we could not reproduce the CAM-B3LYP results for the ES-ECD of S_a -binol reported in the SI of ref 43. Our CAM-B3LYP results are shown in Figure S4. Since

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our results for methyloxirane and norcamphor are consistent with CAM-B3LYP data reported by other authors, we suspect there may be a problem in the results reported by Schmid et al.

According to our calculations, the A and B symmetry excitation pairs have ES-ECD that are almost mirror images of each other across the x-axis. In the lower-energy region, the agreement between the length (origin at center-of-charge) and velocity gauges becomes poorer, as it can be appreciated from the results in Tables S10–S11 and from Figure S4. Our TD-DFT results show the same trend, see Figure S5.

Given the differences between length and velocity ES rotatory strengths at lower energies, we examined the gaugeorigin dependence of the ES-ECD of the L_b -1 and L_b -2 states of S_a -binol. The gauge origin was manually located at an arbitrary carbon atom. The data reported in Table S13 show that it is only the rotatory strengths for transitions between different symmetries that are affected by the change of gauge origin. Overall, the effect of this shift of origin is fairly small, and it did neither significantly improve nor worsen the agreement between the two gauges. It could be interesting to test the effect of locating the gauge origin at the center-of-mass (or -charge) of the two naphthol moieties, respectively, but we have not pursued it here.

4.2. X-ray Circular Dichroism. *4.2.1. Methyloxirane.* The experimental XCD spectrum at the carbon *K*-edge of methyloxirane, measured in vapor phase, has been reported by Turchini et al.⁸⁵ and by Alberti et al.⁸⁶ Computational results at different levels of theory have also been reported.^{33,87,88} A later study by Piancastelli et al.⁸⁹ focused on the nonchiral core-level photoelectron spectroscopy, the XAS at both C and O *K*-shells, and on resonant and normal Auger spectroscopies.

As explained by Turchini et al., a complicating factor in XCD measurements is that, to the first approximation, the magnetic dipole transition element of *K*-edge excitations is zero, since magnetic dipole transitions arising from *s* orbitals are forbidden. Consequently, the only possible source of magnetic dipole intensity involves 1s-np (particularly, 1s-2p) mixing. Theoretical studies^{87,90} had indicated that this mixing could be sufficient to produce observable CD for simple organic molecules.

In the experimental measurement of Turchini et al., a nonlinear sloping background was present in the XCD of the two isomers, as well as their racemate, indicated as [S(-) +R(+)]. To obtain a monosignate signal, the measured spectra of the two enantiomers were halved and algebraically subtracted. This yielded the composite spectrum, labeled as $S(-)_{o}$ of S(-)-methyloxirane without the baseline background, since $S(-)_c = S(-)_m - \frac{1}{2}[S(-) + R(+)]_m =$ $\frac{1}{2}[S(-)_m - R(+)_m]$ (where the subscript *m* stands for measured). Turchini et al. assigned the CD spectrum to the methyne and methylene carbon atoms (i.e., the oxygen-bound ones) and suggested that the methyl carbon's CD signal would essentially cancel out to zero because of the small energy splitting and the resolution of the experiment. A photoemission experiment revealed three binding energies of 291.2, 292.2, and 292.6 eV. With the d-aug-cc-pVDZ basis set, the three lowest ionization energies are 293.5, 294.8, and 294.9 eV, whereas with the d-aug-cc-pVTZ basis set the IEs are 291.3, 292.6, and 292.7 eV.

The simulation of the XCD (and XAS) spectra of methyloxirane proved to be rather challenging. We explored



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Figure 6. S_a -binol. Ground-state (GS) and excited-state (L_{ar} L_{br} and B_b states) absorption (bottom panels) and ECD (upper panels) spectra in the length gauge computed at the EOM-CCSD/6-31G(d) level. Twenty excitations were considered in each irrep of the C_2 point group. Experimental values from ref 43. The CCSD energies have been shifted by -0.9 eV to align the main peaks in the experimental OPA spectrum. Lorentzian broadening with HWHM = 0.2 eV.

different basis sets, including d-aug-cc-pVDZ and d-aug-cc-pVTZ on all atoms, aug-cc-pVTZ on the C and O atoms and aug-cc-pVDZ on the H atoms, as well as Pople's $6-311++G^{**}$ and $6-311(2+,+)G^{**}$, also uncontracting the inner functions. Two different optimized structures were considered. Comparcompared between EOM-CCSD and CCSD-RSP results were carried out. Note that we report results for the *R* enantiomer, whereas the XCD spectra of ref 11 refer to the *S* enantiomer.

The simulated spectra for two different structures (yielded by EOM-CCSD and CC-RSP using the $6-311++G^{**}$ basis set) are shown in Figure 7, along with experimental results. EOM-CCSD and CCSD-RSP results are consistent, though with a few noticeable differences in the XCD intensity in the length gauge. The moderate differences between velocity and length XCD results depend, to a certain extent, on the absolute size of the rotatory strength, as transitions with extremely small rotatory strengths sometimes have oppositely signed strengths.

The spectra stem from a number of closely lying excitations, whose rotatory strengths may significantly vary with the basis set. The spectra computed for the two optimized equilibrium geometries considered here show large differences. For the structure labeled "Geometry 2" in Figure 7, which is the one from ref 44 also used for ES-ECD, the excited states are less clustered, so the XAS spectral features are more smeared out. The most dramatic difference is, however, observed in the XCD spectra, where the first negative and weak broad band is replaced by a positive one, and the second negative one is far more pronounced. Changing the basis also affects the spectra, as illustrated in Figure 8 for "Geometry 1" (the MP2 optimized structure from ref 76).

The computed XAS spectra agree with the experiments, with overall energy shifts that vary between 0.06 and 2.3 eV, depending on the basis set. The shifts were computed with respect to the first peak of the spectrum of Piancastelli et al. Clearly identifiable XCD spectral patterns are reproduced by all basis sets and for both geometries, yet strikingly different from the measured ones. Given the results, we cannot conclude whether there is a problem with the measured XCD spectrum or whether the differences are due to deficiencies in our simulation. One possible reason for discrepancy is that our calculations do not include dynamical sampling of the structures. We note in passing, though, that the computed rotatory strengths Turchini et al.⁸⁵ report as taken from ref 88 do not appear to correspond to the values tabulated in ref 88. Also, to the best of our understanding, the calculation of ref 88 was carried out on the *R* isomer and not the *S* one.

It is important to identify the origin of the main peaks in our spectra. Inspection of the NTOs reveals that all three carbon atoms are optically active, in agreement with ref 87. In the 6-311++G** basis, the first XAS transition at Geometry 1 (287.5 eV) is due to the methyl C ("C3"), which is dark in XCD. The second and third electronic transitions combine to form the broad feature around 288.5 eV, which changes sign across the two geometries. The two transitions originate both from C3. Three excitations are responsible for the following (negative) band, the one with the largest (negative) rotatory strength coming from the nonchiral oxygen-bound C ("C2"). The next, positive, peak (at around 289.5 eV) stems from two transitions, both with positive rotatory strength, the first one from the chiral center C ("C1"), and the next one from C3. The following negative feature originates mainly from the net balance of two closely lying and oppositely signed sticks at Geometry 1, one positive from C2 and one negative from C1, whereas at Geometry 2 this feature comes from two negative sticks, the strongest due to C2. The positive band at around 290 eV is a convolution of several transitions, from all three carbon atoms.

The first broad band in the XCD spectra of both geometries is, as mentioned, due to two excitations from only the methyl carbon. This is also the band that changes sign between the



Figure 7. (R)-Methyloxirane. Carbon K-edge XCD (upper panels) and XAS (bottom panels) spectra at two different ground-state optimized geometries. Basis set $6-311++G^{**}$. Length gauge pictured in solid line, velocity in dashed. Experimental XAS^{65,86,89} and XCD^{85,86} are also shown. The experimental XCD of the S enantiomer is here reported as its mirror image. Lorentzian broadening with HWHM = 0.2 eV.

two geometries. It is therefore possible that a conformational average, which takes into account the group's free rotation, would result in a net zero contribution from these C3 excitations. However, at higher energies, excitations from C3 do not appear to cancel out.

4.2.2. L-Alanine. The XCD of alanine has previously been theoretically investigated using the STEX approach, the RPA method, as well at the complex polarization propagator (CPP) approach at the TDDFT/CAM-B3LYP level of theory.⁹¹⁻⁹³ A basis-set study⁹² highlighted a strong basis-set dependence of the rotatory strengths, especially for the oxygen and nitrogen *K*-edges.

We calculated the XAS and XCD spectra at all three edges (carbon, oxygen, and nitrogen). The computed rotatory strengths are in general small and therefore sensitive to the convergence threshold adopted. Even with thresholds as tight as 10^{-7} (or even 10^{-8}), in particular, the oxygen-edge *R* values

showed some variations. The results obtained with 10^{-7} are discussed below.

Our XAS and XCD spectra are illustrated in Figures 9 (C and O) and 10 (N). Raw spectral data for all figures can be found in Tables S27-S31 in the SI. NTOs of the main transitions are shown in Tables S32 and S33.

The computed carbon XAS of the neutral structure shows one dominating peak (third excited state) at 290.75 eV ($f^{\text{fg}} =$ 0.076). This corresponds to a transition from the 1s orbital of C2 into the π^* of the carboxyl group (see Figure 1 for atom labeling). The majority of the computed states are transitions from the methyl carbon. It is the equivalent C $1s \rightarrow \pi^*$ transition that dominates the carbon XAS spectrum of the zwitterion at 291.18 eV ($f^{\text{fg}} = 0.066$).

The oxygen XAS spectrum of the neutral structure has a simple profile with one major peak as the first transition at 536.45 eV ($f^{dg} = 0.039$) with the second transition at 3 eV higher in energy. The lowest transition occurs between the 1s

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Figure 8. (*R*)-Methyloxirane. EOM-CCSD Carbon K-edge XCD (upper panels) and XAS (bottom panels) spectra with different basis sets (Geometry 1). The short notation dD stands for d-aug-cc-pVDZ; aT/aD/aD means aug-cc-pVTZ on the C atoms and aug-cc-pVDZ on the remaining atoms. Length gauge pictured in solid line, velocity in dashed. Experimental XAS^{85,86,89} and XCD^{85,86} are also shown. The experimental XCD of the S enantiomer is here reported as its mirror image. Lorentzian broadening with HWHM = 0.2 eV.

orbital of the doubly bonded oxygen (O2) into the π^*_{COOH} orbital. The corresponding transition from the protonated oxygen atom (O1) gives rise to the third peak observed in the spectrum. The second peak, i.e., the first in the split band, is due to a 1s transition from O2 into a p-type oxygen orbital. In the zwitterion, the carboxyl group is deprotonated, making the two oxygen atoms nearly equivalent. The oxygen K-edge XAS spectrum of the zwitterion shows two close-lying peaks of equal magnitude belonging to the O $1s \rightarrow \pi^*_{\text{COO}^-}$ transitions. The first transition at 536.55 eV ($f^{lg} = 0.029$) is from the O1 1s orbital, and the fourth transition (second peak) at 536.89 eV $(f^{\text{lg}} = 0.029)$ originates from the O2 1s orbital. Two almost dark excitations lie between the O $1s \rightarrow \pi^*_{COO^-}$ transitions. The first peak of the nitrogen XAS spectrum of both neutral and zwitterionic L-alanine arises from a transition from the N 1s into a diffuse orbital very localized around the N atom. For the second spectral peak for both forms, the particle orbital is of $\sigma^*_{
m N-H}$ character. For the neutral form, the trailing transitions are weak and diffuse. The third peak in the zwitterion spectrum is

due to a transition into an orbital localized around the N atom with slight σ_{N-H}^* character. The feature in the high-energy region arises from a transition into the σ_{N-C}^* orbital.

The XCD results indicate that all carbon atoms are optically active for both structures, where the majority of transitions are from the methyl carbon 1s orbital. At this K-edge, length and velocity gauge results are rather similar. At the nitrogen and oxygen K-edges, pronounced disagreement between the two gauges (length and velocity) is observed. In the nitrogen case, for instance, the velocity-gauge rotatory strengths are orders of magnitude smaller than the corresponding strengths in the length gauge. The large difference could be due to strong origin dependence of the rotatory strengths. To investigate this further, we tried moving the gauge origin to different locations. In the case of the N K-edge, we moved the origin on the nitrogen atom. The XCD spectra at the default and shifted origins are depicted in Figure 10. The effect of the origin shift from the center of charge to the N atom is striking, leading to almost complete overlap of the length and velocity gauge XCD



Figure 9. L-Alanine in its neutral and zwitter-ionic forms. Carbon (left, 12 states) and oxygen (right, 10 states) fc-CVS-EOM-CCSD/daug-cc-pVDZ K-edge XAS (bottom panels) and XCD (upper panels). Length gauge in solid lines; velocity in dashed. Lorentzian broadening with HWHM = 0.2 eV.



Figure 10. L-Alanine in its neutral and zwitter-ionic forms. Nitrogen K-edge fc-CVS-EOM-CCSD/d-aug-cc-pVDZ XAS (bottom panels) and XCD (upper and middle panels) spectra. Length gauge in solid lines; velocity in dashed. The top row shows the XCD with gauge origin in the center of charge; the middle row the ones with gauge origin at the position of the nitrogen atom. The spectra in gray (top panels) have been magnified by 10^2 . Lorentzian broadening with HWHM = 0.125 eV.

spectra. A closer look at the NTOs of the N 1s transitions reveals that these transitions are highly localized on the N atom. We note, however, that the rotatory strength values are very small, so it remains a general concern whether the agreement after the gauge-origin shift of the length gauge is the mere consequence of having computed equally small residual errors in the two gauges. As an additional test, we carried out calculations on the neutral D-isomer (geometry produced by mirroring the L-structure in the *xy* plane). This produced the exact mirror image of the L-alanine N K-edge XCD spectra at both gauge origins.

Two shifted origins were tested for the O K-edge of neutral L-alanine: one at the doubly bonded oxygen atom and one at the center of mass of the carboxyl moiety. While applying these gauge shifts does have an impact on the oxygen K-edge XCD

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spectrum, it is not as clear-cut as for the nitrogen *K*-edge XCD. A nice overlap between the gauges was, however, obtained for some of the bands, e.g., the first peak in the XCD spectrum, when the origin is located at the doubly bonded oxygen atom. XCD spectra from the gauge-dependence study are shown in Figure S7.

Comparing the XCD spectra of this work with the ones simulated with the CPP/CAM-B3LYP/d-aug-cc-pVDZ method reported in ref 93, we observe that the N K-edge spectra of the neutral structures have similar features for the two methods, if one considers the gauge-shifted EOM-CCSD one. Meanwhile, the corresponding spectra of the zwitterion are quite different, although slight similarity can be found between the TD-DFT spectrum and the CCSD one with center-of-charge origin. The computed XAS spectra are similar. The oxygen XCD spectra of the zwitterionic structure are very different at any gauge origins. Note that we here used the structure of the Ala-I conformer fully optimized at the CCSD(T) level from ref 94, whereas a B3LYP optimized structure was used in ref 93.

4.2.3. Chloroethanol. Inspired by ref 80, where chloroethanol was used as an illustrative case for XCD of larger chloro-compounds, we considered the chlorine $L_{2,3}$ -edge XCD, focusing on the effect of spin-orbit coupling.

At the *L*-edge, the core transitions occur from the 2*p* orbitals of the targeted atom. The degeneracy of the three *p*-orbitals is split by the SOC, which is clearly seen in the X-ray absorption spectra. This splitting is expected to be observed in the XCD spectra as well.

Some of us recently reported an extension of EOM-CCSD for computation of *L*-edge XAS (and XPS) spectra,⁶⁹ employing a state-interaction two-step scheme. First, a set of nonrelativistic EOM-CC states is computed and used to evaluate SOCs using Breit–Pauli operator and mean-field approximation of the two-electron part, as described in refs 95 and 96. Then the resulting SOC-perturbed Hamiltonian matrix is diagonalized, giving rise to SOC-mixed states. Using the computed transformation between zero-order and SOC-perturbed states, the non-Hermitian electric dipole transition strengths are then transformed into a basis of SOC-split states, according to

$$\overline{S}_{\alpha}^{nf} = \mathbf{U}^{\dagger} \langle \hat{\mu}_{\alpha}^{nf} \rangle \langle \hat{\mu}_{\alpha}^{fn} \rangle \mathbf{U}$$
(46)

where the matrix U contains the eigenvectors of the spin-orbit mean-field Hamiltonian matrix. In the present work, the property of interest is the CD rotatory strength, so we considered the (anti)symmetrized product of the electric dipole and magnetic dipole transition moments (eq 18):

$$\bar{R}_{\alpha}^{nf} = \frac{1}{2} \mathbf{U}^{\dagger} \{ \langle \hat{r}_{\alpha}^{nf} \rangle \langle \hat{L}_{\alpha}^{fn} \rangle - \langle \hat{L}_{\alpha}^{nf} \rangle \langle \hat{r}_{\alpha}^{fn} \rangle \} \mathbf{U}$$
(47)

and, likewise, for the velocity formulation (eq 19). Ten singlet excited states were computed for nonrelativistic transition properties, and equally many singlet and (spin-flip) triplet states were computed for the SOC calculations.

As for the nitrogen and oxygen K-edge XCD signals of alanine, we observe strong origin dependence of the *L*-edge XCD spectrum of chloroethanol. The simulated signals in the length gauge with gauge origin at the center of charge are an order of magnitude larger than the velocity-gauge equivalents. Shifting the origin from the center of charge to the chlorine atom improves the agreement between the two gauges 34 PUBLICATIONS AND MANUSCRIPTS

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significantly. The numerical values of the computed signals are very small, especially in the velocity gauge and in the length gauge with origin on Cl. Figure 11 shows the nonrelativistic and SOC spectra for gauge origin at the Cl atom. Figure S8 in the SI illustrates the gauge effect. Raw data are given in Table S31 in the SI.



Figure 11. L-Chloroethanol. fc-CVS-EOM-CCSD/6-311(2+,+)G** nonrelativistic (NR, 10 states) and SOC Cl $L_{2,3}$ -edge XAS (bottom panels) and XCD (upper panels). Gauge origin on the Cl atom, dashed lines are velocity gauge. Geometry from ref 80. Lorentzian broadening with HWHM = 0.124 eV.

The nonrelativistic XAS spectrum shows two peaks separated by 1.3 eV. The first peak is a convolution of two near-degenerate excited states at 201.68 eV of the same magnitude. The NTOs reveal that these transitions are of $2p \rightarrow \sigma^{2}_{C-Cl}$ type for the 2p orbitals perpendicular to the C–Cl bond (see Table S35). Their rotatory strengths have opposite signs and nearly the same magnitude. The second peak comprises three states: two near-degenerate at 202.97 eV, both with weak CD signals (note the sign disagreement between length and velocity gauge results for one of the transitions), and a single state at 203.11 eV with a positive CD signal. The near-degenerate states are transitions from the two perpendicular 2p-orbitals into diffuse orbitals, and the single state is a transition between the 2p orbital lying along the C–Cl bond into diffuse orbitals.

The introduction of SOC splits the XAS spectrum into three peaks, where the middle one contains contributions from both the up-shifted splitting of the lowest NR peak and downshifted splitting from the highest NR peak. Introducing SOC into XCD results in a richer (but slightly less intense) spectrum, with the intense band at 204 eV in the NR redistributing over several peaks. The individual transitions in this region have both positive and negative rotatory strengths, but the overall XCD cross section remains positive.

5. CONCLUSION

We implemented a computational scheme for simulating optical rotation and circular dichroism spectra based on the EOM-CCSD framework in the Q-Chem package. We applied these new tools to calculate ground-state and excited-state circular dichroism spectra of the selected compounds. The circular dichroism spectra were computed for both valence excitations and for core excitations at the K- and L-edges. In the calculations of L-edge X-ray circular dichroism, spin—orbit effects were included via the state-interaction procedure.

We observed generally good agreement between the simulated spectra obtained from EOM-CCSD with those from response theory at the CCSD level, and from TDDFT/ CAM-B3LYP calculations. The assessment of the accuracy of the XCD results proved challenging. For methyloxirane, the computed spectra at the C K-edge do not bear clear resemblance with the experimental ones. A strong origin dependence of the XCD in the length gauge was observed at the oxygen and nitrogen K-edges of L-alanine, as well as the chlorine $L_{2,3}$ -edge in chloroethanol. When the transition is highly localized, locating the gauge origin at the atom of excitation improves the agreement between the spectra from origin-dependent length gauge and those from the velocity gauge. In the X-ray regime, all computed signals, especially for the ones with strong gauge dependence, are extremely small and possibly at the limit of what the methodology can reliably reproduce. Also, without further studies, one cannot determine whether the sign of the experimental spectrum is dominated by vibronic effects, such as the Herzberg-Teller borrowing mechanisms-an aspect that goes beyond the present approach.

APPENDIX: EXPRESSIONS FOR TRANSITION 1PDMS

For brevity, in the following subsections, the left and right amplitudes of target EOM-EE-CCSD and fc-CVS-EOM-EE-CCSD states do not carry the state indices n and f. The CCSD Λ amplitudes do not carry the state index 0.

$$\gamma_{ia}^{f \leftarrow 0} = \sum_{jb} (t_{ij}^{ab} - t_i^b t_j^a) l_j^b - \sum_j \tilde{l}_{ji} t_j^a - \sum_b \tilde{l}^{ba}_i t_i^b$$
(48)

$$\gamma_{ai}^{f \leftarrow 0} = l_i^a \tag{49}$$

$$\gamma_{ji}^{f \leftarrow 0} = -\tilde{l}_{ij} - \sum_{a} l_i^a t_j^a \tag{50}$$

$$\gamma_{ab}^{f \leftarrow 0} = \tilde{l}^{ab} + \sum_{i} l_i^a t_i^b \tag{51}$$

CCSD State \leftarrow **EOM-EE-CCSD State Transition** Here, *l* represents the amplitudes of CCSD Λ .

$$\begin{split} \gamma_{ia}^{0 \leftarrow f} &= r_{i}^{a} + \sum_{jb} (\tilde{r}_{ij}^{ab} - \tilde{r}_{i}^{b} t_{j}^{a} - \tilde{r}_{j}^{a} t_{i}^{b}) l_{j}^{b} + \sum_{jb} (t_{ij}^{ab} - t_{j}^{a} t_{i}^{b}) Y_{jb} \\ &- \sum_{k} \tilde{l}_{k} t_{k}^{a} - \sum_{c} \tilde{l}^{ca} r_{i}^{c} - \sum_{j} \tilde{l}_{j} t_{j}^{a} - \sum_{b} \tilde{l}^{ba} t_{i}^{b} \end{split}$$
(52)

$$\gamma_{ai}^{0 \leftarrow f} = r_0 l_i^a + Y_{ia} \tag{53}$$

$$\gamma_{ji}^{0\leftarrow f} = -\tilde{l}_{ij} - \sum_{a} l_i^a \tilde{r}_j^a - \sum_{a} Y_{ia} t_j^a \tag{54}$$

$$\gamma_{ab}^{0\leftarrow f} = \tilde{l}^{ab} + \sum_{i} l_i^{a\tilde{r}_i^b} + \sum_{i} Y_{ia} t_i^b$$
(55)

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EOM-EE-CCSD State $f \leftarrow$ EOM-EE-CCSD State n Transition

$$\begin{split} \gamma_{ia}^{f \leftarrow n} &= \sum_{jb} \left(\tilde{\tilde{r}}_{ij}^{ab} - \tilde{r}_{i}^{b} t_{j}^{a} - \tilde{r}_{j}^{a} t_{i}^{b} \right) l_{j}^{b} + \sum_{jb} \left(t_{ij}^{ab} - t_{j}^{a} t_{i}^{b} \right) Y_{jb} \\ &- \sum_{k} \tilde{\tilde{l}}_{kl} r_{k}^{a} - \sum_{c} \tilde{l}^{ca} r_{i}^{c} - \sum_{j} \tilde{l}_{ji} t_{j}^{a} - \sum_{b} \tilde{l}^{ba} t_{i}^{b} \end{split}$$

$$(56)$$

$$\gamma_{ai}^{f \leftarrow n} = r_0 l_i^a + Y_{ia} \tag{57}$$

$$\gamma_{ji}^{f \leftarrow n} = -\tilde{l}_{ij} - \sum_{a} l_i^a \tilde{r}_j^a - \sum_{a} Y_{ia} t_j^a$$
(58)

$$\gamma_{ab}^{f \leftarrow n} = \tilde{l}^{ab} + \sum_{i} l_i^a \tilde{\tilde{r}}_i^b + \sum_{i} Y_{ia} t_i^b \tag{59}$$

fc-CVS-EOM-EE-CCSD State ← CCSD State Transition

$$\gamma_{jl}^{f \leftarrow 0} = -\tilde{\tilde{l}}_{lj} - \sum_{a} l_l^a t_j^a \tag{60}$$

$$\gamma_{aI}^{f \leftarrow 0} = l_I^a \tag{61}$$

CCSD State \leftarrow **fc-CVS-EOM-EE-CCSD State Transition** Here, *l* represents the amplitudes of CCSD Λ .

$$\gamma_{j_i}^{0 \leftarrow f} = -\tilde{l}_{iJ} - \sum_{a} l_i^a r_J^a$$

$$\gamma_{j_i}^{0 \leftarrow f} = r_i^a + \sum_{a} (r_i^{ab} - r_i^b t_i^a) l_i^b - \sum_{a} \tilde{l}_i^{ca} r_i^c - \sum_{a} \tilde{l}_i t_i^a$$
(62)

$$\gamma_{Ia}^{0-rJ} = r_I^a + \sum_{jb} \left(r_{Ij}^{ab} - r_I^b t_j^a \right) l_j^b - \sum_c l r_I^c - \sum_j l_{jl} t_j^a$$
(63)

Intermediates

$$Y_{ia} = \sum_{jb} l_{ij}^{ab} r_j^b \tag{64}$$

$$\tilde{\tilde{r}}_{ij}^{ab} = r_{ij}^{ab} + r_0 t_{ij}^{ab} \tag{65}$$

$$\tilde{r}_{i}^{a} = r_{i}^{a} + \frac{1}{2}r_{0}t_{i}^{a}$$
(66)

$$\tilde{\tilde{r}}_i^a = r_i^a + r_0 t_i^a \tag{67}$$

$$\tilde{\tilde{l}}_{ij} = \frac{1}{2} \sum_{kab} l^{ab}_{ik} t^{ab}_{jk}$$
(68)

$$\tilde{\tilde{l}}^{ab} = \frac{1}{2} \sum_{ijc} l^{ac}_{ij} t^{bc}_{ij}$$
(69)

$$\tilde{l}_{ij} = \frac{1}{2} \sum_{kab} l^{ab}_{ik} \tilde{r}^{ab}_{jk}$$
(70)

$$\tilde{l}^{ab} = \frac{1}{2} \sum_{ijc} l^{ac}_{ij} \tilde{r}^{bc}_{ij}$$
(71)

$$\tilde{\tilde{l}}_{lj} = \frac{1}{2} \sum_{kab} l^{ab}_{lk} t^{ab}_{jk}$$
(72)

$$\tilde{l}_{ij} = \frac{1}{2} l^{ab}_{ik} r^{ab}_{jk} \tag{73}$$

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jctc.1c00937.

Additional information: Tables of raw data, Additional spectra, CAM-B3LYP results for Binol, Geometrical parameters. (PDF)

AUTHOR INFORMATION

Corresponding Author

Sonia Coriani – DTU Chemistry, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark;
orcid.org/0000-0002-4487-897X; Email: soco@ kemi.dtu.dk

Authors

- Josefine H. Andersen DTU Chemistry, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark; orcid.org/0000-0002-0534-7463
- Kaushik D. Nanda Department of Chemistry, University of Southern California, Los Angeles, California 90089, United States; ◎ orcid.org/0000-0002-3447-6678

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jctc.1c00937

Notes

The authors declare the following competing financial interest(s): A.I.K. is the president and a part-owner of Q-Chem, Inc.

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Anna I. Krylov – Department of Chemistry, University of Southern California, Los Angeles, California 90089, United States; Orcid.org/0000-0001-6788-5016

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5.2 PUBLICATION II

"Cherry-picking resolvents: Recovering the valence contribution in X-ray two-photon absorption within the core-valence-separated equation-ofmotion coupled-cluster response theory"

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Cherry-Picking Resolvents: Recovering the Valence Contribution in X-ray Two-Photon Absorption within the Core–Valence-Separated Equation-of-Motion Coupled-Cluster Response Theory

Josefine H. Andersen,[§] Kaushik D. Nanda,^{*,§} Anna I. Krylov,* and Sonia Coriani*

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ABSTRACT: Calculations of first-order response wave functions in the X-ray regime often diverge within correlated frameworks such as equation-of-motion coupled-cluster singles and doubles (EOM-CCSD), a consequence of the coupling with the valence ionization continuum. Here, we extend our strategy of introducing a hierarchy of approximations to the EOM-EE-CCSD resolvent (or, inversely, the model Hamiltonian) involved in the response equations for the calculation of X-ray two-photon absorption (X2PA) cross sections. We exploit the frozen-core core–valence separation (fc-CVS) scheme to first decouple the core and valence Fock spaces, followed by a separate approximate treatment of the valence resolvent. We demonstrate the robust convergence of X-ray response calculations within this framework and compare X2PA spectra of small benchmark molecules with the previously reported density functional theory results.

1. INTRODUCTION

Correlated electronic-structure methods, such as those based on coupled-cluster (CC) theory, provide a robust platform for computing ground and excited states in a variety of closed- and open-shell systems. The scope of molecules that can be treated by these high-level methods is expanding, thanks to advances in algorithmic strategies and computing hardware. In the past three decades, CC methods such as the equation-of-motion coupledcluster¹⁻ ⁻³ (EOM-CC) and the coupled-cluster response^{4,5} (CC-RSP) theories have been vigorously developed to afford computations of an ever-growing list of molecular properties,⁶ greatly enhancing our capabilities for reliable first-principles modeling of spectroscopic experiments. These methods are now routinely employed for computing ground- and excited-state properties in linear and nonlinear regimes. Examples of nonlinear properties include multiphoton absorption cross sections,^{7–9} inelastic scattering cross sections,^{10–13} first and second hyperpolarizabilities,^{14–17} excited-state polarizabilities^{18,19} and multiphoton transition moments between excited states,²⁰ multiphoton and magnetic circular dichroism strengths,²¹⁻²⁴ and g-tensors,²⁵ to mention just a few. In addition, the high-level CC methods provide the gold standard for benchmarking approximate and computationally less expensive methods, such as those based on density functional theory (DFT), which can treat much larger systems. Concomitant developments of embedding schemes $^{26-30}$ have afforded robust CC condensed-phase modeling of molecular processes and properties in solutions, protein environments, and periodic systems. Further, advances in orbital concepts^{17,31}



and wave function analysis tools^{37–40} have facilitated robust molecular-level understanding of the molecular processes within the framework of correlated methods.

The EOM-CC theory offers a powerful single-reference framework for computing a variety of electronic states: excited states, ionized states, electron-attached states, and so on. The level of correlation treatment can be systematically improved following the hierarchy of CC/EOM-CC approximations (CC2, CCSD, CC3, CCSDT, ...) up to the exact limit. A crucially important trait of this framework is its flexibility in the choice of the EOM operators and the reference Slater determinant, which are adapted to provide a balanced treatment of the set of target states. EOM-CC and CC-RSP formalisms produce the same excitation energies, but they can differ in their treatment of state and transition properties.^{6,41} The EOM-CC framework allows for the description of properties as generalized expectation values that are obtained by parametrizing exact expressions using eigenenergies and left and right eigenvectors of the (non-Hermitian) similarity-transformed EOM-CC Hamiltonian. EOM-CC response properties within this "expectation-value approach" are identical to the response properties derived from the coupled-cluster configuration interaction (CC-CI) model,

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where the time-dependent Schrödinger equation is solved using an exponential parametrization to describe the unperturbed system and a linear parametrization to describe the time evolution of the unperturbed system.⁴²

In CC (and CC-CI) response theory, the expressions for properties are given by derivatives of appropriate (quasi)energy Lagrangians with respect to the strength of the external perturbation(s) 6,7,20,43,44 or, equivalently, from the response of a generalized time-dependent expectation value of a timeindependent one-electron operator.⁴ Note that properties computed within the alternative analytic-derivative EOM-CC approach, involving derivatives of (quasi)energy Lagrangians with respect to the strength of the external perturbation(s), are identical to those from CC-RSP. 19,45,46 CC-RSP requires additional response intermediates for computing multiphoton absorption moments, relative to the EOM-CC expectation-value approach.5,7 The EOM-CC expectation-value approach for properties becomes exact in the limit of full configuration interaction. This parametrization ensures that the pole structures of frequency-dependent properties are not spoiled by artificial poles, which may negatively impact higher-order excited state properties computed with the CC-RSP approach.¹⁹

This paper presents a new extension of EOM-CC theory for modeling two-photon absorption (2PA) cross sections in the Xray regime (X2PA). This development is motivated by the need for robust and accurate tools for modeling X2PA processes, which occur in experiments involving intense X-ray radiation sources such as X-ray free-electron lasers⁴⁷⁻⁵² (XFEL). Similarly to the UV-vis domain, X2PA has different selection rules compared to one-photon X-ray absorption (XAS) and could, therefore, deliver complementary information. X2P techniques combine the advantages of core-electron transitions with those of standard 2P techniques: the quadratic dependence on intensity endows 2P techniques with better spatial resolution, whereas core-level transitions afford elemental and orbital sensitivity to the local environment and oxidation states. On the downside, in the high-intensity regime, X2PA is competing against a slew of single-photon and sequential multiphoton processes, such as core photoionization, stimulated emission, and scattering, which complicates the interpretation of the experimental observations.^{48,52} So far, the published experimental papers have focused on transition metals.^{48,52} Competing processes such as photoionization and molecular fragmentation have hampered experiments on small molecules.

In view of the high activity in experimental nonlinear X-ray spectroscopies, the paucity of robust *ab initio* methods capable of describing the underlying nonlinear properties limits the potential impact of new experimental techniques, especially given the above-mentioned contributions from competing processes in the experimental signal. Being the simplest higher-order process from the theoretical point of view, X2PA can serve as a platform for future developments of theoretical methods for modeling higher-order multiphoton processes, such as X-ray sum-frequency generation^{53–55} and X-ray second-harmonic generation.^{56,57}

2PA cross sections can be computed using different approaches. Formally, 2PA moments can be obtained from the first residues of quadratic response functions (first electric-dipole hyperpolarizability tensor) to build the 2PA strength tensor and cross sections. ^{7,58–60} Alternatively, elements of the 2PA strength tensor can be evaluated as first residues of the cubic response functions (second electric-dipole hyperpolarizability tensor). ^{7,9,10,58–60} In practice, these relationships are

exploited in the resonance convergent complex polarization propagator (CPP) approach⁶¹ and in damped response theory.^{6,62} In these approaches, a phenomenological imaginary inverse lifetime (damping) parameter is introduced to compute the 2PA strengths from the imaginary part of the cubic response function. The CPP approach has been exploited within the framework of time-dependent DFT (TD-DFT) for computing both valence 2PA⁶³ and X2PA spectra.⁶⁴ Reference 64 by Fahleson et al. is the only published theoretical work on X2PA until now. Here, we explore a computational strategy based on the many-body EOM-CC framework.

CC-RSP^{7,8} and EOM-CC expectation-value⁹ frameworks have also been developed for computing valence 2PA cross sections; the latter employs first-order response wave functions to compute the EOM-CC-parameterized exact sum-over-states expressions for the 2PA moments.⁹ Within the EOM-CC framework, an implementation based on damped response theory also exists (unreported⁶⁵), which computes complexvalued 2PA moments following the introduction of the phenomenological damping for avoiding divergences in modeling doubly resonant 2PA processes. However, the extension of the EOM-CC formalism for computing valence 2PA to X2PA is not straightforward.

In X2PA transitions (Figure 1), the final states are coreexcited states. Such states are high-lying and, therefore, difficult to compute with standard numerical solvers. Moreover, these states are Feshbach resonances embedded in the valence ionization continuum. As a result, standard correlated methods designed for computing electronically bound states cannot be used for these resonances, whose wave functions are not L2integrable.⁶⁶⁻⁶⁹ Without special modifications, attempts to compute core-excited states with these methods are plagued by the erratic (often, divergent) behavior of solvers, a lack of systematic convergence with basis-set increase, and, often, unphysical solutions.^{12,13,70,71} This issue is effectively addressed by the core-valence separation (CVS) approach⁷² in which the core resonances are decoupled from the valence continuum by removing the purely valence-excited determinants from the EOM-CC configuration space. This pruning of the Fock space makes the core-level states artificially bound in the computation, leading to convergent results. The errors in energies introduced due to the CVS dilution of dynamical correlation in methods such as EOM-CC are typically of the order of less than 1 eV.73,74 The effect of the continuum can be reincorporated, e.g., via a perturbative approach^{73,75} or via the Feshbach–Fano formalism.^{76,77} Further, the CVS treatment is not state specific, so multiple states can be computed simultaneously, just as in the case of standard EOM-CC calculations; this feature is attractive in the context of spectroscopy modeling.

Within the CC domain, the CVS scheme was pioneered by Coriani and Koch^{73,75} for computing core-excitation energies (and spectral intensities) as well as core-ionization energies. Since then, the CVS strategy has been used in several CC-RSP and EOM-CC frameworks,^{73,74,78,79} enabling the modeling of XAS, XPS, XCD, and XES spectra.^{11,80–82} The theory was further extended to higher-order properties such as resonant inelastic X-ray scattering (RIXS) cross sections.^{11–13} Similar to 2PA, RIXS is a two-photon process; RIXS moments are also formally given by sum-over-states (SOS) expressions within the EOM-CC expectation-value framework. In practical calculations, the SOS expressions are recast into closed-form expressions by using first-order response wave functions. The RIXS response calculations for these wave functions are affected

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Figure 1. In X2PA, two X-ray photons of energies ω_1 and ω_2 are coherently absorbed such that $\omega_1 + \omega_2$ equals the excitation energy $E_j - E_g$ of the final state *f* that is core excited relative to the initial state *g*. The X2PA moments have contributions from all states of the system, including the ground and bound valence-excited states (black lines), core-excited states (blue lines), valence resonances (magenta lines), and valence continuum states (ultrafine gray dashes).

by their coupling with the continuum, and CVS has been recently adapted to deal with this issue.^{11–13} The limitations of straightforward application of CVS and possible extensions have been discussed in ref 13, giving rise to series of approximations such as CVS-0, CVS-uS, etc. (see section 2.3).

In this contribution, we explore the performance of the CVSuS approach for computing X2PA cross sections within the EOM-CC singles and doubles framework for electronic excitations (EOM-EE-CCSD). We compare the X2PA spectra computed with the CVS-0 and CVS-uS approaches for small benchmark molecules to highlight the importance of including the valence contribution for modeling X2PA. We also compare these computed X2PA spectra with those from ref 64.

2. THEORY

To distinguish between the canonical EOM-EE-CCSD and fc-CVS-EOM-EE-CCSD methods, we use different symbols below. The calligraphic symbols, \mathcal{H} , \mathcal{T} , \mathcal{L} , \mathcal{R} , \mathcal{E} , X, and \mathcal{G} , are associated with the canonical EOM-EE-CCSD method, and regular symbols, H, T, L, R, E, X, and G, are associated with the fc-CVS-EOM-EE-CCSD method.

2.1. The CVS EOM-EE-CCSD Method. The EOM-EE-CCSD method describes the right $(\hat{\mathcal{R}}|\Phi_0\rangle)$ and left $(\langle \Phi_0|\hat{\mathcal{L}})$ wave functions of target states according to the eigenvalue equations

$$\hat{\bar{\mathcal{H}}}\hat{\mathcal{R}}^{k}|\Phi_{0}\rangle = \mathcal{E}_{k}\hat{\mathcal{R}}^{k}|\Phi_{0}\rangle \tag{1}$$

and

$$\langle \Phi_0 | \hat{\mathcal{L}}^k \bar{\mathcal{H}} = \langle \Phi_0 | \hat{\mathcal{L}}^k \mathcal{E}_k \tag{2}$$

where $\hat{\mathcal{H}} = e^{-\hat{\mathcal{T}}} \hat{\mathcal{H}} e^{\hat{\mathcal{T}}}$ is the similarity-transformed EOM-EE-CCSD Hamiltonian, \mathcal{E}_k is the energy of the target state k, and $\hat{\mathcal{T}}$ is the CC operator satisfying the CC equations

$$\langle \Phi_0 | \hat{\mathcal{H}} | \Phi_0 \rangle = \mathcal{E}_0; \quad \langle \Phi_\nu | \hat{\mathcal{H}} | \Phi_0 \rangle = 0 \tag{3}$$

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Here, \mathcal{E}_0 is the energy of the CCSD state defined by the reference determinant Φ_0 , and Φ_{ν} are the singly and doubly excited determinants relative to Φ_0 . The operators $\hat{\mathcal{T}}$, $\hat{\mathcal{R}}$, and $\hat{\mathcal{L}}$ are given in terms of creation $(a^{\dagger}, b^{\dagger})$ and annihilation (i, j) operators as follows:

$$\hat{\mathcal{T}} = \hat{\mathcal{T}}_1 + \hat{\mathcal{T}}_2; \quad \hat{\mathcal{T}}_1 = \sum_{ia} t_i^a a^{\dagger} i; \quad \hat{\mathcal{T}}_2 = \sum_{ijab} t_{ij}^{ab} a^{\dagger} b^{\dagger} j i$$
(4)

$$\hat{\mathcal{R}} = r_0 + \hat{\mathcal{R}}_1 + \hat{\mathcal{R}}_2;$$

$$\hat{\mathcal{R}}_1 = \sum_{ia} r_i^a a^{\dagger} i; \qquad \hat{\mathcal{R}}_2 = \sum_{ijab} r_{ij}^{ab} a^{\dagger} b^{\dagger} j i \qquad (5)$$

and

ģ

$$\hat{\mathcal{L}} = l_0 + \hat{\mathcal{L}}_1 + \hat{\mathcal{L}}_2;$$

$$\hat{\mathcal{L}}_1 = \sum_{ia} l_i^{a\,i\,\dagger}a; \quad \hat{\mathcal{L}}_2 = \sum_{ijab} l_{ij}^{ab\,i\,\dagger}i^{\dagger}j^{\dagger}ba \qquad (6)$$

For the CCSD state, $\hat{\mathcal{R}} = r_0 = 1$ and $\hat{\mathcal{L}} = 1 + \hat{\Lambda}$, where $\hat{\Lambda} = \hat{\Lambda}_1 + \hat{\Lambda}_2$ is the CCSD lambda operator. For EOM-EE-CCSD target states, $l_0 = 0$.

