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ABSTRACT

A computational expression for the Faraday $\mathscr{A}$ term of magnetic circular dichroism (MCD) is derived within coupled cluster response theory and alternative computational expressions for the $\mathscr{B}$ term are discussed. Moreover, an approach to compute the (temperature-independent) MCD ellipticity in the context of coupled cluster damped response is presented, and its equivalence with the stick-spectrum approach in the limit of infinite lifetimes is demonstrated. The damped response approach has advantages for molecular systems or spectral ranges with a high density of states. Illustrative results are reported at the coupled cluster singles and doubles level and compared to time-dependent density functional theory results.

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I. INTRODUCTION

In magnetic circular dichroism (MCD) spectroscopy, the sample is probed with circularly polarized light in the presence of a relatively strong magnetic field oriented parallel to the direction of propagation of the light beam. The external magnetic field induces a differential absorption of the right- and left-circularly polarized light.[1] MCD can provide insight into the geometric, electronic, and magnetic properties of chemical systems. The applied magnetic field couples with the (spin and/or orbital) angular momentum, lifting the degeneracies among ground and excited states (by Zeeman splitting) and giving rise to additional spectroscopic features compared to the zero-field case. Since the MCD spectral features are signed and depend on molecular magnetic moments in electronic states and the direction of the field, MCD yields additional information when combined with conventional absorption spectroscopy. MCD spectra can be obtained from gases, solutions, or isotropic solids. Also, MCD can be observed for any sample of molecules independent of whether they are chiral or not. One can use MCD to study molecules of high symmetry and to probe degenerate electronic ground and excited states.

About 50 years ago, Buckingham and Stephens[2] described the theoretical foundation of MCD in an elegant and incisive way. For an electronic transition, the intensity of the signal is given by the contribution of three effects called $\mathscr{A}$, $\mathscr{B}$, and $\mathscr{C}$ terms. The $\mathscr{A}$ term originates from the Zeeman splitting of degenerate excited states. The $\mathscr{B}$ term arises from the mixing of the zero-field wave functions between non-degenerate states in the presence of a magnetic field. The $\mathscr{C}$ term is a temperature-dependent effect and originates from the Zeeman splitting of a degenerate ground state. Each term is associated with a characteristic band shape. After the seminal work of Buckingham and Stephens, the MCD spectra of several molecules were rationalized and understood qualitatively based on the Hückel molecular orbital, the Pariser–Parr–Pople (PPP) model, and the Complete Neglect of Differential Overlap/Spectroscopic (CNDO/S) method.[3–5]

The challenging aspect of the *ab initio* computation of MCD spectra derives from the need to consider both the perturbation of

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a static magnetic field and the perturbation of an oscillating electric field. In the last 20 years, several approaches have been proposed for the simulation of MCD; see, for example, Ref. 6 for a review up to 2012. Among them, response theory[7–9] has been employed to formulate MCD in different forms, for instance, as single residue of dipole–dipole–magnetic dipole quadratic response functions,[10] as a complex polarization propagator,[11,12] or a damped response function[13] to avoid divergences, and by magnetically perturbed time-dependent density functional theory (MP-TDDFT) evaluating the perturbations induced into TDDFT excitation energies and transition densities by a static magnetic field.[12,14] In the complex polarization propagator/damped response frameworks, the MCD signal is computed directly, without separation into MCD $\mathscr{A}$ and $\mathscr{B}$ terms.[15] MCD spectra have also been calculated with sum-over-states (SOS) methods for the individual terms at the Hartree–Fock and DFT levels[16] of theory and within full configuration interaction (CI).[17] For the treatment of MCD arising from transition metals, DFT and HF may be inadequate; thus, multi-configurational self-consistent-field with the treatment of spin–orbit coupling (SOC) and spin–spin coupling (SSC) using the complete active space self-consistent field (CASSCF)[18] and restricted active space (RAS)[19] wave functions have been implemented. Gauge-origin independent formulations of MCD using the perturbative approach with London orbitals have been developed within DFT,[20,21] Hartree–Fock,[21] and coupled cluster (CC) frameworks.[22,23] Calculations of MCD within a variational treatment of the magnetic field have also been proposed.[24,25]

In this work, we re-analyze the derivation of the MCD $\mathscr{B}$ term within resonant CC response function theory and extend the theory to the computation of the $\mathscr{A}$ term. Then, we derive the CC damped response expression for the MCD ellipticity. Compared to the computation of induced transition strengths for stick spectra, the calculation of the damped response function is computationally more efficient for large chromophores or spectral regions with a high density of states.[9,26] In these cases, the computation of the stick spectra requires the convergence of eigenvectors and the calculation of (derivatives of) transition moments for many states. The costs for the calculations of the damped response function depend mainly on the size of the frequency range and the frequency resolution, but are almost insensitive to the density of states. To show the equivalence of the two approaches, illustrative numerical results are reported at the coupled cluster singles and doubles (CCSD) level for the molecular systems cyclopropane and urea. These are compared with TDDFT results at the CAM-B3LYP[27,28]/aug-cc-pVDZ[29] level.

II. THEORY

A. $\mathscr{A}$ and $\mathscr{B}$ terms from resonant CC response theory

Following Ref. 13, we write the ellipticity θ of plane-polarized light traveling in the Z direction of a space-fixed frame through a sample of randomly moving molecules in the presence of a magnetic field directed along Z as

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

where, in atomic units,

$$\theta_{MCD} = -\omega \sum_f \left\{ \frac{\partial g(\omega,\omega_f)}{\partial \omega} \mathscr{A}(0\to f) + g(\omega,\omega_f)\mathscr{B}(0\to f) \right\}. \tag{2}$$

Here, N is the number density, c is the velocity of light *in vacuo*, μ_0 is the permeability *in vacuo*, l is the length of the sample, ω is the circular frequency of the light wave, B_z is the strength of the external magnetic field, and $g(\omega, \omega_f)$ is a lineshape function. We adopt the sign convention used by Michl.[30] Thus, the contribution to θ_{MCD} of a transition $0 \to f$ can consist of a positive (when $\mathscr{B} < 0$) or negative (when $\mathscr{B} > 0$) band of absorption-like shape centered at the position of the absorption band. If the transition is degenerate, the absorption-like band is superimposed to a s-like (dispersive) shape, centered at the position of the absorption band, with a positive wing at lower energies and a negative one at higher energies (when $\mathscr{A} < 0$) or with a negative wing at lower energies and a positive one at higher energies (when $\mathscr{A} > 0$). Note that, in the expression of the MCD ellipticity θ_{MCD} in Eq. (2), we have omitted the temperature-dependent term, proportional to $\frac{\mathscr{C}(0\to f)}{kT}$, as it only contributes for systems with a degenerate ground state.