The amplitudes of $\hat{\mathcal{R}}$ and $\hat{\mathcal{L}}$ in eqs 5 and 6 for target states are computed by diagonalizing $\hat{\mathcal{H}}$ in the space of the reference, singly excited, and doubly excited determinants using standard techniques such as the generalized Davidson procedure. Whereas such strategies are effective for computing low-lying excited states, their straightforward application to obtain highlying core-excited states is impractical.⁸³ Further, the presence of the valence continuum and the diagonal preconditioner being inappropriate for the doubles-doubles block of the Hamiltonian result in erratic behavior of such calculations of core-level states. For computing core-excited states, the core-excited block of $\overline{\mathcal{H}}$, defined by omitting the reference and purely valenceexcited determinants from the configuration space, is diagonalized instead of $\overline{\mathcal{H}}$. In ref 13 and this study, we call this block the CVS-0 model Hamiltonian $\hat{\overline{H}}^{\rm core}$. Whereas only the couplings of the core-excited configurations with the purely valence doubly excited configurations are problematic from the convergence viewpoint, the removal of the purely valence singly excited determinants makes the spectrum of the CVS-0 Hamiltonian be that of purely core-excited states. This is an attractive feature as it enables direct calculations of the lowest core-excited states without a significant loss of dynamical correlation. We denote the EOM-EE-CCSD operators that diagonalize $\hat{\vec{H}}^{core}$ as \hat{R}^{core} and \hat{L}^{core} .

Here, we compute the ground and valence-excited states with (specific) core electrons frozen. Hence, these states (and, therefore, CCSD \hat{T} and the corresponding EOM-EE-CCSD \hat{R}^{val} and \hat{L}^{val} amplitudes) are computed in the configuration space spanning the reference and purely valence-excited determinants only. Therefore, in our frozen-core (fc) CVS-EOM-EE-CCSD model, the valence-excitation space is uncoupled to the core-excitation space by construction. This is in contrast to the CVS model from ref 73, where the two spaces are decoupled by applying dedicated projectors. Our strategy for computing X2PA spectra is general and applicable to both of these variants of CVS-EOM-EE-CCSD. We refer to the Hamiltonian block defined by the reference and valence-excited determinants as

 \hat{H}^{val} . The fc-CVS-EOM-EE-CCSD Hamiltonian, \hat{H} , is then block diagonal and made up of \hat{H}^{val} and \hat{H}^{core} blocks.

2.2. 2PA Moments within EOM-EE-CCSD Response Theory. The right and left 2PA moments for transitions between states g and f within exact theory are given by the following sum-over-states expressions:

$$M_{xy}^{f \leftarrow g}(\omega_{1}, \omega_{2}) = -\sum_{n} \left(\frac{\langle \Psi^{f} | \hat{\mu}_{y} | \Psi^{n} \rangle \langle \Psi^{n} | \hat{\mu}_{x} | \Psi^{g} \rangle}{\mathcal{E}_{n} - \mathcal{E}_{g} - \omega_{1}} + \frac{\langle \Psi^{f} | \hat{\mu}_{x} | \Psi^{n} \rangle \langle \Psi^{n} | \hat{\mu}_{y} | \Psi^{g} \rangle}{\mathcal{E}_{n} - \mathcal{E}_{g} - \omega_{2}} \right)$$
(7)

and

$$M_{xy}^{g \leftarrow f}(-\omega_1, -\omega_2) = -\sum_n \left(\frac{\langle \Psi^g | \hat{\mu}_x | \Psi^n \rangle \langle \Psi^n | \hat{\mu}_y | \Psi^f \rangle}{\mathcal{E}_n - \mathcal{E}_f + \omega_2} + \frac{\langle \Psi^g | \hat{\mu}_y | \Psi^n \rangle \langle \Psi^n | \hat{\mu}_x | \Psi^f \rangle}{\mathcal{E}_n - \mathcal{E}_f + \omega_1} \right)$$
(8)

where ω_1 and ω_2 are the energies of the two photons absorbed such that $\omega_1 + \omega_2 = \mathcal{E}_f - \mathcal{E}_g$, Ψ s are the zero-order wave functions, and $\hat{\mu}_x(\hat{\mu}_y)$ is the dipole-moment operator along the Cartesian coordinate $x(y) \in \{x, y, z\}$. Within the EOM-EE-CCSD expectation-value approach, eqs 7 and 8 are parameterized by EOM-EE-CCSD wave functions and energies by replacing $\langle \Psi^k |$ with $\langle \Phi_0 | \hat{\mathcal{L}}^k \equiv \langle \mathcal{L}^k |, |\Psi^k \rangle$ with $\hat{\mathcal{R}}^k | \Phi_0 \rangle \equiv |\mathcal{R}^k \rangle$, and $\hat{\mu}$ with the similarity-transformed dipole operator $\hat{\mu}$. This EOM-EE-CCSD approach, previously used to compute valence 2PA transitions,⁹ then recasts eqs 7 and 8 into closed-form expressions using the first-order response wave function $(|\mathcal{X}^k_x(\omega)\rangle \equiv |\mathcal{X}^{k,\omega}_x\rangle)$ as follows:

$$M_{xy}^{f \leftarrow g}(\omega_1, \omega_2) = -(\langle \mathcal{L}^f | \hat{\mu}_y | X_x^{g, \omega_1} \rangle + \langle \mathcal{L}^f | \hat{\mu}_x | X_y^{g, \omega_2} \rangle) \tag{9}$$

and

$$M_{xy}^{g \leftarrow f}(-\omega_1, -\omega_2) = -(\langle \mathcal{L}^g | \hat{\mu}_x | \mathcal{X}_y^{f, -\omega_2} \rangle + \langle \mathcal{L}^g | \hat{\mu}_y | \mathcal{X}_x^{f, -\omega_1} \rangle)$$
(10)

The first-order response wave functions can be expressed as

$$\langle \Phi_{\rho} | X_{x}^{k,\omega} \rangle = \sum_{n} \langle \Phi_{\rho} | \mathcal{R}^{n} \rangle \frac{\langle \mathcal{L}^{n} | \hat{l}_{x}^{k} | \mathcal{R}^{k} \rangle}{\mathcal{E}_{n} - \mathcal{E}_{k} - \omega}$$
(11)

In practice, they are computed by solving the following system of linear equations:

$$\sum_{\rho} \langle \Phi_{\nu} | (\hat{\mathcal{H}} - \mathcal{E}_{k} - \omega) | \Phi_{\rho} \rangle \langle \Phi_{\rho} | \mathcal{X}_{x}^{k,\omega} \rangle = \langle \Phi_{\nu} | \hat{\mu}_{x} | \mathcal{R}^{k} \rangle$$
(12)

Equations 11 and 12 are related by the EOM-EE-CCSD resolvent ($\mathcal{G}^k(\omega)$) expression

$$\begin{aligned} \mathcal{G}_{\nu\rho}^{k}(\omega) &= \langle \Phi_{\nu}|(\hat{\mathcal{H}} - \mathcal{E}_{k} - \omega)^{-1}|\Phi_{\rho}\rangle \\ &= \sum_{n} \frac{\langle \Phi_{\nu}|\mathcal{R}^{n}\rangle \langle \mathcal{L}^{n}|\Phi_{\rho}\rangle}{\mathcal{E}_{n} - \mathcal{E}_{k} - \omega} \end{aligned}$$
(13)

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For EOM-EE-CCSD, Φ_{ν} and Φ_{ρ} in eqs 11–13 span the reference, singly excited, and doubly excited determinant spaces; terms with higher excited determinants do not survive.

Once the 2PA moments are computed, the 2PA strength tensor is constructed according to

$$S_{wx,yz}^{gf}(\omega_{1}, \omega_{2}) = \frac{1}{2} (M_{wx}^{g \leftarrow f}(-\omega_{1}, -\omega_{2})) (M_{yz}^{f \leftarrow g}(\omega_{1}, \omega_{2})) + \frac{1}{2} (M_{yz}^{g \leftarrow f}(-\omega_{1}, -\omega_{2}))^{*} (M_{wx}^{f \leftarrow g}(\omega_{1}, \omega_{2}))^{*}$$
(14)

where "*" denotes complex conjugation. The 2PA strength tensor elements are then used for computing the microscopic 2PA cross section δ^{2PA} (in atomic units (au)) as follows:

$$\delta^{2PA}(\omega_1, \omega_2) = \frac{F}{30} \sum_{x,y} S_{xx,yy}(\omega_1, \omega_2) + \frac{G}{30} \sum_{x,y} S_{xy,xy}(\omega_1, \omega_2) + \frac{H}{30} \sum_{x,y} S_{xy,yx}(\omega_1, \omega_2)$$
(15)

with F = G = H = 2 for parallel linearly polarized light. For degenerate photons of frequency ω , δ^{2PA} is then converted to the macroscopic 2PA cross section σ^{2PA} in GMs according to

$$\sigma^{2\text{PA}}(\omega) = \frac{4\pi^2 \alpha a_0^{5} \omega^2}{c\Gamma} (\delta^{2\text{PA}}(\omega))$$
(16)

where *c* is the speed of light, a_0 is the Bohr radius, α is the finestructure constant, and Γ is the phenomenological lifetime broadening.

2.3. Dealing with the Continuum in the Response Domain. For ω in the X-ray regime, computing first-order response wave functions within standard EOM-CC (eq 12) often results in erratic behavior of solvers.¹¹⁻¹³ One reason for this is similar to the case of computing core-level states with standard EOM-CC. Since the response wave functions can be expressed as a linear combination of all states of the system (eq 11) and the contribution of high-lying states to the response states is often dominant due to the near-resonance condition, the coupling of these response states to the valence continuum is significant and leads to divergences.

This coupling can be omitted by using the CVS Hamiltonian \hat{H} , which is block diagonal in the core-excited and valenceexcited determinant spaces. However, simply using \hat{H} instead of $\hat{\mathcal{H}}$ for computing response wave functions in eq 12 is not sufficient for fixing the erratic behavior of the solvers. The X-ray response wave functions can include non-negligible contributions (coming from \hat{H}^{val}) from high-lying valence resonances, which can also decay via the coupling to the valence doubly excited determinants; this coupling contributes to the erratic behavior of the valence doubly excited determinants in the course of the iterative procedure. In addition, the diagonal preconditioner associated with the doubles—doubles block of \hat{H}^{val} is no longer a good approximation to it in the X-ray energy

range, crippling the convergence. As noted in refs 11, 12, and 13, lower-level theories such as TD-DFT, CIS (configuration interaction singles), CC2, and ADC(2) either do not have doubly excited determinants (which are primarily responsible for the erratic behavior of solvers) or include them in a perturbative fashion with a diagonal doubles—doubles block (the preconditioner is exact). Therefore, the decay channels are

blocked and the response equations typically converge without a problem.

References 11, 12, and 13 introduced the CVS-0 approach, which simply substitutes $\hat{\mathcal{H}}$ with the CVS-0 Hamiltonian ($\hat{\mathcal{H}}^{\text{core}}$) in eq 12. Thus, the X-ray response wave functions are computed within the configuration space of core-excited determinants only, leading to convergent solutions. Note that, in contrast to ref 13, refs 11 and 12 use a different nomenclature and refer to $\hat{\mathcal{H}}^{\text{core}}$ as the CVS-CC-RSP and fc-CVS-EOM-CC Hamiltonian, respectively. The use of the CVS-0 Hamiltonian effectively replaces the sum over all states in the EOM-CC expectation-value approach for computing 2P moments with a sum over just the core-excited states; the contribution of valence-excited states to the SOS moments is omitted. This is justified for most RIXS transitions for which the dominant contribution to the moments arises from nearly resonant core-excited states.³⁶

In contrast to RIXS, in X2PA, the core-excitation energies can be significantly different from the energies of the two absorbed photons. Then, it is reasonable to assume that the nearresonance contribution can arise from not only the core-excited states but also from low-lying and high-lying valence states. For such cases, the CVS-0 approach would miss important contributions to the X2PA moments; therefore, approaches that can include the valence contribution are desirable.

To recover the valence contribution to the SOS moments without spoiling the convergence of X-ray response solutions, ref 13 introduced a hierarchy of approximations in which the fc-CVS-EOM-CCSD resolvent $\mathcal{G}^{k}(\omega)$ was approximated as a sum of a core fc-CVS-EOM-CCSD resolvent $G^{\operatorname{core},k}(\omega)$ and a valence resolvent $F^{\operatorname{val},k}(\omega)$ that approximates the valence fc-CVS-EOM-CCSD resolvent $G^{\operatorname{val},k}(\omega)$, where

$$G_{\nu\rho}^{\text{core},k}(\omega) = \langle \Phi_{\nu} | (\hat{H}^{\text{core}} - E_k - \omega)^{-1} | \Phi_{\rho} \rangle$$
(17)

and

$$G_{\nu\rho}^{\text{val},k}(\omega) = \langle \Phi_{\nu} | (\hat{H}^{\text{val}} - E_k - \omega)^{-1} | \Phi_{\rho} \rangle$$
(18)

where E_k is the energy of the k^{th} eigenstate of the fc-CVS-EOM-CCSD Hamiltonian. The approximate valence resolvent can, for example, originate from lower-level methods (e.g., valence fc-CVS-EOM-CCS, valence fc-CVS-EOM-CC2, etc.) for which the valence response is restricted to the valence singly excited determinant space and the doubly excited determinants are either omitted or included in a perturbative fashion in the response equations. An alternative approach involves approximating the \hat{H}^{val} block of the fc-CVS-EOM-CCSD Hamiltonian by its valence singles-singles block, omitting the problematic coupling of the valence singly and doubly excited determinants and the preconditioning of valence doubles-doubles block in the X-ray regime. When the CVS-0 approach is augmented by this latter approximate valence resolvent $F^{uS,k}(\omega)$, the approach is referred to as the CVS-uS ("uS" stands for "uncoupled valence singles") approach. In effect, such approaches only approximate the intermediate states in the SOS expressions of two-photon moments while still using the high-level correlated energies and wave functions of the initial and final states. Further, since the intermediate states in the SOS expressions dominated by doubly excited valence determinants do not couple significantly with the ground state via the one-electron dipole moment operator, the impact of the omission (or perturbative inclusion) of valence doubly excited determinants is primarily through the dilution of dynamical correlation in the energies and wave functions of the intermediate states involved in the valence resolvent.

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Since the computed multiphoton properties such as 2PA cross sections can be strongly sensitive to the level of electronic correlation,⁶⁰ independent approximations to the valence and core resolvents in our cherry-picking approach may lead to an unbalanced treatment of the core and valence contributions to the X2PA spectra. Therefore, different approximations of the valence resolvent (fc-CVS-EOM-CCS, fc-CVS-EOM-CC2, CVS-uS) may yield different X2PA spectra; similar differences were noted in ref 13 in the context of RIXS. Here, we focus on the CVS-uS approach and leave the search for the most balanced approximation for modeling X2PA spectra for future studies as it will require comparisons with experiments. On the basis of a configurational analysis of 2PA channels in section 2.5, we expect the CVS-uS approximation to give a fairly balanced description of the valence and core contributions to the X2PA spectra for the benchmark systems studied here.

2.4. 2PA Moments within the CVS-uS Approach. Within the CVS-uS approach, the EOM-EE-CCSD-parameterized sum over states for the 2PA moments is a combination of a sum over valence-excited "uS" states plus the contribution from the CCSD state as an intermediate and a sum over core-excited states as follows:

$$\begin{split} M_{xy}^{J \leftarrow g}(\omega_{1}, \omega_{2}) &= \\ &- \frac{\langle L^{f} | \hat{\mu}_{j} | \mathbb{R}^{0} \rangle \langle L^{0} | \hat{\mu}_{x}^{j} | \mathbb{R}^{g} \rangle}{E_{0} - E_{g} - \omega_{1}} - \frac{\langle L^{f} | \hat{\mu}_{x}^{j} | \mathbb{R}^{0} \rangle \langle L^{0} | \hat{\mu}_{j}^{j} | \mathbb{R}^{g} \rangle}{E_{0} - E_{g} - \omega_{2}} \\ &- \sum_{n \neq 0}^{uS} \left(\frac{\langle L^{f} | \hat{\mu}_{j} | \tilde{\mathbb{R}}^{n} \rangle \langle \tilde{L}^{n} | \hat{\mu}_{x}^{j} | \mathbb{R}^{g} \rangle}{\tilde{E}_{n} - E_{g} - \omega_{1}} + \frac{\langle L^{f} | \hat{\mu}_{x}^{j} | \tilde{\mathbb{R}}^{n} \rangle \langle \tilde{L}^{n} | \hat{\mu}_{j} | \mathbb{R}^{g} \rangle}{\tilde{E}_{n} - E_{g} - \omega_{2}} \right) \\ &- \sum_{n}^{core} \left(\frac{\langle L^{f} | \hat{\mu}_{j} | \mathbb{R}^{n} \rangle \langle L^{n} | \hat{\mu}_{x}^{j} | \mathbb{R}^{g} \rangle}{E_{n} - E_{g} - \omega_{1}} + \frac{\langle L^{f} | \hat{\mu}_{x}^{j} | \mathbb{R}^{n} \rangle \langle L^{n} | \hat{\mu}_{j} | \mathbb{R}^{g} \rangle}{E_{n} - E_{g} - \omega_{2}} \right) \end{split}$$
(19)

and

$$\begin{split} M_{xy}^{g \neq j}(-\omega_{1}, -\omega_{2}) &= \\ &- \frac{\langle L^{g} | \hat{\mu}_{x} | R^{0} \rangle \langle L^{0} | \hat{\mu}_{y} | R^{f} \rangle}{E_{0} - E_{f} + \omega_{2}} - \frac{\langle L^{g} | \hat{\mu}_{y} | R^{0} \rangle \langle L^{0} | \hat{\mu}_{x} | R^{f} \rangle}{E_{0} - E_{f} + \omega_{1}} \\ &- \sum_{n \neq 0}^{uS} \left(\frac{\langle L^{g} | \hat{\mu}_{x} | \tilde{R}^{n} \rangle \langle \tilde{L}^{n} | \hat{\mu}_{y} | R^{f} \rangle}{\tilde{E}_{n} - E_{f} + \omega_{2}} + \frac{\langle L^{g} | \hat{\mu}_{y} | \tilde{R}^{n} \rangle \langle \tilde{L}^{n} | \hat{\mu}_{x} | R^{f} \rangle}{\tilde{E}_{n} - E_{f} + \omega_{1}} \right) \\ &- \sum_{n}^{core} \left(\frac{\langle L^{g} | \hat{\mu}_{x} | R^{n} \rangle \langle L^{n} | \hat{\mu}_{y} | R^{f} \rangle}{E_{n} - E_{f} + \omega_{2}} + \frac{\langle L^{g} | \hat{\mu}_{y} | R^{n} \rangle \langle L^{n} | \hat{\mu}_{x} | R^{f} \rangle}{E_{n} - E_{f} + \omega_{1}} \right) \end{split}$$

$$(20)$$

Here, $\langle L^0 |$ and $|R^0 \rangle$ correspond to the CCSD state; note that often, for X2PA, the CCSD state is the initial state g. \tilde{E}_n and $\langle \tilde{L}^n |$ and $|\tilde{R}^n \rangle$ are the n^{th} eigenenergy and left and right eigenvectors, respectively, that diagonalize the \hat{H}^{uS} block, which is defined as the \hat{H}^{val} block with singles-doubles, doubles-singles, and doubles-doubles blocks zeroed out and the CCSD state projected out. These sums in eqs 19 and 20 are separately recast into closed-form expressions using response wave functions that span separate determinant spaces as follows:

$$\begin{split} M_{xy}^{f \leftarrow g}(\omega_{1}, \omega_{2}) &= \\ &- \frac{\langle L^{f} | \hat{\mu}_{y} | \mathbb{R}^{0} \rangle \langle L^{0} | \hat{\mu}_{x} | \mathbb{R}^{g} \rangle}{E_{0} - E_{g} - \omega_{1}} - \frac{\langle L^{f} | \hat{\mu}_{x} | \mathbb{R}^{0} \rangle \langle L^{0} | \hat{\mu}_{y} | \mathbb{R}^{g} \rangle}{E_{0} - E_{g} - \omega_{2}} \\ &- \langle L^{f} | \hat{\mu}_{y} | X_{x}^{uS,g,\omega_{1}} \rangle - \langle L^{f} | \hat{\mu}_{x} | X_{y}^{uS,g,\omega_{2}} \rangle \\ &- \langle L^{f} | \hat{\mu}_{y} | X_{x}^{core,g,\omega_{1}} \rangle - \langle L^{f} | \hat{\mu}_{x} | X_{y}^{core,g,\omega_{2}} \rangle \end{split}$$
(21)

and

$$\begin{split} M_{xy}^{g \leftarrow f}(-\omega_{1}, -\omega_{2}) &= \\ &-\frac{\langle L^{g}|\hat{\mu}_{x}|\mathbb{R}^{0}\rangle\langle L^{0}|\hat{\mu}_{y}|\mathbb{R}^{f}\rangle}{E_{0} - E_{f} + \omega_{2}} - \frac{\langle L^{g}|\hat{\mu}_{y}|\mathbb{R}^{0}\rangle\langle L^{0}|\hat{\mu}_{x}|\mathbb{R}^{f}\rangle}{E_{0} - E_{f} + \omega_{1}} \\ &- \langle L^{g}|\hat{\mu}_{x}|X_{y}^{\mathrm{uS}f, -\omega_{2}}\rangle - \langle L^{g}|\hat{\mu}_{y}|X_{x}^{\mathrm{uS}f, -\omega_{1}}\rangle \\ &- \langle L^{g}|\hat{\mu}_{x}|X_{y}^{\mathrm{core}_{f}, -\omega_{2}}\rangle - \langle L^{g}|\hat{\mu}_{y}|X_{x}^{\mathrm{core}_{f}, -\omega_{1}}\rangle \end{split}$$
(22)

The CVS-uS response equations are given by

$$\sum_{\rho} \langle \Phi_{\nu} | (\hat{H}^{uS} - E_{k} - \omega) | \Phi_{\rho} \rangle \langle \Phi_{\rho} | X_{x}^{uS,k,\omega} \rangle$$
$$= \langle \Phi_{\nu} | \hat{\mu}_{x}^{i} | R^{k} \rangle - \langle \Phi_{\nu} | R^{0} \rangle \langle L^{0} | \hat{\mu}_{x}^{i} | R^{k} \rangle; \quad \Phi_{\nu}, \ \Phi_{\rho} \in \{ \Phi_{0}, \ \Phi_{i}^{a} \}$$
(23)

and

$$\begin{split} \sum_{\rho} \langle \Phi_{\nu} | (\hat{\hat{H}}^{\text{core}} - E_k - \omega) | \Phi_{\rho} \rangle \langle \Phi_{\rho} | X_x^{\text{core},k,\omega} \rangle \\ &= \langle \Phi_{\nu} | \hat{\mu}_x | \mathbb{R}^k \rangle; \quad \Phi_{\nu}, \, \Phi_{\rho} \in \{ \Phi_{I}^a, \, \Phi_{Ij}^{ab}, \, \Phi_{IJ}^{ab} \} \end{split}$$
(24)

Here, *i*, *j*, … represent the valence occupied orbitals; *I*, *J*, … represent the core occupied orbitals; and *a*, *b*, … represent the unoccupied orbitals. The state index *k* in $|R^k\rangle$ refers to either the ground state *g* or the final state *f*. Note that we have projected out the CCSD state in the right-hand side of eq 23 to account for its omission in the sum over valence "uS" states in eqs 19 and 20.

2.5. Configurational Analysis of 2PA Channels. To better understand the CVS-uS approximation to the fc-CVS-EOM-EE-CCSD resolvent for computing X2PA moments and to provide a rationale for it, here, we analyze contributions to the 2PA moments in terms of leading electronic configurations. Tables 1 and 2 present the configurational channel analysis of the X2PA moments between an initial (EOM-EE-)CCSD state with frozen core and a final fc-CVS-EOM-EE-CCSD wave function. We define these 2PA configurational channels as the 2PA coupling terms between Slater determinants involved in the wave functions of the initial and final states through the Slater determinants involved in the intermediate wave function. Here, we neglect dynamical correlation effects arising from the cluster operator \hat{T} . Our aim is to understand which 2PA channels are fully captured, approximated, or not captured by the CVS-uS approximation to the fc-CVS-EOM-EE-CCSD resolvent. In addition, the channel analysis can help us better understand the impact of different types of bound and continuum intermediate states on the 2PA moments.

First, we consider only the dominant electronic configuration in the initial wave function such that $\Psi^g \sim \Phi_0$ for the CCSD state and $\Psi^f \sim \Phi_j^b$ for the core-excited final state. Within this simplified model, there are just four 2PA channels that need to be considered: channels (1), (2), (21), and (22) in Tables 1 and

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2. Channels (1) and (2) are captured exactly by the CVS-0 resolvent, relative to the fc-CVS-EOM-EE-CCSD resolvent, and dominate the contributions of core-excited pre-edge states that lie below the respective core-ionization energy. These channels can also show resonance enhancement when one of the two absorbed photons is in the infrared/UV-vis regime and the other is an X-ray photon that is nearly resonant with a core-excited state. Similarly, channels (21) and (22), which are only approximated by the uS resolvent, relative to the fc-CVS-EOM-EE-CCSD resolvent, can show resonance enhancement when the infrared/UV-vis photon is nearly resonant with a valence-excited state.

Next, if we include other core-excited determinants in the final wave function, the CVS-uS approximation captures all channels involving Φ_0 (channels (1)–(4) and channels (21)–(23) in Tables 1 and 2). Significantly, the couplings of Φ_0 with the dominant singly core-excited configurations (CV) of the final wave function involve only the singly excited valence or core excited determinants as intermediates, which are captured in the CVS-uS approach.

CVS-uS, however, does not capture all the channels involving the dominant configuration when $\Psi^g \sim \Phi^a_i$ is an EOM-EE-CCSD state (channels (30) and (31)). Unless enhanced by near-resonance consideration, these channels only give small contributions due to the small coefficients of the nondominant COVV configurations in Ψ^f with which the dominant OV configurations in Ψ^g couple. Further, when ω is an X-ray frequency, the near-resonance conditions in these channels in Table 1 ($\epsilon_b - \epsilon_l \approx \omega$ and $\epsilon_c - \epsilon_k \approx \omega$ in channels (30) and (31), respectively) imply that the unoccupied orbitals b and c are highlying and highly oscillatory, resulting in negligible couplings in the numerators of these channels. Similarly, for these missed channels in Table 2, near-resonance conditions ($\epsilon_l - \epsilon_l \approx \omega$) are rare due to the sparsity of occupied and core orbitals in typical molecular systems; therefore, these channels do not contribute significantly in general.

Next, we analyze the couplings of different types of valence and core states with the initial and final states involved in the X2PA process within the uncorrelated picture. The valence doubly excited determinants do not couple with the reference and CV determinants through the dipole moment operator. Within the fc-CVS-EOM-EE-CCSD framework, the final states are predominantly singly excited with leading CV configurations involving low-lying unoccupied orbitals. These states do not couple through the dipole moment operator with the leading OV configurations in valence shape resonances in which the unoccupied orbitals are high-lying continuum orbitals. On the other hand, the leading OV configurations of valence Feshbach resonances can couple to these leading CV configurations in the final states through the one-electron operator (channels (22), (24), and (28)). The 2PA channels corresponding to these couplings are captured in the CVS-uS approach. Only the couplings between the nondominant COVV configurations in the final wave function and OOVV configurations in the intermediate wave functions are omitted through the omitted 2PA channels (30)–(33), which can only be significant through resonance enhancement.

3. COMPUTATIONAL DETAILS

The CVS-0 and CVS-uS resolvent approaches for X2PA cross sections within the (fc-CVS-)EOM-EE-CCSD framework are implemented in a development version of the Q-Chem

Table 1. Configurational Analysis of the Leading Channels in X2PA Moment, $M^{f \leftarrow g}$, Where $\Psi^g = r_0 \Phi_0 + \sum_{ia} r_i^a \Phi_i^a + (1/4) \sum_{Ijab} r_{ij}^{ab} \Phi_{Ij}^{ab}$ Is the Wave Function of the Initial State g and $\Psi^f = \sum_{Ia} l_I^a \Phi_I^a + (1/2) \sum_{Ijab} l_{ij}^{ab} \Phi_{Ij}^{ab} + (1/4) \sum_{IJab} l_{iJ}^{ab} \Phi_{IJ}^{ab}$ Is the Wave Function of the Final State f^a

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| (i) Channels captured by CVS | 5-0 | | |
|---|---|--|---|
| $\left\langle \varPhi^b_{\!I} \mu \mid \varPhi^b_{\!I} \right\rangle \left\langle \varPhi^b_{\!I} \mu \mid \varPhi_0 \right\rangle$ | $\langle \varPhi^b_J \mid \mu \mid \varPhi^a_J angle \left\langle \varPhi^a_J \mid \mu \mid \varPhi_0 ight angle$ | $\left\langle \boldsymbol{\varPhi}_{\!J\!K}^{bc} \left \right. \! \mu \left. \right \right. \boldsymbol{\varPhi}_{\!J}^{b} \right\rangle \left\langle \boldsymbol{\varPhi}_{\!J}^{b} \left \right. \! \mu \left. \right \right. \! \boldsymbol{\varPhi}_{\!0} \right\rangle$ | $\left< \varPhi^{bc}_{Jk} \mid \mu \mid \varPhi^{b}_{J} \right> \left< \varPhi^{b}_{J} \mid \mu \mid \varPhi_{0} \right>$ |
| $\epsilon_b - \epsilon_I - \omega$ | $\epsilon_a - \epsilon_J - \omega$ | $\epsilon_b - \epsilon_J - \omega$ | $\epsilon_b - \epsilon_J - \omega$ |
| (1) | (2) | (3) | (4) |
| $\left< \varPhi^b_{J} \mid \mu \mid \varPhi^{ba}_{Ji} \right> \left< \varPhi^{ba}_{Ji} \mid \mu \mid \varPhi^a_i \right>$ | $\left< \varPhi^b_J \mid \mu \mid \varPhi^{ba}_{Ji} \right> \left< \varPhi^{ba}_{Ji} \mid \mu \mid \varPhi^b_i \right>$ | $ig \langle \varPhi^b_I \mu \varPhi^b_I ig angle ig \langle \varPhi^b_I \mu \varPhi^b_i ig angle$ | $\left< \varPhi^b_J \mid \mu \mid \varPhi^a_J \right> \left< \varPhi^a_J \mid \mu \mid \varPhi^a_i \right>$ |
| $\epsilon_b - \epsilon_J - \omega$ | $\epsilon_a - \epsilon_J - \omega$ | $\epsilon_i - \epsilon_I - \omega$ | $\epsilon_i - \epsilon_J - \omega$ |
| (5) | (6) | (7) | (8) |
| $\frac{\left< \varPhi_{Jk}^{bc} \right \mu \mid \varPhi_{J}^{b} \right> \left< \varPhi_{J}^{b} \mid \mu \mid \varPhi_{i}^{b} \right>}{\left< \varPhi_{J}^{b} \mid \mu \mid \varPhi_{i}^{b} \right>}$ | $\left< \varPhi_{JK}^{cb} \mid \mu \mid \varPhi_{Ji}^{cb} \right> \left< \varPhi_{Ji}^{cb} \mid \mu \mid \varPhi_{i}^{b} \right>$ | $\left< \varPhi^{bc}_{Jk} \mid \mu \mid \varPhi^{b}_{J} \right> \left< \varPhi^{b}_{J} \mid \mu \mid \varPhi^{b}_{i} \right>$ | $ \left< \Phi^{bc}_{Jk} \mid \mu \mid \Phi^{bc}_{Jl} \right> \left< \Phi^{bc}_{Jl} \mid \mu \mid \Phi^{c}_{l} \right> $ |
| $\epsilon_i - \epsilon_J - \omega$ | $\epsilon_c - \epsilon_J - \omega$ | $\epsilon_i - \epsilon_J - \omega$ | $\epsilon_b - \epsilon_J - \omega$ |
| (9) | (10) | (11) | (12) |
| $\left< \Phi^{bc}_{Jk} \mid \mu \mid \Phi^{bc}_{Lk} \right> \left< \Phi^{bc}_{Lk} \mid \mu \mid \Phi^{c}_{k} \right>$ | $\left< \varPhi_{Jk}^{bc} \mu \mid \varPhi_{Jk}^{bd} \right> \left< \varPhi_{Jk}^{bd} \mid \mu \mid \varPhi_{k}^{d} \right>$ | $\left< \varPhi_{Jk}^{bc} \mid \mu \mid \varPhi_{Jk}^{bd} \right> \left< \varPhi_{Jk}^{bd} \mid \mu \mid \varPhi_{k}^{b} \right>$ | $\left< \varPhi^b_J \mid \mu \mid \varPhi^{bc}_{Jk} \right> \left< \varPhi^{bc}_{Jk} \mid \mu \mid \varPhi^{bc}_{lk} \right>$ |
| $\epsilon_b - \epsilon_L - \omega$ | $\epsilon_b - \epsilon_J - \omega$ | $\epsilon_d - \epsilon_J - \omega$ | $\epsilon_l - \epsilon_{\bar{l}} - \omega$ |
| (13) | (14) | (15) | (16) |
| $\frac{\left< \varPhi_{JK}^{bc} \right \mu \mid \varPhi_{Jl}^{bc} \right> \left< \varPhi_{Jl}^{bc} \mid \mu \mid \varPhi_{il}^{bc} \right>}{\left< \varPhi_{Jl}^{bc} \mid \mu \mid \varPhi_{il}^{bc} \right>}$ | $\left< \varPhi_{Jl}^{bc} \left \mu \right. \right \varPhi_{Jl}^{bd} \right> \left< \varPhi_{Jl}^{bd} \left \mu \right. \right \varPhi_{kl}^{bd} \right>$ | $\left< \varPhi^{bc}_{Jl} \mid \mu \mid \varPhi^{bc}_{Kl} \right> \left< \varPhi^{bc}_{Kl} \mid \mu \mid \varPhi^{bc}_{il} \right>$ | $\left\langle \varPhi_{Jl}^{bc} \mid \mu \mid \varPhi_{Jk}^{bc} \right\rangle \left\langle \varPhi_{Jk}^{bc} \mid \mu \mid \varPhi_{ik}^{bc} \right\rangle$ |
| $\epsilon_i - \epsilon_J - \omega$ | $\epsilon_k - \epsilon_J - \omega$ | $\epsilon_i - \epsilon_K - \omega$ | $\epsilon_i - \epsilon_J - \omega$ |
| (17) | (18) | (19) | (20) |
| | | | |

(ii) Channels approximated by uS and the term with the CCSD state as intermediate

| $\left< \varPhi^b_J \mid \mu \mid \varPhi_0 \right> \left< \varPhi_0 \mid \mu \mid \varPhi_0 \right>$ | $\left< \pmb{\varPhi}_{\!J}^b \mid \mu \mid \pmb{\varPhi}_{\!i}^b \right> \left< \pmb{\varPhi}_{\!i}^b \mid \mu \mid \pmb{\varPhi}_{\!0} \right>$ | $\left\langle arPsi_{Jk}^{bc} \left \left. \mu \right. \right \left. arPsi_{k}^{c} ight angle \left\langle arPsi_{k}^{c} \left \left. \mu \right. \right \left. arPsi_{0} ight angle ight angle$ | $\left\langle ec{\Phi}_{\!J}^{b} \left \left. \mu \right. \right \left. ec{\Phi}_{\!i}^{b} ight angle \left\langle ec{\Phi}_{\!i}^{b} \left \left. \mu \right. \right \left. ec{\Phi}_{\!i}^{a} ight angle ight angle$ | | | | | | |
|---|---|---|---|--|--|--|--|--|--|
| $-\omega$ | $\epsilon_b - \epsilon_i - \omega$ | $\epsilon_c - \epsilon_k - \omega$ | $\epsilon_b - \epsilon_a - \omega$ | | | | | | |
| (21) | (22) (ه ⁶ د ا ، ا ه ^۵ د) (هذا ، ا ه ^۹ د) | (23) | (24) | | | | | | |
| $\frac{\langle \Psi_{J} \mid \mu \mid \Psi_{0} \rangle \langle \Psi_{0} \mid \mu \mid \Psi_{i} \rangle}{\langle \Psi_{0} \mid \mu \mid \Psi_{i} \rangle}$ | $\langle \Psi_{Jk} \mid \mu \mid \Psi_k \rangle \langle \Psi_k \mid \mu \mid \Psi_k \rangle$ | $\langle \Psi_{jk} \mid \mu \mid \Psi_k \rangle \langle \Psi_k \mid \mu \mid \Psi_l \rangle$ | $\left\langle \boldsymbol{\varphi}_{j}^{r} \mid \boldsymbol{\mu} \mid \boldsymbol{\varphi}_{i}^{r} \right\rangle \left\langle \boldsymbol{\varphi}_{i}^{r} \mid \boldsymbol{\mu} \mid \boldsymbol{\varphi}_{ij}^{rr} \right\rangle$ | | | | | | |
| $\epsilon_i - \epsilon_a - \omega$ | $\epsilon_c - \epsilon_a - \omega$ | $\epsilon_l - \epsilon_k - \omega$ | $\epsilon_j - \epsilon_c - \omega$ | | | | | | |
| (25) | (26) | (27) | (28) | | | | | | |
| $\frac{\langle \Phi_{Jl}^{bc} \mid \mu \mid \Phi_{l}^{c} \rangle \langle \Phi_{l}^{c} \mid \mu \mid \Phi_{li}^{cd} \rangle}{\langle \Phi_{l}^{c} \mid \mu \mid \Phi_{li}^{cd} \rangle}$ | | | | | | | | | |
| $\epsilon_i - \epsilon_d - \omega$ | | | | | | | | | |
| (29) | | | | | | | | | |
| | | | | | | | | | |
| (iii) Channels captured by the | (iii) Channels captured by the term with the CCSD state as intermediate but not by uS | | | | | | | | |

| $\left< \varPhi_{Jk}^{bc} \mid \mu \mid \varPhi_{lk}^{bc} \right> \left< \varPhi_{lk}^{bc} \mid \mu \mid \varPhi_{k}^{c} \right>$ | $\left< \varPhi_{Jk}^{bc} \left \right. \mu \left. \right \left. \varPhi_{lk}^{bc} \right> \left< \varPhi_{lk}^{bc} \right \left. \mu \left. \right \left. \varPhi_{l}^{b} \right> \right>$ | $\left< \varPhi_{Jl}^{bc} \left \right. \mu \left. \right \left. \varPhi_{kl}^{bc} \right> \left< \varPhi_{kl}^{bc} \left \right. \mu \left. \right \left. \varPhi_{kl}^{bd} \right> \right.$ | $\left< \varPhi_{jl}^{bc} \mid \mu \mid \varPhi_{kl}^{bc} \right> \left< \varPhi_{kl}^{bc} \mid \mu \mid \varPhi_{il}^{bc} \right>$ |
|---|---|---|---|
| $\epsilon_b - \epsilon_l - \omega$ | $\epsilon_c - \epsilon_k - \omega$ | $\epsilon_c - \epsilon_d - \omega$ | $\epsilon_i - \epsilon_k - \omega$ |
| (30) | (31) | (32) | (33) |
| ^a The coefficients of the Slater deter | rminants are omitted in the table | | |

The coefficients of the Stater determinants are offitted in the table.

electronic structure package.⁶⁵ py-CCRSP⁸⁴ was used for code debugging and testing.

As application, we considered several small systems, namely NH_3 , H_2O , HF, Ne, benzene, and *p*-nitroaniline (*p*NA). Despite the lack of published experimental studies on the X2PA spectra of small molecules, these systems can serve as test cases for various theoretical strategies, which can then be developed further by including more (better) physics for tackling more complex systems such as transition-metal compounds.

We use the following Abelian point groups in our calculations: C_s for NH₃; $C_{2\nu}$ for H₂O, HF, and pNA; and D_{2h} for Ne and benzene. We follow Q-Chem symmetry notation (details can be found in refs 45, 85, and 35) instead of Mulliken symmetry notation.⁸⁶ The geometries of HF and H₂O were optimized at the DFT/B3LYP^{87,88} level of theory with the t-aug-cc-pVTZ basis set. For NH₃, the CCSD/aug-cc-pVTZ optimized

geometry was used. The geometries of benzene and *p*NA were taken from previous studies.^{12,13,89} All basis sets and geometries used in this study are provided in the Supporting Information.