The spectral representation of the $\mathscr{A}$ term for a non-degenerate ground state 0 is[2,31]

$$\mathscr{A}(0\to f) = \tfrac{1}{2}\varepsilon_{\alpha\beta\gamma} \sum_{f'\in\mathfrak{D}_f} \mathrm{Im}\left[\langle 0|\mu_\alpha|f\rangle\langle f|m_\gamma|f'\rangle\langle f'|\mu_\beta|0\rangle\right], \tag{3}$$

where μ_α and μ_β are components of the electric dipole operator, m_γ is a component of the magnetic dipole operator, and $\varepsilon_{\alpha\beta\gamma}$ is the Levi-Civita tensor. Implicit summation over repeated Greek indices is assumed. $\mathfrak{D}_f$ is the set of degenerate states of which f is a part.[2] The $\mathscr{A}$ term vanishes for a non-degenerate excited state (as the magnetic moment is quenched).[32]

The spectral representation of the $\mathscr{B}$ term is given by[2,31]

$$\mathscr{B}(0\to f) = \varepsilon_{\alpha\beta\gamma}\mathrm{Im}\left[\sum_{k\neq 0}\frac{\langle k|m_\gamma|0\rangle}{\omega_k}\langle 0|\mu_\alpha|f\rangle\langle f|\mu_\beta|k\rangle + \sum_{k\notin\mathfrak{D}_f}\frac{\langle f|m_\gamma|k\rangle}{\omega_k-\omega_f}\langle 0|\mu_\alpha|f\rangle\langle k|\mu_\beta|0\rangle\right]. \tag{4}$$

A connection has previously been made between the $\mathscr{B}$ term of a non-degenerate state and the derivative of the transition strength matrix.[22] We will here extend this definition in order to include the $\mathscr{A}$-term. For exact states, the magnetic-field derivative of the electric–dipole transition strength (for the molecule exposed to the magnetic field), $S_{0f}^{\mu_\alpha\mu_\beta} = \langle 0|\mu_\alpha|f\rangle\langle f|\mu_\beta|0\rangle$, is

$$\tfrac{1}{2}\mathrm{Im}\left(\frac{dS_{0f}^{\mu_\alpha\mu_\beta}}{dB_\gamma}\right) = \mathrm{Im}\left[\sum_{k\neq 0}\frac{\langle k|m_\gamma|0\rangle}{\omega_k}\langle 0|\mu_\alpha|f\rangle\langle f|\mu_\beta|k\rangle + \sum_{k\neq f}\frac{\langle f|m_\gamma|k\rangle}{\omega_k-\omega_f}\langle 0|\mu_\alpha|f\rangle\langle k|\mu_\beta|0\rangle\right], \tag{5}$$

which is exactly the expression for the contributions to the $\mathscr{B}$ term if the state f is non-degenerate. If f is degenerate, however, the second sum contains additional terms, explicitly excluded from Eq. (4), involving the states degenerate with the final state. If we assume

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that the degeneracy can be broken by an infinitesimal amount, $\upsilon = \omega_{f'} - \omega_f$, the $\mathscr{A}$ term can be defined as the residue

$$\mathscr{A}(0 \to f) = \tfrac{1}{4}\varepsilon_{\alpha\beta\gamma} \lim_{\upsilon \to 0} \upsilon \mathrm{Im}\left(\frac{dS_{0f}^{\mu_\alpha \mu_\beta}}{dB_\gamma}\right). \tag{6}$$

Similarly, the expression for the $\mathscr{B}$ term in Eq. (4) is obtained by defining the $\mathscr{B}$ term as what remains of the transition-moment derivative once the singularities are removed, i.e., any degeneracy is projected out of the excited state wave function response.

In CC response theory, the transition strength is given as the product of distinct left and right transition moments[8,10,33,34]

$$S_{0f}^{\mu_\alpha \mu_\beta} = \tfrac{1}{2} T_{0f}^{\mu_\alpha} T_{f0}^{\mu_\beta} + \tfrac{1}{2} (T_{0f}^{\mu_\beta} T_{f0}^{\mu_\alpha})^*, \tag{7}$$

$$T_{0f}^{\mu_\alpha} = \eta^{\mu_\alpha} R_f + M_f \xi^{\mu_\alpha}, \tag{8}$$

and

$$T_{f0}^{\mu_\beta} = L_f \xi^{\mu_\beta}. \tag{9}$$

The eigenvectors are obtained by solving the right and left eigenvalue equations

$$\left(\mathbf{A} - \omega_f \mathbf{1}\right) R_f = \mathbf{0} \tag{10}$$

and

$$L_f (\mathbf{A} - \omega_f \mathbf{1}) = \mathbf{0} \tag{11}$$

under the biorthogonality condition $L_k R_l = \delta_{lk}$, and the transition multipliers $M_f(\omega_f)$ are the solutions of the linear equations

$$M_f(\omega_f)(\mathbf{A} + \omega_f \mathbf{1}) = -\mathbf{F} R_f. \tag{12}$$

For ease of notation, we have omitted the overbar on the transition multiplier. The definitions of the Jacobian matrix **A**, the matrix **F**, and of the property gradients, ξ^X and η^X, for any generic operator X, are summarized in Table S1 in the supplementary material. Additional information can be found, e.g., in Ref. 33.

Let us start by considering the case where the final state f is not degenerate. Under the assumption that the atomic orbital basis does not depend on the magnetic field, straightforward differentiation of the CC left and right ground-to-excited-state transition moments yields

$$\frac{dT_{0f}^{\mu_\alpha}}{dB_\gamma} = -T_{0f}^{\mu_\alpha m_\gamma} = \eta^{\mu_\alpha} R_f^{m_\gamma} + (\mathbf{F}^{\mu_\alpha} t^{m_\gamma} + \bar{t}^{m_\gamma} \mathbf{A}^{\mu_\alpha}) R_f + M_f^{m_\gamma} \xi^{\mu_\alpha} + M_f \mathbf{A}^{\mu_\alpha} t^{m_\gamma}, \tag{13}$$

$$\frac{dT_{f0}^{\mu_\beta}}{dB_\gamma} = -T_{f0}^{\mu_\beta m_\gamma} = L_f^{m_\gamma} \xi^{\mu_\beta} + L_f \mathbf{A}^{\mu_\beta} t^{m_\gamma}, \tag{14}$$

where t^{m_γ} and $\bar{t}^{m_\gamma}$ are the zero-frequency derivatives, with respect to the magnetic field, of the CC amplitudes and Lagrangian multipliers, respectively, obtained solving usual right and left response equations,[33]

$$(\mathbf{A} - \omega_X \mathbf{1}) t^X(\omega_X) = -\xi^X, \tag{15}$$

$$\bar{t}^X(\omega_X)(\mathbf{A} + \omega_X \mathbf{1}) = -(\eta^X + \mathbf{F} t^X(\omega_X)) = -\bar{\xi}^X(\omega_X), \tag{16}$$

for operator X equal to m_γ and $\omega_X = 0$.

The equations determining the magnetic-field derivatives, $L_f^{m_\gamma}$ and $R_f^{m_\gamma}$, of the left and right eigenvectors, as well as the magnetic-field derivative $M_f^{m_\gamma}$ of the transition multipliers, are

$$(\mathbf{A} - \omega_f \mathbf{1}) R_f^{m_\gamma} = -\left(\mathbf{A}^{m_\gamma} + \mathbf{B} t^{m_\gamma} - \omega_f^{m_\gamma} \mathbf{1}\right) R_f, \tag{17}$$

$$L_f^{m_\gamma} (\mathbf{A} - \omega_f \mathbf{1}) = -L_f \left(\mathbf{A}^{m_\gamma} + \mathbf{B} t^{m_\gamma} - \omega_f^{m_\gamma} \mathbf{1}\right), \tag{18}$$

$$M_f^{m_\gamma}(\mathbf{A} + \omega_f \mathbf{1}) = -\mathbf{F} R_f^{m_\gamma} - (\mathbf{F}^{m_\gamma} + \mathbf{G} t^{m_\gamma} + \bar{t}^{m_\gamma} \mathbf{B}) R_f - M_f (\mathbf{A}^{m_\gamma} + \omega_f^{m_\gamma} \mathbf{1} + \mathbf{B} t^{m_\gamma}), \tag{19}$$

where

$$\omega_f^{m_\gamma} = L_f (\mathbf{A}^{m_\gamma} + \mathbf{B} t^{m_\gamma}) R_f \,. \tag{20}$$

See again Ref. 33 for the definition of the remaining CC matrices.

While $(\mathbf{A} - \omega_f \mathbf{1})$ in Eqs. (17) and (18) is singular, it is easy to show that the right hand sides are orthogonal to R_f and L_f, respectively. It is sufficient to insert $\omega_f^{m_\gamma}$ in their definition and to project them against L_f and R_f, respectively. Thus, for non-degenerate final states f, Eqs. (17) and (18) can be solved in the orthogonal complement to the singularity without loss of generality.[22,34,35] In practice, this is achieved by introducing the projector

$$P_f = 1 - R_f \otimes L_f \tag{21}$$

where $R_f \otimes L_f$ is the outer product of the eigenvectors and the projected derivative eigenvectors

$${}^{\perp}R_f^{m_\gamma} = P_f R_f^{m_\gamma} \tag{22}$$

and

$${}^{\perp}L_f^{m_\gamma} = L_f^{m_\gamma} P_f, \tag{23}$$

which are obtained solving

$$P_f (\mathbf{A} - \omega_f \mathbf{1}) {}^{\perp}R_f^{m_\gamma} = -P_f \left(\mathbf{A}^{m_\gamma} + \mathbf{B} t^{m_\gamma}\right) R_f \tag{24}$$

and

$${}^{\perp}L_f^{m_\gamma} (\mathbf{A} - \omega_f \mathbf{1}) P_f = -L_f \left(\mathbf{A}^{m_\gamma} + \mathbf{B} t^{m_\gamma}\right) P_f. \tag{25}$$

In addition, we use the notation ${}^{\perp}M_f^{m_\gamma}$ to emphasize that the Lagrange multiplier responses are calculated using the non-singular derivative of the eigenvector, i.e.,

$${}^{\perp}M_f^{m_\gamma}(\mathbf{A} + \omega_f \mathbf{1}) = -\mathbf{F}^{\perp} R_f^{m_\gamma} - (\mathbf{F}^{m_\gamma} + \mathbf{G} t^{m_\gamma} + \bar{t}^{m_\gamma} \mathbf{B}) R_f - M_f (\mathbf{A}^{m_\gamma} + \omega_f^{m_\gamma} \mathbf{1} + \mathbf{B} t^{m_\gamma}). \tag{26}$$

If the final state f is degenerate (i.e., it belongs to the set $\mathfrak{D}_f$), the projector is generalized as

$$P_f = 1 - \sum_{f' \in \mathfrak{D}_f} R_{f'} \otimes L_{f'}. \tag{27}$$

Then, we introduce a distinction between the two kinds of contributions, i.e., the $\mathscr{A}$ and the $\mathscr{B}$ term. In accordance with exact theory, we define the $\mathscr{B}$ term as the term obtained by projecting out the singularity and otherwise continuing as in the non-degenerate case. The

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$\mathscr{A}$ term, on the other hand, will be defined as the residue of the term involving the singularity.

Thus, the CC $\mathscr{B}$ term will be obtained as

$$\mathscr{B}_{\mathrm{CC}}(0\to f) = -\tfrac{1}{2}\varepsilon_{\alpha\beta\gamma}\left({}^{\perp}T_{0f}^{\mu_\alpha m_\gamma}T_{f0}^{\mu_\beta} + T_{0f}^{\mu_\alpha}{}^{\perp}T_{f0}^{\mu_\beta m_\gamma}\right), \tag{28}$$

where the perpendicular perturbed transition moments (${}^{\perp}T_{0f}^{\mu_\alpha m_\gamma}$ and ${}^{\perp}T_{f0}^{\mu_\beta m_\gamma}$) are defined by introducing ${}^{\perp}R_f^{m_\gamma}$, ${}^{\perp}L_f^{m_\gamma}$ and ${}^{\perp}M_f^{m_\gamma}$ in place of their non-$\perp$ equivalents into Eqs. (13) and (14). The formulation of the derivative transition moments as in Eqs. (13) and (14) is attractive as all dependencies on the electric dipole components μ_α and μ_β are explicit, allowing for the identification of derivative left and right transition densities.