Core orbitals were frozen in all calculations as prescribed by the (fc-CVS-)EOM-EE-CCSD framework, except for the N and O K-edge calculations for pNA wherein the lowest four and two core orbitals were frozen, respectively. The CVS-0 and CVS-uS 2PA cross sections with degenerate photons were computed between the CCSD and core-excited states, with the latter obtained within the fc-CVS-EOM-EE-CCSD framework. We used the d-aug-cc-pVTZ basis set for NH₃, t-aug-cc-pVTZ basis set for H₂O and HF, t-aug-cc-pCVTZ basis set augmented with s and p Rydberg functions for Ne, uC-6-311(2+,+)G^{**} for benzene, and uC-6-311++G^{**} basis set for pNA. For each system, we considered all core-excited states below the respective core-ionization energies, i.e., 10, 22, 24, 32, 65, and

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Table 2. Configurational Analysis of the Leading Channels in X2PA Moment, $M^{g \leftarrow f}$, Where $\Psi^g = l_0 \Phi_0 + \sum_{ia} l_i^a \Phi_i^a + (1/4) \sum_{ijab} l_{ij}^{ab} \Phi_{ij}^{ab}$ Is the Wave Function of the Initial State g and $\Psi^{f} = \sum_{Ia} r_I^a \Phi_I^a + (1/2) \sum_{Ijab} r_{Ij}^{ab} \Phi_{Ij}^{ab} + (1/4) \sum_{IJab} r_{IJ}^{ab} \Phi_{IJ}^{ab}$ Is the Wave Function of the Final State f^a

| (i) Channels captured by CVS- | -0 | | |
|---|---|--|---|
| $\left\langle arPsi_{0} \mu\midarPsi_{I}^{b} ight angle \left\langle arPsi_{I}^{b} \mu\midarPsi_{J}^{b} ight angle$ | $\left\langle arPsi_{0}\mid\mu\midarPsi_{J}^{a} ight angle \left\langle arPsi_{J}^{a}\mid\mu\midarPsi_{J}^{b} ight angle$ | $\left\langle arPsi_{0}\mid\mu\midarPsi_{J}^{b} ight angle \left\langle arPsi_{J}^{b}\mid\mu\midarPsi_{JK}^{bc} ight angle$ | $\left< arPsi_{0} \mid \mu \mid arPsi_{J}^{b} \right> \left< arPsi_{J}^{b} \mid \mu \mid arPsi_{Jk}^{bc} \right>$ |
| $\epsilon_I - \epsilon_I + \omega$ | $\epsilon_a - \epsilon_b + \omega$ | $\epsilon_K - \epsilon_c + \omega$ | $\epsilon_k - \epsilon_c + \omega$ |
| (1) | (2) | (3) | (4) |
| $\left< \varPhi_{i}^{a} \mid \mu \mid \varPhi_{Ji}^{ba} \right> \left< \varPhi_{Ji}^{ba} \mid \mu \mid \varPhi_{J}^{b} \right>$ | $\left< \varPhi^b_i \mid \mu \mid \varPhi^{ba}_{Ji} \right> \left< \varPhi^{ba}_{Ji} \mid \mu \mid \varPhi^b_{J} \right>$ | $\left< \varPhi^b_i \mid \mu \mid \varPhi^b_I \right> \left< \varPhi^b_I \mid \mu \mid \varPhi^b_J \right>$ | $\left\langle arPsi_{i}^{a} \mid \mu \mid arPsi_{J}^{a} ight angle \left\langle arPsi_{J}^{a} \mid \mu \mid arPsi_{J}^{b} ight angle$ |
| $\epsilon_a - \epsilon_i + \omega$ | $\epsilon_a - \epsilon_i + \omega$ | $\epsilon_I - \epsilon_I + \omega$ | $\epsilon_a - \epsilon_b + \omega$ |
| (5) | (6) | (7) | (8) |
| $\left< \boldsymbol{\varPhi}_{i}^{b} \mid \boldsymbol{\mu} \mid \boldsymbol{\varPhi}_{J}^{b} \right> \left< \boldsymbol{\varPhi}_{J}^{b} \mid \boldsymbol{\mu} \mid \boldsymbol{\varPhi}_{Jk}^{bc} \right>$ | $\left\langle \boldsymbol{\varPhi}_{i}^{b} \mid \boldsymbol{\mu} \mid \boldsymbol{\varPhi}_{Ji}^{cb} \right\rangle \left\langle \boldsymbol{\varPhi}_{Ji}^{cb} \mid \boldsymbol{\mu} \mid \boldsymbol{\varPhi}_{JK}^{cb} \right\rangle$ | $\left< \varPhi^b_i \mid \mu \mid \varPhi^b_J \right> \left< \varPhi^b_J \mid \mu \mid \varPhi^{bc}_{Jk} \right>$ | $\langle \boldsymbol{\Phi}_{l}^{c} \mid \boldsymbol{\mu} \mid \boldsymbol{\Phi}_{Jl}^{bc} \rangle \langle \boldsymbol{\Phi}_{Jl}^{bc} \mid \boldsymbol{\mu} \mid \boldsymbol{\Phi}_{Jk}^{bc} \rangle$ |
| $\epsilon_k - \epsilon_c + \omega$ | $\epsilon_{K} - \epsilon_{i} + \omega$ | $\epsilon_k - \epsilon_c + \omega$ | $\epsilon_k - \epsilon_l + \omega$ |
| (9) | (10) | (11) | (12) |
| $\frac{\langle \Phi_{k}^{c} \mid \mu \mid \Phi_{Lk}^{bc} \rangle \langle \Phi_{Lk}^{bc} \mid \mu \mid \Phi_{Jk}^{bc} \rangle}{\langle \Phi_{Lk}^{bc} \mid \mu \mid \Phi_{Jk}^{bc} \rangle}$ | $\langle \Phi_k^d \mid \mu \mid \Phi_{Jk}^{bd} \rangle \langle \Phi_{Jk}^{bd} \mid \mu \mid \Phi_{Jk}^{bc} \rangle$ | $\left\langle \boldsymbol{\varPhi}_{k}^{b} \mid \boldsymbol{\mu} \mid \boldsymbol{\varPhi}_{Jk}^{bd} \right\rangle \left\langle \boldsymbol{\varPhi}_{Jk}^{bd} \mid \boldsymbol{\mu} \mid \boldsymbol{\varPhi}_{Jk}^{bc} \right\rangle$ | $\left\langle \Phi^{bc}_{lk} \mid \mu \mid \Phi^{bc}_{Jk} \right\rangle \left\langle \Phi^{bc}_{Jk} \mid \mu \mid \Phi^{b}_{J} \right\rangle$ |
| $\epsilon_J - \epsilon_L + \omega$ | $\epsilon_d - \epsilon_c + \omega$ | $\epsilon_d - \epsilon_c + \omega$ | $\epsilon_c - \epsilon_K + \omega$ |
| (13) | (14) | (15) | (16) |
| $\left\langle \Phi_{il}^{bc} \mid \mu \mid \Phi_{Jl}^{bc} \right\rangle \left\langle \Phi_{Jl}^{bc} \mid \mu \mid \Phi_{JK}^{bc} \right\rangle$ | $\langle \Phi_{kl}^{bd} \mid \mu \mid \Phi_{Jl}^{bd} \rangle \langle \Phi_{Jl}^{bd} \mid \mu \mid \Phi_{Jl}^{bc} \rangle$ | $\left\langle \mathbf{\Phi}_{il}^{bc} \mid \mu \mid \mathbf{\Phi}_{Kl}^{bc} \right\rangle \left\langle \mathbf{\Phi}_{Kl}^{bc} \mid \mu \mid \mathbf{\Phi}_{Jl}^{bc} \right\rangle$ | $\left\langle \Phi_{ik}^{bc} \mid \mu \mid \Phi_{Jk}^{bc} \right\rangle \left\langle \Phi_{Jk}^{bc} \mid \mu \mid \Phi_{Jl}^{bc} \right\rangle$ |
| $\epsilon_K - \epsilon_l + \omega$ | $\epsilon_d - \epsilon_c + \omega$ | $\epsilon_J - \epsilon_K + \omega$ | $\epsilon_l - \epsilon_k + \omega$ |
| (17) | (18) | (19) | (20) |
| (ii) Channels approximated by | uS and the term with the CCSD | state as intermediate | |
| $\left\langle arPsi_{0} \mu\midarPsi_{0} ight angle \left\langle arPsi_{0} \mu\midarPsi_{I}^{b} ight angle$ | $\left\langle arPsi_{0}\mid\mu\midarPsi_{i}^{b} ight angle \left\langle arPsi_{i}^{b}\mid\mu\midarPsi_{I}^{b} ight angle$ | $\left\langle arPsi_{0} \left \left. \mu \right. \right arPsi_{k}^{ c} ight angle \left\langle arPsi_{k}^{ c} \left \left. \mu \right. \right arPsi_{lk}^{bc} ight angle$ | $ig\langle arPsi_{i}^{a} \mu \mid arPsi_{i}^{b} ig angle ig\langle arPsi_{i}^{b} \mu \mid arPsi_{I}^{b} ig angle$ |
| $\epsilon_I - \epsilon_b + \omega$ | $\epsilon_I - \epsilon_i + \omega$ | $\epsilon_I - \epsilon_b + \omega$ | $\epsilon_i - \epsilon_i + \omega$ |
| (21) | (22) | (23) | (24) |
| $\left\langle arPsi_{i}^{a} \left ight. \mu \left \left. arPsi_{0} ight angle \left\langle arPsi_{0} \left ight. \mu \left \left. arPsi_{J}^{b} ight angle ight angle$ | $\left\langle arPsi_{k}^{a} \mid \mu \mid arPsi_{k}^{c} ight angle \left\langle arPsi_{k}^{c} \mid \mu \mid arPsi_{Jk}^{bc} ight angle$ | $\left\langle {{\pmb{\Phi }_{l}^{c}}\left \left. \mu \right.} \right \left. {{\pmb{\Phi }_{k}^{c}}} \right\rangle \left\langle {{\pmb{\Phi }_{k}^{c}}\left \left. \mu \right.} \right \left. {{\pmb{\Phi }_{Jk}^{bc}}} \right angle ight angle$ | $\left\langle \mathbf{\Phi}_{ij}^{bc} \mid \mu \mid \mathbf{\Phi}_{i}^{b} \right\rangle \left\langle \mathbf{\Phi}_{i}^{b} \mid \mu \mid \mathbf{\Phi}_{I}^{b} ight angle$ |
| $\epsilon_J - \epsilon_b + \omega$ | $\epsilon_J - \epsilon_b + \omega$ | $\epsilon_J - \epsilon_b + \omega$ | $\epsilon_i - \epsilon_i + \omega$ |
| (25) | (26) | (27) | (28) |
| $\langle \varPhi_{li}^{\mathit{cd}} \mid \mu \mid \varPhi_{l}^{\mathit{c}} angle \langle \varPhi_{l}^{\mathit{c}} \mid \mu \mid \varPhi_{Jl}^{\mathit{bc}} angle$ | | | |
| $\epsilon_J - \epsilon_b + \omega$ | | | |
| (29) | | | |
| (iii) Channels captured by the | term with the CCSD state as inte | rmediate but not by uS | |
| $\langle \Phi_{k}^{c} \mid \mu \mid \Phi_{lk}^{bc} angle \langle \Phi_{lk}^{bc} \mid \mu \mid \Phi_{lk}^{bc} angle$ | $\langle \pmb{\Phi}_{l}^{b} \mid \mu \mid \pmb{\Phi}_{lk}^{bc} angle \langle \pmb{\Phi}_{lk}^{bc} \mid \mu \mid \pmb{\Phi}_{lk}^{bc} angle$ | $\langle \pmb{\varPhi}_{kl}^{bd} \mu \pmb{\varPhi}_{kl}^{bc} angle \langle \pmb{\varPhi}_{kl}^{bc} \mu \pmb{\varPhi}_{ll}^{bc} angle$ | $\langle \varPhi^{bc}_{ll} \mid \mu \mid \varPhi^{bc}_{kl} angle \langle \varPhi^{bc}_{kl} \mid \mu \mid \varPhi^{bc}_{ll} angle$ |

| (30) | | | | (3 | 1) | | |
|------|--|--|--|----|----|--|--|
| | | | | | | | |

 $\epsilon_{l} - \epsilon_{l} + \omega$

^aThe coefficients of the Slater determinants are omitted in the table.

63 states for NH₃, H₂O, HF, Ne, benzene, and *p*NA, respectively. The response equations were solved by using an iterative Davidson-like subspace procedure. All spectra were convoluted by using a Lorentzian broadening function with a half-width at half-maximum of 0.3 eV. In the discussion below, "X" labels the ground state and "c" is a core-excited state.

4. RESULTS AND DISCUSSION

 $\epsilon_{I} - \epsilon_{I} + \omega$

The bottom panels of Figure 2(a)-(h) compare the experimental and computed XAS spectra of our benchmark systems. The computed XAS spectra are shifted to align with the respective first experimental peak; the shifts are given in the figure legends. These shifts are <1.1 eV and significantly smaller than the corresponding shifts computed at the lower TD-DFT/CAM-B3LYP_{100%} level of theory in ref 64. The XAS spectra

yielded by (fc-CVS-)EOM-EE-CCSD show only small discrepancies with respect to experimental spectra in terms of peak positions and intensities of dominant peaks, compared to similar discrepancies with the TD-DFT approach in ref 64, further highlighting its robustness relative to TD-DFT in modeling XAS. Below, all computed energy values are shifted values. The nonshifted peak positions are reported in the Supporting Information.

 $\epsilon_I - \epsilon_k + \omega$

(32)

The top two panels in Figure 2(a)-(h) provide the X2PA spectra computed, respectively, with the CVS-0 and CVS-uS resolvents within the (fc-CVS-)EOM-EE-CCSD framework for the benchmark systems (shifted similar to XAS). We note that the CVS-0 results are not to be construed as an approximation to the CVS-uS results; rather, the CVS-0 data provide separate estimates of the core and valence contributions to the X2PA

 $\epsilon_I - \epsilon_k + \omega$

(33)



Figure 2. fc-CVS-EOM-EE-CCSD with the d-aug-cc-pVTZ (NH₃), t-aug-cc-pCVTZ (H₂O, HF), t-aug-cc-pCVTZ+Rydberg (Ne), uC-6-311(2+, +)G** (benzene), and uC-6-311++G** (pNA) basis sets. XAS and (CVS-0 and CVS-uS) X2PA spectra of (a) NH₃, (b) H₂O, (c) HF, (d) Ne, (e) benzene, (f) pNA (C K-edge), (g) pNA (N K-edge), and (h) pNA (O K-edge). Experimental spectra from ref 90 (NH₃ and H₂O), ref 91 (HF), ref 92 (benzene), ref 93 (Ne), and ref 94 (pNA). Black vertical lines correspond to excited states that are dark in the given spectrum. Dark states are omitted from the benzene spectra.

cross sections. Compared to CVS-0, the intensities of the spectra computed with CVS-uS are one order of magnitude smaller across all systems. This is a consequence of cancellation of contributions from the valence states as intermediates and the core states as intermediates. Further, the shapes of these spectra with the two approaches show significant differences. We also note that the magnitudes of the X2PA cross sections ($\sim 10^{-6}$) in atomic units (au) are orders of magnitude smaller than typical

valence 2PA cross sections for these systems, a consequence of small overlaps of core orbitals with unoccupied orbitals. However, the X2PA moments used for computing the cross sections are greater than the precision thresholds set in our calculations and, therefore, these moments are numerically reliable.

Response equations for all systems converge within our CVS-0 and CVS-uS setups. Whereas the convergence is, in general,

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|---------------------|---------|--|
|---------------------|---------|--|

quick for most systems, for pNA, a few "uS" response equations take ~80 iterations before convergence—a consequence of the very diffuse basis set used for pNA and larger valence contributions in pNA compared to other systems.

The XAS spectrum of NH₃, discussed in depth in ref 74, is dominated by the peak at 402.2 eV corresponding to the degenerate XA' $\rightarrow c2A'$ and XA' $\rightarrow c1A''$ transitions, i.e., the 1s $\rightarrow 3p$ (XA₁ $\rightarrow cE$) transition, with smaller features around 400.5 eV (1s \rightarrow 3s), 402.8 eV, and 403.5 eV. In contrast, both the CVS-0 and CVS-uS X2PA spectra are dominated by the XA' $\rightarrow c1A''$ (1s \rightarrow 3s) transition at 400.5 eV. The 2PA cross section for the XA' $\rightarrow c2A'$ transition is, in particular, negligible for the CVS-uS approach. Small features at 402.8 eV and 403.5 eV are also present in the CVS-uS spectrum.

Similar to NH₃, the XAS spectrum for H₂O is richer relative to the X2PA spectra (from both the CVS-0 and CVS-uS approaches) and dominated by the three features around S34.0 eV, S35.7 eV, and S37.0 eV. The first feature results from the XA₁ \rightarrow c1A₁ transition, the second results from the XA₁ \rightarrow c1B₁ transition, and the third results from XA₁ \rightarrow c1B₂ and XA₁ \rightarrow c2A₁ transitions; see also refs 74 and 95. The X2PA spectrum for both CVS-0 and CVS-uS has a dominant peak corresponding to the XA₁ \rightarrow c1A₁ transition with a tail of small features observed in the high-energy region. The CVS-uS X2PA spectrum is also similar to the X2PA spectrum in ref 64.

The computed XAS spectrum for HF shows two dominant peaks around 687.2 eV and 690.8 eV. The former peak arises from the $XA_1 \rightarrow c1A_1$ transition, while the latter originated from the close-lying $XA_1 \rightarrow c2A_1$ and degenerate $XA_1 \rightarrow c1B_1$ and XA_1 $\rightarrow c1B_2$ transitions. Both CVS-0 and CVS-uS X2PA spectra are dominated by the $XA_1 \rightarrow c1A_1$ transition. However, whereas the CVS-0 spectrum also shows a dominant $XA_1 \rightarrow c2A_1$ peak, this transition is not as important in the CVS-uS spectrum. The CVS-uS spectrum instead features close-lying peaks around 692.4 eV and 692.8 eV, arising from the $XA_1 \rightarrow c4A_1$ and $XA_1 \rightarrow$ $c7A_1$ transitions, respectively. Although the shape of the CVS-uS spectrum resembles the X2PA spectrum in ref 64, the smaller features are slightly blue shifted in the former.

XAS and X2PA spectra for neon are complementary to each other. The XAS spectrum, consisting entirely of Rydberg transitions, is dominated by the $1s \rightarrow 3p$ transition, peaked at 867.1 eV, followed by $1s \rightarrow 4p$, $1s \rightarrow 5p$ and $1s \rightarrow 6p$, as allowed according to dipole selection rules.^{74,93,95} Relative to the shifts applied to the XAS spectrum in ref 64, the shifts applied in this study are much smaller. The CVS-0 X2PA spectrum has a dominant $1s \rightarrow 3s (XA_g \rightarrow c1A_g)$ feature at 865.3 eV, along with smaller features at 868.3 eV and 869.9 eV; the latter arises from $1s \rightarrow 3d$ transitions. In contrast, the CVS-uS spectrum has a dominant feature at 870.1 eV, arising from the $XA_g \rightarrow c11A_g$ transition, followed by a smaller peak at 869.9 eV corresponding to the $1s \rightarrow 3d$ transition. The CVS-uS spectrum resembles the X2PA spectrum in ref 64, even though the $1s \rightarrow 3d$ transitions, which are indicated as the dominant ones in the case of X2PA spectrum in ref 64, are no longer the most dominant. The difference between the CVS-0 and CVS-uS spectra further highlights the importance of including the valence resolvent for computing X2PA cross sections.

Benzene's XAS, also studied in refs 89 and 12, features a dominant peak at 285.2 eV arising from the $XA_g \rightarrow c2B_{1u}$ transition. Smaller features including the ones at 287.0 eV and 289.0 eV are also present, with the former originating from degenerate $XA_g \rightarrow c1B_{2u}$ and $XA_g \rightarrow c2B_{3u}$ transitions and the latter originating from degenerate $XA_g \rightarrow c9B_{2u}$ and $XA_g \rightarrow c9B_{2u}$ and X

 $c12B_{3u}$ transitions. Benzene is centrosymmetric, and its XAS and X2PA are complementary to each other. Whereas the dominant X2PA peak for both CVS-0 and CVS-uS approaches originates from the same $XA_g \rightarrow c2A_g$ transition at 287.1 eV, the shapes of the two spectra are slightly different for the smaller features. Among the smaller features for CVS-uS, the peak at 289.0 eV arising from the $XA_g \rightarrow c12A_g$ transition is dominant. The complementary XAS and X2PA modeling augmented by the corresponding orbital analysis can, in principle, provide rich information on the electronic structure of this highly symmetric molecule.

pNA has a large dipole moment and features numerous charge-transfer valence excitations. The computed C K-edge XAS spectrum is comparable with the experimental spectrum in ref 94, although experimental features, except the ones around 285.0 eV and 287.5 eV and the shoulder around 286.0 eV, are not well resolved. The dominant feature around 285.0 eV originates from the $XA_1 \rightarrow c1B_2$ and $XA_1 \rightarrow c2B_2$ transitions, both of $1s_{\rm C} \rightarrow \pi^*$ character. The former transition is characterized by $b_1 \rightarrow a_2$ and $a_1 \rightarrow b_2$ orbital transitions with the core hole delocalized over the two carbons at the meta position relative to the nitro group (see the raw data in Table S7 and NTO analysis in Table S8 in the Supporting Information). The latter transition is characterized by a $b_1 \rightarrow a_2$ orbital transition with the core hole delocalized over the two carbons at the meta position relative to the amine group. The next two features, one at \approx 285.9 eV and the other at 286.5 eV, arise from the $XA_1 \rightarrow c3B_2$ and $XA_1 \rightarrow c5B_2$ transitions, respectively. The first one is due to $1s \rightarrow \pi^*$ transition from the carbon atom bearing the nitro group. The second, also of $1s \rightarrow \pi^*$ type, is an $a_1 \rightarrow b_2$ transition with the core hole originating primarily from the C atom bearing the amino group, with some delocalization over the two nearest carbons. The computed XAS spectrum has a few other relatively intense features such as $XA_1 \rightarrow c1B_1$ at 287.0 eV, $XA_1 \rightarrow c7B_2$ at 288.2 eV, $XA_1 \rightarrow c13A_1$ at 289.5 eV, $XA_1 \rightarrow c11B_2$ at 289.5 eV, $XA_1 \rightarrow c15B_1$ at 290.1 eV, and $XA_1 \rightarrow c15B_1$ *c*20A₁ at 290.3 eV. Their character (π^* , σ^* , Rydberg) becomes apparent upon inspecting the NTOs in Table S8.

In the CVS-0 X2PA spectrum, many of these same transitions are important along with $XA_1 \rightarrow c1A_1$ at 287.0 eV, $XA_1 \rightarrow c2A_1$ at 287.9 eV, $XA_1 \rightarrow c5A_1$ at 288.7 eV, $XA_1 \rightarrow c7A_1$ at 288.8 eV, $XA_1 \rightarrow c12A_1$ at 289.4 eV, $XA_1 \rightarrow c2B_1$ at 287.9 eV, and $XA_1 \rightarrow$ c5B1 at 288.7 eV. The CVS-uS spectrum, in contrast, is less rich, with only the $XA_1 \rightarrow c1A_1, XA_1 \rightarrow c2A_1, XA_1 \rightarrow c5A_1, XA_1 \rightarrow c5A_2$ $c8A_1$ (at 288.9 eV), $XA_1 \rightarrow c14A_1$ (at 289.6 eV), $XA_1 \rightarrow c19A_1$ (at 290.3 eV), $XA_1 \rightarrow c20A_1$, and $XA_1 \rightarrow c15B_1$ transitions dominant. pNA, therefore, represents yet another system that features a large valence contribution to the X2PA cross sections, highlighting the importance of including the valence resolvent in our model. The dominant transitions in the CVS-uS spectrum, $XA_1 \rightarrow c1A_1$ and $XA_1 \rightarrow c2A_1$, are characterized by different pairs of $a_1 \rightarrow a_1$ and $b_1 \rightarrow b_1$ orbital transitions, and are of $\sigma^*/\text{Rydberg}$ type. For the former, the core hole is delocalized on the carbons meta to the amine group, whereas for the latter, the core hole is predominantly centered on the carbons meta to the nitro group. The next most intense peak is due to the $XA_1 \rightarrow c20A_1$ transition, characterized by an $a_1 \rightarrow a_1$ transition with the core hole on the carbon atom connected to the nitro group; see Table **S8**

Compared to the C *K*-edge spectra, the N and O *K*-edge XAS and X2PA spectra of *p*NA are not as rich, a direct consequence of fewer N and O atoms. The computed N *K*-edge XAS spectrum, which compares well with the experimental spectrum from ref

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94, is dominated by the $XA_1 \rightarrow c2B_2$ (1s $\rightarrow \pi^*$) transition at 403.7 eV, which is also dominant in the CVS-0 spectrum. This transition is characterized by the $a_1 \rightarrow b_2$ orbital transition with the core hole localized on the N atom of the nitro group and a delocalized π^* particle orbital (see the raw data in Table S7 and NTO analysis in Table S8). The second dominant feature in the XAS transition originates from two transitions: $XA_1 \rightarrow c1B_2$ at 402.6 eV and $XA_1 \rightarrow c1B_1$ at 402.8 eV. The former is also quite strong in the CVS-0 spectrum and is characterized by the $a_1 \rightarrow b_2$ orbital transition with the core hole localized on N atom of the amine group and another delocalized π^* particle orbital. In contrast to the XAS and CVS-0 spectra, the CVS-uS spectrum shows different dominant features arising from the $XA_1 \rightarrow c1A_1$ and $XA_1 \rightarrow c4A_1$ transitions at 401.8 eV and 405.0 eV, respectively. Remarkably, in both these transitions, the core hole is localized on the amine group's N atom and the nitro group does not participate in the particle orbital. The core transitions from the N atom in the nitro group are basically quenched in the XTPA CVS-uS spectrum.

The O K-edge XAS spectrum of pNA is even more featureless than the N K-edge XAS spectrum and compares well with the experimental spectrum from ref 94. The XAS spectrum has a dominant feature at 531.1 eV originating from the $XA_1 \rightarrow c1B_2$ transition, characterized by an $a_1 \rightarrow b_2$ orbital transition with a delocalized π^* particle orbital and the core hole delocalized on the two oxygen atoms (see the raw data in Table S11 and NTO analysis in Table S12 in the Supporting Information). This transition, along with the degenerate $XA_1 \rightarrow c1A_2$ transition, is also dominant in the CVS-0 spectrum but quenched in the CVSuS spectrum. These two transitions have the same characteristic π^* particle orbital, with the hole orbitals different (one is the symmetric and the other the antisymmetric combination of the oxygen 1s orbitals). Similar to the N K-edge CVS-uS spectrum, the O K-edge CVS-uS spectrum is dominated by fully symmetric transitions. In this case, the dominant transitions are $XA_1 \rightarrow$ $c6A_1, XA_1 \rightarrow c7A_1$, and $XA_1 \rightarrow c1A_1$ at 538.1 eV, 538.8 eV, and 536.2 eV, respectively. Whereas the first two transitions feature particle orbitals delocalized on the entire molecule, the third transition features a particle orbital that is largely localized at the nitro end of pNA. For details on the NTOs involved in the smaller features, we refer to the tabulated raw data used to construct the spectra shown in Figure 2 and the corresponding NTO analyses in the Supporting Information.

5. CONCLUSIONS

We have presented an approach for computing X2PA spectra within the EOM-EE-CCSD framework. Standard iterative procedures for computing the X-ray response wave functions diverge within the EOM-EE-CCSD framework; in this study, we have extended our frozen-core CVS-based strategy of cherrypicking resolvents, mitigating this issue in the computations of X2PA cross sections. The fc-CVS scheme allows us to fragment the EOM-EE-CCSD resolvent into a direct sum of independent core (called "CVS-0") and valence resolvents; X-ray response wave functions in the core- and valence-excitation spaces can, therefore, be computed separately. The valence resolvent is then approximated using the valence singles-singles block of the fc-CVS-EOM-EE-CCSD Hamiltonian, which is the "uS" approximation. We also provided the configurational analysis of X2PA channels to rationalize the CVS-uS approach and showed that the approach captures the most important channels for the 2PA transitions between the CCSD or singly excited valence-excited states and singly excited core-excited states. The X2PA spectra

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for small benchmark systems computed with this approach are comparable in shape to those from the CPP-TD-DFT approach in ref 64, yet with smaller discrepancies for the (fc-CVS-uS-)EOM-EE-CCSD framework in the peak positions relative to XAS experiments. We also highlighted the importance of the valence contribution to the X2PA moments by comparing the CVS-0 and CVS-uS spectra.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jctc.2c00541.

Tabulated data for transition properties, natural transition orbital (NTO) pairs of relevant core transitions at the *C*, N, and O *K*-edges of *p*NA, Cartesian coordinates, basis sets (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Kaushik D. Nanda Department of Chemistry, University of Southern California, Los Angeles, California 90089, United States; Orcid.org/0000-0002-3447-6678; Email: kaushikdnanda@gmail.com
- Anna I. Krylov Department of Chemistry, University of Southern California, Los Angeles, California 90089, United States; o orcid.org/0000-0001-6788-5016; Email: krylov@ usc.edu
- Sonia Coriani DTU Chemistry, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark;
 orcid.org/0000-0002-4487-897X; Email: soco@ kemi.dtu.dk

Author

Josefine H. Andersen – DTU Chemistry, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark; orcid.org/0000-0002-0534-7463

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jctc.2c00541

Author Contributions

[§]J.H.A. and K.D.N. contributed equally.

Notes

The authors declare the following competing financial interest(s): A.I.K. is the president and a part-owner of Q-Chem, Inc.

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5.3 MANUSCRIPT I

"An efficient protocol for computing MCD spectra in a broad frequency range combining resonant and damped CC2 quadratic response theory" Josefine H. Andersen, S. Coriani, and C. Hättig **2023** (*Submitted*)

Supporting information can be found in Appendix A.
An efficient protocol for computing MCD spectra in a broad frequency range combining resonant and damped CC2 quadratic response theory

Josefine H. Andersen,*,[†] Sonia Coriani,*,[†] and Christof Hättig*,[‡]

†Department of Chemistry, Technical University of Denmark, Kemitorvet Building 207, DK-2800 Kongens Lyngby, Denmark

‡Arbeitsgruppe Quantenchemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

E-mail: johvan@kemi.dtu.dk; soco@kemi.dtu.dk; christof.haettig@rub.de

Abstract

Coupled-cluster response theory offers a path to high-accuracy calculations of spectroscopic properties, such as magnetic circular dichroism (MCD). However, divergence or slow convergence issues or are often encountered for electronic transitions in high-energy regions with a high density of states. This is here addressed for MCD by an implementation of damped quadratic response theory for resolution-of-identity coupled cluster singles-and-approximate-doubles (RI-CC2), along with an implementation of the MCD \mathcal{A} term from resonant response theory. Combined, damped and resonant response theory provide an efficient strategy to calculate MCD spectra over a broad frequency range and for systems that include highly symmetric molecules with degenerate excited states. The protocol is illustrated by application to Zink Tetrabenzoporphyrin in the energy region 2–8 eV and comparison to experimental data.

Timings are reported for the resonant and damped approaches, showing that the greater part of the calculation time is consumed by the construction of the building blocks for the final MCD ellipticity. A recommendation on how to utilize the procedure is outlined.

1 Introduction

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Magnetic circular dichroism (MCD) spectroscopy is a technique based on the measurement of the differential absorption of left and right circular polarized light passing through a sample immersed in a (relatively strong) magnetic field parallel to the direction of propagation of the light.¹ The frequency of the light is typically in a region of electronic absorption of the sample, that is UV/vis, near IR or X-ray,¹ but magnetic circular dichroism of vibrational transitions can also be recorded.² A recently proposed experimental protocol utilizes pulsed vector beams, where the magnetic field generated by the vector beams replaces the external static field applied in conventional MCD experiments.³ MCD has been applied with success to molecular systems to gain insight into structural, electronic, and magnetic properties, and experiments are moving into the investigation of nanosystems as well.⁴

Traditionally, the MCD signal is analyzed in terms of three characteristic band shapes, whose underlying electronic-structure intensity descriptors are known as the Faraday \mathcal{A} , \mathcal{B} , and \mathcal{C} terms. The \mathcal{C} term relates to the Zeeman splitting of degenerate ground states due to the external field, and its absorption-shaped band is temperature dependent. Only paramagnetic compounds exhibit \mathcal{C} term signals.^{1,5,6} \mathcal{A} and \mathcal{B} terms have different physical origins and are both independent of temperature. While the \mathcal{A} term arises from the magnetic field-induced Zeeman splitting of degenerate electronic states, the \mathcal{B} term is the result of mixing of non-degenerate states under the influence of the magnetic field. Thus, all molecules exhibit \mathcal{B} -type signals while only molecules with a three-fold or higher symmetry axis will have nonzero \mathcal{A} terms.^{1,5,6} A derivative line shape indicates the presence of an \mathcal{A} term and, thus, excited-state degeneracy, while a transition with only a \mathcal{B} term contribution gives rise to a Gaussian-shaped absorption feature. When present, the \mathcal{A} term dominates the spectrum.^{1,5,6}

MCD experiments can help to deconvolute bands observed in a regular absorption spectrum. Since the MCD signals taking both positive and negative values, transitions can be better distinguished and, as mentioned, (near-)degenerate states can be identified from derivative lineshapes. In the interpretation of experimental MCD spectra, computational spectroscopy can provide valuable support. From quantum chemical calculation, it is possible to gain insight into the underlying electronic transitions, which in a spectrum are convoluted in a band of varying resolution. Among the most recent developments of theoretical approaches targeting MCD are implementations based on response theory⁷ within the algebraic diagrammatic construction (ADC) scheme,⁸ coupled cluster singles and doubles (CCSD),⁹ and resolution-of-identity coupled cluster singles and approximate doubles (RI-CC2)¹⁰, as well as the linear-response (LR-) time-dependent (TD-) density functional theory (DFT) approach, in which excited states are calculated in a finite magnetic field.¹¹

The calculation of the individual Faraday terms requires an explicit solution of the final excited states. This approach is limited by the convergence of the excited state eigenvectors and their derivatives which becomes increasingly difficult in regions with a high density of states. Damped response theory and the complex polarization propagator framework offer an alternative approach where the spectrum is computed directly as an interpolation of cross-section grid points in any frequency region.^{12–14} Implementations of this type of approach have been presented for various electronic-structure methods for the computation of linear spectroscopies such as one-photon absorption and electronic circular dichroism (ECD),^{15–20} of C_6 dispersion coefficients,^{21–23} and of the nonlinear spectroscopies such as MCD,^{9,24} nuclear spin-induced circular dichroism (NSCD),²⁵ magneto-chiral dichroism (MChD) and magneto-chiral birefringence dispersion,²⁶ as well as resonant inelastic X-ray scattering (RIXS)^{27–31} and two-photon absorption.^{32–34}

In this work we extend the RI-CC2 framework for MCD spectroscopy¹⁰ in TURBO-MOLE³⁵ to include the calculation of the \mathcal{A} term. Moreover, we address the shortcomings of the explicit calculation of the Faraday terms in regions where many close-lying electronic states can be expected by presenting an RI-CC2 implementation of damped quadratic response. The RI-CC2 method allows for applications to molecular systems of sizes that are not amenable for CCSD and higher-order methods, while still producing reasonably accurate excitation energies and, thus, spectra.

Our protocol then combines the explicit calculation of individual \mathcal{A} and \mathcal{B} terms in regions of well-separated electronic transitions with damped response calculations of the MCD signal in dense spectral regions. This opens for the investigation of the MCD of molecules in a broad frequency range including cases with degenerate excited states. Furthermore, the implementation of damped quadratic response can straightforwardly be extended to compute other perturbation-induced spectra such as NSCD and MChD.

To assess the time consumption of the resonant and damped pathways, we compare the timings for converging the equations and computing the MCD ellipticities for two degenerate resonant states and for one complex frequency.

2 Theory

For a randomly oriented sample in a static magnetic field placed along the z axis, the ellipticity of plane-polarized light passing through the sample parallel to the field can be determined as³⁶

$$\theta = \frac{1}{6} \mu_0 c \, l N B_z \, \theta_{\rm MCD} \tag{1}$$

where μ_0 is the permeability, c is the velocity of light, l is the path length through the sample, N is the number density, and B_z is the strength of the external magnetic field along the z axis.

The MCD ellipticity, θ_{MCD} , can be computed using different approaches. Within resonant (standard) response theory, the traditional expression for the MCD ellipticity of a system with a non-degenerate ground state takes the form (in atomic units)^{9,36}

$$\theta_{\rm MCD} = -\omega \sum_{j} \left\{ \frac{\partial g(\omega_j, \omega)}{\partial \omega} \,\mathcal{A}(0 \to j) + g(\omega_j, \omega) \,\mathcal{B}(0 \to j) \right\}$$
(2)

where ω is the frequency of the incoming light, ω_j is the excitation energy of the electronic transition $0 \to j$, and $g(\omega_j, \omega)$ is a lineshape function, *e.g.*, a Gaussian or a Lorentzian. We refer to Section 3 for details on the type of lineshape function applied in the present work.

The exact sum-over-states (SOS) representation of the \mathcal{B} term is 37,38

$$\mathcal{B}(0 \to j) = \varepsilon_{\alpha\beta\zeta} \operatorname{Im}\left[\sum_{k \neq 0} \frac{\langle k | m_{\zeta} | 0 \rangle}{\omega_{k}} \langle 0 | \mu_{\alpha} | j \rangle \langle j | \mu_{\beta} | k \rangle + \sum_{k \notin \mathcal{D}_{j}} \frac{\langle j | m_{\zeta} | k \rangle}{\omega_{k} - \omega_{j}} \langle 0 | \mu_{\alpha} | j \rangle \langle k | \mu_{\beta} | 0 \rangle\right] \quad (3)$$

where μ_{α} and m_{α} are Cartesian components of the electric dipole and magnetic dipole operators, respectively, and $\varepsilon_{\alpha\beta\zeta}$ is the Levi-Civita tensor. Implicit summation for α , β , and ζ is implied throughout. \mathcal{D}_j is a set of degenerate states of which j is part $(j \in \mathcal{D}_j)$. These degenerate states, if included in the sum over k, would make the second term of Eq. (3) diverge and are therefore explicitly excluded from the sum. The MCD signal of the \mathcal{D}_j set is instead described via the non-divergent \mathcal{A} term and the derivative of the lineshape function (Eq. 2). Assuming a non-degenerate ground state, the exact SOS expression for the \mathcal{A} term of an excited state j within the degenerate set \mathcal{D}_j is ^{37,38}

$$\mathcal{A}(0 \to j) = \frac{1}{2} \varepsilon_{\alpha\beta\zeta} \operatorname{Im}_{\substack{j' \in \mathcal{D}_j \\ j' \neq j}} \left\langle 0 | \mu_{\alpha} | j \right\rangle \left\langle j | m_{\zeta} | j' \right\rangle \left\langle j' | \mu_{\beta} | 0 \right\rangle \tag{4}$$

which can be recognized as the residue of the dispersive term of Eq. (3) in the limit of $(\omega_k - \omega_j) \rightarrow 0.$

In general, computing the Faraday terms from their SOS expressions is highly inefficient. Instead, the \mathcal{A} and \mathcal{B} terms can be obtained, *e.g.*, from the double and single residues of appropriate quadratic response functions,^{36,39} or from the magnetic field-derivatives of the excitation energy and the one-photon dipole transition strength.^{40–42}

2.1 Implementation of the Faraday A and B terms

In the work of Faber et al.,⁹ the expression for the MCD \mathcal{A} term within CC theory was derived from a residue analysis of the magnetic field-derivative of the dipole-dipole transition strength. Following this derivation, we calculate the \mathcal{A} term as

$$\mathcal{A}(0 \to j) = -\frac{1}{4} \varepsilon_{\alpha\beta\zeta} \operatorname{Im}_{\substack{j' \in \mathcal{D}_j \\ j' \neq j}} \left(T^{\mu_{\alpha}}_{0j'} T^{m_{\zeta}}_{j'j} T^{\mu_{\beta}}_{j0} + T^{\mu_{\alpha}}_{0j} T^{m_{\zeta}}_{jj'} T^{\mu_{\beta}}_{j'0} \right) .$$

$$(5)$$

 T_{0j}^{μ} and T_{j0}^{μ} are the CC one-photon dipole transition moments, whose computation has been discussed several times elsewhere, see, e.g., Refs. 7,9. In general, the one-photon transition moment for the magnetic dipole operator m_{ζ} between the degenerate states j and j', $T_{jj'}^{m_{\zeta}}$, can be expressed in two ways,⁷

$$T_{jj'}^{m_{\zeta}} = \bar{E}_j(-\omega_j)(\mathbf{A}^{m_{\zeta}} + \mathbf{B}\,t^{m_{\zeta}}(0))E_{j'}(\omega_{j'}) \tag{6}$$

or

$$T_{jj'}^{m_{\zeta}} = \bar{E}_j(-\omega_j) \mathbf{A}^{m_{\zeta}} E_{j'}(\omega_{j'}) + \bar{N}_{jj'}(\omega_j, \omega_{j'}) \xi^{m_{\zeta}}$$
(7)

where the multipliers $\bar{N}_{jj'}$ are determined by solving the linear equation 7

$$\bar{N}_{jj'}(-\omega_j,\omega_{j'})\left(\mathbf{A} + (\omega_j - \omega_{j'})\mathbf{1}\right) = -\bar{E}_j(-\omega_j)\mathbf{B}E_{j'}(\omega_{j'}) .$$
(8)

In the equations above, \bar{E}_j and E_j are the left and right eigenvectors of the excited state j, obtained by solving the CC eigenvalue equations

$$\mathbf{A}E_j(\omega_j) = \omega_j E_j(\omega_j) \quad \text{and} \quad \bar{E}_j(-\omega_j)\mathbf{A} = \omega_j \bar{E}_j(-\omega_j) \ . \tag{9}$$

The CC Jacobian matrix, \mathbf{A} , as well as the matrices \mathbf{A}^m and \mathbf{B} are partial derivatives of

the CC Lagrangian,⁷ and we refer to Table S1 in the SI for a summary of the CC building blocks. Additional definitions can be found in Refs. 7,9,40.

In order to apply Eq. (6), one must solve for the response amplitudes $t^{m_{\zeta}}$ at zero frequency, whereas solving for the $\bar{N}_{jj'}$ multipliers is necessary for Eq. (7). Since the $t^{m_{\zeta}}(0)$ vectors are also involved in the calculation of the \mathcal{B} term (and do not scale with the number of excited states), it is advantageous to use Eq. (6) to obtain the MCD \mathcal{A} term. Details on the implementation of the contractions needed to evaluate the above quantities for RI-CC2 in TURBOMOLE can be found in Refs. 43,44.

Continuing to follow the derivations for CC methods of Ref. 9, the \mathcal{B} term is calculated as

$$\mathcal{B}(0 \to j) = -\frac{1}{2} \varepsilon_{\alpha\beta\zeta} \operatorname{Im} \left({}^{\perp}T_{0j}^{\mu\alpha m_{\zeta}} T_{j0}^{\mu\beta} + T_{0j}^{\mu\alpha \perp} T_{j0}^{\mu\beta m_{\zeta}} \right) .$$
(10)

 ${}^{\perp}T_{0j}^{\mu_{\alpha}m_{\zeta}}$ and ${}^{\perp}T_{j0}^{\mu_{\beta}m_{\zeta}}$ are the (right and left) magnetic field-derivatives of the one-photon dipole transition moments⁴⁰

$${}^{\perp}T_{0j}^{\mu_{\alpha},m_{\zeta}} = \left. \frac{\mathrm{d}T_{0j}^{\mu_{\alpha}}}{\mathrm{d}B_{\zeta}} \right|_{\mathbf{B}=\mathbf{0}} = \left[\mathbf{G}t^{m_{\zeta}}(0)t^{\mu_{\alpha}}(-\omega_{j}) + \mathbf{F}^{m_{\zeta}}t^{\mu_{\alpha}}(-\omega_{j}) + \mathbf{F}^{\mu_{\alpha}}t^{m_{\zeta}}(0) \right] E_{j}(\omega_{j}) + \bar{M}_{j}(\omega_{j}) \left[\mathbf{A}^{\mu_{\alpha}}t^{m_{\zeta}}(0) + \mathbf{A}^{m_{\zeta}}(0)t^{\mu_{\alpha}}(-\omega_{j}) + \mathbf{B}t^{m_{\zeta}}(0)t^{\mu_{\alpha}}(-\omega_{j}) \right] + \omega_{j}^{m_{\zeta}}[\bar{M}_{j}(\omega_{j})t^{\mu_{\alpha}}(-\omega_{j})] + \bar{\xi}^{\mu_{\alpha}}(-\omega_{j}) \,^{\perp}E_{j}^{m_{\zeta}}(\omega_{j}, 0) + \bar{\xi}^{m_{\zeta}}(0)E_{j}^{\mu_{\alpha}}(\omega_{j}, -\omega_{j})$$
(11)

and

$${}^{\perp}T_{j0}^{\mu_{\alpha},m_{\zeta}} = \frac{\mathrm{d}T_{j0}^{\mu_{\alpha}}}{\mathrm{d}B_{\zeta}} = {}^{\perp}\bar{E}_{j}^{m_{\zeta}}(-\omega_{j},0)\xi^{\mu_{\alpha}} + \bar{E}_{j}(-\omega_{j})\mathbf{A}^{\mu_{\alpha}}t^{m_{\zeta}}(0) \ .$$
(12)

As before, we refer to Refs. 7,9,45 for definitions of most of CC building blocks, and only

draw attention to some of the relevant quantities for our discussion.

The term in Eq. (11) involving ω_j^m (*i.e.*, the derivative of the excitation energy with respect to the magnetic field) is only nonzero for a degenerate j, since ω_j^m corresponds to the definition of the excited-state expectation value $T_{jj}^{m_{\zeta}}$ of the imaginary angular momentum operator.

The first-order responses of the eigenvectors are determined according to^{9,10,40}

$$[\mathbf{A} - (\omega_j - \omega_j)\mathbf{1}]E_j^{\mu\alpha}(\omega_j, -\omega_j) = [\mathbf{A}^{\mu\alpha} + \mathbf{B}t^{\mu\alpha}(-\omega_j)]E_j(\omega_j)$$
(13)

$$\left(P_{j}[\mathbf{A} - (\omega_{j} + 0)\mathbf{1}]P_{j}\right) \ ^{\perp} E_{j}^{m_{\zeta}}(\omega_{j}, 0) = -P_{j}[\mathbf{A}^{m_{\zeta}} + \mathbf{B}t^{m_{\zeta}}(0)]E_{j}(\omega_{j}) \tag{14}$$

$${}^{\perp}\bar{E}_{j}^{m_{\zeta}}(-\omega_{j},0)\Big(P_{j}[\mathbf{A}+(0-\omega_{j})\mathbf{1}]P_{j}\Big) = -\bar{E}_{j}(-\omega_{j})[\mathbf{A}^{m_{\zeta}}+\mathbf{B}t^{m_{\zeta}}(0)]P_{j}.$$
(15)

The projector P_j removes singularities in the responses of the eigenvectors to the magnetic field $({}^{\perp}\bar{E}_j^m \text{ and } {}^{\perp}E_j^m)$ by projecting onto the orthogonal complement of the undifferentiated eigenvectors,^{9,10} as indicated by the \perp superscript:

$${}^{\perp}E_j^m = P_j E_j^m \tag{16}$$

$${}^{\perp}\bar{E}_j^m = \bar{E}_j^m P_j .$$
⁽¹⁷⁾

Generalized for a degenerate state j, P_j takes the form of the outer product of the eigenvectors summed over the set \mathcal{D}_j :

$$P_j = 1 - \sum_{j' \in \mathcal{D}_j} E_{j'} \otimes \bar{E}_{j'} .$$
⁽¹⁸⁾

In the case where j is not degenerate, \mathcal{D}_j is simply of size 1.

The implementation of the MCD \mathcal{B} term for non-degenerate cases and of the derivative transition moments for RI-CC2 in TURBOMOLE have been reported in Refs. 10 and 46, respectively. This has now been generalized for degenerate states by adding the $\omega_j^m[\bar{M}_j(\omega_j)t^\mu(-\omega_j)]$ contribution to $\mathcal{B}(0 \to j)$ for $j \in \mathcal{D}_j$, and by keeping the magnetic fieldderivatives of the eigenvector of state j orthogonal to the entire set \mathcal{D}_j according to Eq (18). The calculation of the \mathcal{A} term has also been added, together with an automated procedure to detect degeneracies.

Thus, in resonant response theory, the \mathcal{A} and \mathcal{B} terms are computed separately for each individual excited state and the ellipticity is put together according to Eq. (2).

2.2 Implementation of the quadratic response function

Alternative to the resonant approach, one can obtain the MCD ellipticity from damped response theory, either as the real part of the dipole-dipole-magnetic dipole damped quadratic response function^{24,36}

$$\theta_{\rm MCD} = -\omega \,\epsilon_{\alpha\beta\zeta} \,\mathrm{Re} \,\langle\langle\mu_{\alpha};\mu_{\beta},m_{\zeta}\rangle\rangle_{\omega+i\gamma,0} \tag{19}$$

or, equivalently, as the magnetic field-derivative of the damped dynamic polarizability⁹

$$\theta_{\rm MCD} = -\omega \,\epsilon_{\alpha\beta\zeta} \,\mathrm{Re} \left(\frac{\mathrm{d} \langle \langle \mu_{\alpha}; \mu_{\beta} \rangle \rangle_{\omega+i\gamma}}{\mathrm{d} B_{\zeta}} \right)_{\mathbf{B}=\mathbf{0}} \,. \tag{20}$$

The final working equations are the same.

In damped response theory, a finite lifetime of the electronically excited states is implemented by introducing a complex excitation energy. The generalization of standard to damped response theory is effectively carried out by making the replacement $^{12-14}$

$$\omega \to \omega + i\gamma \tag{21}$$

for all frequency-dependent components of the response functions. The damping factor γ is the inverse lifetime and takes an empirical value. Contributions from both the \mathcal{A} and \mathcal{B} terms are contained within the damped response function,⁴⁷ where also the band profiles are built into the formula in the form of Lorentzian broadening functions.^{13,48}

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Within CC theory, the quadratic response function⁷ can be expressed as

$$\langle \langle A; B, C \rangle \rangle_{\bar{\omega}_B, \bar{\omega}_C} = \frac{1}{2} \hat{C}^{\pm \omega} \Big[\mathbf{G} t^A(\bar{\omega}_A) t^B(\bar{\omega}_B) t^C(\bar{\omega}_C) + \frac{1}{2} \hat{P}^{ABC} \bar{t}^A(\bar{\omega}_A) \mathbf{B} t^B(\bar{\omega}_B) t^C(\bar{\omega}_C) + \frac{1}{2} \hat{P}^{ABC} \mathbf{F}^A t^B(\bar{\omega}_B) t^C(\bar{\omega}_C) + \hat{P}^{ABC} \bar{t}^A(\bar{\omega}_A) \mathbf{A}^B t^C(\bar{\omega}_C) \Big]$$
(22)

where $\bar{\omega}_A = -\bar{\omega}_B - \bar{\omega}_C$, the permutation operator \hat{P}^{ABC} symmetrizes with respect to permutations of the operators A, B, and C together with the accompanied frequencies, and $\hat{C}^{\pm\omega}$ symmetrizes with respect to a change of sign of the real parts of the frequencies (denoted by ω_A , ω_B , and ω_C) followed by complex conjugation. While $\bar{\omega}_C$ is assumed to be real, the frequencies $\bar{\omega}_A$ and $\bar{\omega}_B$ can be either real or complex. In the former case, the quadratic response function is purely real or purely imaginary (depending on the combination of A, B and C), and the building blocks are computed according to standard response theory. An example of an observable that can be calculated from the standard formulation of the quadratic response function with real frequencies is the ground state hyperpolarizability. For the case that $\bar{\omega}_A$ and $\bar{\omega}_B$, on the other hand, are complex, we allow the replacement of Eq. (21) and the response function becomes complex, *i.e.*, damped. It follows that the implementation of the damped quadratic response function of Eq. (19) is a (conceptually) simple generalization of the implementation for real frequencies.

To compute the MCD ellipticity from the damped quadratic response function according to Eq. (19) the frequencies are set to $\bar{\omega}_B = \omega + i\gamma$ and $\bar{\omega}_C = 0$, and we thus need both damped response amplitudes and damped response multipliers. In other words, we must solve the right and left linear response equations for the dipole moment operator with complex frequencies, i.e.

$$\left[\mathbf{A} - (\omega + i\gamma)\mathbf{1}\right]t^{\mu}(\omega + i\gamma) = -\xi^{\mu} \tag{23}$$

$$\bar{t}^{\mu}(-\omega - i\gamma) \left[\mathbf{A} - (\omega + i\gamma) \mathbf{1} \right] = -\eta^{\mu} - \mathbf{F} t^{\mu}(-\omega - i\gamma) \equiv -\bar{\xi}^{\mu}(-\omega - i\gamma) .$$
(24)

In the RI-CC2 implementation in TURBOMOLE, the above response equations are effectively solved only in the space of single excitations, *i.e.*, only the singles components of all vectors are explicitly computed and stored; contributions from the doubles are computed on-the-fly. The derivation and implementation of Eq. (23) for (RI-)CC2 in TURBOMOLE are described in detail in the work by Fedotov et al.¹⁵ It boils down to iteratively solving the effective linear CC2 response equations for the singles amplitudes

$$\begin{bmatrix} \mathbf{A}_{SS}^{\text{eff}} - \omega \mathbf{1}_{SS} & -\mathbf{\Gamma}_{SS}^{\text{eff}} + \gamma \mathbf{1}_{SS} \\ \mathbf{\Gamma}_{SS}^{\text{eff}} - \gamma \mathbf{1}_{SS} & \mathbf{A}_{SS}^{\text{eff}} - \omega \mathbf{1}_{SS} \end{bmatrix} \begin{bmatrix} t_{R,S}^{\mu} \\ t_{I,S}^{\mu} \end{bmatrix} = -\begin{bmatrix} \xi_{R,S}^{\mu,\text{eff}} \\ \xi_{I,S}^{\mu,\text{eff}} \end{bmatrix}$$
(25)

where the ω - and γ -dependent effective matrices are defined as

$$\mathbf{A}_{SS}^{\text{eff}}(\omega,\gamma) = \mathbf{A}_{SS} - \mathbf{A}_{SD} \frac{\Delta}{\Delta^2 + \gamma^2} \mathbf{A}_{DS}$$
(26a)

$$\mathbf{\Gamma}_{SS}^{\text{eff}}(\omega,\gamma) = -\mathbf{A}_{SD} \frac{\gamma}{\Delta^2 + \gamma^2} \mathbf{A}_{DS}$$
(26b)

with the diagonal matrix $\Delta = \mathbf{A}_{DD} - \omega \mathbf{1}_{DD}$ and the effective right hand sides (RHS)

$$\xi_{R,S}^{\mu,\text{eff}}(\omega,\gamma) = \xi_{R,S}^{\mu} - \mathbf{A}_{SD} \frac{\Delta}{\Delta^2 + \gamma^2} \xi_{R,D}^{\mu} + \mathbf{A}_{SD} \frac{\gamma}{\Delta^2 + \gamma^2} \xi_{I,D}^{\mu}$$
(27a)

$$\xi_{I,S}^{\mu,\text{eff}}(\omega,\gamma) = \xi_{I,S}^{\mu} - \mathbf{A}_{SD} \frac{\Delta}{\Delta^2 + \gamma^2} \xi_{I,D}^{\mu} - \mathbf{A}_{SD} \frac{\gamma}{\Delta^2 + \gamma^2} \xi_{R,D}^{\mu} .$$
(27b)

Above and in the following, indices R and I label the real and imaginary component of the given vectors (e.g., $t = t_R + it_I$), and subscripts S and D refer to the singles and doubles spaces, respectively.

The corresponding derivation of the (RI-)CC2 response multiplier equations for complex frequencies, Eq. (24), is discussed in detail in Section S5 in the SI. In compact matrix form, the effective damped CC2 multiplier equations of Eq. (24) become

$$\begin{bmatrix} \bar{t}_{R,S}^{\mu} & \bar{t}_{I,S}^{\mu} \end{bmatrix} \begin{bmatrix} \mathbf{A}_{SS}^{\text{eff}} - \omega \mathbf{1}_{SS} & \mathbf{\Gamma}_{SS}^{\text{eff}} - \gamma \mathbf{1}_{SS} \\ -\mathbf{\Gamma}_{SS}^{\text{eff}} + \gamma \mathbf{1}_{SS} & \mathbf{A}_{SS}^{\text{eff}} - \omega \mathbf{1}_{SS} \end{bmatrix} = -\begin{bmatrix} \bar{\xi}_{R,S}^{\mu,\text{eff}} & \bar{\xi}_{I,S}^{\mu,\text{eff}} \end{bmatrix}.$$
(28)

and the effective RHSs take the form

$$\bar{\xi}_{S}^{R,\text{eff}} = \bar{\xi}_{S}^{R} - \bar{\xi}_{D}^{R} \frac{\Delta}{\Delta^{2} + \gamma^{2}} \mathbf{A}_{DS} + \bar{\xi}_{D}^{I} \frac{\gamma}{\Delta^{2} + \gamma^{2}} \mathbf{A}_{DS} , \qquad (29a)$$

$$\bar{\xi}_{S}^{I,\text{eff}} = \bar{\xi}_{S}^{I} - \bar{\xi}_{D}^{I} \frac{\Delta}{\Delta^{2} + \gamma^{2}} \mathbf{A}_{DS} - \bar{\xi}_{D}^{R} \frac{\gamma}{\Delta^{2} + \gamma^{2}} \mathbf{A}_{DS} .$$
(29b)

In connection with the current work, the convergence of the iterative solution of the CC2 response equations has been improved by determining the coefficients for the expansion of the solution vectors on the basis of the trial vectors by the requirement that the residual in the full space is minimized, instead of solving (as otherwise described in Ref. 15) the equations projected to the subspace of trial vectors. For further details, we refer to Section S6 in the SI.

After computation of the (singles only) complex response amplitudes and multipliers via Eqs. (23) and (24), the damped response function for MCD is constructed. The first term of Eq. (22) is the contractions of three response vectors with the **G** matrix: $\mathbf{G}t^{\mu\alpha}(\omega + i\gamma)t^{\mu\beta}(-\omega - i\gamma)t^{m_{\zeta}}(0)$. For details on the implementation of the **G**-matrix contractions, see Section S7. The contraction of the **B** matrix with one (complex) vector from the left and two from the right in the second term of Eq. (22) is evaluated analogously to the **F**-matrix contractions described in Ref. 49. There, the singles components of $\sigma(\bar{t}^x, t^y)$ are contracted with the singles components of the t^z amplitudes, whereas the contraction of the doubles is evaluated directly from the intermediates for constructing $\sigma(\bar{t}^x, t^y)_D$, thereby avoiding the storage of any doubles intermediates. For the **B**-matrix contractions, the unperturbed Lagrange multipliers are replaced by response multipliers, and a contribution that originates from the projection onto the Hartree-Fock state is skipped.

The last two terms of Eq. (22) are rewritten as contractions between complex perturbed one-particle densities and one-electron integrals⁴⁹:

$$\mathbf{F}^{\mu_{\alpha}} t^{\mu_{\beta}} (-\omega - i\gamma) t^{m_{\zeta}}(0) = \hat{h}^{\mu_{\alpha}} D^{F} (t^{\mu_{\beta}}, t^{m_{\zeta}}) , \qquad (30)$$

$$\bar{t}^{\mu\alpha}(\omega + i\gamma)\mathbf{A}^{\mu\beta}t^{m_{\zeta}}(0) = \hat{h}^{\mu\beta}D^{A}(\bar{t}^{\mu\alpha}, t^{m_{\zeta}}) .$$
(31)

The generalization of the implementation for the damped quadratic response function entailed generalizing the construction of the RHS for the response multiplier equations, the **G**-matrix contraction routines to handle two complex vectors, the **B**-matrix contraction routines to handle complex vectors from the left, the D^F density to handle complex amplitudes, and the D^A density to handle complex multipliers. The generalization of the latter also involved the on-the-fly evaluation of the doubles parts of the complex response vectors.

3 Computational details

To illustrate the results, we examined the Zink Tetrabenzoporphyrin (ZnTBP) complex in a planar geometry of D_{4h} symmetry, sketched in Figure 1. A DFT-optimized geometry was obtained from Ref. 50 and reoptimized at the MP2/cc-pVTZ level of theory. The MCD spectra were computed with both resonant and damped response using a development version of TURBOMOLE 7.6.^{35,51} The molecule was treated in its largest Abelian point group, D_{2h} , and the aug-cc-pVDZ basis set^{52,53} was applied as orbital and auxiliary basis for H, C, and N. The energy-consistent pseudo potential (ECP) for Zn from Figgen et al.⁵⁴ was used in combination with the aug-cc-pVDZ-PP basis set⁵⁵ for both the orbital and auxiliary basis.

In the resonant response calculations, the MCD \mathcal{B} terms were computed with the preexisting implementation,¹⁰ whereas the \mathcal{A} terms were obtained using our new contribution to the program. Lorentzian broadening functions were applied to the resonant results such that

$$g(\omega, \omega_j) = \frac{1}{\pi} \frac{\gamma}{(\omega - \omega_j)^2 + \gamma^2}$$
(32)

$$\frac{\partial g(\omega, \omega_j)}{\partial \omega} = -\frac{2}{\pi} \frac{(\omega - \omega_j)\gamma}{\left[(\omega - \omega_j)^2 + \gamma^2\right]^2} \,. \tag{33}$$

By setting the half-width-at-half-maximum (HWHM) in the lineshape functions equal to the damping factor applied in damped calculations, one obtains identical spectra from resonant and damped response, provided the latter is multiplied by a factor of π^{-1} . A damping factor of $4.5563 \cdot 10^{-3}$ au ($\approx 1000 \text{ cm}^{-1}$), as often used in the literature, was applied. The stick spectra were broadened with an HWHM of the same value, unless otherwise stated.

The 18 lowest electronically excited states were converged for resonant response; 8 of B_{2u} , 8 of B_{3u} , and 2 of B_{1u} symmetries. Oscillator strengths were calculated for all 18 states, while the MCD terms were calculated for the lowest 15 states. With the damped approach, the high-energy spectrum was initially built between 0.15 and 0.30 a.u. with a distance of 0.01 a.u. between the grid points. To obtain a higher resolution of some spectral features, additional grid points were calculated in the ranges 0.145–0.18 a.u. and 0.19–0.23 a.u., such that the separation between points in these intervals was 0.005 a.u. The damped spectrum was drawn by cubic interpolation of the grid points. The absorption and MCD spectra



Figure 1: Zinc Tetrabenzoporphyrine (ZnTBP).

obtained from interpolation of the coarse grid are depicted in Figure S1. All raw data are available in the SI.

All calculations were carried out with the frozen core approximation. For the damped calculations, a convergence threshold of 10^{-4} was applied for both the linear equations and the numerical Laplace transformation; the qualitative results were found to be rather insensitive to the threshold. In the resonant case, the residuals of the eigenvalue and linear equations were converged below thresholds of 10^{-8} and 10^{-6} , respectively.

4 Results and discussion

4.1 Absorption and MCD Spectra

The ZnTBP molecule was chosen as an illustrative example due to the availability of an experimental MCD spectrum reaching energies as high as 8 eV ($65\,000 \text{ cm}^{-1}$), 56 covering what is referred to as the Q- ($15\,800-18\,000 \text{ cm}^{-1}$), B- ($23\,500-29\,000 \text{ cm}^{-1}$), N-, L-, and X-band ($28\,000-65\,000 \text{ cm}^{-1}$) regions. 56,57 The experimental measurements were carried out in an Argon matrix. It is noted that in the experiment, several nonequivalent sites in the Argon matrix together with crystal field (CF) splitting result in absorption and MCD spectra with a rich structure. 56 This is not reproduced by the calculations carried out in gas phase. The Q- and B-band regions also reveal vibrational overtones in the experimental measurements. 56

The simulated absorption and MCD spectra in the full energy range are depicted in Figure 2, where the broadened stick spectra cover the Q-, B-, N-, and L-bands, while the N-, L-, C-, and X-bands are covered by the damped results. An overlap between the resonant and damped spectra ensures a complete description.

While the electronic transitions of the Q- and B-bands are well separated, the spectrum above 4 eV convolutes more close-lying states. Especially the C- and X-band regions contain a high density of states stemming from the large aromatic system of the TBP ligand. In the absorption spectrum of Figure 2, it is seen that the B-band has much higher intensity than 72



Figure 2: ZnTBP. Absorption (lower panel) and MCD (upper panel) spectra from standard (blue) and damped (red) response in the energy region 2-8 eV ($15\,000-65\,000 \text{ cm}^{-1}$. Energies have been shifted by -0.349 eV (-2818 cm^{-1}).

the Q-band, consistent with previous findings.⁵⁶ The MCD spectrum is predominantly given by \mathcal{A} terms, occurring in all bands except the X-band. The \mathcal{A} terms are positive, as it can be seen from the negative wing at lower energies.

Experimental absorption and MCD spectra in three energy ranges are shown alongside the theoretical ones in Figures 3 and 4, respectively. The broadening factors of the stick spectra in the low- and mid-energy panels have been reduced to the values indicated in the figure captions to be comparable to experiment which reports very high resolution of the Qand B-bands.⁵⁶

All theoretical spectra have been red-shifted by $0.35 \text{ eV} (2818 \text{ cm}^{-1})$ to align the first absorption peak with the corresponding peak of the major matrix site of the Q-band in the experimental absorption spectrum (Figure 3, upper left panel). The size of this shift is considered to be within what can be attributed to environmental effects, the deviation between computed vertical excitation energies and experimental band maxima in addition to the general overestimation of excitation energies within CC2.^{58,59} The shift also aligns the maxima of the C- and X-bands in the high-energy region fairly well with experiment, although the separations between the spectral features in the simulated spectrum are slightly larger. Nevertheless, the features are well reproduced by our calculations. The MCD in the N-band region is, however, far more pronounced in the simulated spectrum. A better fit could be brought about by increasing the damping factor, *i.e.*, the broadening of the spectrum.

The (shifted) B-band is located approximately $0.12 \text{ eV} (994 \text{ cm}^{-1})$ to the red of the corresponding peak in experiment, indicating that the computed energy gap between the first and second peak is too small. This is again within the error of CC2. If we align the spectra according to the B-band instead of the Q-band, the overall red shift is reduced to $0.23 \text{ eV} (1825 \text{ cm}^{-1})$. However, this worsens the alignment of the high-energy region. Spectra shifted to align with the B-band are available in Figures S2 and S3 in the SI.

While the spectrum that convolutes the excitations underlying the X-band in the absorption spectrum is of similar intensity as the C-band, the MCD spectrum above 6 eV has a much lower intensity and is less rich in features. Looking at the lower panel in Figure 4, we see that a flattening of the spectrum in the X-band region is also observed experimentally. This observation suggests that this part of the spectrum is made of \mathcal{B} terms, *i.e.*, the convoluted states are non-degenerate, as the \mathcal{B} terms are usually (much) smaller than the \mathcal{A} terms, as previously mentioned. Figure 5 shows separate broadened \mathcal{A} - and \mathcal{B} -term spectra to illustrate this point. Note that the spectra are plotted on individual y axes. Interestingly, the \mathcal{B} term spectrum reveals two oppositely signed terms of same magnitude between 4-4.5 eV (N-band region), a phenomenon referred to as a pseudo- \mathcal{A} term.⁶⁰ It has here its origin in two ¹E_u states that contribute to the N-band which are only separated by $\approx 0.1 \text{ eV}$ and coupled with a non-vanishing transition moment for the z component of the magnetic



Figure 3: ZnTBP. Absorption spectra in three energy regions with experimental spectra from Ref. 56. Theoretical energies have been shifted by $-0.349 \text{ eV} (-2818 \text{ cm}^{-1})$. HWHMs of 7 cm⁻¹ (Q-band, upper left), 20 cm⁻¹ (B-band, upper right), and 1000 cm⁻¹ (N-X region, lower panel). The experimental spectra are presented without ε values.

dipole operator.

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In the experiment, it is reported that the zero-crossings of the MCD spectra do not fully coincide with the maxima in the absorption spectra, as is exhibited by true \mathcal{A} terms.⁵⁶ The observed shift is attributed to symmetry-lowering effects arising from Jahn-Teller effects and CF splitting. The lowering of symmetry lifts the degeneracy between the pairs, which now instead appear as close-lying \mathcal{B} terms of equal magnitude and opposite sign, *i.e.*, as pseudo- \mathcal{A} terms. Meanwhile, the splitting of the degenerate pair affects the absorption spectrum by resulting in two transitions with oscillator strengths that are likely to be different. This



Figure 4: ZnTBP. MCD spectra in three energy regions with experimental spectra from Ref. 56. Theoretical energies have been shifted by $-0.349 \text{ eV} (-2818 \text{ cm}^{-1})$. HWHMs of 7 cm⁻¹ (Q-band, upper left), 20 cm⁻¹ (B-band, upper right), and 1000 cm⁻¹ (N-X region, lower panel). The experimental spectra are presented without θ values.

alters the position of the absorption maxima compared to the fully symmetric structure. Also, the superposition of nearby bands with different intensities in absorption and different ellipticities for MCD contributes to shifts between the maxima in the absorption and zerocrossings in the MCD spectra. All in all, one cannot, even at the most accurate theoretical level, expect a complete agreement with the experimental spectra used for comparison in the current work, since the experimental measurements do not reflect the perfectly symmetric molecule applied in the calculations. That the zero-crossing of the pseudo- \mathcal{A} term feature under the (shifted) N-band (~ 4.1 eV) in the calculated spectrum aligns almost perfectly



Figure 5: ZnTBP. MCD \mathcal{A} (left y-axis, light blue) and \mathcal{B} (right y-axis, navy) spectra. The sticks are $-\mathcal{B}$ terms scaled by a factor of 8 for visibility. Energies have been shifted by $-0.349 \text{ eV} (-2818 \text{ cm}^{-1})$.

with the experimental one is mostly coincidental.

Since this is a showcase example, and ZnTBP is a well-studied system, ${}^{50,61-64}$ we will not go further into analyzing the spectra.

4.2 Timings

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For the evaluation of the time consumption of the two approaches, a damped calculation was carried out with a real frequency of 0.20 a.u. and a damping factor of $4.5563 \cdot 10^{-3}$ a.u.. The frequency of 0.20 a.u. lies in the upper L-band region, right "at the border" with the spectrally dense region. The resonant calculations were carried out for the lowest-energy degenerate set consisting of the first transitions of B_{2u} and B_{3u} symmetry.

These calculations were carried out in shared-memory (OpenMP) parallel modality on 40 cores of two Intel Xeon Gold 6230 CPUs running at 2.1 GHz.

4.2.1 Calculation of the quadratic response function

Table 1 summarizes the timings of a calculation of the quadratic response function with one complex frequency as well as a calculation with only a real frequency. Two RHSs, two sets of linear equations, four types of densities, and two types of matrix contractions are involved, see the table for details. The ground state amplitudes, multipliers, and densities, the RHSs and linear solvers for the static magnetic perturbation, and the densities only perturbed by the magnetic dipole are all independent of the number of complex frequencies. The remaining components scale linearly.

It is clearly seen that the most time-consuming steps are the computation of the densities and matrix-vector contractions for building the quadratic response function: more than 70% of the total wall time was spent by those operations in both the real and complex cases. From the timings it is observed that the RHSs and matrix-vector contractions take roughly twice as long for the complex response function, while the left- and right-hand transformations are faster when the frequency is complex. We note that the linear solver required nearly twice as many iterations for converging the response equations without a damping factor.

For an approximate evaluation of the time demand per frequency, we subtract from the total wall time the frequency-independent steps mentioned previously. This amounts to almost 35 hours per complex frequency and 24 hours per real frequency. There is thus only a 50% increase in the time consumption from regular to damped quadratic response, demonstrating the efficiency of the implementation of damped response theory.

4.2.2 State-by-state calculation

The timings from the resonant calculation are summarized in Table 2. Note that no timings for the CC eigenequations are reported; in the setup, these were solved in a sequence of a CCS pre-optimization, a quasi-linear CC2 pre-optimization, and a final DIIS eigensolver for the non-linear eigenvalue problem for $\mathbf{A}_{SS}^{\text{eff}}$.

In a resonant calculation, four sets of linear equations are solved and their respective

Table 1: ZnTBP. Timings from a regular and damped quadratic response calculation with $\omega = 0.20$ au and $\gamma = 4.5563 \cdot 10^{-3}$ au. Data for right-hand sides (RHS), right- and left-hand transformations (RHTR, LHTR), densities, and contractions, along with the number of vectors, densities, or contractions of the given 'Type', as well as the scaling of the number of 'Types' with the number of frequencies, $n_{\rm freq}$. Times are normalized over all symmetries and/or permutations; "int." = intermediate(s).

| Туре | Time (damped) | Time (regular) | Unit | # | Scaling |
|---|---------------|----------------|--------------|----|----------------------|
| RHS (t^A) | 363.58 | 175.00 | sec/vec | 9 | $3 + 6 n_{\rm freq}$ |
| RHS (\bar{t}^A) | 471.26 | 234.39 | sec/vec | 9 | $3 + 6 n_{\rm freq}$ |
| RHTR (t^A) | 37.69 | 62.59 | sec/iter/vec | 18 | $2 n_{\rm RHS}$ |
| LHTR (\bar{t}^A) | 37.22 | 42.28 | sec/iter/vec | 18 | $2 n_{\rm RHS}$ |
| $D^{\eta}(\bar{t}, t^A) + \text{int. for } D^F$ | 814.60 | 506.93 | m sec/dens | 9 | $3 + 6 n_{\rm freq}$ |
| $D^F(\bar{t}, t^A, t^B)$ | 0.24 | 0.11 | m sec/dens | 18 | $18 n_{\rm freq}$ |
| $D^{\xi}(\bar{t}^A, t) + \text{int. for } D^A$ | 1392.87 | 806.60 | m sec/dens | 9 | $3 + 6 n_{\rm freq}$ |
| $D^A(\bar{t}^A, t^B)$ | 1651.43 | 1226.67 | seco/dens | 36 | $36 n_{\rm freq}$ |
| $ar{t}^A {f B} t^B t^C$ | 1114.67 | 586.21 | sec/contr | 18 | $18 n_{\rm freq}$ |
| $\mathbf{G} t^A t^B t^C$ | 123.83 | 67.67 | sec/contr | 6 | $6 n_{\rm freq}$ |

RHSs are built. For putting together the MCD ellipticity, 10 densities are computed and four matrix-vector contractions are carried out, see Table 2 for details. Besides the calculations related to just the ground state, only the RHS and linear solver for the magnetic fieldperturbed amplitudes are state-independent. All remaining steps scale linearly with the number of excited states.

Again, the computation of the property building blocks takes up a large part of the total wall time, amounting to 50% of the total wall time in the presented case. This is 20 percentage points less than observed for the quadratic response function and is a reflection of the substantial amount of additional linear equations that are required for the state-by-state approach, besides, of course, the lower computational cost and scaling of the densities.

The time required per resonant state was approximately 9 hours. This measure represents a lower limit for the cost of the resonant approach. As the number of requested states increases, so will the number of iterations required before reaching convergence in the eigenand linear solvers.

Table 2: ZnTBP. Timings from a resonant response calculation of the MCD of the first degenerate set of excited states. Data for right hand sides (RHS), right- and left hand transformations (RHTR, LHTR), densities and contractions, along with the number of vectors, densities, or contractions of the given 'Type'. Times are normalized over all symmetries and/or permutations. "int." = intermediate(s)

| Туре | Time | Unit | # |
|--|---------|--------------------------|----------------|
| RHS (\bar{M}_i) | 115.44 | seconds/vector | 2 |
| RHS (t^A) | 194.25 | seconds/vector | 7 |
| RHS (E_i^A) | 956.55 | seconds/vector | 8 |
| RHS (\vec{E}_i^A) | 309.58 | seconds/vector | 4 |
| LHTR (\bar{M}_j) | 53.37 | seconds/iteration/vector | 2 |
| RHTR (t^{A}) | 80.61 | seconds/iteration/vector | $\overline{7}$ |
| RHTR (E_i^A) | 360.03 | seconds/iteration/vector | 12 |
| LHTR (\bar{E}_{j}^{A}) | 25.45 | seconds/iteration/vector | 8 |
| $D^{\xi}(\bar{E}_j, t)$ + int. for $D^A(\bar{E}_j, t^A)$ | 47.70 | seconds/density | 2 |
| $D^{\xi}(\bar{M}_j, t) + \text{int. for } D^A(\bar{M}_j, t^A)$ | 50.10 | seconds/density | 2 |
| $D^{\eta}(\bar{t}, E_j^A)$ | 1381.28 | seconds/density | 8 |
| $D^{\eta}(\bar{t}, E_j) + \text{int. for } D^F(\bar{t}, E_j, t^A)$ | 85.80 | seconds/density | 2 |
| $D^{\eta}(\bar{t}, t^A)$ + int. for $D^F(\bar{t}, E_j, t^A)$ | 691.89 | seconds/density | 7 |
| $D^A(\bar{E}_j, t^A)$ | 697.50 | seconds/density | 4 |
| $D^A(\bar{M}_j, t^A)$ | 699.90 | seconds/density | 8 |
| $D^A(\bar{E}_j, E_{j'})$ | 103.20 | seconds/density | 2 |
| $D^F(\bar{t}, E_j, t^A)$ | 0.11 | seconds/density | 8 |
| $D^{\xi}(\bar{E}_{j}^{A},t)$ | 1040.70 | seconds/density | 4 |
| $\bar{M}_j \mathbf{B} t^A t^B$ | 428.86 | seconds/contraction | 4 |
| $\mathbf{F} E_i^A t^B$ | 530.28 | seconds/contraction | 8 |
| $\bar{E}_j \check{\mathbf{B}} t^A E_{j'}$ | 233.74 | seconds/contraction | 6 |
| $\mathbf{G}E_{j}t^{A}t^{B}$ | 105.50 | seconds/contraction | 4 |

5 Concluding remarks

We have presented the implementation of the MCD \mathcal{A} term and of the quadratic response function for real and complex frequencies to include the damped response case for MCD at the (RI-)CC2 level of theory in Turbomole.^{35,51} We applied them to the highly symmetric ZnTBP molecule to show how a combination of resonant and damped response theory can be used to compute efficiently MCD spectra for relatively large chromophores. By combining the resonant and damped response results, the absorption and MCD spectra have been simulated in the region 2–8 eV (16 000–65 000 cm⁻¹) and compared to experimental data from the literature. Good agreement was found between the theoretical and experimental spectra, where the errors of the computed excitation energies were assigned to the neglect of environmental effects, deviations between vertical excitations and band maxima, as well as the general error of CC2.

Timings have been reported for a resonant calculation of a set of degenerate states and for a damped calculation with one complex frequency. It was found that the computation of the building blocks of the final property is by far the most time-consuming for both the resonant and damped case, although the former spends thrice the amount of percentage points on the construction of RHSs compared to the damped approach.

The final recommendation for the application of our procedure is to use the resonant approach for the low-energy region of the MCD spectrum, where the density of states is typically low and the resonant approach is expected to be the most efficient one. The spectrum is then extended to higher energies by producing a grid of cross sections with damped calculations. An overlap with the low-energy spectrum is advised for a complete description of the spectrum. The damping factor can be chosen based on the resolution of an experimental spectrum. If no experiment is available, or if no resolution is reported, a factor of 1000 cm⁻¹ typically gives a reasonable theoretical spectrum. The step size should roughly correspond to the damping factor. In the current work, this was the case in regions with stronger spectral features, while less rich regions were treated with a step twice this size.

For the damped spectrum, an initial calculation with larger damping factor and smaller basis can be used to identify important regions in the spectrum that need a denser grid or smaller damping factor. At least, it is beneficial to first produce a coarse grid and then supplement it with more points in regions where more pronounced spectral features are expected.

Furthermore, it should be exploited that the damped approach can be used at any frequency interval (including the X-ray regime), meaning that several batches of, *e.g.*, four complex frequencies each, can be carried out simultaneously, thereby scanning a large frequency range in a (relatively) short amount of time. It is our experience that a cubic spline provides the best interpolation of the data points with respect to reproducing a broadened stick spectrum and avoiding an overfitting of the parameters.

Supporting Information Available

Cartesian coordinates, numerical data, additional figures, generalization of response multipliers equations, reduced space residual minimization, **G**-matrix contractions.

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5.4 MANUSCRIPT II

"Insights into localization, energy ordering, and substituent effect in excited states of azobenzenes from coupled cluster calculations of nuclear spin-induced circular dichroism"

Josefine H. Andersen, C. Hättig, S. Coriani, and P. Štěpánek **2023** (*Submitted*)

Supporting information can be found in Appendix B.
Insights into localization, energy ordering, and substituent effect in excited states of azobenzenes from coupled cluster calculations of nuclear spin-induced circular dichroism

Josefine H. Andersen,¹ Christof Hättig,² Sonia Coriani,³ and Petr Štěpánek⁴

¹⁾DTU Chemistry, Technical University of Denmark, Kemitorvet Building 207, DK-2800 Kongens Lyngby, Denmark

²⁾Arbeitsgruppe Quantenchemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

³⁾DTU Chemistry, Technical University of Denmark, Kemitorvet, Building 207, DK-2800 Kongens Lyngby, Denmark^{a)}

⁴⁾NMR Research Unit, Faculty of Science, University of Oulu, PO Box 3000, FI-90014 Oulu, Finland^{b)}

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Nuclear spin-induced circular dichroism (NSCD) is a molecular effect of differential absorption of left- and right-circularly polarized light due to nuclear spins in the molecule. In this work, new tools for its calculation are presented. Analytic expressions for the computation of the \mathcal{B}_K term of NSCD have been derived and implemented for the second-order coupled cluster singles and doubles (CC2) model. NSCD results obtained thereby for three derivatives of azobenzenes have been compared with results from time-dependent density functional theory (TD-DFT). The complementary information that could be obtained from NSCD measurements compared to NMR for these three species is discussed.

^{a)}soco@kemi.dtu.dk

 $^{^{\}rm b)}$ petr.stepanek@oulu.fi

I. INTRODUCTION

Nuclear magneto-optic (NMO) effects are molecular properties that arise as a consequence of the simultaneous interaction of the molecular electronic cloud with a beam of light and with the nuclear magnetic moments. They manifest as a change in the polarization state of the probing beam of light as it passes through a sample with anisotropically oriented nuclear magnetic moments.^{1–21}

The character of the change of the polarization induced in the light beam depends on the NMO effect. Nuclear spin-induced optical rotation (NSOR) is a circular birefringence that rotates the plane of polarization of the light beam.^{1,4,14,19} The nuclear Cotton-Mouton-like effects are linear birefringences and cause the linearly polarized beam to acquire an ellipticity.^{2,5,10–12} Nuclear spin-induced circular dichroism (NSCD) is the differential absorption of the left- and right-circularly polarized (LCP, RCP) components.^{15,17}

NSCD is particularly different from the other NMO effects mentioned above in that it is a property that only occurs when the wavelength of the light beam corresponds to the energy of a transition between two electronic states. In other words, NSCD only appears in the energy region of electronic absorption bands, which is usually in the visible or near ultraviolet (UV/vis) frequency range. In contrast, the other known NMO effects are birefringences and are also present in dispersive regions.

Broadly speaking, NSCD can be seen as a localized version of classical magnetic circular dichroism (MCD).^{22–27} In MCD the sample exhibits different coefficients of molar absorption for the LCP and RCP components of light when it is placed in a magnetic field with a component parallel to the path of the propagation of the beam.²⁶ In NSCD, the magnetic field perturbation is not introduced from the outside, but from within the molecule by the individual nuclear magnetic moments. In analogy to MCD, NSCD is then observed when the average magnetization of the sample from the nuclear magnetic moments is at least partially aligned with the direction of the light beam.¹⁵

Since NSCD arises from differential absorption coefficients for RCP and LCP, a proper characterization of the excited states is important for its faithful description. In addition, since it also involves interactions with the nuclear magnetic moments via a hyperfine interaction operator (\hat{h}^{hf}) , capturing the electronic properties near the nucleus is also essential. This places a high demand on the basis set as well as on the computational method. The calculation of NSCD spectra has so far only been implemented within the framework of time-dependent (TD-) density functional theory (DFT).^{15,20} One TD-DFT protocol for NSCD is based on the complex polarization propagator (CPP) method.^{28,29} This approach allows to simulate directly the absorption spectra with broadened bands and to investigate regions of arbitrary energy without the explicit need to calculate all excited states of lower energy. However, it partly obscures the contributions of individual excited states as the resulting spectrum is a sum of all contributions that are implicitly convoluted with Lorentzian broadening bands. More recently, a TD-DFT quadratic-response-based approach has been developed for calculating the NSCD strengths of individual transitions.²⁰ This approach produces NSCD data in the form of "stick spectra", *i.e.*, NSCD strengths of a particular nucleus K over a given set of excited states, known as NSCD \mathcal{B}_K terms.