An alternative expression of the (orthogonal) left moment is obtained by eliminating $M_f^{m_\gamma}$ (or ${}^{\perp}M_f^{m_\gamma}$) from Eq. (13) using Eq. (19) [or Eq. (26)],

$$\begin{aligned} M_f^{m_\gamma}\xi^{\mu_\alpha} &= -\Big[\mathbf{F}R_f^{m_\gamma} + (\mathbf{F}^{m_\gamma} + \mathbf{G}t^{m_\gamma} + \bar{t}^{m_\gamma}\mathbf{B})R_f \\ &\quad + M_f(\mathbf{A}^{m_\gamma} + \omega_f^{m_\gamma}\mathbf{1} + \mathbf{B}t^{m_\gamma})\Big](\mathbf{A}+\omega_f\mathbf{1})^{-1}\xi^{\mu_\alpha} \\ &= \Big[\mathbf{F}R_f^{m_\gamma} + (\mathbf{F}^{m_\gamma} + \mathbf{G}t^{m_\gamma} + \bar{t}^{m_\gamma}\mathbf{B})R_f \\ &\quad + M_f(\mathbf{A}^{m_\gamma} + \omega_f^{m_\gamma}\mathbf{1} + \mathbf{B}t^{m_\gamma})\Big]t^{\mu_\alpha}(-\omega_f), \end{aligned} \tag{29}$$

$$\begin{aligned} T_{0f}^{\mu_\alpha m_\gamma} &= \big[\mathbf{G}t^{m_\gamma}t^{\mu_\alpha}(-\omega_f) + \mathbf{F}^{m_\gamma}t^{\mu_\alpha}(-\omega_f) + \mathbf{F}^{\mu_\alpha}t^{m_\gamma}\big]R_f \\ &\quad + M_f\big[\mathbf{A}^{\mu_\alpha}t^{m_\gamma} + \mathbf{A}^{m_\gamma}t^{\mu_\alpha}(-\omega_f) + \mathbf{B}t^{m_\gamma}t^{\mu_\alpha}(-\omega_f)\big] \\ &\quad + \big[\eta^{\mu_\alpha} + \mathbf{F}t^{\mu_\alpha}(-\omega_f)\big]R_f^{m_\gamma} \\ &\quad + \omega_f^{m_\gamma}\cdot M_f t^{\mu_\alpha}(-\omega_f) + \bar{t}^{m_\gamma}\big[\mathbf{A}^{\mu_\alpha} + \mathbf{B}t^{\mu_\alpha}(-\omega_f)\big]R_f. \end{aligned} \tag{30}$$

The last term in Eq. (30) can further be recast as

$$\begin{aligned} \bar{t}^{m_\gamma}\big[\mathbf{A}^{\mu_\alpha} + \mathbf{B}t^{\mu_\alpha}(-\omega_f)\big]R_f &= \big(\eta^{m_\gamma} + \mathbf{F}t^{m_\gamma}\big)R_f^{\mu_\alpha}(-\omega_f) \\ &= \bar{\xi}^{m_\gamma}(0)R_f^{\mu_\alpha}(-\omega_f), \end{aligned} \tag{31}$$

which now involves $R_f^{\mu_\alpha}(-\omega_f)$, the first-order response to the electric field of the right eigenvector in a non-phase-isolated (i.e., unprojected) form.[35] Similarly, the third term can be recast as

$$\big[\eta^{\mu_\alpha} + \mathbf{F}t^{\mu_\alpha}(-\omega_f)\big]^{\perp}R_f^{m_\gamma} = -{}^{\perp}\bar{t}(-\omega_f)\big(\mathbf{A}^{m_\gamma} + \mathbf{B}t^{m_\gamma} - \omega_f^{m_\gamma}\mathbf{1}\big)R_f. \tag{32}$$

Equation (30) is formally the approach taken in the implementation in Dalton[22,36] and Turbomole,[37,38] the latter also employing Eq. (31).[37,38] If the final states f are non-degenerate, both approaches [Eqs. (13) and (30)] require the solution of the same amount of linear equations. In the case of degenerate states, however, the latter is advantageous as the dipole response amplitudes $t^{\mu_\alpha}(-\omega_f)$ need to be calculated only once for each degenerate set.

To obtain the CC expression for the $\mathscr{A}$ term, we perform a residue analysis according to Eq. (6), i.e.,

$$\mathscr{A}_{\mathrm{CC}}(0\to f) = -\tfrac{1}{4}\varepsilon_{\alpha\beta\gamma}\lim_{\upsilon\to 0}\upsilon\mathrm{Im}\left(T_{0f}^{\mu_\alpha m_\gamma}T_{f0}^{\mu_\beta} + T_{0f}^{\mu_\alpha}T_{f0}^{\mu_\beta m_\gamma}\right), \tag{33}$$

which requires the residues

$${}^{\parallel}T_{0f}^{\mu_\alpha m_\gamma} = \lim_{\upsilon\to 0}\upsilon\, T_{0f}^{\mu_\alpha m_\gamma} = -\eta^{\mu_\alpha}\,{}^{\parallel}R_f^{m_\gamma} - {}^{\parallel}M_f^{m_\gamma}\,\xi^{\mu_\alpha}, \tag{34}$$

$${}^{\parallel}T_{f0}^{\mu_\beta m_\gamma} = \lim_{\upsilon\to 0}\upsilon\, T_{f0}^{\mu_\beta m_\gamma} = -{}^{\parallel}L_f^{m_\gamma}\xi^{\mu_\beta}. \tag{35}$$

The response of the eigenvectors parallel to the degenerate set $\mathscr{D}_f$ is defined as residues of non-phase isolated derivatives of the eigenvectors[35]

$${}^{\parallel}R_f^{m_\gamma} = \lim_{\upsilon\to 0}\upsilon\, R_f^{m_\gamma} = -\sum_{\substack{f'\in\mathfrak{D}_f,\\ f'\neq f}} R_{f'}L_{f'}(\mathbf{A}^{m_\gamma} + \mathbf{B}t^{m_\gamma})R_f = -\sum_{\substack{f'\in\mathfrak{D}_f,\\ f'\neq f}} R_{f'}T_{f'f}^{m_\gamma}, \tag{36}$$

$${}^{\parallel}L_f^{m_\gamma} = \lim_{\upsilon\to 0}\upsilon\, L_f^{m_\gamma} = -\sum_{\substack{f'\in\mathfrak{D}_f,\\ f'\neq f}} L_f(\mathbf{A}^{m_\gamma} + \mathbf{B}t^{m_\gamma})R_{f'}L_{f'} = -\sum_{\substack{f'\in\mathfrak{D}_f,\\ f'\neq f}} T_{ff'}^{m_\gamma}L_{f'}, \tag{37}$$

and

$${}^{\parallel}M_f^{m_\gamma} = -\mathbf{F}\,{}^{\parallel}R_f^{m_\gamma}(\mathbf{A}+\omega_f\mathbf{1})^{-1} = -\sum_{\substack{f'\in\mathfrak{D}_f,\\ f'\neq f}} M_{f'}T_{f'f}^{m_\gamma}. \tag{38}$$