(TD-)DFT methods depend on the choice of functional, which is still often designed in a semi-empirical way for specific properties and/or molecular systems, and, as such, it is hard to improve in a systematic way. The reliable performance of a certain functional for new properties is therefore not assured. Oftentimes, (TD-)DFT methods need to be benchmarked against high-end methods, such as those based on the coupled cluster (CC) ansatz.³⁰ The fully *ab initio* CC methods do not contain or require *a priori* assumptions about the nature of the studied system, which are common in the construction of many DFT functionals. Thus, CC methods treat different molecules on more equal footing and provide less biased results compared to DFT, which on the other hand can be sensitive to particular combinations of molecules and functionals. The CC ansatz also offers a clear and systematic path toward the full theoretical limit, though at the price of a steep increase in the computational costs moving up the hierarchy of CC approximations. However, the CC model only provides a good approximation when the system can be well described by a single determinant.

Among the CC approximations, the second-order approximate coupled cluster singles and doubles model $(CC2)^{31-33}$ has emerged as a cost-effective and relatively accurate approach for a variety of molecular properties and UV/vis spectra of medium-to-large molecular systems. It is our goal here to present a method to calculate stick spectra of NSCD based on the CC ansatz, with a specific implementation at the CC2 level. The approach gives access to NSCD values for specific excited states, and it can be used for direct investigation of moderately-sized molecules and as a first benchmark for DFT models. It is based on a generalization

of the resolution-of-identity CC2 (RI-CC2)^{32,33} implementation of the MCD \mathcal{B} term³⁴ in Turbomole³⁵ to the computation of the NSCD \mathcal{B}_K term. The new RI-CC2 protocol is applied to a selection of para-substituted azobenzenes and its results are compared to those obtained with TD-DFT using the BH+HLYP functional.^{36,37}

II. THEORY

Since NSCD can be considered as magnetic circular dichroism induced by the nuclear spin, the mathematical expressions for its fundamental molecular descriptors can be derived along the lines of the derivation of conventional circular dichroism induced by an external (static) magnetic field. Buckingham and Stephens²² were first to obtain the sum-over-states (SOS) expressions for the Faraday \mathcal{A} , \mathcal{B} , and \mathcal{C} terms of MCD. For closed-shell molecular systems with no degenerate ground or excited states, only the \mathcal{B} term is of relevance.^{22–25,27}

Early attempts to compute the MCD terms were based on such SOS expressions. It was later shown³⁸ that the \mathcal{B} term can be obtained from the first-order residues of a quadratic response function involving the electric dipole operator ($\hat{\mu}$) and, in a non-relativistic context, the orbital Zeeman interaction operator (relative to a common origin O), $\hat{h}^{OZ} = \frac{e}{2m_e} \sum_i \hat{l}_{iO}$ (\hat{l}_{iO} being the angular momentum operator relative to the origin O). For a given electronic transition from state 0 to state f with an excitation energy of frequency ω_f , this is expressed as follows:

$$\mathcal{B}(0 \to f) = i\varepsilon_{\alpha\beta\gamma} \lim_{\omega \to \omega_f} (\omega - \omega_f) \langle \langle \hat{\mu}_{\alpha}; \hat{\mu}_{\beta}, \hat{h}_{\gamma}^{\text{OZ}} \rangle \rangle_{\omega,0} .$$
(1)

An alternative, yet equivalent, computational route is to express it as the magnetic fieldderivative of the one-photon dipole transition strength, $S^{0f}_{\alpha\beta}(\mathbf{B})$, in the presence of the magnetic field³⁹

$$\mathcal{B}(0 \to f) = \frac{1}{2} \varepsilon_{\alpha\beta\gamma} \operatorname{Im} \frac{\mathrm{d}S^{0f}_{\alpha\beta}(\mathbf{B})}{\mathrm{d}B_{\gamma}} \Big|_{\mathbf{B}=\mathbf{0}},\tag{2}$$

where $S^{0f}_{\alpha\beta} = \langle 0|\hat{\mu}_{\alpha}|f\rangle\langle f|\hat{\mu}_{\beta}|0\rangle$. In the equations above, ω is the frequency of the external electric field (the incident light beam), $\varepsilon_{\alpha\beta\gamma}$ is the Levi-Civita tensor, and implicit summation over repeated indices is implied, where indices α , β , and γ run over the three Cartesian coordinates x, y, and z.

In analogy with the case of MCD, and inspired by the CPP formulation of NSCD by Vaara et al.,¹⁵ an SOS expression for the NSCD \mathcal{B}_K term of nucleus K and its connection to the residues of a quadratic response function has been derived.^{18,20} The approach used a nonrelativistic formulation where the orbital hyperfine interaction operator of nucleus K, a.k.a. the paramagnetic (nuclear) spin-(electron) orbit (PSO) operator, $\hat{h}_K^{\text{pso}} = \frac{e\hbar}{m_e} \frac{\mu_0 \gamma_K}{4\pi} \sum_i \frac{\hat{l}_{iK}}{r_{iK}^3}$, replaces the orbital Zeeman interaction operator in Eq. (1)

$$\mathcal{B}_{K}(0 \to f) \propto i \varepsilon_{\alpha\beta\gamma} \lim_{\omega \to \omega_{f}} (\omega - \omega_{f}) \langle \langle \hat{\mu}_{\alpha}; \hat{\mu}_{\beta}, \hat{h}_{K,\gamma}^{\text{pso}} \rangle \rangle_{\omega,0} .$$
(3)

The NSCD equivalent of the derivative expression, Eq. (2), is

$$\mathcal{B}_{K}(0 \to f) = \frac{1}{2} \varepsilon_{\alpha\beta\gamma} \operatorname{Im} \frac{\mathrm{d}S^{0f}_{\alpha\beta}(\mathbf{I}_{K})}{\mathrm{d}I_{K,\gamma}} \bigg|_{\mathbf{I}_{K}=\mathbf{0}}$$
(4)

where \mathbf{I}_{K} is the nuclear spin.

As in the case of MCD, the NSCD signal of a molecule with no degenerate ground and excited states is solely determined by the \mathcal{B}_K term. The total NSCD ellipticity spectrum of nucleus K can then be computed as²⁰

$$\eta_K(\omega) = \omega \mathcal{L}_K \sum_f \mathcal{B}_K(0 \to f) g_f(\omega, \omega_f)$$
(5)

where \mathcal{L}_K is a product of physical constants, and $g_f(\omega, \omega_f)$ is a broadening function. The ellipticity in Eq. (5) is given per unit path length, unit of spin polarization, and unit concentration of the nucleus. The numerical values of \mathcal{L}_K used in the current study are reported in the ESI.

Within CC response theory, computational expressions for the \mathcal{B} term of MCD are most conveniently obtained using the derivative approach.^{34,39,40} Following a similar strategy, we can formulate the \mathcal{B}_K term as

$$\mathcal{B}_{K}(0 \to f) = -\frac{1}{2} \epsilon_{\alpha\beta\gamma} \left({}^{\perp}T_{0f}^{\mu_{\alpha},K_{\gamma}} T_{f0}^{\mu_{\beta}} + T_{0f}^{\mu_{\alpha}\perp} T_{f0}^{\mu_{\beta},K_{\gamma}} \right)$$
(6)

where T_{0f}^{μ} and T_{f0}^{μ} are the left and right one-photon transition moments,⁴¹ and ${}^{\perp}T_{0f}^{\mu,K}$ and ${}^{\perp}T_{f0}^{\mu K}$ are the nuclear spin-derivatives of the one-photon dipole transition moments; note the use of the compact notation K_{γ} in place of $\hat{h}_{K\gamma}^{\text{pso}}$. The CC response expressions for these

transition moment derivatives are promptly derived in analogy with the MCD ${\cal B}~{\rm term}^{34,39,40}$

$${}^{\perp}T_{0f}^{\mu,K} = \frac{\mathrm{d}T_{0f}^{\mu}}{\mathrm{d}I_{K}} = \left[\mathbf{G}t^{K}(0)t^{\mu}(-\omega_{f}) + \mathbf{F}^{K}t^{\mu}(-\omega_{f}) + \mathbf{F}^{\mu}t^{K}(0)\right]E_{f}(\omega_{f}) + \bar{M}_{f}(\omega_{f})\left[\mathbf{A}^{\mu}t^{K}(0) + \mathbf{A}^{K}(0)t^{\mu}(-\omega_{f}) + \mathbf{B}t^{K}(0)t^{\mu}(-\omega_{f})\right] + \omega_{f}^{K}[\bar{M}_{f}(\omega_{f})t^{\mu}(-\omega_{f})] + \bar{\xi}^{\mu}(-\omega_{f}) \,{}^{\perp}E_{f}^{K}(\omega_{f}, 0) + \bar{\xi}^{K}(0)E_{f}^{\mu}(\omega_{f}, -\omega_{f})$$
(7)

and

$${}^{\perp}T_{f0}^{\mu,K} = \frac{\mathrm{d}T_{f0}^{\mu}}{\mathrm{d}I_K} = {}^{\perp}\bar{E}_f^K(-\omega_f,0)\xi^{\mu} + \bar{E}_f(-\omega_f)\mathbf{A}^{\mu}t^K(0) \ . \tag{8}$$

Note that, in Equation (7), $\omega_f^K = \frac{d\omega_f}{dI_K} = \bar{E}_f(-\omega_f)[\mathbf{A}^K + \mathbf{B}t^K(0)]E_f(\omega_f)$, which is the definition of the excited-state expectation value T_{ff}^K of the operator $\hat{h}_{K,\gamma}^{\text{pso}}$. Since $\hat{h}_{K,\gamma}^{\text{pso}}$ is imaginary, ω_f^K is zero, unless the final state f is degenerate.

In the equations above, $E_f(\omega_f)$ and $\bar{E}_f(-\omega_f)$ are the right and left CC excited state vectors, obtained by solving the right and left eigenvalue equations

$$\left[\mathbf{A} - \omega_f \mathbf{1}\right] E_f(\omega_f) = \mathbf{0} \tag{9}$$

$$\bar{E}_f(-\omega_f)\left[\mathbf{A} - \omega_f \mathbf{1}\right] = \mathbf{0} \tag{10}$$

and $E_f^{\mathcal{O}}(\omega_f, \omega_{\mathcal{O}})$ and $\bar{E}_f^{\mathcal{O}}(-\omega_f, \omega_{\mathcal{O}})$ are their first-order responses to a general operator $\hat{\mathcal{O}}$, with associated frequency $\omega_{\mathcal{O}}$. The eigenvector responses are obtained from solving the linear equations

$$\left[\mathbf{A} - (\omega_f + \omega_{\mathcal{O}})\mathbf{1}\right] E_f^{\mathcal{O}}(\omega_f, \omega_{\mathcal{O}}) = -\left[\mathbf{B}t^{\mathcal{O}}(\omega_{\mathcal{O}}) + \mathbf{A}^{\mathcal{O}}\right] E_f(\omega_f)$$
(11)

$$\bar{E}_{f}^{\mathcal{O}}(-\omega_{f},\omega_{\mathcal{O}})\left[\mathbf{A}+(\omega_{\mathcal{O}}-\omega_{f})\mathbf{1}\right] = -\bar{E}_{f}(-\omega_{f})\left[\mathbf{B}t^{\mathcal{O}}(\omega_{\mathcal{O}})+\mathbf{A}^{\mathcal{O}}\right]$$
(12)

When $\omega_{\mathcal{O}} = 0$ (as is the case for $\hat{\mathcal{O}} = \hat{h}_{K}^{\text{pso}}$) Equations (11) and (12) may diverge in the case where $[\mathbf{A} - \omega_f \mathbf{1}]$ is singular, *i.e.*, if the solution vector has a component in the direction of the right and left eigenvectors. To avoid these unphysical divergences, the eigenvector derivatives $E_f^K(\omega_f, 0)$ and $\bar{E}_f^K(-\omega_f, 0)$ are projected onto the orthogonal complement of the undifferentiated eigenvectors, as indicated by the superscript \perp .^{34,39,40} Definitions of the remaining CC building blocks can be found, *e.g.*, in Refs. 31, 34, 39, and 41. 98

Since it will be relevant for the discussion of the results in the next sections, we also report here the exact sum-over-states expression for the \mathcal{B}_K term

$$\mathcal{B}_{K} \propto \epsilon_{\alpha\beta\gamma} \left[\sum_{k \neq m} \frac{\langle 0|\hat{\mu}_{\alpha}|k\rangle \langle k|\hat{h}_{\gamma}^{\text{pso}}|m\rangle}{E_{m} - E_{k}} - \sum_{k \neq 0} \frac{\langle 0|\hat{h}_{\gamma}^{\text{pso}}|k\rangle \langle k|\mu_{\alpha}|m\rangle}{E_{k} - E_{0}} \right] \langle m|\hat{\mu}_{\beta}|0\rangle \tag{13}$$

which in CC theory is explicitly symmetrized as follows

$$\mathcal{B}_{K} \propto -\frac{1}{2} \epsilon_{\alpha\beta\gamma} \left[\left\{ \sum_{k \neq m} \frac{\langle 0|\hat{\mu}_{\alpha}|k\rangle \langle k|\hat{h}_{\gamma}^{\text{pso}}|m\rangle}{E_{m} - E_{k}} - \sum_{k \neq 0} \frac{\langle 0|\hat{h}_{\gamma}^{\text{pso}}|k\rangle \langle k|\hat{\mu}_{\alpha}|m\rangle}{E_{k} - E_{0}} \right\} \langle m|\hat{\mu}_{\beta}|0\rangle - \langle 0|\hat{\mu}_{\beta}|m\rangle \left\{ \sum_{k \neq m} \frac{\langle m|\hat{h}_{\gamma}^{\text{pso}}|k\rangle \langle k|\hat{\mu}_{\alpha}|0\rangle}{E_{m} - E_{k}} - \sum_{k \neq 0} \frac{\langle m|\hat{\mu}_{\alpha}|k\rangle \langle k|\hat{h}_{\gamma}^{\text{pso}}|0\rangle}{E_{k} - E_{0}} \right\} \right]$$
(14)

Eq. (14) can be further split into dispersive $(\mathcal{B}_{K,d})$ and absorptive $(\mathcal{B}_{K,a})$ components¹⁸

$$\mathcal{B}_{K,d} = -\frac{1}{2} \epsilon_{\alpha\beta\gamma} \sum_{k \neq m} \left\{ \frac{\langle 0|\hat{\mu}_{\alpha}|k\rangle \langle k|\hat{h}_{\gamma}^{\text{pso}}|m\rangle}{E_m - E_k} \langle m|\hat{\mu}_{\beta}|0\rangle - \langle 0|\hat{\mu}_{\beta}|m\rangle \frac{\langle m|\hat{h}_{\gamma}^{\text{pso}}|k\rangle \langle k|\hat{\mu}_{\alpha}|0\rangle}{E_m - E_k} \right\}$$
(15)

$$\mathcal{B}_{K,a} = -\frac{1}{2} \epsilon_{\alpha\beta\gamma} \sum_{k\neq 0} \left\{ \frac{\langle 0|\hat{h}_{\gamma}^{\rm pso}|k\rangle\langle k|\hat{\mu}_{\alpha}|m\rangle}{E_k - E_0} \langle m|\hat{\mu}_{\beta}|0\rangle - \langle 0|\hat{\mu}_{\beta}|m\rangle \frac{\langle m|\hat{\mu}_{\alpha}|k\rangle\langle k|\hat{h}_{\gamma}^{\rm pso}|0\rangle}{E_k - E_0} \right\}$$
(16)

As discussed in the literature,¹⁸ the importance of each contribution to the total NSCD is modulated by the size of the energy denominators. The denominators in the $\mathcal{B}_{K,a}$ SOS are never smaller than the relative energy of the first excited state, and will progressively increase as energetically higher excited states are considered in the SOS. On the other hand, the energy difference between two excited states in the denominator of the dispersive terms can become very small and result in a very large contribution from this type of term, even dominant in the case of very close-lying excited states. Also, since the \mathcal{B}_K term is a scalar triple product, *i.e.*, it contains the Levi-Civita tensor, and the PSO operator is imaginary, the dispersive contributions from a pair of excited states k and m to each other's NSCD signal will be identical in magnitude but of opposite sign. Thus, energetically close pairs of excited states may contribute to the NSCD spectrum with a bisignate feature if the contribution to $\mathcal{B}_{K,d}$ due to the interaction of the two states is dominant in the SOS. In MCD, this feature is referred to as a pseudo- \mathcal{A} term.⁴²

Since \hat{h}^{pso} and $\hat{\mu}$ are one-electron operators, their matrix elements between two excited states, $\langle k | \hat{\mathcal{O}} | m \rangle$, approximately become

$$\langle k|\hat{\mathcal{O}}|m\rangle \approx \langle \phi_k^h|\hat{\mathcal{O}}|\phi_m^h\rangle \langle \phi_k^p|\phi_m^p\rangle + \left\langle \phi_k^p|\hat{\mathcal{O}}|\phi_m^p\rangle \left\langle \phi_k^h|\phi_m^h\right\rangle \tag{17}$$

where ϕ_i^h and ϕ_i^p indicate the occupied (also called *hole*) and virtual (also called *particle*) natural transition orbital (NTO) of state *i*. Therefore, we can expect these matrix elements to be sizable only if the states *k* and *m* have either similar occupied or virtual NTOs.

III. COMPUTATIONAL DETAILS

Three para-substituted azobenzenes were chosen for investigation as systems of both experimental interest and computational feasibility: 4-hydroxyazobenzene (AZO-1, a.k.a. 4-phenylazophenol or p-(phenylazo)phenol), 4-aminoazobenzene (AZO-2, a.k.a. p-Aminoazobenzene or aniline yellow), and 4-amino-4'-nitroazobenzene (AZO-3). Figure 1 shows the azobenzene molecules with numbered atoms for later reference. The geometries were optimized at the MP2/cc-pVTZ level using Turbomole³⁵ and Cartesian coordinates can be found in the ESI.

The effects of solvation in dimethyl sulfoxide (DMSO), $CHCl_3$, and C_6H_{12} were examined for AZO-3 using the COSMO model.⁴³ Dielectric constants and refractive indices of the solvents are provided in the ESI.

The NSCD ellipticities were calculated with RI-CC2 and TD-DFT using the weighted core-valence correlation-consistent aug-cc-pwCVDZ basis set⁴⁴ and development versions of Turbomole³⁵ and Dalton,⁴⁵ respectively. For the TD-DFT calculations, the BH+HLYP^{36,37} functional was applied. The spectra were generated by broadening the stick spectra with a Lorentzian band of half-width-at-half-maximum of 1000 cm^{-1} .

IV. RESULTS AND DISCUSSION

Our discussion will cover several aspects of the results, and revolve around the character of the considered excited states (ESs), the NSCD spectra, difference densities, and the signs of the individual \mathcal{B}_K terms. Before moving into the analysis, some background on the relation between NSCD and NMR is provided. Then, for each azobenzene species, the CC2 results are considered first. Second, comparisons between CC2 and TD-DFT are carried out. For additional investigation of the origin of conspicuous observations, an SOS study and examination of the natural transition orbitals (NTOs) are carried out. Solvent effects on selected excited-state NSCD terms are also discussed.



FIG. 1. Molecular structures and atom numbering schemes for 4-hydroxyazobenzene (AZO-1),4-aminoazobenzene (AZO-2), and 4-amino-4'-nitroazobenzene (AZO-3).

A. Equivalence of nuclei in NSCD

Experimentally, the NSCD requires the presence and proper orientation of the bulk magnetization of the nuclear spins (\mathbf{M}). This magnetization emerges as the population average of individual nuclear magnetic moments⁴⁶ and its evolution in time is the basis for nuclear magnetic resonance (NMR) spectroscopy. Since the presence of NSCD requires that this nuclear magnetization vector has a component parallel with the light beam, manipulating the direction of \mathbf{M} is essential for the observation of NSCD. In other words, the time evolution of \mathbf{M} will directly influence the time evolution of the NSCD.

From a semi-classical point of view, the magnetization vector from an ensemble of identical nuclear spins K precesses around the direction of the magnetic field present at the position of the nuclei at a well-defined frequency, called Larmor frequency. This Larmor frequency is proportional to the magnetic field B_{loc} experienced locally by the nucleus. B_{loc} is determined by the external magnetic field (B_0) , modified due to the local electronic structure around the nucleus, imparting nuclei in different local environments different Larmor frequencies. These small local differences in B_{loc} and, hence, the Larmor frequencies are observed in NMR spectroscopy as nuclear shielding, a fundamental NMR property used to distinguish different nuclei in molecules.

The instantaneous local magnetic fields depend on the conformation and surroundings

of the molecule and can change in fluids very rapidly due to the molecular motions. However, the nuclear precession frequencies are usually much slower ($\sim 10^{1}-10^{2}$ MHz) than the molecular tumbling. As a consequence, the observed Larmor frequencies are an average of the Larmor frequencies that the nucleus experiences during one period of its precession motion. This means that results of the quantum chemical calculations for properties, whose observation is associated with the precession of magnetization, need to be averaged for the nuclei that can, on the time scale of an NMR experiment, explore different conformations and hence different B_{loc} and Larmor frequencies.

For the molecules here considered, this is the situation of the carbon and hydrogen atoms that are attached in positions equivalent with respect to the N=N bridge. As an example, the hydrogen nuclei H2 and H4 can, on the timescale of the NMR experiment, exchange their positions due to the rotation of the phenyl ring along the N-C2 bond. This is reflected experimentally in the NMR spectrum of azobenzene, which shows a single peak at identical frequencies for these nuclei.^{47,48} As noted above, since NSCD is modulated by the time evolution of the magnetization the same way as NMR, the same effect will also apply here. This means that although the calculated results will show different NSCD for these nuclei in the presented *static* structure, the more appropriate interpretation of the results from the experimental point of view is to average these NSCD signals. This is analogous to a common practice applied in the analysis of calculated NMR chemical shifts. For this reason, the sum of NSCD for nuclei considered as NMR-equivalent is also reported as this is more relevant to the experimental measurements than the individual, practically unobservable, contributions from an instantaneous structure.

B. Similarities between the excited states of the three systems

The three investigated azobenzenes differ in the substituents in *para* positions with respect to the carbons bound to the azo (N=N) group: AZO-1 has the electron-donating hydroxy group (-OH) on one of the phenyl rings, whereas AZO-2 has an electron-donating amino group $(-NH_2)$ in the same position; AZO-3 contains both the electron-donating amino group on one ring and the electron-withdrawing nitro group $(-NO_2)$ on the other ring. AZO-1 and AZO-2 are sometimes referred to as electron-donating azobenzenes; AZO-3 is a prototypical push-pull system (electron donor-acceptor azobenzene).

| | RI-CC2 | | Character (localization) | TD-DFT/BH+HLYP | |
|-----------|--------|-------|--|----------------|-------|
| State n | E_n | f | CC2/TD-DFT | E_n | f |
| | | | AZO-1 | | |
| 1 | 2.959 | 0.000 | $n\pi^*$ (azo) | 3.015 | 0.000 |
| 2 | 3.796 | 0.868 | $\pi\pi^*$ (deloc.) | 3.790 | 0.822 |
| 3 | 4.508 | 0.008 | $\pi\pi^*$ (left) | 4.748 | 0.012 |
| 4 | 4.549 | 0.018 | $\pi\pi^*$ (right) | 4.838 | 0.003 |
| | | | AZO-2 | | |
| 1 | 2.964 | 0.000 | $n\pi^*$ (azo) | 3.031 | 0.000 |
| 2 | 3.589 | 0.919 | $\pi\pi^*$ (deloc.) | 3.657 | 0.894 |
| 3 | 4.437 | 0.028 | $\pi\pi^*$ (right) | 4.720 | 0.010 |
| 4 | 4.528 | 0.008 | $\pi\pi^*$ (left) | 4.781 | 0.014 |
| | | | AZO-3 | | |
| 1 | 2.866 | 0.000 | $n\pi^*$ (azo) | 2.956 | 0.000 |
| 2 | 3.339 | 1.043 | $\pi\pi^*$ (deloc.) | 3.426 | 1.067 |
| 3 | 3.854 | 0.000 | $n\pi^*$ (nitro) | 4.155 | 0.000 |
| 4 | 4.352 | 0.004 | $\pi\pi^*$ (right) / $\pi\pi^*$ (left) | 4.535 | 0.017 |
| 5 | 4.430 | 0.011 | $\pi\pi^*$ (left) / $n\pi^*$ (nitro) | 4.587 | 0.000 |
| 6 | 4.441 | 0.001 | $n\pi^*$ (nitro) / $\pi\pi^*$ (right) | 4.607 | 0.001 |

TABLE I. Excitation energies E_n (eV), oscillator strengths f, character, and localization of the electronic transitions under investigation. The aug-cc-pwCVDZ basis set was used at both levels of theory. Figures S1, S2, S3, and S4 (ESI) collect the NTOs.

Table I collects information on the excited states considered for the three azobenzenes. The first excited state (ES1) of all three molecules has $n\pi^*$ character, with the hole orbital localized on the azo group. ES1 is dark in optical absorption in all three azobenzenes. The second state, ES2, is a delocalized $\pi\pi^*$ electronic state, where the π^* involves the azo group. This is the bright state in optical absorption, which has a distinct charge-transfer character in AZO-3. In AZO-1, ES3 is a $\pi\pi^*$ state mainly localized on the unsubstituted (left) phenyl ring, and ES4 is a $\pi\pi^*$ state mainly localized on the substituted (right) phenyl. In AZO-2, ES3 is dominantly on the substituted ring (similar to ES4 of AZO-1), and ES4 is on the unsubstituted one (similar to ES3 of AZO-1). Both ES3 and ES4 are almost dark in optical absorption in AZO-1 and AZO-2. CC2 and TD-DFT yield equivalent descriptions of the characters of the four excited states of AZO-1 and AZO-2. In AZO-3, ES3 is a dark $n\pi^*$ state at both levels of theory, with the hole localized on the nitro group. The remaining three states of AZO-3 have different energetic ordering for CC2 and TD-DFT. ES4 at CC2 level corresponds to ES6 at TD-DFT level, and ES5 at CC2 level to ES4 at TD-DFT level. Both states have $\pi\pi^*$ character, with noticeable localization on either one or the other of the phenyl rings. Finally, ES6 at CC2 level corresponds to ES5 at TD-DFT level; it is of $n\pi^*$ character and originates from the nitro group with the π^* orbital strongly localized on the phenyl linked to the nitro group.

C. NSCD spectra: observed trends

We will now analyze the CC2 NSCD \mathcal{B}_K data and corresponding spectra for the carbon (K = C) and hydrogen (K = H) nuclei of the three compounds. Note that in the plots discussed in the following, the spectra of the various nuclei have been color-coded such that pairs of NMR-equivalent atoms are colored identically.

The \mathcal{B}_C terms and corresponding NSCD spectra of the carbon atoms in **AZO-1** are shown in Figure 2; those of the hydrogen nuclei are in Figure 3. The corresponding raw data are provided in Table S5 (ESI).

At the CC2 level, the first excited state of AZO-1 is NSCD dark at all nuclei, except for C2 and C7—that is, the nuclei connected to the azo group. This is explained by the fact that ES1 is an $n \to \pi^*$ excitation with the hole orbital localized at the azo group, whose transition dipole moment (entering the \mathcal{B}_K expression) is only non-zero in the direction perpendicular to the molecular plane. At C2, \mathcal{B}_C is positive, whereas it is negative at C7. We attribute the non-negligible NSCD at C2 and C7 to the fact that ES1 is strongly localized on the azo group, see Figure 5.

The \mathcal{B}_C term and the corresponding spectral band of ES2 are positive for all carbons, except C2 and C7, yet with varying intensities. For ES3 and ES4, all carbons on the unsubstituted phenyl ring have two negative \mathcal{B}_C terms, and a resulting negative band. For all carbons of the right ring, ES3 has negative \mathcal{B}_C whereas ES4 has a positive, and larger, 104



FIG. 2. AZO-1. NSCD spectra of the carbon nuclei. RI-CC2 (colored) and TD-DFT/BH+HLYP (grey) results with the aug-cc-pwCVDZ basis set. Vertical dotted lines mark the excitation energies. TD-DFT energies have been shifted by -0.055 eV to align the first transition with RI-CC2. The sticks have been scaled for visibility.



FIG. 3. AZO-1. NSCD spectra of the hydrogen nuclei. RI-CC2 (colored) and TD-DFT/BH+HLYP (grey) results with the aug-cc-pwCVDZ basis set. Vertical dotted lines mark the excitation energies. TD-DFT energies have been shifted by -0.055 eV to align the first transition with RI-CC2. The sticks have been scaled for visibility.

 \mathcal{B}_C value. The resulting convoluted band is positive.

All in all, the NSCD spectra of the C atoms on the left ring have similar positive/negative bisignate shape, with the exception of C7, featuring instead three negative peaks. On the right ring, the unsubstituted carbons (C1, C3, C4, and C6) also have similar spectral shapes

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FIG. 4. AZO-1. Combined NSCD spectra of NMR-equivalent atoms. RI-CC2 and TD-DFT/BH+HLYP results with the aug-cc-pwCVDZ basis set. Vertical dotted lines mark the excitation energies of the excited states. TD-DFT energies have been shifted by -0.055 eV to align the first transition with RI-CC2. The sticks have been scaled for visibility.

with two positive peaks. C5, the –OH substituted carbon, also shows two positive NSCD bands, though with much lower intensity.

Turning our attention to the (CC2) hydrogen NSCD spectra of AZO-1 in Figure 3, we observe that ES1 is completely dark for all hydrogens. All hydrogens on the right ring have oppositely signed \mathcal{B}_H for ES3 and ES4, and the resulting band is negative. All hydrogens on the left ring have two positive \mathcal{B}_H for ES3 and ES4 and an overall positive band. The overall spectra of H5, H6, H7, H8 (left ring) are similar, yet modulated; the spectra of the right ring hydrogens are more dissimilar from each other as could be expected due to their different local environment.

When computing the total NSCD spectra of the NMR-equivalent nuclei, we note that

all carbon pairs combine in a constructive way, see Figure 4. Summing the spectra of the NMR-equivalent H1+H3, however, yields an almost quenched ES2 signal, whereas ES3 and ES4 combine into a stronger negative band. The NSCD signals of H2+H4 and H5+H9 also partly cancel out for ES2, and constructively add up for ES3 and ES4; the NSCD of H6+H8 are combined constructively for all excited states.

In an attempt to identify any peculiar sign patterns of the NSCD and possible connection between the NSCD and the localization of the difference density of the excited states, we plot in Figure 5 the difference densities of the four excited states of AZO-1 together with a signed measure of the $\mathcal{L}_K \mathcal{B}_K$ term for each nucleus. Different from the results of previous studies on other molecules,²⁰ the NSCD intensities of AZO-1 do not appear to clearly connect to the regions of significant change in electronic density, and moderate NSCD signals can be seen at some distance from the main change in the electron density. Nevertheless, it is observed that in all cases the largest NSCD signal does appear in the regions where the density changes are localized the most. It should also be noted that in the previous study,²⁰ the NSCD signal "leaked" outside of the regions of high difference densities up to a distance of few bonds, which in the present case represents a significant fraction of the total molecule. For ES3, we note that the NSCDs of all carbons are negative and those of all hydrogens are positive, independent of where the electronic density is concentrated (*i.e.*, on the left ring). In ES4, the difference density is localized on the right ring, and the signs of the carbon and hydrogen \mathcal{B}_K are flipped compared to ES3. We will return to this observed behavior in a following section.

The NSCD spectra of **AZO-2** are shown in Figures 6 and 7 for carbon and hydrogen, respectively. The underlying raw data can be found in Table S6 (ESI).

Starting from the carbons' spectra, it is seen that ES1 is clearly visible (at the CC2 level) on C2 (negative) and C7 (positive), and only slightly discernible on some of the others. For ES2, all carbons on the left ring have positive NSCD, except for C7. On the right ring, the NMR-equivalent C1 and C3 have both positive NSCD, whereas C6+C4 have oppositely signed NSCD for ES2. The substituted C2 and C5 both have negative $\mathcal{B}_C(0 \rightarrow 2)$. ES3 and ES4 are slightly more energetically separated than in AZO-1. All carbons on the left ring have oppositely signed \mathcal{B}_C terms for these two states. In a few cases, the resulting band is bisignate, yet weak, otherwise it is negative. On the right ring, the NMR-equivalent pairs C1+C3 and C4+C6 have oppositely signed \mathcal{B}_C for ES3, whereas, for ES4, all carbons on the



FIG. 5. AZO-1. RI-CC2 and TD-DFT/BH+HLYP (aug-cc-pwCVDZ basis set) difference densities for the four lowest excited states (ES) with the sign (+/-) of the nuclei's $\mathcal{L}_K \mathcal{B}_K$ terms. The size of the sign indicates the magnitude (magnified by 1000) of the signal (smallest for 1 < |NSCD| < 10, middle size for 10 < |NSCD| < 100 and largest for |NSCD| > 100. NSCD signals with absolute values < 1 are not shown).

right ring have positive NSCD.

Looking at the hydrogen NSCD of AZO-2 in Figure 7, we note that ES1 is dark in NSCD, as also observed for ES1 in AZO-1. For ES3, all hydrogens have negative \mathcal{B}_H ; for ES4, on the other hand, the hydrogens on the left ring have positive \mathcal{B}_H while those on the right ring maintain their negative signal. As a result, the spectral shape of the ES3-ES4 band for the left ring hydrogen atoms resembles a pseudo- \mathcal{A} term.

The combined NSCD of the NMR-equivalent atoms in AZO-2 is shown in Figure 8. Partial cancellation occurs for ES2 on C4+C6. All other carbon pairs have NSCD terms of the same sign and their signals combine constructively. The NMR-equivalent amino hydrogens, H10 and H11, as well as the H6+H8 pair on the left ring have almost identical spectra with only



FIG. 6. AZO-2. NSCD spectra of the carbon nuclei. RI-CC2 (colored) and TD-DFT/BH+HLYP (grey) results with the aug-cc-pwCVDZ basis set. Vertical dotted lines mark the excitation energies of the excited states. TD-DFT energies have been shifted by -0.071 eV to align the first transition with RI-CC2. The sticks have been scaled for visibility.

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FIG. 7. AZO-2. NSCD spectra of the hydrogen nuclei. RI-CC2 (colored) and TD-DFT/BH+HLYP (grey) results with the aug-cc-pwCVDZ basis set. Vertical dotted lines mark the excitation energies of the excited states. TD-DFT energies have been shifted by -0.071 eV to align the first transition with RI-CC2. The sticks have been scaled for visibility.



FIG. 8. AZO-2. Combined NSCD spectra of NMR equivalent atoms. RI-CC2 and TD-DFT/BH+HLYP results with the aug-cc-pwCVDZ basis set. Vertical dotted lines mark the excitation energies of the excited states. TD-DFT energies have been shifted by -0.071 eV to align the first transition with RI-CC2. The sticks have been scaled for visibility.

minor modulation in intensity, and thus combine constructively in the summed spectra. The NMR-equivalent H5+H9 on the left ring, as well as the pairs H1+H3 and H2+H4 on the right ring have oppositely signed \mathcal{B}_H for ES2, resulting in partial quenching of the NSCD of ES2 in the combined spectra. The two summed spectra of the left-ring carbons both exhibit a positive/negative spectral shape, and the right-ring combined spectra share a strong positive peak at higher frequencies, thus making the carbons on the two rings 112



FIG. 9. AZO-2. RI-CC2 and TD-DFT/BH+HLYP (aug-cc-pwCVDZ basis set) difference densities for the four lowest excited states (ES) with the sign (+/-) of the nuclei's $\mathcal{L}_K \mathcal{B}_K$ terms. The size of the sign indicates the magnitude (magnified by 1000) of the signal (smallest for 1 < |NSCD| < 10, middle size for 10 < |NSCD| < 100 and largest for |NSCD| > 100. NSCD signals with absolute values < 1 are not shown).

distinguishable. This also applied to the hydrogens, where the three right-ring spectra have the same positive/negative feature and the left-ring pairs have negative/pseudo- \mathcal{A} spectral shape.

As noted for AZO-1, when considering the density difference vs signed measure of the NSCD in Figure 9, no straightforward connection between the density change and the NSCD emerges. In a cross-comparison between ES3 of AZO-1 and ES4 of AZO-2, the sign pattern of the left ring (where the density difference is dominant) is preserved, whereas it is reversed on the right ring. Conversely, the sign pattern on the left ring of ES3 in AZO-2 is opposite to the one of ES4 in AZO-1. As for the right ring, all hydrogen NSCD signals are negative for both molecules, whereas the carbon NSCD of AZO-2 breaks the pattern with respect to AZO-1.

Finally, we analyze the CC2 NSCD results for AZO-3, illustrated in Figure 10 (carbon) and Figure 11 (hydrogen). Corresponding numerical values are found in Table S7 (ESI).

As in the two azobenzenes previously discussed, ES1 is NSCD-dark at most carbons, except C2 (negative) and C7 (positive); the signs of the NSCD terms on these two atoms are opposite to what we saw in AZO-1 and AZO-2. The \mathcal{B}_C terms of ES2 are positive for the NMR-equivalent pairs C1+C3, C8+C12, and C9+C11. C4 and C6 have oppositely signed \mathcal{B}_C for ES2 (C6 is positive). At the remaining carbon nuclei, \mathcal{B}_C of ES2 is negative. ES3 is dark to NSCD for all carbons. The \mathcal{B}_C terms of the closely spaced ES4, ES5, and ES6 combine to give one spectral band at higher energy. For the left-ring carbons, except C7, the NSCD \mathcal{B}_C of ES5 and ES6 are oppositely signed and of comparable magnitude. The \mathcal{B}_C terms of ES5 and ES6 of the carbon atoms on the right ring, on the other hand, are more dissimilar: C1 has relatively small, oppositely signed \mathcal{B}_C for the two states whereas the \mathcal{B}_C of ES6 at its NMR-equivalent C3 is almost quenched, as it is for C4 and C6.

At the hydrogens, see Figure 11, ES1 and ES3 are NSCD-dark. Weak and all-negative NSCD is obtained for ES4 for the left-ring hydrogens. For this state, all NMR-equivalent hydrogens on the right ring have oppositely signed NSCD, although the amino hydrogens are almost dark. All right-ring hydrogens have negative NSCD for ES5 and are nearly dark in ES6. As for the left-ring hydrogens, ES5 and ES6 have oppositely signed \mathcal{B}_H . The spectral band convoluting ES4-ES6 is always negative. The hydrogens for ES2 have both positive and negative NSCD of medium to high intensities.

Altogether, the NSCD signals of the NMR-equivalent left-ring pairs C8+C12, and C9+C11 are very similar and both combine constructively for all excited states, see Figure 12. Upon convolution of the terms of ES4, ES5 and ES6, an asymmetric bisignate spectral feature emerges for C9+C11, whereas a positive band characterizes this spectral region for C8+C12. On the right ring, C4+C6 combine destructively for ES2 and ES4, and constructively for ES5, which results in two positively signed bands. The combination of the NSCDs of C1+C3 enhances the signal of ES2 and partly quenches the NSCD of ES4, yielding a total positive band for ES4-ES6 which is less intense than the one for ES2. All NMR-equivalent hydrogen pairs have oppositely signed \mathcal{B}_H for at least one excited state in AZO-3. Thus, the summed spectra of the pairs H1+H3, H2+H4, and H5+H8 appear with a damped signal of ES2; ES4 is canceled out for H1+H3, H2+H4, and H9+H10, and the intensities of ES5 and ES6 are reduced in the combined H6+H7 spectrum.



FIG. 10. AZO-3. NSCD spectra of the carbon nuclei. RI-CC2 (colored) and TD-DFT/BH+HLYP (grey) results with aug-cc-pwCVDZ basis set. Vertical dotted lines mark the excitation energies of the excited states. TD-DFT energies have been shifted by -0.090 eV to align the first transition with RI-CC2. The sticks have been scaled for visibility.



FIG. 11. AZO-3. NSCD spectra of the hydrogen nuclei. RI-CC2 (colored) and TD-DFT/BH+HLYP (grey) results with aug-cc-pwCVDZ basis set. Vertical dotted lines mark the excitation energies of the excited states. TD-DFT energies have been shifted by -0.090 eV to align the first transition with RI-CC2. The sticks have been scaled for visibility.

Looking at the density difference plots for AZO-3 in Figure 13, we note that for CC2 in ES6 (ES5 for TD-DFT), where the density change is localized almost entirely on the nitro group, the NSCD of the left-ring carbons (and hydrogens for CC2) is rather strong, while the NSCD on the right ring is almost quenched. Relatively large NSCD is also observed for

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FIG. 12. AZO-3. Combined NSCD spectra of NMR-equivalent atoms. RI-CC2 and TD-DFT/BH+HLYP results with the aug-cc-pwCVDZ basis set. Vertical dotted lines mark the excitation energies of the excited states. TD-DFT energies have been shifted by -0.090 eV to align the first transition with RI-CC2. The sticks have been scaled for visibility.

ES5 on some of the carbons of the left ring, where the density difference is localized, versus smaller NSCD on the right ring. These are the clearest instances observed in this study suggesting a relationship between the size of the NSCD signal and the difference density of the excited state.



FIG. 13. AZO-3. RI-CC2 and TD-DFT/BH+HLYP (aug-cc-pwCVDZ basis set) difference densities for the six lowest excited states (ES) with the signed (+/-) measure of the $\mathcal{L}_K \mathcal{B}_K$ terms. The size of the sign indicates the magnitude (magnified by 1000) of the signal (smallest for 1 < |NSCD| < 10, middle size for 10 < |NSCD| < 100 and largest for |NSCD| > 100. NSCD signals with absolute values < 1 are not shown).

D. CC2 vs DFT

We now move on to compare TD-DFT with CC2, looking at the spectra as well as the density difference plots. The TD-DFT NSCD spectra are provided as grey graphs in Figures 2, 3 and 4 for AZO-1, Figures 6, 7 and 8 for AZO-2, and Figures 10, 11 and 12 for AZO-3. Before comparing the NSCD spectra obtained from CC2 and TD-DFT, it is worth noting that the energy splittings of the electronic excitations are different, see Table I. This can result in the NSCD spectra appearing to be more different than what the numerical results for the \mathcal{B}_K term indicate.

The first observation when comparing CC2 and TD-DFT for **AZO-1** is that the spectral shapes are not strikingly different for most nuclei. The most noticeable differences are the all-zero TD-DFT NSCD signals for the first excited state (C7 is just small here) and the much smaller NSCD for C6 and much larger NSCD of C5 for ES2 at TD-DFT level compared to CC2. Interestingly, as can be seen from Fig. 5, the difference densities of ES2 differ quite significantly between the CC2 and DFT near the C5 and C6, suggesting a possible connection. In all other spectra, TD-DFT and CC2 yield the same sign of the signal of ES2, most often also producing similar intensities. All atoms of the left ring (C7-C12, H5-H8) have the same spectral feature arising from the convolution of ES3 and ES4 when comparing the methods, but closer inspection of the underlying sticks reveals that, at the TD-DFT level, the intensity is almost exclusively in ES3 while with CC2 it is split between the two states. Meanwhile, for all right-ring atoms (C1-C6, H1-H4, H10), the two methods both give NSCD intensities of opposite sign for ES3 and ES4. At the carbon atoms, their convolution yields a single band. Bisignate features are seen for all right-ring hydrogens at TD-DFT level.

Turning our attention to AZO-2, and comparing the CC2 NSCD spectra with the TD-DFT ones (in grey) in Figures 6 and 7, the overall impression is again that the two methods are in qualitative agreement, albeit with more differences than found for AZO-1. Also for this molecule, TD-DFT yields a first excited state with vanishing NSCD signals, whereas at the CC2 level several atoms have visible spectral transitions. Looking at ES2, TD-DFT \mathcal{B}_K terms of opposite sign compared to CC2 are obtained for C6, H1, and H7; C5 has a very strong negative peak in the CC2 spectrum versus no observable strength for TD-DFT. In general, the spectra for the $-NH_2$ substituted C5 strongly differ between TD-DFT and CC2. C6 has also nearly zero NSCD at the TD-DFT level for ES2. It is interesting to note here again that the ES2 difference densities in the surroundings of C5 and C6 noticeably differ between the DFT and CC2, similarly as in the case of AZO-1. At the right ring, TD-DFT and CC2 produce equivalent relative NSCD intensities (and sign) for the third and fourth excitation, except for C1, C5, and C6 for which the two methods yield opposite signs of the NSCD \mathcal{B}_C term of ES3. On the left ring, both methods similarly give oppositely signed \mathcal{B}_C terms for ES3 and ES4, yet with different relative intensities. This results, at TD-DFT level, in one intense convoluted band (negative for carbon and positive for hydrogen), versus a weaker bisignate spectral band at CC2 level.

Considering the summed spectra of AZO-2 in Figure 8, there is a good overlap of the CC2 and TD-DFT spectra for all right-ring nuclei. For the left right the weak bisignate feature predicted by CC2 around ES3 and ES4 for the individual carbon nuclei combines to an overall negative band. As a result, the two methods predict the same positive/negative spectral shape for those nuclei. On the other hand, the combined NSCD for left-ring hydrogens in energy region of ES3 and ES4 provides different signatures, bisignate for CC2 and strong positive for TD-DFT, due to relative intensities of the two transitions.

AZO-3 is the system where CC2 and TD-DFT differ the most, starting already from the ordering of the excited states. Opposite to what we observed for AZO-1 and AZO-2, TD-DFT yields stronger NSCD signals than CC2 for ES1, mainly at C2 and C7 but also at some of the other carbon nuclei (Figure 10). The NSCD of ES2 also shows noticeable differences for C7 as well as the right ring carbons C2, C4, C5, and C6, and for H8, which is basically zero for TD-DFT (Figure 11). ES3 is completely NSCD dark at both levels of theory. ES4-ES6 are closely spaced for both methods, yet differently ordered, as previously mentioned. Because of this, one should take care when comparing the spectral features convoluting those three transitions. In the summed spectra (Figure 12), all peaks at ES2 exhibit the same sign for CC2 and TD-DFT, except for H2+H4. All in all, the combined TD-DFT NSCD spectra appear rather different from the CC2 ones in correspondence with the higher transitions.

Looking at the density difference plots in Figure 13, we note that, despite the similar density difference distributions between ES4 (CC2) and ES6 (TD-DFT), there are noticeable differences in the NSCD sign patterns yielded by the two methods. Comparing ES5 (CC2) with ES4 (TD-DFT), we observe that the left-ring nuclei have similar NSCD with the sole exception of H6. The right-ring nuclei, on the other hand, have reversed sign trends (except for the almost dark C5). ES6 (CC2) and ES5 (TD-DFT) have basically identical NSCD sign patterns on the left ring, on which the density difference is concentrated.

E. Rationalizing trends: a sum-over-states analysis

To rationalize some of the observed trends, we carried out an SOS decomposition of the CC2 \mathcal{B}_K term (cf. Eqs. (15) and (16)) of selected carbon nuclei over a small number of excited states (twice the number of states under investigation). Bar plots of the SOS terms of the selected nuclei are provided in Figures S6-S8 (ESI).

Starting from AZO-1 and AZO-2, the results for excited state m = 1 (ES1, $n\pi^*$) are dominated by the $\mathcal{B}_{C,d}$ contribution arising from the interaction with state k = 2 (ES2, $\pi\pi^*$). This can be easily rationalized since: i) the contribution from $\langle 1|\hat{\mu}|k\rangle$ will only be sizeable when state k also has $n\pi^*$ character, so the $\mathcal{B}_{C,a}$ should be small when k corresponds to a $\pi \to \pi^*$ transition, as in this case; *ii*) ϕ_2^p is very similar to ϕ_1^p , which should lead to a sizeable $\left\langle \phi_k^h | \hat{h}^{\text{pso}} | \phi_m^h \right\rangle$ (and hence PSO transition moment between excited states), for those atoms where the occupied NTOs of both states are sizeable, as it happens here around C2 and C7, see Figure S1 (ESI). For state 2 of AZO-1, we see in the right phenyl ring (C2) strong interactions with state 4, and in the left ring (C9, C12) strong interactions with state 3. This can also be understood, since state 4 is localized mainly on the right ring, and state 3 is mainly on the left ring. For AZO-2, the situation is turned around, consistent with the fact that the characters of ES3 and ES4 of AZO-2 are flipped with respect to AZO-1. At C5, which is the atom bound to the (different) substituents, the situation is more complicated. Here, the \mathcal{B}_K term comprises significant contributions from several intermediate states including, for AZO-2, a coupling to the ground state (k = 0). Especially C5 of AZO-1 has strong contributions from higher-lying states, and it is noted that the small number of states included in the SOS does not produce an NSCD signal of any likeness to the analytic value (Table S9 (ESI).

For state 3 in AZO-1, the most important contributions are of $\mathcal{B}_{K,d}$ type and come from states 2 and 4. Those from state 2 dominate on the left ring (C9 and C12), and those from state 4 dominate on the right ring (C2 and C5). If we compare the SOS for ES3 of AZO-1 with the SOS terms of ES4 for AZO-2 (~ES3 of AZO-1), we see that on the left ring (C9, C12) the dominating SOS contributions from state 2 to the respective states of the two azobenzenes have the same sign. Meanwhile, the smaller contributions on the right ring from state 4 to state 3 (AZO-1) and state 3 to state 4 (AZO-2) flip sign. This is because the energy denominator ($E_m - E_k$) changes sign. The dominating contribution from state 3 to state 4 on the right ring (C2 and C5) in AZO-1 also changes sign compared to the contribution from state 4 to state 3 in AZO-2, again because of the energy denominator.

For state 4 in AZO-1, we have again that the $\mathcal{B}_{K,d}$ term from state 2 dominates on the right ring (C2, C5), while the $\mathcal{B}_{K,d}$ term from state 3 dominates on the left ring (C9, C12). Conversely, in ES3 of AZO-2, the dominating $\mathcal{B}_{K,d}$ contributions are also from state 2 in the right ring, and keep their sign compared to AZO-1, while the dominating contributions in the left ring of AZO-2 (coming now from state 4) flip sign.

As partly anticipated in Section IV B, the first two excited states in AZO-3 are similar to the first two states in AZO-1 and AZO-2, apart from some additional charge-transfer into the $-NO_2$ group in ES2. ES4 and ES5 are similar to the third and fourth states in AZO-2 up to two small differences: in state 4 the nodal planes are slightly rotated and in state 5 there is some additional charge-transfer to the $-NO_2$ group; states 3 and 6 are local excitations at the $-NO_2$ group.

The SOS NSCD of AZO-3 ES1 is dominated by the $\mathcal{B}_{K,d}$ contributions from state 2, but its sign is reversed compared to the corresponding contribution in AZO-1 and AZO-2. For state 2, the contributions are similar to those for state 2 in AZO-2, but with a sign flip for the contribution from state 1 and larger contributions from higher states as well as the ground state, due to the larger ground state dipole moment. Because of its strong localization on the $-NO_2$ group and the $n\pi^*$ character, ES3 cannot strongly interact with any other state, and the $\mathcal{B}_{K,d}$ and $\mathcal{B}_{K,a}$ terms are negligible. In ES4, the contributions arising from states 2 and 5 have some similarity to the corresponding contributions in AZO-2, but in AZO-3 there are significant additional contributions from higher states. Due to the similarity of their virtual NTOs and the small energy gap, states 5 and 6 strongly interact. This gives rise to large (pseudo- \mathcal{A}) \mathcal{B}_K terms in the left ring where the occupied NTOs of the two states are localized.

From the above analysis, we, therefore, conclude that for the valence excitations of these azobenzene compounds in the gas phase, NSCD essentially probes $\frac{\langle k|\hat{h}^{pso}|m\rangle}{E_k - E_m}$, *i.e.*, the transition densities between excited states. Where the result is dominated by one or two states that are energetically close to the probed states, we can understand some of the sign patterns, *e.g.*, when states interchange.

F. Substituent effects

The substituted carbon atoms counts C2, C7, and C5 in all three azobenzenes, as well as C10 in AZO-3.

For the bridged atoms C2 and C7 we make the same (CC2) observations in both AZO-1 and AZO-2, namely that they are bright in ES1, they exhibit similar signals for ES2, where the transition is localized around the N=N group, while at higher energies their respective signals resemble more the ones of their neighbouring carbon nuclei. In AZO-3, on the other hand, the two atoms do not follow each other at ES2. In this case, C2 has a strong signal for ES2 and weaker signals for ES3 and ES4 while the opposite is true for C7, looking at the CC2 results only.

With respect to C5 in AZO-1, the (CC2) signals are significantly damped compared to all other spectra, although the sign pattern follows that of its neighbouring C4+C6 pair. Comparing with TD-DFT, the two methods produce the same signed features in the C5 spectrum and damped NSCD around ES3 and ES4, but here TD-DFT suggests a much stronger ES2. Meanwhile, C5 in AZO-2, compared to the aggregated C4+C6 spectrum, has a significantly different CC2 spectrum with a strong, negative NSCD of ES2 and a weak negative convolution of ES3 and ES4. We note that on the TD-DFT level, ES2 is completely NSCD-dark for C5 (AZO-2) and the spectrum at higher energies shows a weak, positive feature, which is more consistent with a hypothesis of the substituent having a damping effect on the NSCD compared to the carbon nuclei in the local environment.

These observations sum up to the following: CC2 and TD-DFT do not predict similar spectra for C5, and the -OH and $-NH_2$ substituents seem to influence the carbon atom to which they are bound, differently. These substituents do not seem to affect the surrounding atoms.

AZO-3, as AZO-2, has an amino group attached to C5. In fact, the two molecules' C5 have in common the over-all spectral features (for CC2) with two negative features and ES2 being stronger than the (very weak) high-energy region. However, C5 in AZO-2 is visible in ES1, and ES2 is much stronger compared to C5 in AZO-3 which generally has a spectrum of very low intensity.

At the CC2 level, C10, which has no substituent for AZO-2, exhibits a spectrum different from and much weaker than its nearest neighbours while the TD-DFT results indicate similar spectra for all left ring nuclei except C7. Possibly, this carbon (C10) experiences some influence from the N=N group which, in turn, is affected by the amino group in *para* position on C5, where the two methods produce rather different spectra. It could be that TD-DFT fails to capture some effects arising from the $-NH_2$ nitrogen atom which, on the other hand, are captured by the correlated CC model. This propagation of perturbation along the chain C5-C2-C7-C10 could also be an explanation for the quite different NSCD of all of these atoms between AZO-2 and AZO-3 and between TD-DFT and CC2. The difference between TD-DFT and CC2 appear to be enhanced, especially along C5-C2-C7, when comparing AZO-3 to AZO-2, suggesting that the combination of an electron-donating and electron-withdrawing group challenges the suitability of TD-DFT/BH+HLYP for this application.

By adding a nitro group to C10 (AZO-3), stark effects are observed. Firstly, the highenergy states are convoluted by the strongest peak observed for all other nuclei in all three molecules. The increase of \mathcal{B}_C value also applies to the other carbon atoms in the left phenyl ring, especially in the transitions that are localized on the nitro group. The hydrogens seem to be unaffected by the electron-withdrawing group. TD-DFT and CC2 produce similar spectra for C10 but not for C5.

G. Solvent effects

COSMO calculations were carried out for the second excited state of AZO-3 (the chargetransfer transition). The effect of three solvents was examined; C_6H_{12} , $CHCl_3$, and DMSO. These solvents represent both polar and nonpolar ones. The NSCD signals from gas-phase and COSMO calculations are plotted in Figure 14. The results are plotted as bars in the order of increasing polarity, *i.e.*, gas phase $< C_6H_{12} < CHCl_3 < DMSO$. Numerical data are collected in Table S8 and NTOs can be found in Figure S5 (ESI).

The most striking observation is the very strong (and oppositely signed) NSCD of C2 and C7 in DMSO. In the other three environments, those same nuclei have signals that are among the weakest calculated for the carbon nuclei.

With respect to the effect of increasing polarity, we observe in several cases, especially for the hydrogens, a systematic increase or decrease in the NSCD strength with increasing polarity. However, there does not appear to be a trend related to molecular structure and to which nuclei exhibit increasing or decreasing NSCD signals.



FIG. 14. AZO-3. NSCD of excited state 2. RI-CC2/aug-cc-pwCVDZ results from gas phase and COSMO calculations in C₆H₁₂, CHCl₃, and DMSO.

For most nuclei, the NSCD has the same sign in all environments, with modulation of intensities. The exceptions for hydrogen are H3, H7, and the amino hydrogens H9 and H10. In all mentioned cases, it is either the results obtained in gas-phase or DMSO that deviate from the others. For the amino hydrogens the NSCD is positive in gas phase, $C_{6}H_{12}$, and CHCl₃ with a systematic and striking decrease in intensity. Meanwhile, the signals are negative in DMSO. For these hydrogens, one should note that they can form hydrogen bonds to the oxygens in DMSO and to other AZO-3 molecules if the concentration is high. These effects are not captured by COSMO. Nevertheless, for all cases, the NSCD intensity has a monotonic increase or decrease with the increasing polarity of the solvent. There are three exceptions for the carbon nuclei with respect to producing the same sign in all environments: C2, C4, and C5. For C2 the trend is a monotonic increase in NSCD, while for C4 and C5 there is no clear trend. Both C4 and C5 have very weak signals, which makes them more susceptible to switching signs with even small perturbations of intensities, compared to, *e.g.*, similar fluctuations in C1 which has a stronger overall signal.

All in all, the starkest contrast to the signals computed in gas phase is obtained with the very polar DMSO solvent. The solvent effects seem to be most pronounced on the carbons bound to the N=N group, and the amino hydrogens for which proper description of hydrogen bonding between the molecule and the solvent can be of importance.

V. CONCLUDING REMARKS

We have presented a computational approach for the calculation of the nuclear spininduced circular dichroism property at the RI-CC2 level of theory. The implementation was demonstrated on a set of derivates of azobenzene, and the results were compared with the NSCD obtained from TD-DFT (BH+HLYP).

Comparing TD-DFT and CC2, a main observation is that the former seems to be less sensitive to the substituents. The spectra of the substituted C5 nucleus differed between the two methods for all three compounds, and for TD-DFT these spectra were similar in features to the neighboring, non-substituted carbon atoms. Furthermore, the discrepancies between the correlated and density-based methods have been found to follow the substituent character, especially for the chain of substituted atoms C5-C2-C7-C10. While -OH only influenced C5, the perturbative effect of $-NH_2$ propagated along the chain of substituted atoms. This propagation of discrepancies was amplified when adding a nitro group to C10.

This has implications for the selection of the computational method. Previous theoretical studies of NSCD, which were so far limited to the TD-DFT method, adopted the BH+HLYP functional since this had been proven to provide good results for the related NSOR effect,^{8,21} and therefore considered to be also suitable for NSCD. However, our study suggests that the functional does not provide a sufficiently good description of the substituent effects and/or the excited states. With the new implementation of CC2, it is possible to benchmark different functionals for this property, keeping in mind that CC2 is not suited for strongly correlated systems.

The substituent effects were found to be pronounced on the carbon nuclei only. While electron-donating groups appear to have little effect on the NSCD of the neighboring nuclei, the introduction of an electron-withdrawing group (strongly) enhances the strength of the NSCD of the carbon atoms in the local environment. This is especially observed when the transition is localized on the electron-withdrawing group. This relation, if proven more general, might have the potential to enable the experimental identification of the localization of a transition in a molecule with an electron-withdrawing group. The carbons with an electron-donating group exhibit in all cases damped signals at higher energies.

Compared to a previous study,²⁰ no clear cases of the NSCD-bright nuclei following the localization of the excitation were observed, although no strong NSCD was computed for nuclei without any difference density either. ES6 of AZO-3 (at CC2 level) offered the clearest example of this trend, a transition with a density difference strongly localized on the electron-withdrawing nitro group.

Relating our CC2 findings to an expected experiment for these systems, the results for AZO-1 and AZO-2 show that it is possible to distinguish the carbon atoms from the left and right rings based on the spectral shape. The carbons with an electron-donating group can be identified from damped signals, and the atoms connected by the N=N bridge can also be identified and assigned to the left or the right ring based on spectral shape. Distinguishing left from right did not prove to be straightforward for AZO-3.

The solvation study suggests that a solvent has the potential to strongly alter the NSCD of certain nuclei. In the presented case, DMSO enhances the NSCD signals of the bridged C2 and C7 significantly while C_6H_{12} and CHCl₃ did not bring about any striking changes compared to the gas phase calculations. It is interesting to note that previous studies of the influence of implicit solvent^{49,50} on the related NSOR effect showed only quantitative difference, affecting proportionally the strength of the signal, but not its sign. This suggests a larger importance of solvent effects for NSCD than for NSOR.

A major finding is that the ordering of the excited states can directly influence the predictions of the NSCD. From the SOS study it was illustrated how, in some situations, the sign of the \mathcal{B}_C term can flip by interchanging two strongly coupled states. As a result, the predicted NSCD can depend on the ordering of the transitions predicted by the theoretical model which, in turn, depends on the chosen combination of method and basis set. This effect resulted in opposite signs of the NSCD in an entire phenyl group between the equivalent excitations of AZO-1 and AZO-2 and between CC2/ES5 and TD-DFT/ES6 of AZO-3.

From this observation, it can be argued that if the sign of the NSCD depends on the localization of the excited states on the left or right ring as well as their energy order, NSCD can give an idea about the (relative) order of the (left/right localized) excitations. Although this would indeed require further analysis of the NTOs in combination with the NSCD to obtain a well-founded understanding of the observations, the insight into the nature of the excited states obtained from such investigations might provide valuable information in efforts devoted to the development of materials with tailored photophysical properties (e.g., for applications such as organic LEDs, artificial photosynthesis, organic photovoltaic cells, or photocatalysts).

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SUPPLEMENTARY INFORMATION AVAILABLE

Additional information: Cartesian coordinates, transition strengths, numerical NSCD data, NTOs, SOS decomposition

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The published work covering our procedure for computing X2PA with fc-CVS-EOM-CCSD [47] provides the derivations of the CVS-uS approach in the classical EOM notation. The theoretical strategy in a notation resembling the one adopted for response theory in Ref. [7] is presented in the following.

6.1 THE CVS-US APPROXIMATION IN AN ALTERNATIVE NOTATION

The two-photon transition tensor elements for the transition between the ground state 0 and an excited state *f* with excitation energy ω_f can in exact theory be represented by a SOS [44, 48, 49]

$$M_{0f}^{xy} = \frac{1}{\hbar} \sum_{k \in 0, f} \left[\frac{\langle 0|\mu_x|k\rangle \langle k|\mu_y|f\rangle}{\omega_k - \omega_1} + \frac{\langle 0|\mu_y|k\rangle \langle k|\mu_x|f\rangle}{\omega_k - \omega_2} \right]$$
(36)

where $\omega_1 + \omega_2 = \omega_f$ and $\mu^x (\mu^y)$ is a Cartesian component of the dipolemoment operator with $x(y) \in \{x, y, z\}$.

Since CC theory is non-Hermitian, the $0 \rightarrow f$ and $f \rightarrow 0$ transition moments are not the same. We translate the above SOS expression to CC formalism in terms of the CC one-photon transition moments [50]

$$M_{0f}^{xy} = -\sum_{k \in 0, f} \left[\frac{T_{0k}^{x} T_{kf}^{y}}{\omega_{k} - \omega_{2}} + \frac{T_{0k}^{y} T_{kf}^{x}}{\omega_{k} - \omega_{1}} \right]$$
(37)

and

$$M_{f0}^{xy} = -\sum_{k \in 0, f} \left[\frac{T_{fk}^y T_{k0}^x}{\omega_k - \omega_1} + \frac{T_{fk}^x T_{k0}^y}{\omega_k - \omega_2} \right] .$$
(38)

For EOM-CC, the general two-photon right and left transition moments take the form

$$M_{f0}^{xy}(\omega_1, \omega_2) = -P^{xy} \left\{ L_f \left[\mathbf{A}^x t^y(\omega_2) - (\bar{t} \cdot \xi^x) t^y(\omega_2) - (\bar{t} \cdot t^y(\omega_2))\xi^x \right] \right\}$$
(39)

and

$$M_{0f}^{xy}(\omega_1, \omega_2) = -P^{xy} \left\{ \left[\bar{t}^y(-\omega_2) \mathbf{A}^x - (\bar{t} \cdot \xi^x) \bar{t}^y(-\omega_2) \right] R_f - (\bar{t} \cdot R_f) \bar{t}^y(-\omega_2) \cdot \xi^x \right\}$$
(40)

where *P^{xy}* permutes the operator components and their associated frequencies. The response amplitudes and multipliers are solved from the expressions

$$(\mathbf{A} - \omega \mathbf{1}) t^{x}(\omega) = -\xi^{x}$$
(41)

$$\bar{t}^{x}(\omega)(\mathbf{A}-\omega\mathbf{1})=-\eta^{x}.$$
(42)

The details and definitions of the matrices and vectors are unimportant to the purpose of this evalutation; the interested reader is referred to, e.g., Ref. [11]. We recall that we are working within the CCSD approximation, that is, there are only singles and doubles indices.

If we now consider the case where the final state is a core-excited state *F*, we can imagine splitting the SOS transition moments in valence (lower-case *k*) and core (capital *K*) spaces

$$M_{0F}^{xy} = -\sum_{0,k} \left[\frac{T_{0k}^{x} T_{kF}^{y}}{\omega_{k} - \frac{1}{2}\omega_{F}} + \frac{T_{0k}^{y} T_{kF}^{x}}{\omega_{k} - \frac{1}{2}\omega_{F}} \right]$$
(43)

$$-\sum_{K} \left[\frac{T_{0K}^{x} T_{KF}^{y}}{\omega_{K} - \frac{1}{2} \omega_{F}} + \frac{T_{0K}^{y} T_{KF}^{x}}{\omega_{K} - \frac{1}{2} \omega_{F}} \right]$$
(44)

where the two incoming photons are now degenerate and equals half the energy it takes to promote the core electron from its ground state to the excited state F

$$\omega_1 = \omega_2 = \frac{1}{2}\omega_F . \tag{45}$$

By exploiting the fc-CVS framework for computing core-excited states, the constraints to the ground and excited states set the following conditions

- The ground state amplitudes have no core components: $t_{aI} = t_{aIbj} = t_{aibJ} = t_{aIbJ} = 0$
- The ground state multipliers have no core components: $\bar{t}_{aI} = \bar{t}_{aIbj} = \bar{t}_{aibJ} = \bar{t}_{aIbJ} = 0$
- The eigenvectors *R* and *L* have no valence components: $R_{ai} = R_{aibj} = 0$ and $L_{ai} = L_{aibj} = 0$
- The Jacobian is blocked:
 A_{μ_c,ν_v} = A_{ν_v,μ_c} = 0

where indices i, j refer to occupied and a, b to virtual molecular spinorbitals. I, J refer specifically to core occupied orbitals. The subscripts c, v denote general core and valence indices, respectively. Since **A** is blocked, we have decoupled the core and valence response amplitudes. In compact notation, the response amplitude equations then take the form

$$\begin{bmatrix} \mathbf{A}_{cc} - \frac{1}{2}\omega_F \mathbf{1}_{cc} & \mathbf{0} \\ \mathbf{0} & \mathbf{A}_{vv} - \frac{1}{2}\omega_F \mathbf{1}_{vv} \end{bmatrix} \begin{bmatrix} t_c^x \\ t_v^x \end{bmatrix} = -\begin{bmatrix} \boldsymbol{\xi}_c^x \\ \boldsymbol{\xi}_v^x \end{bmatrix} \,. \tag{46}$$

Thus, we have two separate equations for the core and valence components of the response amplitudes

$$\left(\mathbf{A}_{cc} - \frac{1}{2}\omega_F \mathbf{1}_{cc}\right) t_c^x \left(\frac{1}{2}\omega_F\right) = -\xi_c^x \tag{47}$$

$$\left(\mathbf{A}_{vv} - \frac{1}{2}\omega_F \mathbf{1}_{vv}\right) t_v^x(\frac{1}{2}\omega_F) = -\xi_v^x .$$
(48)

This also applies to the response multipliers

$$\bar{t}_c^x(\frac{1}{2}\omega_F)(\mathbf{A}_{cc} - \frac{1}{2}\omega_F \mathbf{1}_{cc}) = -\eta_c^x \tag{49}$$

$$\mathbf{I}_{v}^{\mathbf{x}}(\frac{1}{2}\omega_{F})\left(\mathbf{A}_{vv}-\frac{1}{2}\omega_{F}\mathbf{1}_{vv}\right)=-\eta_{v}^{\mathbf{x}}.$$
(50)

In the spirit of the partitioned SOS expression in Eq. (43), we may then calculate the transition moments in Eqs. (39) and (40) from separate valence and core terms.

In practice, however, the condition of Eq. (45) causes problems. Half the value of a core excitation frequency lies above the ionization limit of valence electrons, i.e., in an area with many close-lying excitations. As a result, $(\mathbf{A} - \frac{1}{2}\omega_f \mathbf{1})$ can become divergent, leading to convergence issues in the response equations. Closer inspection reveals that the divergences occur only in the valence space; the diagonal of the Jacobian in the core space contains (much) larger values than half a core excitation energy. It is thus in the same mindset as in the fc-CVS approximation that we introduce further constraints on the valence response equations by removing all doubles components such that

$$A_{v_n v_m} = 0 \quad \text{for} \quad n, m = 2 \tag{51}$$

$$t_{v_n}^x = 0 \quad \text{for} \quad n = 2 \tag{52}$$

$$f_{v_n}^x = 0 \quad \text{for} \quad n = 2 \tag{53}$$

where *n*,*m* indicate the excitation level. By doing so, we remove unphysical states that are resonant with the photon frequency, and the valence response equations exhibit robust convergence.

Ultimately, the transition moments are put together from terms collecting the core indices and terms collecting the singles-only valence indicies, hence the name of the approximation: "core–valence separation and uncoupled valence singles".

CONCLUSION AND OUTLOOK

A variety of spectroscopies have been made available for calculation with coupled cluster theory, specifically EOM-CCSD and RI-CC2 response theory. Several techniques probing different molecular responses of both core and valence electrons have been implemented: (damped) ECD, optical rotation, (damped) MCD, NSCD, and X2PA. Each of those techniques provides different insights into the system under investigation.

Based on the new implementation of ECD within the EOM-CCSD framework, the ground and excited state ECD of various chiral molecules was investigated in the regimes of valence and core excitations (Publication I). The studies in the X-ray region revealed interesting connections between the gauge origin and spectral shapes when the transitions are particularly localized.

From the combination of resonant and damped response calculations, a methodology for computing an MCD spectrum in a broad frequency range was developed (Manuscript I). Among future prospects is the generalization of the implementation of damped quadratic response for MCD in TURBOMOLE to include damped NSCD and magneto-chiral circular dichroism. Furthermore, an extension of the damped quadratic response function to include solvent effects is within immediate reach.

A localized equivalent of MCD, NSCD, was studied for a small set of substituted azobenzenes (Manuscript II). Connections were made between the NSCD and the effects of substituents and solvents, and the possible identification of the nuclei based on spectral shapes was discussed. Measuring NSCD experimentally continues to be a challenging work in progress.

With a starting point in the divergence issues of the response equations when computing X2PA with the EOM-CCSD method, approximations to the response space was introduced. The efforts resulted in an implementation showing robust convergence while including significant contributions from the valence singles space (Publication II). This work offers a platform for future developments within higher-order multiphoton processes as well as a basis for benchmarking this, at present, much unexplored property. The X2PA of molecules of the modest sizes considered in this study remains experimentally unfeasible to date. However, when the experimental facilities are mature, the theory is ready to provide insight and support.

The diversity of spectroscopies that can be simulated using coupled cluster theory has thus been demonstrated. The various properties are, or will soon be (relative to the time of writing), released to the entire scientific community in two major quantum chemistry codes, Q-Chem and TURBOMOLE. They open the door for further investigations of the phenomena, some of which are still sparsely investigated theoretically and/or experimentally. Hopefully, (parts of) this work will act as platform and/or inspiration for future studies, continuing the expansion of humanity's shared knowledge base. Part III

APPENDIX



SUPPORTING INFORMATION: MANUSCRIPT I

"Supporting Information: An efficient protocol for computing MCD spectra in a broad frequency range combining resonant and damped CC2 quadratic response theory" Josefine H. Andersen, S. Coriani, and C. Hättig **2023** (*Submitted*)

Supporting Information: An efficient protocol for computing MCD spectra in a broad frequency range combining resonant and damped CC2 quadratic response theory.

Josefine H. Andersen, *,† Sonia Coriani, *,† and Christof Hättig*,‡

 †Department of Chemistry, Technical University of Denmark, Kemitorvet Building 207, DK-2800 Kongens Lyngby, Denmark
 ‡Arbeitsgruppe Quantenchemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

E-mail: johvan@kemi.dtu.dk; soco@kemi.dtu.dk; christof.haettig@rub.de

S1 Relevant CC building blocks

Table S1: Definition of the relevant CC building blocks. \mathcal{L} is the time-averaged quasi-energy Lagrangian, T is the cluster operator, τ_{μ} is an excitation operator (for excitation level μ), and ϵ_X is the strength of the perturbation associated with operator X. For additional information, see, e.g., Ref. S1.

| $ \mathrm{CC}\rangle$ | = | $\exp(T) \mathrm{HF}\rangle$ | |
|-----------------------|---|---|---|
| $\langle \Lambda $ | = | $(\langle \mathrm{HF} + \sum_{\mu} \bar{t}_{\mu} \langle \mu) \exp(-T)$ | |
| Matrix elements | | Derivative formulation | Explicit expression |
| $A_{\mu\nu}$ | = | $\frac{\partial^2 \mathcal{L}}{\partial \bar{t}_{\mu} \partial t_{\nu}}$ | $\langle \mu \exp(-T)[H, \tau_{\nu}] \exp(T) \mathrm{HF} \rangle$ |
| $B_{\mu\nu\gamma}$ | = | $\frac{\partial^3 \mathcal{L}}{\partial \bar{t}_{\mu} \partial t_{\nu} \partial t_{\gamma}}$ | $\langle \mu \exp(-T)[[H, \tau_{\nu}], \tau_{\gamma}] \exp(T) \mathrm{HF} \rangle$ |
| $F_{\mu\nu}$ | = | $\frac{\dot{\partial}^2 \mathcal{L}}{\partial t_\mu \partial t_\nu}$ | $\langle \Lambda [[H, \tau_{\mu}], \tau_{\nu}] \mathrm{CC} \rangle$ |
| $G_{\mu\nu\gamma}$ | = | $\frac{\partial^3 \mathcal{L}}{\partial t_\mu \partial t_\nu \partial t_\gamma}$ | $\langle \Lambda [[[H, \tau_{\mu}], \tau_{\nu}], \tau_{\gamma} \mathrm{CC} \rangle$ |
| ξ^X_μ | = | $\frac{\partial^2 \mathcal{L}}{\partial t_{\mu} \partial \varepsilon_X}$ | $\langle \mu \exp(-T) X \exp(T) \mathrm{HF} \rangle$ |
| $A^X_{\mu\nu}$ | = | $\frac{\partial^{3} \mathcal{L}}{\partial \bar{t}_{\mu} \partial t_{\nu} \partial \varepsilon_{X}}$ | $\langle \mu \exp(-T)[X, \tau_{\nu}] \exp(T) \mathrm{HF} \rangle$ |
| η^X_μ | = | $\frac{\partial^2 \mathcal{L}}{\partial \bar{t}_{\mu} \partial \varepsilon_X}$ | $\langle \Lambda [X, \tau_{\mu}] \mathrm{CC} \rangle$ |
| $F^X_{\mu\nu}$ | = | $\frac{\partial^3 \mathcal{L}}{\partial t_\mu \partial t_\nu \partial \varepsilon_X}$ | $\langle \Lambda [[X, \tau_{\mu}], \tau_{\nu}] \mathrm{CC} \rangle$ |

S2 Coordinates

In Angstrom and xyz format. 61 atoms.

| Η | 4.4937189 | -6.2352038 | 0.000000 |
|---|------------|------------|-----------|
| N | 1.4527967 | 1.4527967 | 0.0000000 |
| N | -1.4527967 | 1.4527967 | 0.0000000 |
| N | -1.4527967 | -1.4527967 | 0.0000000 |
| N | 1.4527967 | -1.4527967 | 0.0000000 |
| С | -0.000000 | 3.4285263 | 0.0000000 |
| С | -3.4285263 | 0.0000000 | 0.0000000 |
| С | -0.0000000 | -3.4285263 | 0.0000000 |
| С | 3.4285263 | 0.0000000 | 0.0000000 |
| С | 1.2418640 | 2.8101113 | 0.0000000 |
| С | -2.8101113 | 1.2418640 | 0.0000000 |
| С | -1.2418640 | -2.8101113 | 0.0000000 |
| С | 2.8101113 | -1.2418640 | 0.0000000 |
| С | 2.8101113 | 1.2418640 | 0.0000000 |
| С | -1.2418640 | 2.8101113 | 0.0000000 |
| С | -2.8101113 | -1.2418640 | 0.0000000 |
| С | 1.2418640 | -2.8101113 | 0.0000000 |
| С | 2.5101122 | 3.5058807 | 0.0000000 |
| С | -3.5058807 | 2.5101122 | 0.0000000 |
| С | -2.5101122 | -3.5058807 | 0.0000000 |
| С | 3.5058807 | -2.5101122 | 0.0000000 |
| С | 3.5058807 | 2.5101122 | 0.0000000 |
| С | -2.5101122 | 3.5058807 | 0.0000000 |
| С | -3.5058807 | -2.5101122 | 0.0000000 |
| С | 2.5101122 | -3.5058807 | 0.0000000 |
| С | 2.8511067 | 4.8602058 | 0.0000000 |
| С | -4.8602058 | 2.8511067 | 0.0000000 |
| С | -2.8511067 | -4.8602058 | 0.0000000 |
| С | 4.8602058 | -2.8511067 | 0.0000000 |
| С | 4.8602058 | 2.8511067 | 0.0000000 |

| С | -2.8511067 | 4.8602058 | 0.0000000 |
|----|------------|------------|-----------|
| С | -4.8602058 | -2.8511067 | 0.0000000 |
| С | 2.8511067 | -4.8602058 | 0.0000000 |
| С | 4.2000838 | 5.1940575 | 0.0000000 |
| С | -5.1940575 | 4.2000838 | 0.0000000 |
| С | -4.2000838 | -5.1940575 | 0.0000000 |
| С | 5.1940575 | -4.2000838 | 0.0000000 |
| С | 5.1940575 | 4.2000838 | 0.0000000 |
| С | -4.2000838 | 5.1940575 | 0.0000000 |
| С | -5.1940575 | -4.2000838 | 0.0000000 |
| С | 4.2000838 | -5.1940575 | 0.0000000 |
| Н | 2.0940270 | 5.6341683 | 0.0000000 |
| Н | -5.6341683 | 2.0940270 | 0.0000000 |
| Н | -2.0940270 | -5.6341683 | 0.0000000 |
| Н | 5.6341683 | -2.0940270 | 0.0000000 |
| Н | 5.6341683 | 2.0940270 | 0.000000 |
| Н | -2.0940270 | 5.6341683 | 0.0000000 |
| Н | -5.6341683 | -2.0940270 | 0.0000000 |
| Н | 2.0940270 | -5.6341683 | 0.0000000 |
| Н | 4.4937189 | 6.2352038 | 0.0000000 |
| Н | 6.2352038 | 4.4937189 | 0.0000000 |
| Н | -6.2352038 | -4.4937189 | 0.0000000 |
| Н | -4.4937189 | -6.2352038 | 0.0000000 |
| Н | -6.2352038 | 4.4937189 | 0.000000 |
| Н | -4.4937189 | 6.2352038 | 0.0000000 |
| Н | 6.2352038 | -4.4937189 | 0.000000 |
| Н | 0.000000 | -4.5117982 | 0.000000 |
| Н | -4.5117982 | 0.0000000 | 0.000000 |
| Н | 4.5117982 | 0.0000000 | 0.000000 |
| Н | 0.000000 | 4.5117982 | 0.000000 |
| Zn | 0.000000 | 0.0000000 | 0.000000 |

S3 Raw data

Table S2: ZnTBP. Excitation frequency ω_j (au and eV), oscillator strength f_j , MCD \mathcal{B}_j and \mathcal{A}_j terms for the *j* states of indicated symmetry (Irrep) in the D_{2h} and D_{4h} point groups. The molecule's "true" point group is D_{4h} , the computations were done in D_{2h} .

| Irrep. D_{2h} | Irrep. \mathbf{D}_{4h} | Band | $\omega_j/{\rm au}$ | $\omega_j/{\rm eV}$ | f_j | \mathcal{B}_{j} | \mathcal{A}_{j} |
|---|--------------------------|------|---|---|---|---|----------------------|
| $\begin{array}{c} \mathbf{B}_{2u} \\ \mathbf{B}_{3u} \end{array}$ | E_u | Q | $0.0872 \\ 0.0872$ | $2.37 \\ 2.37$ | $0.1524 \\ 0.1524$ | $\begin{array}{c} 120.5239 \\ 120.5239 \end{array}$ | $-3.3266 \\ -3.3266$ |
| $\begin{array}{c} \mathbf{B}_{2u} \\ \mathbf{B}_{3u} \end{array}$ | E_u | В | $\begin{array}{c} 0.1209 \\ 0.1209 \end{array}$ | $3.29 \\ 3.29$ | $1.3578 \\ 1.3578$ | $-63.3364 \\ -63.3364$ | $-4.1220 \\ -4.1220$ |
| $\begin{array}{c} \mathbf{B}_{2u} \\ \mathbf{B}_{3u} \end{array}$ | E_u | | $\begin{array}{c} 0.1496 \\ 0.1496 \end{array}$ | $\begin{array}{c} 4.07\\ 4.07\end{array}$ | $0.0246 \\ 0.0246$ | $-15.7819 \\ -15.7819$ | $0.0525 \\ 0.0525$ |
| $\begin{array}{c} \mathbf{B}_{2u} \\ \mathbf{B}_{3u} \end{array}$ | E_u | | $\begin{array}{c} 0.1528 \\ 0.1528 \end{array}$ | $\begin{array}{c} 4.16\\ 4.16\end{array}$ | $0.0050 \\ 0.0050$ | $\frac{16.7140}{16.7140}$ | $0.0318 \\ 0.0318$ |
| $\begin{array}{c} \mathbf{B}_{2u} \\ \mathbf{B}_{3u} \end{array}$ | E_u | Ν | $\begin{array}{c} 0.1638 \\ 0.1638 \end{array}$ | $4.46 \\ 4.46$ | $0.0597 \\ 0.0597$ | $-285.9130 \\ -285.9130$ | $-0.0427 \\ -0.0427$ |
| B_{1u} | A_{2u} | | 0.1665 | 4.53 | 0.0016 | -8.3996 | 0.0000 |
| $\begin{array}{c} \mathbf{B}_{2u} \\ \mathbf{B}_{3u} \end{array}$ | E_u | Ν | $\begin{array}{c} 0.1673 \\ 0.1673 \end{array}$ | $4.55 \\ 4.55$ | $\begin{array}{c} 0.1510 \\ 0.1510 \end{array}$ | 271.3286 271.3287 | $-0.2376 \\ -0.2376$ |
| $\begin{array}{c} \mathbf{B}_{2u} \\ \mathbf{B}_{3u} \end{array}$ | E_u | | $\begin{array}{c} 0.1741 \\ 0.1741 \end{array}$ | $\begin{array}{c} 4.74 \\ 4.74 \end{array}$ | $0.0018 \\ 0.0018$ | _ | _ |
| $\begin{array}{c} \mathbf{B}_{2u} \\ \mathbf{B}_{3u} \end{array}$ | E_u | L | $\begin{array}{c} 0.1863 \\ 0.1863 \end{array}$ | $5.07 \\ 5.07$ | $0.1990 \\ 0.1990$ | _ | _ |
| B_{1u} | A_{2u} | | 0.1870 | 5.09 | 0.0052 | — | — |

| ω | Abs. | MCD |
|-------|---------|------------|
| 0.145 | 133.54 | 6534.19 |
| 0.150 | 139.13 | -7713.47 |
| 0.155 | 126.38 | -29517.01 |
| 0.160 | 169.86 | -99212.61 |
| 0.165 | 296.00 | -75991.06 |
| 0.170 | 246.98 | 118076.25 |
| 0.175 | 154.68 | 31567.15 |
| 0.180 | 177.63 | 1115.78 |
| 0.185 | -327.24 | -11332.57 |
| 0.190 | 311.13 | -4226.40 |
| 0.195 | 367.01 | -305.34 |
| 0.200 | 480.70 | -108838.34 |
| 0.205 | 638.34 | -188948.44 |
| 0.210 | 945.05 | -138535.01 |
| 0.215 | 670.33 | 214749.28 |
| 0.220 | 441.63 | 80876.68 |
| 0.225 | 279.47 | 6755.28 |
| 0.230 | 245.02 | 31014.91 |
| 0.240 | 218.25 | -46897.86 |
| 0.250 | 265.45 | -38354.63 |
| 0.260 | 619.71 | -34339.19 |
| 0.270 | 467.79 | -1419.03 |
| 0.280 | 288.17 | 13537.87 |
| 0.290 | 151.33 | 8400.66 |
| 0.300 | 179.63 | 13245.31 |
| | | |

Table S3: ZnTBP. Damped absorption and MCD signals at frequency ω (au).