In the above equations, simplifications have been made by identifying the conventional CC expression for transition moments between excited states, e.g., $T_{ff'}^{m_\gamma} = L_f(\mathbf{A}^{m_\gamma} + \mathbf{B}t^{m_\gamma})R_{f'}$. This allows us to write the $\mathscr{A}_{\mathrm{CC}}$ term as

$$\mathscr{A}_{\mathrm{CC}}(0\to f) = -\tfrac{1}{4}\varepsilon_{\alpha\beta\gamma}\mathrm{Im}\sum_{\substack{f'\in\mathfrak{D}_f,\\ f'\neq f}}\left(T_{0f'}^{\mu_\alpha}T_{f'f}^{m_\gamma}T_{f0}^{\mu_\beta} + T_{0f}^{\mu_\alpha}T_{ff'}^{m_\gamma}T_{f'0}^{\mu_\beta}\right) \tag{39}$$

or, when summed over the whole degenerate set,

$$\mathscr{A}_{\mathrm{CC}}(0\to\mathfrak{D}_f) = -\tfrac{1}{2}\varepsilon_{\alpha\beta\gamma}\mathrm{Im}\sum_{f',f''\in\mathfrak{D}_f}(1-\delta_{f'f''})\left(T_{0f'}^{\mu_\alpha}T_{f'f''}^{m_\gamma}T_{f''0}^{\mu_\beta}\right). \tag{40}$$

Note that the $\mathscr{A}$ term has previously been formulated as the derivative of the excitation energy[13,20,31]

$$\mathscr{A}(0\to f) = -\tfrac{1}{2}\varepsilon_{\alpha\beta\gamma}\sum_{f\in\mathfrak{D}_f}\left(\frac{\partial\omega_f}{\partial B_\gamma}\right)\mathrm{Im}\left\{\tilde{\mu}_\alpha^{0f}\tilde{\mu}_\beta^{f0}\right\}, \tag{41}$$

where the real degenerate states f are (typically) expanded in complex states $\tilde{f}$, which diagonalize the imaginary operator m_γ.[13,20] This is consistent with our derivation, as we can identify

$$\frac{\partial\omega_f}{\partial B_\gamma} = L_f(\mathbf{A}^{m_\gamma} + \mathbf{B}t^{m_\gamma})R_{f'} = T_{ff'}. \tag{42}$$

Our derivation highlights how the transformation to the diagonal basis for m_γ can be avoided.

B. MCD spectra from CC damped response theory

Within damped response theory, the MCD ellipticity can be obtained directly from the magnetic field derivative of the damped dynamic polarizability,

$$\theta_{MCD} = -\,\omega\varepsilon_{\alpha\beta\gamma}\mathrm{Re}\left(\frac{d\langle\langle\mu_\alpha;\mu_\beta\rangle\rangle_{\omega+i\bar{\omega}}}{dB_\gamma}\right)_{B=0}, \tag{43}$$

where ω is the frequency of the perturbing light wave and $\bar{\omega}$ is the damping parameter. General sum-over-state expressions for the damped polarizability can be found, e.g., in Refs. 39 and 40. In

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coupled cluster theory, the damped polarizability can be computed according to the following equation:[40–43]

$$\langle\langle \mu_\alpha;\mu_\beta\rangle\rangle_{\omega+i\varpi} = \frac{1}{2}C^{\pm\omega}\{\eta^{\mu_\alpha}t^{\mu_\beta}(\omega+i\varpi)+\eta^{\mu_\beta}t^{\mu_\alpha}(-\omega-i\varpi) + \mathbf{F}t^{\mu_\beta}(\omega+i\varpi)t^{\mu_\alpha}(-\omega-i\varpi)\}. \quad (44)$$

The complex amplitudes in Eq. (44) are found solving the complex linear equations

$$[\mathbf{A}-(\omega+i\varpi)\mathbf{1}]t^{\mu_\alpha}(\omega+i\varpi) = -\xi^{\mu_\alpha}. \quad (45)$$

We refer to our previous work[41–43] for details on how to solve the complex equations in Eq. (45).

Typically, the CC response functions need to be explicitly symmetrized,[33] as indicated in Eq. (44) by the $\frac{1}{2}C^{\pm\omega}$ operator. However, the Levi-Civita symbol in Eq. (43) makes this symmetrization redundant. Taking the first derivative of the non-symmetric CC linear response function, i.e., the term in brackets in Eq. (44), we obtain the following equation:

$$\begin{aligned}\frac{d\langle\langle \mu_\alpha;\mu_\beta\rangle\rangle_{\omega+i\varpi}}{dB_\gamma} &= \mathbf{F}^{m_\gamma}t^{\mu_\beta}(\omega+i\varpi)t^{\mu_\alpha}(-\omega-i\varpi)+\big[\mathbf{F}^{\mu_\alpha}t^{\mu_\beta}(\omega+i\varpi)\\ &+\mathbf{F}^{\mu_\beta}t^{\mu_\alpha}(-\omega-i\varpi)+\mathbf{G}t^{\mu_\beta}(\omega+i\varpi)t^{\mu_\alpha}(-\omega-i\varpi)\big]t^{m_\gamma}\\ &+\bar{t}^{m_\gamma}\big[\mathbf{A}^{\mu_\alpha}t^{\mu_\beta}(\omega+i\varpi)+\mathbf{A}^{\mu_\beta}t^{\mu_\alpha}(-\omega-i\varpi)\\ &+\mathbf{B}t^{\mu_\beta}(\omega+i\varpi)t^{\mu_\alpha}(-\omega-i\varpi)\big]\\ &+\big[\mathbf{F}t^{\mu_\alpha}(-\omega-i\varpi)+\eta^{\mu_\alpha}\big]t^{\mu_\beta m_\gamma}(\omega+i\varpi)\\ &+\big[\mathbf{F}t^{\mu_\beta}(\omega+i\varpi)+\eta^{\mu_\beta}\big]t^{\mu_\alpha m_\gamma}(-\omega-i\varpi). \quad (46)\end{aligned}$$

The above expression contains the doubly perturbed amplitudes, which are defined by the second-order response equations

$$\begin{aligned}&[\mathbf{A}+(\omega+i\varpi)]t^{\mu_\alpha m_\gamma}(-\omega-i\varpi)\\ &\quad=-\mathbf{A}^{\mu_\alpha}t^{m_\gamma}-\mathbf{A}^{m_\gamma}t^{\mu_\alpha}(-\omega-i\varpi)-\mathbf{B}t^{m_\gamma}t^{\mu_\alpha}(-\omega-i\varpi). \quad (47)\end{aligned}$$