S4 Additional figures



Figure S1: ZnTBP. Absorption (upper) and MCD (lower) spectra from standard and damped response at the RI-CC2/aug-cc-pVDZ level of theory. The interpolated spectrum is built on a uniform coarse grid with energy steps of 0.01 au throughout.



Figure S2: ZnTBP. Absorption spectra in three energy regions with experimental spectra from Ref. S2. RI-CC2/aug-cc-pVDZ results. All theoretical energies have been shifted by -0.226 eV (-1824.6 cm^{-1}) to align with the absorption peak of the B-band. HWHMs of 7 cm⁻¹ (Q-band, upper left), 20 cm⁻¹ (B-band, upper right), and 1000 cm⁻¹ (N–X region, lower panel). The experimental spectra are presented without ε values.



Figure S3: ZnTBP. MCD spectra in three energy regions with experimental spectra from Ref. S2. RI-CC2/aug-cc-pVDZ results. All theoretical energies have been shifted by -0.226 eV (-1824.6 cm^{-1}) to align with the absorption peak of the B-band. HWHMs of 7 cm⁻¹ (Q-band, upper left), 20 cm⁻¹ (B-band, upper right), and 1000 cm⁻¹ (N–X region, lower panel). The experimental spectra are presented without θ values.

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S5 Detailed derivation of the linear response equations for the perturbed Lagrange multipliers with complex frequencies

This derivation closely resembles the derivation of the equivalent equations for the complex perturbed amplitudes from the work of Fedotov et al.^{S3} In the following, the perturbed multipliers (\bar{t}^X) are referred to as L, while the perturbed amplitudes t^X are referred to as R. The reason for this change of notation is that this is how they write it in the Turbomole manual.

The linear equation(s) for the perturbed multipliers with a complex frequency, $\omega + i\gamma$, can be written in block notation

$$\begin{bmatrix} L_S & L_D \end{bmatrix} \left(\begin{bmatrix} \mathbf{A}_{SS} & \mathbf{A}_{SD} \\ \mathbf{A}_{DS} & \mathbf{A}_{DD} \end{bmatrix} + \begin{bmatrix} \mathbf{1}_{SS} & 0 \\ 0 & \mathbf{1}_{DD} \end{bmatrix} (\omega + i\gamma) \right) = -\begin{bmatrix} \xi_S & \xi_D \end{bmatrix}$$
(S1)

where subscripts S, D refer to the singles and doubles excitation components of the vector/matrix, and both L and ξ are frequency dependent. Note that in this notation, ξ is used as a general notation for the right-hand-side (RHS) and is *not* the CC (right) response vector ξ^X .

The RHS of Eq. (S1) is

$$\xi = \eta^X + \mathbf{F}R \ . \tag{S2}$$

Remember here that R is a perturbed amplitude.

From the matrix/vector form, we separate the linear equations into one for singles and one for doubles (with respect to the RHS):

$$L_S \mathbf{A}_{SS} + L_D \mathbf{A}_{DS} + (\omega + i\gamma) L_S = -\xi_S \tag{S3a}$$

$$L_S \mathbf{A}_{SD} + L_D \mathbf{A}_{DD} + (\omega + i\gamma) L_D = -\xi_D .$$
(S3b)

The L vectors are complex and can be written as

$$L_S = L_S^R + iL_S^I, \quad L_D = L_D^R + iL_D^I.$$
(S4)

We insert the above into Eqs. (S3a) and (S3b), which are then each split into two, by collecting separately the real and imaginary parts. With respect to the singles of the RHS, this gives first

$$(L_S^R + iL_S^I)\mathbf{A}_{SS} + (L_D^R + iL_D^I)\mathbf{A}_{DS} + (L_S^R + iL_S^I)(\omega + i\gamma) = -\xi_S^R - i\xi_S^I$$

which further becomes

$$L_S^R \mathbf{A}_{SS} + L_D^R \mathbf{A}_{DS} + L_S^R \omega - L_S^I \gamma = -\xi_S^R \tag{S5a}$$

$$L_S^I \mathbf{A}_{SS} + L_D^I \mathbf{A}_{DS} + L_S^I \omega + L_S^R \gamma = -\xi_S^I .$$
(S5b)

For the doubles, we get

$$(L_{S}^{R}+iL_{S}^{I})\mathbf{A}_{SD}+(L_{D}^{R}+iL_{D}^{I})\mathbf{A}_{DD}+(L_{D}^{R}+iL_{D}^{I})(\omega+i\gamma)=-\xi_{D}^{R}-i\xi_{D}^{I}$$
(S6a)

which becomes

$$L_S^R \mathbf{A}_{SD} + L_D^R \mathbf{A}_{DD} + L_D^R \omega - L_D^I \gamma = -\xi_D^R \tag{S6b}$$

$$L_S^I \mathbf{A}_{SD} + L_D^I \mathbf{A}_{DD} + L_D^I \omega + L_D^R \gamma = -\xi_D^I .$$
(S6c)

The above equations are rewritten to isolate either the singles or doubles on the left hand

side:

$$L_S^R(\mathbf{A}_{SS} + \omega \mathbf{1}_{SS}) - L_S^I \gamma = -\xi_S^R - L_D^R \mathbf{A}_{DS}$$
(S7a)

$$L_S^I(\mathbf{A}_{SS} + \omega \mathbf{1}_{SS}) + L_S^R \gamma = -\xi_S^I - L_D^I \mathbf{A}_{DS}$$
(S7b)

$$L_D^R(\mathbf{A}_{DD} + \omega \mathbf{1}_{DD}) - L_D^I \gamma = -\xi_D^R - L_S^R \mathbf{A}_{SD}$$
(S7c)

$$L_D^I(\mathbf{A}_{DD} + \omega \mathbf{1}_{DD}) + L_D^R \gamma = -\xi_D^I - L_S^I \mathbf{A}_{SD} .$$
 (S7d)

We now introduce the matrix

$$\Delta = \mathbf{A}_{DD} + \omega \mathbf{1}_{DD} \tag{S8}$$

and isolate L_D^R and L_D^I in Eqs. (S7c) and (S7d), respectively

$$L_D^R \mathbf{\Delta} = -\xi_D^R - L_S^R \mathbf{A}_{SD} + L_D^I \gamma$$
(S9a)

$$\Rightarrow L_D^R = -\left(\xi_D^R + L_S^R \mathbf{A}_{SD} - L_D^I \gamma\right) \frac{1}{\Delta}$$
(S9b)

$$L_D^I \boldsymbol{\Delta} = -\xi_D^I - L_S^I \mathbf{A}_{SD} - L_D^R \boldsymbol{\gamma}$$
(S9c)

$$\Rightarrow L_D^I = -\left(\xi_D^I + L_S^I \mathbf{A}_{SD} + L_D^R \gamma\right) \frac{1}{\Delta} .$$
 (S9d)

We insert Eq. (S9c) into (S9a) to obtain an expression for the doubles multipliers in terms of the singles:

$$L_D^R = -\left\{\xi_D^R + L_S^R \mathbf{A}_{SD} - \left[-\left(\xi_D^I + L_S^I \mathbf{A}_{SD} + L_D^R \gamma\right) \frac{1}{\Delta}\right] \gamma\right\} \frac{1}{\Delta}$$
$$= -\left(\xi_D^R + L_S^R \mathbf{A}_{SD}\right) \frac{1}{\Delta} - \left(\xi_D^I + L_S^I \mathbf{A}_{SD} + L_D^R \gamma\right) \frac{\gamma}{\Delta^2} .$$
(S10)

We collect the terms involving L_D on the left hand side and simplify as follows

$$L_D^R + L_D^R \frac{\gamma^2}{\Delta^2} = L_D^R \frac{\Delta^2}{\Delta^2} + L_D^R \frac{\gamma^2}{\Delta^2} = L_D^R \frac{\Delta^2 + \gamma^2}{\Delta^2}$$
(S11)

and obtain

$$L_D^R = \left[-\left(\xi_D^R + L_S^R \mathbf{A}_{SD}\right) \frac{1}{\Delta} - \left(\xi_D^I + L_S^I \mathbf{A}_{SD}\right) \frac{\gamma}{\Delta^2} \right] \frac{\Delta^2}{\Delta^2 + \gamma^2}$$
(S12)

$$= -\left(\xi_D^R + L_S^R \mathbf{A}_{SD}\right) \frac{\boldsymbol{\Delta}}{\boldsymbol{\Delta}^2 + \gamma^2} - \left(\xi_D^I + L_S^I \mathbf{A}_{SD}\right) \frac{\gamma}{\boldsymbol{\Delta}^2 + \gamma^2} \,. \tag{S13}$$

With the exact same procedure, we obtain for ${\cal L}_D^I$ the expression

$$L_D^I = -\left(\xi_D^I + L_S^I \mathbf{A}_{SD}\right) \frac{\mathbf{\Delta}}{\mathbf{\Delta}^2 + \gamma^2} + \left(\xi_D^R + L_S^R \mathbf{A}_{SD}\right) \frac{\gamma}{\mathbf{\Delta}^2 + \gamma^2} \,. \tag{S14}$$

We now return to the linear equations (S7a) and (S7b). In Eq. (S7a) we substitute L_D^R with the expression obtained in (S12):

$$L_{S}^{R}(\mathbf{A}_{SS} + \omega \mathbf{1}_{SS}) - L_{S}^{I}\gamma = -\xi_{S}^{R} - \left[-\left(\xi_{D}^{R} + L_{S}^{R}\mathbf{A}_{SD}\right)\frac{\boldsymbol{\Delta}}{\boldsymbol{\Delta}^{2} + \gamma^{2}} - \left(\xi_{D}^{I} + L_{S}^{I}\mathbf{A}_{SD}\right)\frac{\gamma}{\boldsymbol{\Delta}^{2} + \gamma^{2}} \right] \mathbf{A}_{DS}$$
$$= -\xi_{S}^{R} + \xi_{D}^{R}\frac{\boldsymbol{\Delta}}{\boldsymbol{\Delta}^{2} + \gamma^{2}}\mathbf{A}_{DS} + L_{S}^{R}\mathbf{A}_{SD}\frac{\boldsymbol{\Delta}}{\boldsymbol{\Delta}^{2} + \gamma^{2}}\mathbf{A}_{DS}$$
$$+ \xi_{D}^{I}\frac{\gamma}{\boldsymbol{\Delta}^{2} + \gamma^{2}}\mathbf{A}_{DS} + L_{S}^{I}\mathbf{A}_{SD}\frac{\gamma}{\boldsymbol{\Delta}^{2} + \gamma^{2}}\mathbf{A}_{DS} .$$
(S15)

The above equation is then rearranged to collect all singles multipliers on the left of the equal sign:

$$L_{S}^{R}(\mathbf{A}_{SS} + \omega \mathbf{1}_{SS}) - L_{S}^{I}\gamma - L_{S}^{R}\mathbf{A}_{SD}\frac{\boldsymbol{\Delta}}{\boldsymbol{\Delta}^{2} + \gamma^{2}}\mathbf{A}_{DS} - L_{S}^{I}\mathbf{A}_{SD}\frac{\gamma}{\boldsymbol{\Delta}^{2} + \gamma^{2}}\mathbf{A}_{DS}$$
$$= L_{S}^{R}\left(\mathbf{A}_{SS} + \omega \mathbf{1}_{SS} - \mathbf{A}_{SD}\frac{\boldsymbol{\Delta}}{\boldsymbol{\Delta}^{2} + \gamma^{2}}\mathbf{A}_{DS}\right) - L_{S}^{I}\left(\mathbf{A}_{SD}\frac{\gamma}{\boldsymbol{\Delta}^{2} + \gamma^{2}}\mathbf{A}_{DS} + \gamma\right)$$
$$= -\xi_{S}^{R} + \xi_{D}^{R}\frac{\boldsymbol{\Delta}}{\boldsymbol{\Delta}^{2} + \gamma^{2}}\mathbf{A}_{DS} + \xi_{D}^{I}\frac{\gamma}{\boldsymbol{\Delta}^{2} + \gamma^{2}}\mathbf{A}_{DS} .$$
(S16)

We now introduce the effective matrices

$$\mathbf{A}_{SS}^{\text{eff}} = \mathbf{A}_{SS} - \mathbf{A}_{SD} \frac{\mathbf{\Delta}}{\mathbf{\Delta}^2 + \gamma^2} \mathbf{A}_{DS}$$
(S17)

$$\Gamma_{SS}^{\text{eff}} = \mathbf{A}_{SD} \frac{\gamma}{\mathbf{\Delta}^2 + \gamma^2} \mathbf{A}_{DS}$$
(S18)

and write the effective linear equation

$$L_S^R(\mathbf{A}_{SS}^{\text{eff}} + \omega \mathbf{1}_{SS}) - L_S^I(\Gamma_{SS}^{\text{eff}} + \gamma) = -\xi_S^{R,\text{eff}}$$
(S19)

where the (real) effective RHS is

$$\xi_S^{R,\text{eff}} = \xi_S^R - \xi_D^R \frac{\Delta}{\Delta^2 + \gamma^2} \mathbf{A}_{DS} - \xi_D^I \frac{\gamma}{\Delta^2 + \gamma^2} \mathbf{A}_{DS} .$$
(S20)

Again, we do the same for the imaginary counterparts (Eqs. (S7b) and (S14)) and arrive at the equation

$$L_{S}^{I}\left(\mathbf{A}_{SS}+\omega\mathbf{1}_{SS}-\mathbf{A}_{SD}\frac{\mathbf{\Delta}}{\mathbf{\Delta}^{2}+\gamma^{2}}\mathbf{A}_{DS}\right)+L_{S}^{R}\left(\mathbf{A}_{SD}\frac{\gamma}{\mathbf{\Delta}^{2}+\gamma^{2}}\mathbf{A}_{DS}+\gamma\right)$$
$$=-\xi_{S}^{I}+\xi_{D}^{I}\frac{\mathbf{\Delta}}{\mathbf{\Delta}^{2}+\gamma^{2}}\mathbf{A}_{DS}-\xi_{D}^{R}\frac{\gamma}{\mathbf{\Delta}^{2}+\gamma^{2}}\mathbf{A}_{DS}$$
(S21)

which abbreviates to

$$L_{S}^{I}(\mathbf{A}_{SS}^{\text{eff}} + \omega \mathbf{1}_{SS}) + L_{R}^{I}(\mathbf{\Gamma}_{SS}^{\text{eff}} + \gamma) = -\xi_{S}^{I,\text{eff}}$$
(S22)

with

$$\xi_S^{I,\text{eff}} = \xi_S^I - \xi_D^I \frac{\Delta}{\Delta^2 + \gamma^2} \mathbf{A}_{DS} + \xi_D^R \frac{\gamma}{\Delta^2 + \gamma^2} \mathbf{A}_{DS} .$$
(S23)

In compact matrix-vector form, we thus have

$$\begin{bmatrix} L_S^R & L_S^I \end{bmatrix} \begin{bmatrix} \mathbf{A}_{SS}^{\text{eff}} + \omega \mathbf{1}_{SS} & (\mathbf{\Gamma}_{SS}^{\text{eff}} + \gamma \mathbf{1}_{SS}) \\ -(\mathbf{\Gamma}_{SS}^{\text{eff}} + \gamma \mathbf{1}_{SS}) & \mathbf{A}_{SS}^{\text{eff}} + \omega \mathbf{1}_{SS} \end{bmatrix} = -\begin{bmatrix} \xi_S^{R,\text{eff}} & \xi_S^{I,\text{eff}} \end{bmatrix}.$$
(S24)

SS5.1 The RHS of the complex perturbed multipliers

The right-hand-side of the perturbed multipliers equations is

$$\xi = \eta^X + \mathbf{F}R \ . \tag{S25}$$

As for the complex solution vectors, the RHS can be written in matrix/vector form and split into real and imaginary components

$$\begin{bmatrix} \xi_{S}^{R} \\ \xi_{D}^{R} \\ \xi_{D}^{I} \\ \xi_{S}^{I} \\ \xi_{D}^{I} \end{bmatrix}^{\mathrm{T}} = \begin{bmatrix} \eta_{S}^{X,R} \\ \eta_{D}^{X,R} \\ \eta_{S}^{X,I} \\ \eta_{D}^{X,I} \end{bmatrix}^{\mathrm{T}} + \begin{pmatrix} \begin{bmatrix} \mathbf{F}_{SS} & \mathbf{F}_{SD} & \mathbf{0} \\ \mathbf{F}_{DS} & \mathbf{0} & \mathbf{0} \\ \mathbf{F}_{DS} & \mathbf{F}_{SD} \\ \mathbf{0} & \mathbf{F}_{DS} & \mathbf{0} \end{bmatrix} \begin{bmatrix} R_{S}^{R} \\ R_{D}^{R} \\ R_{S}^{I} \\ R_{D}^{I} \end{bmatrix} \end{pmatrix}^{\mathrm{T}}$$
(S26)

where also we used the fact that $\mathbf{F}_{DD} = \mathbf{0}$ for CC2. The above corresponds to the four equations

$$\xi_S^R = \eta_S^{X,R} + \mathbf{F}_{SS} R_S^R + \mathbf{F}_{SD} R_D^R \tag{S27a}$$

$$\xi_D^R = \eta_D^{X,R} + \mathbf{F}_{DS} R_S^R \tag{S27b}$$

$$\xi_S^I = \eta_S^{X,I} + \mathbf{F}_{SS} R_S^I + \mathbf{F}_{SD} R_D^I \tag{S27c}$$

$$\xi_D^I = \eta_D^{X,I} + \mathbf{F}_{DS} R_S^I \ . \tag{S27d}$$

The R vectors are the complex perturbed amplitudes and there will thus always be both a real and an imaginary contribution to the RHS.

S6 Minimization of the residual for the CPP response equations in RI-CC2

SS6.1 Theory

If the approximate solution of a (real-valued) linear equation $\mathbf{M}\mathbf{x} = -\mathbf{y}$ is expanded in a set of orthonormal basis vectors \mathbf{b}_i , the coefficients c_i for the solution $\sum_i c_i \mathbf{b}_i$ which minimize the squared norm $||\mathbf{R}||^2$ of the residual $\mathbf{R} = \mathbf{M}\mathbf{x} + \mathbf{y}$ are determined by the condition:

$$0 = \frac{\mathrm{d}||\mathbf{R}||^2}{\mathrm{d}c_k} \quad \forall c_k \;. \tag{S28}$$

Inserting the expansion of the solution vector \mathbf{x} in the basis vectors

$$\mathbf{R} = \sum_{i} c_i \mathbf{M} \mathbf{b}_i + \mathbf{y} = \sum_{i} c_i \boldsymbol{\sigma}_i + \mathbf{y}$$
(S29)

with the transformed basis vectors $\sigma_i = \mathbf{M}\mathbf{b}_i$, we obtain the condition for optimal coefficients c_i :

$$0 = \frac{d}{dc_k} \left(\sum_i c_i \boldsymbol{\sigma}_i + \mathbf{y} \right) \cdot \left(\sum_j c_j \boldsymbol{\sigma}_j + \mathbf{y} \right)$$
(S30)

$$= \boldsymbol{\sigma}_{k} \cdot \left(\sum_{j} c_{j} \boldsymbol{\sigma}_{j} + \mathbf{y}\right) + \left(\sum_{i} c_{i} \sigma_{i} + \mathbf{y}\right) \cdot \boldsymbol{\sigma}_{k}$$
(S31)

The first and the second term give identical results so that the latter equations can be written in matrix-vector form as:

$$\mathbf{M}^{\mathrm{red}}\mathbf{c} = -\mathbf{y}^{\mathrm{red}} , \qquad (S32)$$

with

$$\mathbf{M}_{ij}^{\text{red}} = (\mathbf{M}\mathbf{b}_i) \cdot (\mathbf{M}\mathbf{b}_j) = \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j , \qquad (S33)$$

$$\mathbf{y}_i^{\text{red}} = (\mathbf{M}\mathbf{b}_i) \cdot \mathbf{y} = \boldsymbol{\sigma}_i \cdot \mathbf{y} .$$
 (S34)

With the solution vector in the reduced space, \mathbf{c} , the squared norm of the remaining residual can be expressed as:

$$||\mathbf{R}||^{2} = \mathbf{c}^{t} \mathbf{M}^{\text{red}} \mathbf{c} + 2\mathbf{c} \cdot \mathbf{y}^{\text{red}} + ||\mathbf{y}||^{2}$$
(S35)

For the linear equations in damped CC2 response theory in its partitioned doubles-direct form:

$$\begin{bmatrix} \mathbf{A}_{SS}^{\text{eff}}(\omega,\gamma) - \omega \mathbf{1}_{SS} & -\mathbf{\Gamma}_{SS}^{\text{eff}}(\omega,\gamma) + \gamma \mathbf{1}_{SS} \\ \mathbf{\Gamma}_{SS}^{\text{eff}}(\omega,\gamma) - \gamma \mathbf{1}_{SS} & \mathbf{A}_{SS}^{\text{eff}}(\omega,\gamma) - \omega \mathbf{1}_{SS} \end{bmatrix} \begin{bmatrix} \mathbf{t}_{S}^{R} \\ \mathbf{t}_{S}^{I} \end{bmatrix} = -\begin{bmatrix} \xi_{S}^{R,\text{eff}}(\omega,\gamma) \\ \xi_{S}^{I,\text{eff}}(\omega,\gamma) \end{bmatrix} , \quad (S36)$$

with use of the following ansatz for the solution vector

$$\mathbf{t}_{S}^{R} = \sum_{i} c_{i}^{R} \mathbf{b}_{i} \quad \text{and} \quad \mathbf{t}_{S}^{I} = \sum_{i} c_{i}^{I} \mathbf{b}_{i} , \qquad (S37)$$

and of the following short-hand notation for the linearly transformed basis vectors

$$\boldsymbol{\sigma}_{i}^{R} = \mathbf{A}_{SS}^{\text{eff}}(\omega, \gamma) \mathbf{b}_{i}$$
 and $\boldsymbol{\sigma}_{i}^{I} = \boldsymbol{\Gamma}_{SS}^{\text{eff}}(\omega, \gamma) \mathbf{b}_{i}$, (S38)

the residual vector is thus given by:

$$\mathbf{R} = \begin{bmatrix} \sum_{i} c_{i}^{R} (\boldsymbol{\sigma}_{i}^{R} - \omega \mathbf{b}_{i}) - \sum_{i} c_{i}^{I} (\boldsymbol{\sigma}_{i}^{I} - \gamma \mathbf{b}_{i}) \\ \sum_{i} c_{i}^{R} (\boldsymbol{\sigma}_{i}^{I} - \gamma \mathbf{b}_{i}) + \sum_{i} c_{i}^{I} (\boldsymbol{\sigma}_{i}^{R} - \omega \mathbf{b}_{i}) \end{bmatrix} + \begin{bmatrix} \xi_{S}^{R,\text{eff}}(\omega, \gamma) \\ \xi_{S}^{I,\text{eff}}(\omega, \gamma) \end{bmatrix}$$
(S39)

We split the squared norm into two contributions:

$$||\mathbf{R}||^2 = ||\mathbf{R}^R||^2 + ||\mathbf{R}^I||^2 , \qquad (S40)$$

and introduce the auxiliary reduced space quantities:

$$A_{ij}^{\text{red}} = \mathbf{b}_i \cdot \boldsymbol{\sigma}_j^R$$
 and $\Gamma_{ij}^{\text{red}} = \mathbf{b}_i \cdot \boldsymbol{\sigma}_j^I$ (S41)

$$g_i^{\text{red},R} = \mathbf{b}_i \cdot \xi_S^{R,\text{eff}}(\omega,\gamma) \quad \text{and} \quad g_i^{\text{red},I} = \mathbf{b}_i \cdot \xi_S^{I,\text{eff}}(\omega,\gamma)$$
(S42)

as well as:

$$\mathbf{B}^{\mathrm{red}} = \begin{bmatrix} \mathbf{B}^{\mathrm{red},RR} & \mathbf{B}^{\mathrm{red},RI} \\ \mathbf{B}^{\mathrm{red},IR} & \mathbf{B}^{\mathrm{red},II} \end{bmatrix} \quad \text{with} \quad B_{ij}^{\mathrm{red},KL} = \boldsymbol{\sigma}_{i}^{K} \cdot \boldsymbol{\sigma}_{j}^{L} , \quad (S43)$$
$$\mathbf{h}^{\mathrm{red}} = \begin{bmatrix} \mathbf{h}^{\mathrm{red},RR} & \mathbf{h}^{\mathrm{red},RI} \\ \mathbf{h}^{\mathrm{red},IR} & \mathbf{h}^{\mathrm{red},II} \end{bmatrix} \quad \text{with} \quad h_{i}^{\mathrm{red},KL} = \boldsymbol{\sigma}_{i}^{K} \cdot \boldsymbol{\xi}_{S}^{L,\mathrm{eff}}(\omega,\gamma) . \quad (S44)$$

The first contribution is given by:

$$\begin{split} ||R^{R}|| &= \left(\sum_{i} c_{i}^{R} (\boldsymbol{\sigma}_{i}^{R} - \omega \mathbf{b}_{i}) - \sum_{i} c_{i}^{I} (\boldsymbol{\sigma}_{i}^{I} - \gamma \mathbf{b}_{i}) + \xi_{S}^{R,\text{eff}}(\omega, \gamma)\right) \tag{S45} \\ &\quad \cdot \left(\sum_{j} c_{j}^{R} (\boldsymbol{\sigma}_{i}^{R} - \omega \mathbf{b}_{j}) - \sum_{j} c_{j}^{I} (\boldsymbol{\sigma}_{j}^{I} - \gamma \mathbf{b}_{j}) + \xi_{S}^{R,\text{eff}}(\omega, \gamma)\right) \\ &= \sum_{ij} c_{i}^{R} (\boldsymbol{\sigma}_{i}^{R} - \omega \mathbf{b}_{i}) \cdot (\boldsymbol{\sigma}_{j}^{R} - \omega \mathbf{b}_{j}) c_{j}^{R} - \sum_{ij} c_{i}^{R} (\boldsymbol{\sigma}_{i}^{R} - \omega \mathbf{b}_{i}) \cdot (\boldsymbol{\sigma}_{j}^{I} - \gamma \mathbf{b}_{j}) c_{j}^{I} \qquad (S46) \\ &\quad - \sum_{ij} c_{i}^{I} (\boldsymbol{\sigma}_{i}^{I} - \gamma \mathbf{b}_{i}) \cdot (\boldsymbol{\sigma}_{j}^{R} - \omega \mathbf{b}_{j}) c_{j}^{R} + \sum_{ij} c_{i}^{I} (\boldsymbol{\sigma}_{i}^{I} - \gamma \mathbf{b}_{i}) \cdot (\boldsymbol{\sigma}_{j}^{I} - \gamma \mathbf{b}_{j}) c_{j}^{I} \\ &\quad + \sum_{i} c_{i}^{R} (\boldsymbol{\sigma}_{i}^{R} - \omega \mathbf{b}_{i}) \xi_{S}^{R,\text{eff}}(\omega, \gamma) - \sum_{i} c_{i}^{I} (\boldsymbol{\sigma}_{i}^{I} - \gamma \mathbf{b}_{i}) \xi_{S}^{R,\text{eff}}(\omega, \gamma) \\ &\quad + \sum_{i} c_{i}^{R} (\boldsymbol{\sigma}_{i}^{R} - \omega \mathbf{b}_{i}) \xi_{S}^{R,\text{eff}}(\omega, \gamma) - \sum_{j} c_{j}^{I} (\boldsymbol{\sigma}_{j}^{I} - \gamma \mathbf{b}_{j}) \xi_{S}^{R,\text{eff}}(\omega, \gamma) \\ &\quad + \sum_{j} c_{j}^{R} (\boldsymbol{\sigma}_{j}^{R} - \omega \mathbf{b}_{j}) \xi_{S}^{R,\text{eff}}(\omega, \gamma) - \sum_{j} c_{j}^{I} (\boldsymbol{\sigma}_{j}^{I} - \gamma \mathbf{b}_{j}) \xi_{S}^{R,\text{eff}}(\omega, \gamma) \\ &\quad + \left[\mathbf{c}^{R} \quad \mathbf{c}I \right]^{t} \begin{bmatrix} (\mathbf{B}^{\text{red},RR} - \omega \mathbf{A}^{\text{red}} - \omega (\mathbf{A}^{\text{red}})^{t} + \omega^{2}\mathbf{1}) & -(\mathbf{B}^{\text{red},RI} - \omega \mathbf{\Gamma}^{\text{red}} - \gamma (\mathbf{\Gamma}^{\text{red}})^{t} + \gamma^{2}\mathbf{1}) \end{bmatrix} \begin{bmatrix} \mathbf{c}^{R} \\ \mathbf{c}I \end{bmatrix} \\ &\quad + \left[\mathbf{c}^{R} \quad \mathbf{c}I \right]^{t} \begin{bmatrix} \mathbf{h}^{\text{red},RR} - \omega \mathbf{g}^{\text{red},R} \\ -\mathbf{h}^{\text{red},IR} + \gamma \mathbf{g}^{\text{red},R} \end{bmatrix} + \left[\mathbf{h}^{\text{red},RR} - \omega \mathbf{g}^{\text{red},R} - \mathbf{h}^{\text{red},IR} + \gamma \mathbf{g}^{\text{red},R} \right]^{t} \begin{bmatrix} \mathbf{c}^{R} \\ \mathbf{c}I \end{bmatrix} \\ &\quad + ||\xi_{S}^{R,\text{eff}}(\omega,\gamma)||^{2} \end{aligned}$$

The second contribution is given by:

$$\begin{split} ||R^{I}|| &= \left(\sum_{i} c_{i}^{R} (\boldsymbol{\sigma}_{i}^{I} - \gamma \mathbf{b}_{i}) + \sum_{i} c_{i}^{I} (\boldsymbol{\sigma}_{i}^{R} - \omega \mathbf{b}_{i}) + \xi_{S}^{I,\text{eff}}(\omega, \gamma)\right) \tag{S47} \\ &\quad \cdot \left(\sum_{j} c_{j}^{R} (\boldsymbol{\sigma}_{j}^{I} - \gamma \mathbf{b}_{j}) + \sum_{j} c_{j}^{I} (\boldsymbol{\sigma}_{j}^{R} - \omega \mathbf{b}_{j}) + \xi_{S}^{I,\text{eff}}(\omega, \gamma)\right) \\ &= \left[\mathbf{c}^{R} \ \mathbf{c}^{I}\right]^{t} \begin{bmatrix} (\mathbf{B}^{\text{red},II} - \gamma \mathbf{\Gamma}^{\text{red}} - \gamma (\mathbf{\Gamma}^{\text{red}})^{t} + \gamma^{2} \mathbf{1}) & (\mathbf{B}^{\text{red},IR} - \omega (\mathbf{\Gamma}^{\text{red}})^{t} - \gamma \mathbf{A}^{\text{red}} + \omega \gamma \mathbf{1}) \\ (\mathbf{B}^{\text{red},RI} - \omega \mathbf{\Gamma}^{\text{red}} - \gamma (\mathbf{A}^{\text{red}})^{t} + \omega \gamma \mathbf{1}) & (\mathbf{B}^{\text{red},RR} - \omega \mathbf{A}^{\text{red}} - \omega (\mathbf{A}^{\text{red}})^{t} + \omega^{2} \mathbf{1}) \end{bmatrix} \begin{bmatrix} \mathbf{c}^{R} \\ \mathbf{c}^{I} \end{bmatrix} \\ &+ \left[\mathbf{c}^{R} \ \mathbf{c}^{I}\right]^{t} \begin{bmatrix} \mathbf{h}^{\text{red},II} - \gamma \mathbf{g}^{\text{red},I} \\ \mathbf{h}^{\text{red},RI} - \omega \mathbf{g}^{\text{red},I} \end{bmatrix} + \left[\mathbf{h}^{\text{red},II} - \gamma \mathbf{g}^{\text{red},I} - \omega \mathbf{g}^{\text{red},I} \right]^{t} \begin{bmatrix} \mathbf{c}^{R} \\ \mathbf{c}^{I} \end{bmatrix} \\ &+ ||\xi_{S}^{I,\text{eff}}(\omega,\gamma)||^{2} \end{split}$$

The stationarity condition for $||\mathbf{R}||^2$ leads to the linear equation:

$$\begin{bmatrix} \mathbf{M}^{\mathrm{red},RR} & \mathbf{M}^{\mathrm{red},RI} \\ \mathbf{M}^{\mathrm{red},IR} & \mathbf{M}^{\mathrm{red},II} \end{bmatrix} \begin{bmatrix} \mathbf{c}^{R} \\ \mathbf{c}^{I} \end{bmatrix} = -\begin{bmatrix} \mathbf{y}^{\mathrm{red},R} \\ \mathbf{y}^{\mathrm{red},I} \end{bmatrix}$$
(S48)

and

$$\begin{bmatrix} \mathbf{M}^{\mathrm{red},RR} & \mathbf{M}^{\mathrm{red},RI} \\ \mathbf{M}^{\mathrm{red},IR} & \mathbf{M}^{\mathrm{red},II} \end{bmatrix} \begin{bmatrix} \mathbf{c}^{R} \\ \mathbf{c}^{I} \end{bmatrix} = -\begin{bmatrix} \mathbf{y}^{\mathrm{red},R} \\ \mathbf{y}^{\mathrm{red},I} \end{bmatrix}$$
(S48)

(S49)

(S50)

(S51)

(S52)

 $\mathbf{M}^{\mathrm{red},II} = \mathbf{M}^{RR} = (\mathbf{M}^{RR})^t$

 $\mathbf{M}^{\mathrm{red},IR} = -\mathbf{M}^{\mathrm{red},RI} = (\mathbf{M}^{\mathrm{red},RI})^t$

$$\begin{bmatrix} \mathbf{M}^{\mathrm{red},RR} & \mathbf{M}^{\mathrm{red},RI} \\ \mathbf{M}^{\mathrm{red},IR} & \mathbf{M}^{\mathrm{red},II} \end{bmatrix} \begin{bmatrix} \mathbf{c}^{R} \\ \mathbf{c}^{I} \end{bmatrix} = -\begin{bmatrix} \mathbf{y}^{\mathrm{red},R} \\ \mathbf{y}^{\mathrm{red},I} \end{bmatrix}$$
(S48)

with

$$\begin{bmatrix} \mathbf{M}^{\mathrm{red},RR} & \mathbf{M}^{\mathrm{red},RI} \\ \mathbf{M}^{\mathrm{red},IR} & \mathbf{M}^{\mathrm{red},II} \end{bmatrix} \begin{bmatrix} \mathbf{c}^{R} \\ \mathbf{c}^{I} \end{bmatrix} = -\begin{bmatrix} \mathbf{y}^{\mathrm{red},R} \\ \mathbf{y}^{\mathrm{red},I} \end{bmatrix}$$

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$$\mathbf{y}^{\mathrm{red},I} = -\mathbf{h}^{\mathrm{red},IR} + \gamma \mathbf{g}^{\mathrm{red},R} + \mathbf{h}^{\mathrm{red},RI} - \omega \mathbf{g}^{\mathrm{red},I}$$
(S54)

$$\mathbf{y}^{\mathrm{red},R} = \mathbf{h}^{\mathrm{red},RR} - \omega \mathbf{g}^{\mathrm{red},R} + \mathbf{h}^{\mathrm{red},II} - \gamma \mathbf{g}^{\mathrm{red},I}$$
(S53)

$$red_R$$
 red_R red_R red_R red_R

 $\mathbf{M}^{\mathrm{red},RI} = \mathbf{B}^{\mathrm{red},IR} - \mathbf{B}^{\mathrm{red},RI} - \boldsymbol{\omega}[(\mathbf{\Gamma}^{\mathrm{red}})^t - \mathbf{\Gamma}^{\mathrm{red}}] - \boldsymbol{\gamma}[\mathbf{A}^{\mathrm{red}} - (\mathbf{A}^{\mathrm{red}})^t]$

 $\mathbf{M}^{\mathrm{red},RR} = \mathbf{B}^{\mathrm{red},RR} + \mathbf{B}^{\mathrm{red},II} - \boldsymbol{\omega}[\mathbf{A}^{\mathrm{red}} + (\mathbf{A}^{\mathrm{red}})^t] - \gamma[\mathbf{\Gamma}^{\mathrm{red}} + (\mathbf{\Gamma}^{\mathrm{red}})^t] + (\boldsymbol{\omega}^2 + \gamma^2)\mathbf{1}$

As above, the squared norm of the total residual can be calculated from the solution vector in the reduced space, \mathbf{c} , with \mathbf{M}^{red} , \mathbf{y}^{red} and $||\xi_S^{\text{eff}}||^2$. Alternatively, one can calculate separately the squared norms of the real and imaginary parts of the residual vector with the reduced space quantities:

$$\tilde{\mathbf{M}}^{R,\mathrm{red}} = \begin{bmatrix} \left(\mathbf{B}^{\mathrm{red},RR} - \omega \mathbf{A}^{\mathrm{red}} - \omega (\mathbf{A}^{\mathrm{red}})^t + \omega^2 \mathbf{1} \right) & -\left(\mathbf{B}^{\mathrm{red},RI} - \omega \mathbf{\Gamma}^{\mathrm{red}} - \gamma (\mathbf{A}^{\mathrm{red}})^t + \omega\gamma \mathbf{1} \right) \\ -\left(\mathbf{B}^{\mathrm{red},IR} - \omega (\mathbf{\Gamma}^{\mathrm{red}})^t - \gamma \mathbf{A}^{\mathrm{red}} + \omega\gamma \mathbf{1} \right) & \left(\mathbf{B}^{\mathrm{red},II} - \gamma \mathbf{\Gamma}^{\mathrm{red}} - \gamma (\mathbf{\Gamma}^{\mathrm{red}})^t + \gamma^2 \mathbf{1} \right) \end{bmatrix}$$
(S55)

$$\tilde{\mathbf{y}}^{R,\text{red}} = \begin{bmatrix} \mathbf{h}^{\text{red},RR} - \omega \mathbf{g}^{\text{red},R} \\ -\mathbf{h}^{\text{red},IR} + \gamma \mathbf{g}^{\text{red},R} \end{bmatrix}$$
(S56)

and

$$\tilde{\mathbf{M}}^{I,\mathrm{red}} = \begin{bmatrix} \left(\mathbf{B}^{\mathrm{red},II} - \gamma \mathbf{\Gamma}^{\mathrm{red}} - \gamma (\mathbf{\Gamma}^{\mathrm{red}})^t + \gamma^2 \mathbf{1} \right) & \left(\mathbf{B}^{\mathrm{red},IR} - \omega (\mathbf{\Gamma}^{\mathrm{red}})^t - \gamma \mathbf{A}^{\mathrm{red}} + \omega \gamma \mathbf{1} \right) \\ \left(\mathbf{B}^{\mathrm{red},RI} - \omega \mathbf{\Gamma}^{\mathrm{red}} - \gamma (\mathbf{A}^{\mathrm{red}})^t + \omega \gamma \mathbf{1} \right) & \left(\mathbf{B}^{\mathrm{red},RR} - \omega \mathbf{A}^{\mathrm{red}} - \omega (\mathbf{A}^{\mathrm{red}})^t + \omega^2 \mathbf{1} \right) \end{bmatrix}$$
(S57)

$$\tilde{\mathbf{y}}^{I,\text{red}} = \begin{bmatrix} \mathbf{h}^{\text{red},II} - \gamma \mathbf{g}^{\text{red},I} \\ \mathbf{h}^{\text{red},RI} - \omega \mathbf{g}^{\text{red},I} \end{bmatrix}$$
(S58)

as:

$$||\mathbf{R}^{R}||^{2} = \mathbf{c}^{t} \tilde{\mathbf{M}}^{R, \text{red}} \mathbf{c} + 2\mathbf{c} \cdot \tilde{\mathbf{y}}^{R, \text{red}} + ||\xi_{S}^{R, \text{eff}}||^{2}$$
(S59)

$$||\mathbf{R}^{I}||^{2} = \mathbf{c}^{t} \tilde{\mathbf{M}}^{I, \text{red}} \mathbf{c} + 2\mathbf{c} \cdot \tilde{\mathbf{y}}^{I, \text{red}} + ||\boldsymbol{\xi}_{S}^{I, \text{eff}}||^{2}$$
(S60)

SS6.2 Comparison with the limit $\gamma = 0$

In the limit $\gamma = 0$, the quantities $\Gamma_{SS}^{\text{eff}}(\omega, \gamma)$ and $\xi_{S}^{I,\text{eff}}(\omega, \gamma)$ and thus also σ_{i}^{I} , Γ^{red} , $\mathbf{g}^{\text{red},I}$, \mathbf{B}^{IR} , \mathbf{B}^{RI} , \mathbf{II} , $\mathbf{h}^{\text{red},IR}$, \mathbf{h}^{RI} , \mathbf{h}^{II} , \mathbf{M}^{RI} , \mathbf{M}^{IR} , and \mathbf{y}^{I} vanish. The minimization condition reduces,

in this limit, to:

$$\begin{bmatrix} \mathbf{B}^{\mathrm{red},RR} - \omega[\mathbf{A}^{\mathrm{red}} + (\mathbf{A}^{\mathrm{red}})^{t}] + \omega^{2}\mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{B}^{\mathrm{red},RR} - \omega[\mathbf{A}^{\mathrm{red}} + (\mathbf{A}^{\mathrm{red}})^{t}] + \omega^{2}\mathbf{1} \end{bmatrix} \begin{bmatrix} \mathbf{c}^{R} \\ \mathbf{c}^{I} \end{bmatrix}$$
(S61)
$$= -\begin{bmatrix} \mathbf{h}^{\mathrm{red},RR} - \omega \mathbf{g}^{\mathrm{red},R} \\ \mathbf{0} \end{bmatrix}$$

From the block-diagonal form, it follows that $\mathbf{c}^{I} = \mathbf{0}$, and the coefficients for the real part of the solution vector are determined by the equation:

$$\left[\mathbf{B}^{\mathrm{red},RR} - \omega[\mathbf{A}^{\mathrm{red}} + (\mathbf{A}^{\mathrm{red}})^t] + \omega^2 \mathbf{1}\right] \mathbf{c}^R = -\left[\mathbf{h}^{\mathrm{red},RR} - \omega \mathbf{g}^{\mathrm{red},R}\right]$$
(S62)

The last equation is used by the solver for the non-CPP response equations.