However, the expression by which $t^{\mu_\alpha m_\gamma}(-\omega-i\varpi)$ is multiplied is exactly the right hand side of the equations that determine $\bar{t}^{\mu_\beta}(\omega+i\varpi)$, so that this term can be eliminated according to the following equation:

$$\begin{aligned}&\big[\mathbf{F}t^{\mu_\beta}(\omega+i\gamma)+\eta^{\mu_\beta}\big]t^{\mu_\alpha m_\gamma}(-\omega-i\varpi)\\ &\quad=\bar{t}^{\mu_\beta}(\omega+i\gamma)\big[\mathbf{A}^{\mu_\alpha}t^{m_\gamma}+\mathbf{A}^{m_\gamma}t^{\mu_\alpha}(-\omega-i\varpi)\\ &\quad+\mathbf{B}t^{m_\gamma}t^{\mu_\alpha}(-\omega-i\varpi)\big]. \quad (48)\end{aligned}$$

This leads to a more convenient computational expression, which shows the symmetry between the perturbations as follows:

$$\begin{aligned}&\frac{d\langle\langle \mu_\alpha;\mu_\beta\rangle\rangle_{\omega+i\varpi}}{dB_\gamma}\\ &=\mathbf{F}^{m_\gamma}t^{\mu_\beta}(\omega+i\varpi)t^{\mu_\alpha}(-\omega-i\varpi)+\big[\mathbf{F}^{\mu_\alpha}t^{\mu_\beta}(\omega+i\varpi)\\ &+\mathbf{F}^{\mu_\beta}t^{\mu_\alpha}(-\omega-i\varpi)+\mathbf{G}t^{\mu_\beta}(\omega+i\varpi)t^{\mu_\alpha}(-\omega-i\varpi)\big]t^{m_\gamma}\\ &+\bar{t}^{m_\gamma}\big[\mathbf{A}^{\mu_\alpha}t^{\mu_\beta}(\omega+i\varpi)+\mathbf{A}^{\mu_\beta}t^{\mu_\alpha}(-\omega-i\varpi)\\ &+\mathbf{B}t^{\mu_\beta}(\omega+i\varpi)t^{\mu_\alpha}(-\omega-i\varpi)\big]+\bar{t}^{\mu_\alpha}(-\omega-i\varpi)\big[\mathbf{A}^{\mu_\beta}t^{m_\gamma}\\ &+\mathbf{A}^{m_\gamma}t^{\mu_\beta}(\omega+i\varpi)+\mathbf{B}t^{m_\gamma}t^{\mu_\beta}(\omega+i\varpi)\big]+\bar{t}^{\mu_\beta}(\omega+i\varpi)\\ &\times\big[\mathbf{A}^{\mu_\alpha}t^{m_\gamma}+\mathbf{A}^{m_\gamma}t^{\mu_\alpha}(-\omega-i\varpi)+\mathbf{B}t^{m_\gamma}t^{\mu_\alpha}(-\omega-i\varpi)\big]. \quad (49)\end{aligned}$$

The connection to the quadratic response function expression $\langle\langle \mu_\alpha;\mu_\beta,m_\gamma\rangle\rangle_{\omega,0}$ (in the limit of $\varpi=0$) is apparent.[22,33]

III. RESULTS AND DISCUSSION

The calculation of the $\mathscr{A}_{\mathrm{CC}}(0\to f)$ and $\mathscr{B}_{\mathrm{CC}}(0\to f)$ terms in gas phase according to the expressions in Eqs. (28) and (40) as well as that of the MCD ellipticity according to the damped-response algorithm discussed in Section IIB have been implemented at the CCSD level in our stand-alone python CC response platform for code prototyping.[42,44] Two illustrative cases were considered, cyclopropane, C_3H_6, and urea, $H_2N(CO)NH_2$. Cyclopropane has D_{3h} symmetry and, thus, possesses degenerate excited states, yielding spectral features that arise from the $\mathscr{A}$-term. Urea belongs to the C_{2v} (or lower) point group and does not support degenerate excited states per symmetry. Explicit point group symmetry is not implemented in PY-CCRSP. In the current implementation, the eigenvalue

TABLE I. Cyclopropane. Computed spectral parameters from resonant response theory: excitation energies (ω_f), dipole oscillator strengths (f), and MCD $\mathscr{A}$ and $\mathscr{B}$ terms.

Symm	ω_f (eV)	f (adim)	$\mathscr{A}$ (a.u.) [LAO $\mathscr{A}$ (a.u.)]	$\mathscr{B}$ (a.u.) [LAO $\mathscr{B}$ (a.u.)]
			CCSD/aug-cc-pVDZ	
E′	7.686	0.0001	−0.000 187 85	0.241 235 51
E′	8.305	0.16	0.059 157 07	2.572 666 36
E′	9.361	0.009	−0.011 416 25	3.482 804 34
A_2''	9.557	0.0098	0.000 000 00	−4.516 438 87
			CAM-B3LYP/aug-cc-pVDZ	
E′	7.476	0.0001	−0.000 030 14(−0.000 028 71)	0.187 982 69(0.197 459 4)
E′	8.105	0.156	0.052 788 49(0.045 171 5)	1.972 667 12(1.881 245 2)
E′	9.168	0.0088	−0.010 795 84(−0.011 294 6)	2.964 045 89(2.713 459 9)
A_2''	9.286	0.0096	0.000 000 00(0.000 000 00)	−3.617 143 00(−3.147 974)

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problem is solved first. The solutions are then analyzed to identify eigenvalues that are degenerate within a preset threshold. For each degenerate state, the $\mathscr{A}$-term is computed. Experimental results in gas phase as well as computational (TDDFT and SOS-HF) results for cyclopropane are available in the literature.[11,45] To the best of our knowledge, the MCD spectrum of urea has neither been measured nor simulated before.

The geometry of urea was optimized at the CCSD/aug-cc-pVDZ level, whereas the geometry of cyclopropane was optimized at the CCSD(T)/aug-cc-pVTZ level.

The MCD spectra resulting from the calculated individual $\mathscr{A}_{\mathrm{CC}}(0 \to f)$ and $\mathscr{B}_{\mathrm{CC}}(0 \to f)$ terms were generated according to Eq. (2) with a Lorentzian lineshape function

$$g(\omega, \omega_f) = \frac{\varpi}{\pi} \frac{1}{(\omega - \omega_f)^2 + \varpi^2}, \tag{50}$$

$$\frac{\partial g(\omega, \omega_f)}{\partial \omega} = -\frac{2\varpi}{\pi} \frac{\omega - \omega_f}{\left[(\omega - \omega_f)^2 + \varpi^2\right]^2}, \tag{51}$$

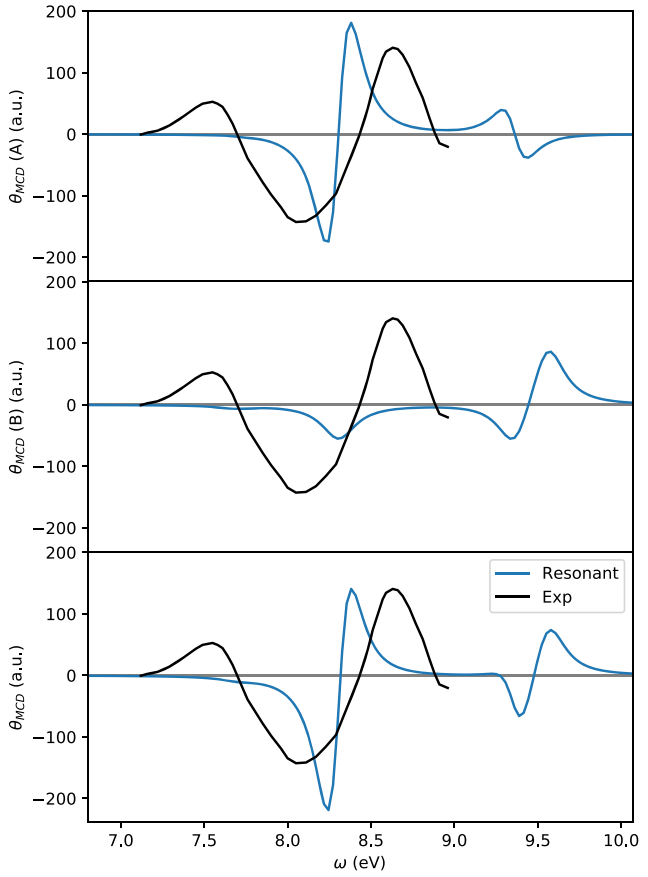


FIG. 1. Cyclopropane. CCSD relative contributions of $\mathscr{A}_{\mathrm{CC}}$ (upper panel) and $\mathscr{B}_{\mathrm{CC}}$ (middle panel) terms of resonant response theory to the total (lower panel) broadened MCD spectrum. The experimental spectrum was taken from Ref. 46. The computed ellipticity is reported in atomic units. The experiment is plotted in arbitrary units and scaled to match the height of the second peak in the total computed spectrum.

and the same $\varpi = 0.004\,556\,3$ a.u. ≈ 1000 cm^{-1} was used for the broadening adopted in the damped response calculations. The frequency step in the damped-response calculations was 0.001 a.u. The CCSD results are compared with CAM-B3LYP results obtained using LSDalton,[36] including results obtained using London atomic orbitals (LAO). The values of the excitation energies, electric dipole oscillator strengths f, and MCD terms for cyclopropane, obtained from resonant response theory, are collected in Table I.

Based on the values in Table I, Fig. 1 illustrates the relative importance of the $\mathscr{A}$ and $\mathscr{B}$ terms. Clearly, the bisignate spectral feature centered at 8.30 eV is dominated by the positive $\mathscr{A}$ term contribution of the second E′ excited state, where the $\mathscr{B}$ term is causing the slightly asymmetry of the dispersion band. The second bisignate feature at around 9.5 eV is the result of the fine balance of the negative $\mathscr{A}$ term for the third E′ state and the oppositely signed pseudo $\mathscr{A}$ due to the $\mathscr{B}$ terms of the close-lying third E′ state and the non-degenerate A_2'' state.

The total MCD spectrum generated by Lorentzian broadening of the $\mathscr{A}$ and $\mathscr{B}$ terms is compared with the spectrum obtained directly from damped response theory in Fig. 2. The broadened spectrum is basically identical to the one of damped response theory. The CAM-B3LYP spectrum is red-shifted compared to the CCSD one, and with slightly weaker intensities, but otherwise the spectral profiles are similar.

Table II collects the values of the excitation energies, oscillator strengths and MCD spectral parameters for urea, as obtained from resonant response theory. Only $\mathscr{B}$ terms are possible by symmetry. The corresponding MCD spectra, including the ones obtained from damped response, are shown in Fig. 3. Also in this case, damped and resonant theories yield almost identical spectra up to the number of frequencies that have been considered. The CAM-B3LYP spectrum is qualitatively very similar, yet with larger intensities from the two excited states at around 8 eV.

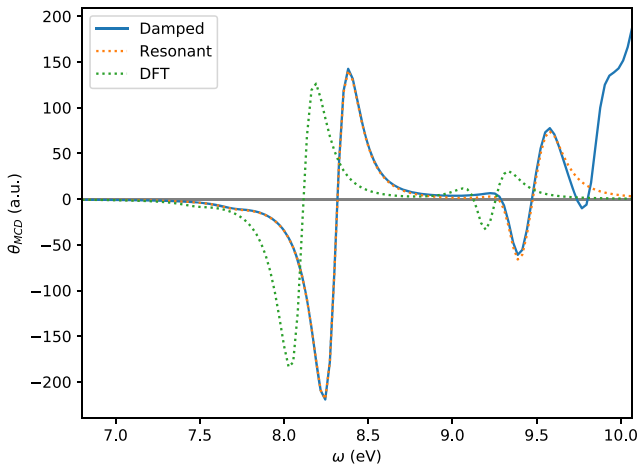


FIG. 2. Cyclopropane. CCSD/aug-cc-pVDZ MCD spectra from damped and resonant response theory, and comparison with the CAM-B3LYP spectrum from resonant response theory. The ellipticity is reported in atomic units.

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TABLE II. Urea. Computed spectral parameters (from resonant response theory): excitation energies (ω_f), oscillator strengths (f), and MCD $\mathscr{B}$ terms. Basis set aug-cc-pVDZ.

CCSD			CAM-B3LYP		
ω_f (eV)	f (adim)	$\mathscr{B}$ (a.u.)	ω_f (eV)	f (adim)	$\mathscr{B}$ (a.u) [LAO $\mathscr{B}$ (a.u.)].
6.420	0.031	−4.787 69	6.354	0.025	−4.918 73(−4.731 65)
6.754	0.033	5.235 36	6.612	0.033	5.663 15(5.365 14)
7.524	0.009	−0.676 20	7.371	0.012	−0.625 43(−0.779 52)
7.623	0.036	−7.464 70	7.463	0.021	−7.639 75(−6.929 1)
7.731	0.014)	1.536 04	7.587	0.020	1.832 69(−1.652 01)
7.832	0.002	5.050 75	7.674	0.009	4.953 39(4.992 14)
8.019	0.14	84.020 8	7.928	0.18	80.306 1(77.841 0)
8.054	0.20	−84.070 5	8.010	0.13	−80.255 2(−78.022 81)
8.634	0.059	−4.236 49	8.518	0.07	−4.097 54(−3.886 4)
8.671	0.003	3.058 57	8.557	0.004	3.010 59(3.614 1)