S7 Implementation of the G-matrix contractions

For CC2 only the following two terms contribute to the **G**-matrix contractions:

$$G_{\mu_{1}\nu_{1}\gamma_{1}} = \langle \bar{t}_{1} | [[[\hat{H}, \tau_{\mu_{1}}], \tau_{\nu_{1}}], \tau_{\gamma_{1}}] | \mathrm{HF} \rangle + \langle \bar{t}_{2} | [[[\hat{H}, \tau_{\mu_{1}}], \tau_{\nu_{1}}], \tau_{\gamma_{1}}] | \mathrm{HF} \rangle$$
(S63)

where \bar{t} are the unperturbed ground-state CC Lagrange multipliers. For the quadratic response function, only contractions of **G** with three vectors are needed, which can be written as:

$$G_{XYZ} = \sum_{\mu\nu\gamma} G_{\mu\nu\gamma} t^X_{\mu} t^Y_{\nu} t^Z_{\gamma} = G^{\bar{t}_1}_{XYZ} + G^{\bar{t}_2}_{XYZ} , \qquad (S64)$$

where $G_{XYZ}^{\bar{t}_1}$ comprises the contributions from the singles part of the Lagrange multipliers \bar{t} and $G_{XYZ}^{\bar{t}_2}$ those from the doubles part of the Lagrange multipliers. We use in the following the convention that the indices i, j, k, and l run over active occupied and the indices a, b, c, and d over active virtual orbitals. The indices p, q, r, and s are used to denote the union of active occupied and virtual orbitals and α , β , κ , and λ for atomic orbitals.

The first contribution to the **G**-matrix contraction is evaluated as:

$$G_{XYZ}^{\bar{t}_1} = \sum_{ck} \zeta_{ck}^{YZ} F_{ck}^X + \sum_{ck} \zeta_{ck}^{XZ} F_{ck}^Y + \sum_{ck} \zeta_{ck}^{XY} F_{ck}^Z$$
(S65)

with the intermediates:

$$\zeta_{ck}^{XY} = -\sum_{bj} \bar{t}_{bj} \left(t_{cj}^X t_{bk}^Y + t_{cj}^Y t_{bk}^X \right) = -\sum_j \left(\sum_b t_{bk}^Y \bar{t}_{bj} \right) t_{cj}^X + \sum_j \left(\sum_b t_{bk}^X \bar{t}_{bj} \right) t_{cj}^Y \tag{S66}$$

and the singly dressed Fock matrices:

$$F_{pq}^{X} = h_{pq}^{X} + \sum_{j} \left[2(pq\hat{j}j)^{X} - (jq\hat{p}j)^{X} \right]$$
(S67)

$$h_{pq}^{X} = \sum_{\alpha\beta} \left[\Lambda_{p\alpha}^{p,X} \Lambda_{q\beta}^{h} + \Lambda_{p\alpha}^{p} \Lambda_{q\beta}^{h,X} \right] h_{\alpha\beta}$$
(S68)

$$(pq\hat{|}rs)^X = \sum_{\alpha\beta} \left[\Lambda^{p,X}_{\alpha p} \Lambda^h_{\beta q} + \Lambda^p_{\alpha p} \Lambda^{h,X}_{\beta q} \right] \sum_{\kappa\lambda} (\alpha\beta|\kappa\lambda) \Lambda^p_{\kappa r} \Lambda^h_{\lambda s}$$
(S69)

$$+\sum_{\alpha\beta} \left[\Lambda_{\alpha r}^{p,X} \Lambda_{\beta s}^{h} + \Lambda_{\alpha r}^{p} \Lambda_{\beta s}^{h,X} \right] \sum_{\kappa\lambda} (\alpha\beta|\kappa\lambda) \Lambda_{\kappa p}^{p} \Lambda_{\lambda q}^{h}$$
$$\mathbf{\Lambda}^{p,X} = -\mathbf{C} (\mathbf{t}_{1}^{X})^{T}$$
(S70)

$$\mathbf{\Lambda}^{h,X} = +\mathbf{C}\mathbf{t}_1^X \tag{S71}$$

The two-electron repulsion integrals are evaluated within the RI approximation. The second contribution, $G_{XYZ}^{\bar{t}_2}$, is evaluated as:

$$G_{XYZ}^{\bar{t}_2} = -\sum_{dl} H_{dl}^{YZ} t_{dl}^X - \sum_{dl} H_{dl}^{XZ} t_{dl}^Y - \sum_{dl} H_{dl}^{XY} t_{dl}^Z$$
(S72)

with

$$H_{dl}^{XY} = \sum_{Qi} \check{Y}_{Qdi}^Y \hat{B}_{Qli}^X + \sum_{Qi} \check{Y}_{Qdi}^X \hat{B}_{Qli}^Y$$
(S73)
where

$$\breve{Y}_{Qdi}^X = \sum_{ck} \bar{t}_{ki}^{cd} \hat{B}_{Qck}^X \tag{S74}$$

$$\hat{B}_{Qpq}^{X} = \sum_{P} \sum_{\alpha\beta} \left[\Lambda_{\alpha p}^{p,X} \Lambda_{\beta q}^{h} + \Lambda_{\alpha p}^{p} \Lambda_{\beta q}^{h,X} \right] (\alpha\beta|P) [\mathbf{V}^{-1/2}]_{PQ}$$
(S75)

Algorithm for G-matrix contractions:

- compute Lambda matrices dressed with amplitude responses (X, Y, and Z):
 - read t_1^X from file
 - compute $\Lambda_{\mu a}^{p,X} = -\sum_{i} C_{\mu i} t_{ai}^{X}$ and $\Lambda_{\mu i}^{h,X} = +\sum_{a} C_{\mu a} t_{ai}^{X}$
- compute 3-index integrals dressed with amplitude responses (X, Y, and Z):

$$\hat{B}_{Qai}^{X} = \sum_{P\mu\nu} V_{QP}^{-1/2} (P|\mu\nu) \Lambda_{\mu a}^{p} \bar{\Lambda}_{\nu i}^{h,X} - \hat{B}_{Qji} t_{aj}^{X}$$
(S76)

$$\hat{B}_{Qji}^{X} = \sum_{P\mu\nu} V_{QP}^{-1/2} (P|\mu\nu) \Lambda_{\mu j}^{p} \bar{\Lambda}_{\nu i}^{h,X}$$
(S77)

- compute F_{ia}^X (for X, Y, and Z):
 - calculate $i_Q^X = \sum_{ai} B_{Qia} t_{ai}^X$ - calculate $F_{ia}^X = 2 \sum_Q B_{Qia} \bar{i}_Q^X - \sum_{Qk} B_{Qka} \bar{B}_{Qik}^X$
- compute \check{Y}_{Qai}^X :

$$\check{Y}_{Qai}^X = \sum_{bj} \bar{t}_{ij}^{ab} \bar{B}_{Qbj}^X \tag{S78}$$

• for all pairs (XY, XZ, and YZ) compute:

$$\zeta_{ck}^{XY} = \hat{P}^{XY} \sum_{jb} t_{bk}^X \bar{t}_{bj} t_{cj}^Y \tag{S79}$$

• compute the \bar{t}_1 contribution to the G-matrix contraction:

$$G^{\bar{t}_1} = \sum_{ck} \left(\zeta_{ck}^{XY} \bar{F}_{ck}^Z + \zeta_{ck}^{XZ} \bar{F}_{ck}^Y + \zeta_{ck}^{YZ} \bar{F}_{ck}^X \right)$$
(S80)

• for all pairs (XY, XZ, and YZ) compute:

$$H_{ck}^{XY} = \hat{P}^{XY} \sum_{Qi} \breve{Y}_{Qci}^X \bar{B}_{Qki}^Y$$
(S81)

• compute the \bar{t}_2 contribution to the G matrix contraction:

$$G^{\bar{t}_2} = -\sum_{ck} \left(H_{ck}^{XY} t_{ck}^Z + H_{ck}^{XZ} t_{ck}^Y + H_{ck}^{YZ} t_{ck}^X \right)$$
(S82)

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B

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Supplementary Information: Insights into localization, energy ordering, and substituent effect in excited states of azobenzenes from coupled cluster calculations of nuclear spin-induced circular dichroism

Josefine H. Andersen,¹ Christof Hättig,² Sonia Coriani,¹ and Petr Štěpánek³ ¹⁾ DTU Chemistry, Technical University of Denmark, Kemitorvet, Building 207, DK-2800 Kongens Lyngby, Denmark ²⁾ Arbeitsgruppe Quantenchemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany ³⁾ NMR Research Unit, Faculty of Science, University of Oulu, PO Box 3000, FI-90014 Oulu, Finland^a)

 $^{^{}a)}$ petr.stepanek@oulu.fi

S1. PHYSICAL CONSTANTS

NSCD prefactors

For carbon (\mathcal{L}_C) and hydrogen (\mathcal{L}_H) :

 $\mathcal{L}_C = 1.3125973044$ $\mathcal{L}_H = 5.2189931889$

Solvents

TABLE S1. Dielectric constants ϵ_r and refractive indices η_D for the three solvents.

| Solvent | ϵ_r | η_D |
|------------------------|--------------|----------|
| DMSO | 46.45 | 1.479 |
| $\mathrm{C_6H_{12}^1}$ | 2.023 | 1.4264 |
| $\mathrm{CHCl}_3{}^2$ | 4.8069 | 1.4459 |

S2. TRANSITION STRENGTHS

TABLE S2. AZO-1. aug-cc-pwCVDZ. Transition strength components $S_{0f}^{\alpha\alpha} = T_{0f}^{\alpha}T_{f0}^{\alpha}$ for $\alpha \in x, y, z$. The molecule lies (roughly) on the xy plane, with the long axis along y.

| State n | E_n | f | S_{0f}^{xx} | S_{0f}^{yy} | S_{0f}^{zz} |
|-----------|-------|-------|---------------|---------------|---------------|
| 1 | 2.959 | 0.000 | 0.0000 | 0.0000 | 0.0000 |
| 2 | 3.796 | 0.868 | 0.0366 | 9.2925 | 0.0000 |
| 3 | 4.508 | 0.008 | 0.0698 | 0.0010 | 0.0000 |
| 4 | 4.549 | 0.018 | 0.0087 | 0.1515 | 0.0000 |

TABLE S3. AZO-2. aug-cc-pwCVDZ. Transition strength components $S_{0f}^{\alpha\alpha} = T_{0f}^{\alpha}T_{f0}^{\alpha}$ for $\alpha \in x, y, z$. The molecule lies (roughly) on the xz plane, with the long axis along z.

| State n | E_n | f | S_{0f}^{xx} | S_{0f}^{yy} | S_{0f}^{zz} |
|---------|-------|-------|---------------|---------------|---------------|
| 1 | 2.964 | 0.000 | 0.0000 | 0.0000 | 0.0000 |
| 2 | 3.589 | 0.919 | 0.0298 | 0.0001 | 10.4251 |
| 3 | 4.437 | 0.028 | 0.0141 | 0.0000 | 0.2459 |
| 4 | 4.528 | 0.008 | 0.0637 | 0.0000 | 0.0065 |

| x, y, z. The molecule lies (roughly) on the xz plane, with the long axis along z . | | | | | | | |
|--|-------|-----------------------|---------------|---------------|---------------|--|--|
| State n | E_n | f | S_{0f}^{xx} | S_{0f}^{yy} | S_{0f}^{zz} | | |
| 1 | 2.866 | $1.12\cdot 10^{-6}$ | 0.0000 | 0.0000 | 0.0000 | | |
| 2 | 3.339 | 1.043 | 0.0252 | 0.0001 | 12.7198 | | |
| 3 | 3.854 | $3.05 \cdot 10^{-10}$ | 0.0000 | 0.0000 | 0.0000 | | |
| 4 | 4.352 | 0.004 | 0.0000 | 0.0000 | 0.0407 | | |
| 5 | 4.430 | 0.011 | 0.0941 | 0.0000 | 0.0049 | | |
| 6 | 4.441 | 0.001 | 0.0002 | 0.0057 | 0.0000 | | |

TABLE S4. AZO-3. aug-cc-pwCVDZ. Transition strength components $S_{0f}^{\alpha\alpha} = T_{0f}^{\alpha}T_{f0}^{\alpha}$ for $\alpha \in r$ as \tilde{r} . The molecula lies (roughly) on the $r\tilde{r}$ plane, with the long axis along \tilde{r} .

S3. NSCD INTENSITIES

| | | R | I-CC2 | | DFT/BH+HLYP | | | |
|-----------------|--------|---------|---------|------------------------|------------------------------|---------|---------|--------|
| Atom | ES1 | ES2 | ES3 | ES4 | ES1 | ES2 | ES3 | ES4 |
| E (eV) | 2.959 | 3.796 | 4.508 | 4.549 | 3.015 | 3.790 | 4.748 | 4.838 |
| ω (a.u.) | 0.109 | 0.140 | 0.166 | 0.167 | 0.111 | 0.139 | 0.175 | 0.178 |
| f | 0.000 | 0.868 | 0.008 | 0.018 | 0.000 | 0.822 | 0.012 | 0.003 |
| Atom# | | | | NSCD (\mathcal{L}_K) | $\mathcal{B}_K \times 1000)$ | | | |
| C1 | -2.57 | 235.83 | -75.99 | 148.82 | -0.38 | 139.88 | -28.42 | 51.03 |
| C2 | 51.02 | -318.52 | -109.29 | 201.89 | 5.74 | -139.57 | -35.97 | 56.83 |
| C3 | 4.71 | 50.43 | -95.07 | 259.93 | 0.55 | 71.24 | -40.82 | 99.75 |
| C4 | -0.57 | 58.04 | -67.64 | 151.45 | -0.04 | 62.88 | -29.86 | 51.19 |
| C5 | -3.26 | 14.97 | -37.41 | 53.91 | -0.35 | 109.02 | -11.36 | 19.72 |
| C6 | -4.38 | 68.22 | -80.65 | 146.64 | -0.46 | 9.62 | -34.48 | 64.00 |
| C7 | -40.25 | -111.27 | -27.46 | -71.77 | -4.82 | -50.78 | -131.43 | -8.27 |
| C8 | 4.09 | 245.35 | -41.59 | -58.78 | 0.51 | 180.70 | -112.76 | -6.99 |
| C9 | 2.39 | 117.22 | -76.92 | -63.95 | 0.28 | 80.70 | -183.47 | -10.35 |
| C10 | 3.13 | 66.04 | -14.09 | -66.29 | 0.37 | 73.77 | -98.53 | -8.26 |
| C11 | 0.36 | 155.70 | -58.70 | -61.68 | 0.03 | 139.55 | -151.54 | -7.94 |
| C12 | -4.79 | 92.05 | -114.41 | -80.22 | -0.57 | 106.55 | -259.41 | -15.13 |
| H1 | -0.95 | -23.53 | 85.51 | -144.19 | -0.09 | -11.67 | 37.87 | -47.25 |
| H2 | -0.33 | 226.24 | 94.42 | -179.60 | -0.06 | 161.96 | 46.65 | -63.37 |
| H3 | -0.16 | 40.33 | 80.73 | -176.71 | -0.01 | 23.65 | 38.31 | -56.56 |
| H4 | -0.41 | -53.08 | 109.84 | -126.35 | 0.08 | -150.61 | 40.45 | -39.59 |
| H5 | -1.08 | -250.94 | 53.20 | 37.11 | -0.15 | -217.89 | 124.26 | 0.76 |
| H6 | 0.07 | -168.79 | 64.75 | 61.27 | 0.00 | -135.76 | 158.23 | 5.23 |
| H7 | 0.31 | -89.18 | 70.36 | 67.57 | 0.05 | -24.17 | 172.59 | 7.25 |
| H8 | 0.62 | -127.98 | 51.92 | 64.05 | 0.06 | -106.13 | 146.90 | 3.96 |
| H9 | 0.63 | 46.40 | 72.67 | 58.19 | 0.12 | 54.28 | 192.75 | 3.60 |
| H10 | -0.62 | 92.10 | 60.08 | -103.19 | -0.06 | 89.39 | 24.90 | -36.35 |

TABLE S5. AZO-1. aug-cc-pwCVDZ.

| | | R | I-CC2 | | DFT/BH+HLYP | | | |
|-------------------|--------|---------|---------|------------------------|-------------------------------|---------|---------|---------|
| Atom | ES1 | ES2 | ES3 | ES4 | ES1 | ES2 | ES3 | ES4 |
| E (eV) | 2.964 | 3.589 | 4.437 | 4.528 | 3.031 | 3.657 | 4.720 | 4.781 |
| ω (a.u.) | 0.109 | 0.132 | 0.163 | 0.166 | 0.111 | 0.134 | 0.173 | 0.176 |
| f | 0.000 | 0.919 | 0.028 | 0.008 | 0.000 | 0.894 | 0.010 | 0.014 |
| $\mathrm{Atom}\#$ | | | | NSCD (\mathcal{L}_F) | $(\mathcal{B}_K \times 1000)$ | | | |
| C1 | -3.25 | 311.97 | -12.27 | 35.86 | 0.03 | 197.83 | 7.09 | 48.20 |
| C2 | 86.44 | -305.82 | 136.18 | 38.27 | 0.14 | -139.39 | 79.59 | 42.52 |
| C3 | 7.74 | 91.72 | 344.45 | 44.08 | 0.02 | 89.07 | 196.44 | 92.41 |
| C4 | -0.94 | -122.20 | 258.29 | 42.86 | 0.00 | -83.76 | 146.87 | 79.42 |
| C5 | -6.02 | -113.85 | -19.57 | 6.46 | 0.01 | -0.57 | 3.62 | 12.37 |
| C6 | -8.21 | 88.08 | -11.17 | 35.24 | 0.00 | -4.20 | 31.64 | 69.04 |
| C7 | -57.34 | -108.88 | 37.37 | -33.59 | -0.20 | -67.20 | 42.86 | -109.98 |
| C8 | 5.77 | 175.98 | 33.26 | -53.22 | 0.02 | 143.69 | 30.86 | -101.41 |
| C9 | 3.46 | 63.23 | 31.77 | -80.66 | 0.01 | 51.04 | 40.84 | -171.49 |
| C10 | 4.78 | 6.01 | 27.28 | -19.15 | 0.01 | 24.31 | 30.56 | -82.05 |
| C11 | 0.44 | 102.04 | 30.86 | -62.77 | 0.00 | 110.72 | 34.21 | -137.05 |
| C12 | -7.18 | 49.84 | 38.67 | -136.85 | -0.03 | 74.24 | 56.38 | -251.69 |
| H1 | -1.86 | -12.39 | -36.40 | -29.32 | 0.00 | 6.37 | -35.92 | -41.57 |
| H2 | -0.39 | 272.84 | -142.58 | -28.76 | 0.00 | 207.37 | -97.35 | -43.66 |
| H3 | -0.35 | 115.35 | -225.26 | -36.09 | 0.00 | 86.22 | -128.26 | -56.74 |
| H4 | 0.11 | -147.41 | -32.98 | -26.89 | 0.00 | -148.73 | -37.49 | -18.86 |
| H5 | -2.07 | -187.65 | -40.59 | 30.71 | -0.01 | -185.37 | -36.05 | 94.99 |
| H6 | 0.06 | -106.36 | -44.88 | 59.22 | 0.00 | -99.59 | -44.49 | 133.50 |
| H7 | 0.54 | -33.85 | -35.67 | 65.22 | 0.00 | 11.87 | -39.51 | 151.34 |
| H8 | 0.88 | -68.78 | -41.11 | 51.13 | 0.00 | -70.38 | -43.54 | 122.62 |
| H9 | 1.72 | 79.74 | -36.84 | 55.91 | 0.00 | 83.95 | -49.55 | 160.50 |
| H10 | -0.83 | 90.06 | -42.85 | -15.92 | 0.04 | 115.47 | -38.07 | -27.91 |
| H11 | -0.99 | 115.40 | -66.82 | -26.12 | 0.00 | 110.54 | -40.90 | -26.91 |

TABLE S6. AZO-2. aug-cc-pwCVDZ.

| | | | R | I-CC2 | | | | | DFT/BE | I+HLYP | | |
|-----------------|--------|---------|-------|--------|---------|----------------------|-----------------------------------|---------|--------|---------|---------|--------|
| | ES1 | ES2 | ES3 | ES4 | ES5 | ES6 | ES1 | ES2 | ES3 | ES4 | ES5 | ES6 |
| E (eV) | 2.866 | 3.339 | 3.854 | 4.352 | 4.430 | 4.441 | 2.956 | 3.426 | 4.155 | 4.535 | 4.587 | 4.607 |
| ω (a.u.) | 0.105 | 0.123 | 0.142 | 0.160 | 0.163 | 0.163 | 0.109 | 0.126 | 0.153 | 0.167 | 0.169 | 0.169 |
| f | 0.000 | 1.043 | 0.000 | 0.004 | 0.011 | 0.000 | 0.000 | 1.067 | 0.000 | 0.017 | 0.000 | 0.000 |
| Atom# | | | | | | NSCD (\mathcal{L}) | $_{K}\mathcal{B}_{K} \times 1000$ |) | | | | |
| C1 | 1.30 | 323.72 | 0.00 | -30.64 | 81.12 | -45.71 | 12.14 | 227.75 | 0.02 | -63.31 | -7.78 | 60.06 |
| C2 | -33.90 | -144.08 | 0.00 | -15.02 | 51.61 | 1.14 | -208.71 | 73.98 | -0.08 | -84.01 | 6.27 | 76.33 |
| C3 | -2.86 | 206.39 | 0.00 | 51.90 | 59.84 | -0.34 | -17.52 | 204.19 | 0.00 | -85.72 | 1.51 | 89.77 |
| C4 | 0.30 | -20.31 | 0.00 | 27.55 | 41.48 | 2.66 | 1.06 | 7.16 | 0.01 | -66.63 | 0.49 | 62.80 |
| C5 | 2.42 | -35.48 | 0.00 | -4.47 | -5.95 | 6.57 | 13.10 | 62.80 | 0.00 | -8.02 | 3.50 | 8.69 |
| C6 | 3.31 | 129.92 | 0.00 | -36.96 | 41.22 | 1.18 | 19.82 | 53.57 | 0.02 | -64.70 | -3.61 | 67.29 |
| C7 | 18.66 | -16.36 | 0.00 | 25.58 | 94.16 | 28.11 | 118.68 | 51.32 | 0.03 | 22.71 | 20.17 | 2.30 |
| C8 | -2.02 | 204.87 | 0.00 | 39.29 | -631.14 | 663.89 | -13.38 | 229.81 | 0.17 | -202.03 | 127.96 | 17.57 |
| C9 | -1.08 | 125.98 | 0.00 | -0.36 | 2454.17 | -2372.76 | -5.79 | 189.49 | 0.11 | 463.36 | -379.53 | -98.41 |
| C10 | -2.25 | -242.08 | 0.00 | -40.75 | 120.38 | -781.70 | -13.69 | -205.94 | -0.02 | 18.89 | -430.57 | 11.68 |
| C11 | -0.10 | 146.01 | 0.00 | 22.90 | 2235.44 | -2184.57 | -0.62 | 210.13 | -0.18 | 564.01 | -559.69 | -59.05 |
| C12 | 2.62 | 146.28 | 0.00 | 6.46 | -231.58 | 240.60 | 16.44 | 205.83 | -0.15 | -189.23 | 61.01 | 0.41 |
| H1 | 0.70 | -45.34 | 0.00 | 20.17 | -40.92 | -2.44 | 4.01 | -40.30 | 0.00 | 62.84 | -0.48 | -59.26 |
| H2 | -0.09 | 201.63 | 0.00 | -14.17 | -47.84 | 6.35 | 0.46 | 119.59 | 0.00 | 71.63 | -0.03 | -73.13 |
| H3 | 0.11 | 31.83 | 0.00 | -25.53 | -47.51 | 0.13 | 0.56 | 12.98 | 0.00 | 65.12 | 0.14 | -63.44 |
| H4 | -0.03 | -157.05 | 0.00 | 17.57 | -41.05 | -3.43 | -0.92 | -166.58 | 0.00 | 57.35 | -1.76 | -52.31 |
| H5 | 1.09 | -154.32 | 0.00 | -17.05 | 100.84 | -149.35 | 6.83 | -205.99 | -0.03 | 72.00 | -23.31 | -13.73 |
| H6 | 0.02 | -47.26 | 0.00 | -6.84 | -44.14 | 5.22 | 0.11 | -70.79 | 0.06 | 76.85 | -2.80 | -1.00 |
| H7 | -0.27 | -38.52 | 0.00 | -20.10 | 77.96 | -111.16 | -1.21 | -73.38 | -0.04 | 92.02 | -5.32 | -7.92 |
| H8 | -0.68 | 38.42 | 0.00 | -3.78 | 59.43 | -105.90 | -7.39 | -0.62 | 0.03 | 107.38 | -32.83 | -8.72 |
| H9 | 0.39 | 40.37 | 0.00 | 6.39 | -25.17 | 0.44 | 1.56 | 61.49 | 0.00 | 33.69 | 0.23 | -34.68 |
| H10 | 0.32 | 57.99 | 0.00 | -1.99 | -24.85 | 0.17 | 1.84 | 59.33 | 0.00 | 36.11 | -0.07 | -35.02 |

TABLE S7. AZO-3. aug-cc-pwCVDZ.

| | DMSO | C_6H_{12} | CHCl ₃ |
|-----------------|----------|--|-------------------|
| E (eV) | 2.918 | 3.110 | 3.019 |
| ω (a.u.) | 0.107 | 0.114 | 0.111 |
| f | 1.134 | 1.134 | 1.134 |
| Atom# | | NSCD ($\mathcal{L}_K \mathcal{B}_K$ values) | |
| C1 | 350.02 | 392.98 | 388.71 |
| C2 | 1,752.74 | -41.93 | 98.17 |
| C3 | 429.66 | 278.82 | 304.37 |
| C4 | 42.04 | 25.32 | 44.30 |
| C5 | -46.51 | 31.86 | 54.86 |
| C6 | 9.34 | 179.03 | 176.89 |
| C7 | -610.94 | -32.52 | -69.60 |
| C8 | 278.74 | 227.72 | 223.27 |
| C9 | 177.03 | 151.74 | 149.31 |
| C10 | -67.72 | -176.31 | -159.86 |
| C11 | 163.43 | 171.20 | 167.29 |
| C12 | 35.00 | 146.38 | 132.83 |
| H1 | -137.25 | -80.72 | -91.58 |
| H2 | 173.76 | 201.58 | 191.73 |
| H3 | -62.10 | -22.35 | -37.87 |
| H4 | -247.00 | -223.36 | -230.24 |
| H5 | -224.79 | -177.28 | -176.97 |
| H6 | -23.25 | -34.73 | -28.56 |
| H7 | 3.88 | -16.65 | -9.50 |
| H8 | 123.77 | 53.29 | 59.35 |
| H9 | -28.95 | 15.68 | 2.29 |
| H10 | -15.58 | 32.91 | 17.61 |

TABLE S8. AZO-3. Excited state 2. COSMO-RI-CC2/aug-cc-pVDZ.



S4. NATURAL TRANSITION ORBITALS

FIG. S1. RI-CC2/aug-cc-pwCVDZ. Natural transition orbitals for the first four electronic transitions of AZO-1 (left) and AZO-2 (right). Isosurface value 0.015.



FIG. S2. TD-DFT/BH+HLYP/aug-cc-pwCVDZ. Natural transition orbitals for the first four electronic transitions of AZO-1 (left) and AZO-2 (right). Isosurface value 0.015.



FIG. S3. RI-CC2/aug-cc-pwCVDZ. Natural transition orbitals for the first six electronic transitions of AZO-3. Isosurface value 0.015.



FIG. S4. TD-DFT/BH+HLYP/aug-cc-pwCVDZ. Natural transition orbitals for the first six electronic transitions of AZO-3. Isosurface value 0.015. S10

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C6H12



FIG. S5. COSMO-CC2/aug-cc-pwCVDZ. Natural transition orbitals for the second electronic transitions of AZO-3. Isosurface value 0.015.

S5. SUM-OVER-STATES ANALYSIS

The CC sum-over-states expression for the \mathcal{B}_K term is

$$\mathcal{B}_{K} \propto -\frac{1}{2} \epsilon_{\alpha\beta\gamma} \left[\left\{ \sum_{k \neq m} \frac{\langle 0|\hat{\mu}_{\alpha}|k\rangle \langle k|\hat{h}_{\gamma}^{\mathrm{pso}}|m\rangle}{E_{m} - E_{k}} - \sum_{k \neq 0} \frac{\langle 0|\hat{h}_{\gamma}^{\mathrm{pso}}|k\rangle \langle k|\hat{\mu}_{\alpha}|m\rangle}{E_{k} - E_{0}} \right\} \langle m|\hat{\mu}_{\beta}|0\rangle$$
(S1)

$$- \langle 0|\hat{\mu}_{\beta}|m\rangle \left\{ \sum_{k\neq m} \frac{\langle m|\hat{h}_{\gamma}^{\rm pso}|k\rangle \langle k|\hat{\mu}_{\alpha}|0\rangle}{E_m - E_k} - \sum_{k\neq 0} \frac{\langle m|\hat{\mu}_{\alpha}|k\rangle \langle k|\hat{h}_{\gamma}^{\rm pso}|0\rangle}{E_k - E_0} \right\} \right] .$$
(S2)

We split the SOS expression into dispersive and absorptive components³

$$\mathcal{B}_{K,d} = -\frac{1}{2} \epsilon_{\alpha\beta\gamma} \sum_{k \neq m} \left\{ \frac{\langle 0|\hat{\mu}_{\alpha}|k\rangle \langle k|\hat{h}_{\gamma}^{\text{pso}}|m\rangle}{E_m - E_k} \langle m|\hat{\mu}_{\beta}|0\rangle - \langle 0|\hat{\mu}_{\beta}|m\rangle \frac{\langle m|\hat{h}_{\gamma}^{\text{pso}}|k\rangle \langle k|\hat{\mu}_{\alpha}|0\rangle}{E_m - E_k} \right\}$$
(S3)

$$\mathcal{B}_{K,a} = -\frac{1}{2} \epsilon_{\alpha\beta\gamma} \sum_{k\neq 0} \left\{ \frac{\langle 0|\hat{h}_{\gamma}^{\mathrm{pso}}|k\rangle \langle k|\hat{\mu}_{\alpha}|m\rangle}{E_k - E_0} \langle m|\hat{\mu}_{\beta}|0\rangle - \langle 0|\hat{\mu}_{\beta}|m\rangle \frac{\langle m|\hat{\mu}_{\alpha}|k\rangle \langle k|\hat{h}_{\gamma}^{\mathrm{pso}}|0\rangle}{E_k - E_0} \right\} .$$
(S4)

The atoms selected for the SOS study are C2, C5, C9, and C12. The number of states included in the sum is twice the number of states under investigation (as specified in captions). Tables S9, S10, and S11 show the exact (analytic) and SOS NSCD values for AZO-1, AZO-2 and AZO-3, respectively. The values of the $\mathcal{B}_{K,d}$ and $\mathcal{B}_{K,a}$ terms are plotted separately as bar plots in Figures S6 (AZO-1), S7 (AZO-2), and S8 (AZO-3). Note that the numbers are scaled by 1000 but not multiplied by the unit prefactor \mathcal{L}_C .

TABLE S9. AZO-1. RI-CC2/aug-cc-pwCVDZ. Exact and sum-over-states $(n_k = 8) \mathcal{B}_K \times 1000$ of C2, C5, C9, and C12..

| | $\mathrm{ES}\#$ | 1 | 2 | 3 | 4 |
|------|-----------------|-------|---------|--------|--------|
| Ga | Exact | 38.87 | -242.66 | -83.27 | 153.81 |
| 02 | SOS | 34.01 | -105.17 | -79.82 | 145.61 |
| CIT. | Exact | -4.59 | -86.73 | -14.91 | 4.92 |
| C5 | SOS | -2.59 | 6.66 | -31.07 | 70.40 |
| Go | Exact | 1.82 | 89.31 | -58.60 | -48.72 |
| C9 | SOS | 1.54 | 118.68 | -22.22 | -47.46 |
| | Exact | -3.65 | 70.13 | -87.17 | -61.12 |
| C12 | SOS | -2.76 | 90.44 | -18.83 | -47.06 |



FIG. S6. AZO-1. RI-CC2/aug-cc-pwCVDZ. Bar plots of $\mathcal{B}_{C,d}(k \to m)$ (red) and $\mathcal{B}_{C,a}(k \to m)$ (blue) of C2, C5, C9, and C12 for the four lowest excited states. Number of intermediate states $n_k = 8$. Note the offset of the y-values given above the axes.

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TABLE S10. AZO-2. RI-CC2/aug-cc-pwCVDZ. Exact and sum-over-states $(n_k = 8) \mathcal{B}_K \times 1000$ of C2, C5, C9, and C12.

| | $\mathrm{ES}\#$ | 1 | 2 | 3 | 4 | |
|------------|-----------------|-------|---------|--------|---------|--|
| <i>a</i> . | Exact | 65.86 | -232.98 | 103.75 | 29.15 | |
| 02 | SOS | 59.74 | -107.89 | 99.82 | 33.12 | |
| a 5 | Exact | -4.59 | -86.73 | -14.91 | 4.92 | |
| C_{2} | SOS | -4.84 | -86.67 | 23.05 | 11.15 | |
| Go | Exact | 2.63 | 48.17 | 24.20 | -61.45 | |
| C9 | SOS | 2.24 | 70.27 | 22.26 | -24.55 | |
| | Exact | -5.47 | 37.97 | 29.46 | -104.26 | |
| C12 | SOS | -4.34 | 52.19 | 27.21 | -23.12 | |



FIG. S7. AZO-2. RI-CC2/aug-cc-pwCVDZ. Bar plots of $\mathcal{B}_{C,d}(k \to m)$ (red) and $\mathcal{B}_{C,a}(k \to m)$ (blue) of C2, C5, C9, and C12 for the four lowest excited states. Number of intermediate states $n_k = 8$. Note the offset of the y-values given above the axes.

TABLE S11. AZO-3. RI-CC2/aug-cc-pwCVDZ. Exact and sum-over-states ($n_k = 12$) $\mathcal{B}_K \times 1000$ of C2, C5, C9, and C12. _

| | $\mathrm{ES}\#$ | 1 | 2 | 3 | 4 | 5 | 6 |
|---------|-----------------|--------|---------|-------|--------|---------|----------|
| Co | Exact | -25.83 | -109.76 | 0.00 | -11.44 | 39.32 | 0.87 |
| 02 | SOS | -24.75 | 27.09 | -0.00 | -19.13 | 40.90 | -11.71 |
| | Exact | 2.85 | -27.03 | 0.00 | -3.41 | -4.54 | 5.01 |
| C_{2} | SOS | 1.86 | -53.28 | 0.00 | -2.08 | 6.17 | 4.88 |
| Go | Exact | -0.82 | 95.97 | 0.00 | -0.28 | 1869.70 | -1807.68 |
| C9 | SOS | -1.06 | 107.66 | 0.00 | -0.15 | 1920.39 | -1844.30 |
| ~ ~ | Exact | 1.99 | 111.45 | 0.00 | 4.92 | -176.43 | 183.30 |
| C12 | SOS | 1.62 | 107.98 | 0.00 | 6.06 | -100.84 | 170.87 |



FIG. S8. AZO-3. RI-CC2/aug-cc-pwCVDZ. Bar plots of $\mathcal{B}_{C,d}(k \to m)$ (red) and $\mathcal{B}_{C,a}(k \to m)$ (blue) of C2, C5, C9, and C12 for the six lowest excited states. Number of intermediate states $n_k = 12$. Note the offset of the y-values given above the axes.

S6. CARTESIAN COORDINATES

The coordinates are provided in Angstrom and $\verb".xyz"$ format.

AZO-1

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| С | 1.0357887 | -2.0353758 | 0.0006766 |
|---|------------|------------|------------|
| С | -0.2565927 | -1.4965821 | 0.0002726 |
| С | -1.3626410 | -2.3515573 | -0.0003573 |
| С | -1.1934234 | -3.7282563 | -0.0005237 |
| С | 0.0947305 | -4.2615577 | -0.0002036 |
| С | 1.2055258 | -3.4107999 | 0.0004448 |
| N | -0.5548141 | -0.1172454 | 0.0003184 |
| N | 0.4705064 | 0.6310168 | 0.0004193 |
| С | 0.1659645 | 2.0145128 | 0.0003292 |
| С | -1.1304066 | 2.5443198 | 0.0006897 |
| С | -1.3020669 | 3.9220753 | 0.0003706 |
| С | -0.1953763 | 4.7755535 | -0.0002874 |
| С | 1.0931160 | 4.2454362 | -0.0006321 |
| С | 1.2732546 | 2.8658121 | -0.0002831 |
| 0 | 0.2118701 | -5.6195230 | -0.0005667 |
| Η | 2.2035091 | -3.8333257 | 0.0007386 |
| Η | 1.8852879 | -1.3687292 | 0.0011038 |
| Η | -2.0390292 | -4.4008634 | -0.0008599 |
| H | -2.3508346 | -1.9127315 | -0.0008502 |
| H | 2.2600432 | 2.4235006 | -0.0005380 |
| H | 1.9512518 | 4.9031105 | -0.0012208 |
| H | -0.3401306 | 5.8472298 | -0.0005037 |
| Η | -2.3008539 | 4.3370765 | 0.0005835 |
| H | -1.9734575 | 1.8697411 | 0.0011645 |
| Н | 1.1487778 | -5.8428373 | -0.0002853 |

| С | 1.0527302 | 0.0325583 | 1.8403427 |
|---|------------|-----------|------------|
| С | -0.2366122 | 0.0222357 | 1.2903279 |
| С | -1.3445158 | 0.0230522 | 2.1420936 |
| С | -1.1777059 | 0.0341979 | 3.5187191 |
| С | 0.1060409 | 0.0479658 | 4.0764812 |
| С | 1.2149219 | 0.0428400 | 3.2141678 |
| N | -0.5282765 | 0.0124603 | -0.0870202 |
| N | 0.4996235 | 0.0111704 | -0.8339255 |
| С | 0.1964631 | 0.0015885 | -2.2174378 |
| С | -1.0991601 | 0.0010802 | -2.7494077 |

| С | -1.2697246 | -0.0084430 | -4.1273553 |
|---|------------|------------|------------|
| С | -0.1624559 | -0.0176988 | -4.9799709 |
| С | 1.1254203 | -0.0171661 | -4.4482717 |
| С | 1.3040921 | -0.0072797 | -3.0684584 |
| N | 0.2859971 | -0.0071984 | 5.4555693 |
| Н | 2.2117720 | 0.0455223 | 3.6379429 |
| Н | 1.9068110 | 0.0325888 | 1.1793613 |
| Н | -2.0421990 | 0.0306114 | 4.1704887 |
| Н | -2.3318231 | 0.0156988 | 1.7007928 |
| Н | 2.2905099 | -0.0065954 | -2.6252640 |
| Н | 1.9843511 | -0.0243526 | -5.1049532 |
| Н | -0.3061530 | -0.0252178 | -6.0517891 |
| Н | -2.2682373 | -0.0087672 | -4.5431717 |
| Н | -1.9426921 | 0.0081521 | -2.0754755 |
| Н | 1.1626942 | 0.3725353 | 5.7753286 |
| Н | -0.4872619 | 0.3551849 | 5.9901982 |

| С | 1.0578959 | 0.0033142 | 1.8459808 |
|---|------------|------------|------------|
| С | -0.2289174 | -0.0045857 | 1.2885601 |
| С | -1.3429169 | -0.0137353 | 2.1333649 |
| С | -1.1843443 | -0.0151715 | 3.5101324 |
| С | 0.0965083 | -0.0106374 | 4.0760544 |
| С | 1.2112028 | 0.0026930 | 3.2199706 |
| С | 0.2077954 | 0.0017575 | -2.2148239 |
| С | -1.0907427 | -0.0082698 | -2.7401938 |
| С | -1.2798329 | -0.0086591 | -4.1138518 |
| С | -0.1623482 | 0.0012050 | -4.9442103 |
| С | 1.1349826 | 0.0115116 | -4.4502403 |
| С | 1.3107029 | 0.0116291 | -3.0720006 |
| Н | 2.2052834 | 0.0140889 | 3.6498178 |
| Н | 1.9170276 | 0.0097096 | 1.1915797 |
| Н | -2.0528152 | -0.0183976 | 4.1564187 |
| Н | -2.3275405 | -0.0205797 | 1.6862017 |
| Н | 2.3000522 | 0.0194317 | -2.6364233 |
| Н | 1.9684946 | 0.0191423 | -5.1346279 |
| Н | -2.2657581 | -0.0162560 | -4.5516676 |
| Н | -1.9304564 | -0.0155677 | -2.0619480 |
| Н | 1.1493368 | -0.2992726 | 5.7863350 |
| Н | -0.5064157 | -0.2993101 | 5.9919319 |
| Ν | -0.5127848 | -0.0056434 | -0.0869416 |
| Ν | 0.5161518 | 0.0027739 | -0.8321503 |
| Ν | 0.2672165 | 0.0535821 | 5.4522322 |
| N | -0.3640701 | 0.0006728 | -6.3995285 |
| 0 | -1.5219277 | -0.0111654 | -6.8107910 |

0 0.6381130 0.0120177 -7.1103172

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