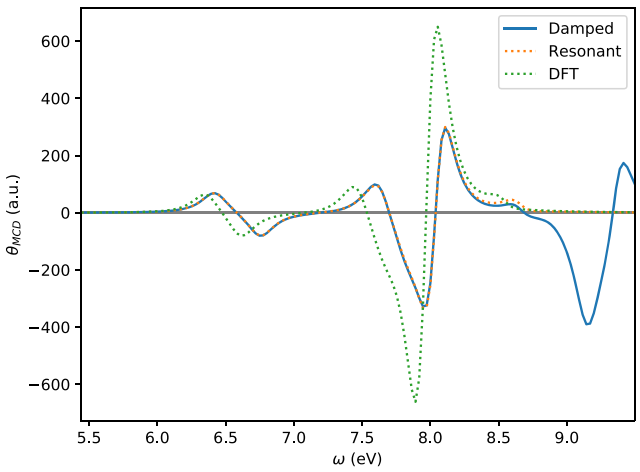


FIG. 3. Urea. CCSD/aug-cc-pVDZ MCD spectra from damped and resonant response theory, and comparison with the CAM-B3LYP one from resonant response theory. The ellipticity is reported in atomic units.

IV. CONCLUSIONS

We have presented a computational approach to obtain the $\mathscr{A}$ term of MCD within CC (resonant) response theory together with alternative computational recipes for the $\mathscr{B}$ term. Moreover, we have derived the computational expression of the MCD ellipticity (temperature-independent part) within CC damped response theory. The latter can prove particularly convenient when the system under investigation is characterized by a large density of excited states. The presented expressions are valid for standard atomic orbital bases, i.e., when the atomic orbital basis does not depend on the magnetic field. Therefore, the results are gauge-origin dependent. The dependence on the gauge origin is expected to be rather modest for the chosen systems, as also indicated by the small differences between CAM-B3LYP LAO and non-LAO results. The expressions can be generalized, e.g., London orbitals, along the lines of Ref. 22, to ensure gauge-origin independence. Such generalization is under development and will be presented at a later point. Illustrative results have been reported for cyclopropane and urea and compared with results from a previous CAM-B3LYP implementation of the $\mathscr{A}$ and $\mathscr{B}$ terms. The spectral profiles were found qualitatively similar though with noticeable differences on the intensity scale and the usual shifts in the position of the excited states.

SUPPLEMENTARY MATERIAL

See the supplementary material for a table with definitions of the main building blocks of CC response theory and for the Cartesian coordinates of the molecules investigated.

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APPENDIX: THE RESIDUES OF THE DERIVATIVE OF THE DAMPED CC LINEAR RESPONSE FUNCTION

For the analysis of the residues of the derivative of $\langle\langle \mu_\alpha; \mu_\beta \rangle\rangle_{\omega+i\omega}$ with respect to B_γ, we define the non-phase-isolated derivatives of the eigenvectors with respect to the electric fields as follows:

$$R_f^{\mu_\alpha}(-\omega) = -\left(\mathbf{A} - (\omega_f - \omega)\mathbf{1}\right)^{-1}\left(\mathbf{A}^{\mu_\alpha} + \mathbf{B}t^{\mu_\alpha}(\omega)\right)R_f. \tag{A1}$$

Of the amplitude and Lagrange multiplier vectors in Eq. (46), only the vectors $t^{\mu_\beta}(\omega)$, $\bar{t}^{\mu_\beta}(\omega)$, and $\bar{t}^{\mu_\alpha}(-\omega)$ have non-vanishing residues in the limit $\omega \to \omega_f$,

$$\lim_{\omega\to\omega_f}(\omega - \omega_f)t^{\mu_\beta}(\omega) = \sum_{f'\in\mathfrak{D}_f} R_{f'}T^{\mu_\beta}_{f'0}, \tag{A2}$$

$$\lim_{\omega\to\omega_f}(\omega - \omega_f)\bar{t}^{\mu_\beta}(\omega) = \sum_{f'\in\mathfrak{D}_f} T^{\mu_\beta}_{f'0}\cdot M_{f'}, \tag{A3}$$

$$\lim_{\omega\to\omega_f}(\omega - \omega_f)\bar{t}^{\mu_\alpha}(-\omega) = \sum_{f'\in\mathfrak{D}_f} T^{\mu_\alpha}_{0f'}\cdot L_{f'}. \tag{A4}$$

We get for the non-singular part of residue (simple pole) at the limit $\omega \to \omega_f$

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$$\lim_{\omega+i\bar{\omega}\to\omega_f}(\omega+i\bar{\omega}-\omega_f)\left.\frac{d\langle\langle\mu_\alpha;\mu_\beta\rangle\rangle_{\omega+i\bar{\omega}}}{d\varepsilon_\gamma}\right|_{\text{non-res}}$$

$$=\frac{1}{2}\mathscr{P}^{\alpha\beta}\sum_{f'\in\mathfrak{D}_f}\Big\{\Big(\mathbf{F}^{m_\gamma}t^{\mu_\alpha}(-\omega_f)R_{f'}\Big)\cdot T^{\mu_\beta}_{f'0}$$
$$+\Big(\Big[\mathbf{F}^{\mu_\alpha}+\mathbf{G}t^{\mu_\alpha}(-\omega_f)\Big]R_{f'}t^{m_\gamma}\Big)\cdot T^{\mu_\beta}_{f'0}$$
$$+\Big(\tilde{t}^{m_\gamma}\Big[\mathbf{A}^{\mu_\alpha}+\mathbf{B}t^{\mu_\alpha}(-\omega_f)\Big]R_{f'}\Big)\cdot T^{\mu_\beta}_{f'0}$$
$$+\Big({}^{\perp}\tilde{t}^{\mu_\alpha}(-\omega_f)\Big[\mathbf{A}^{m_\gamma}+\mathbf{B}t^{m_\gamma}\Big]R_{f'}\Big)\cdot T^{\mu_\beta}_{f'0}$$
$$+L_{f'}\Big[\mathbf{A}^{\mu_\beta}t^{m_\gamma}+\mathbf{A}^{m_\gamma\perp}t^{\mu_\beta}(\omega_f)+\mathbf{B}t^{m_\gamma\perp}t^{\mu_\beta}(\omega_f)\Big]\cdot T^{\mu_\alpha}_{0f'}$$
$$+M_{f'}\Big[\mathbf{A}^{\mu_\alpha}t^{m_\gamma}+\mathbf{A}^{m_\gamma}t^{\mu_\alpha}(-\omega_f)+\mathbf{B}t^{m_\gamma}t^{\mu_\alpha}(-\omega_f)\Big]\cdot T^{\mu_\beta}_{f'0}\Big\}\quad\text{(A5)}$$

$$=\frac{1}{2}\mathscr{P}^{\alpha\beta}\sum_{f'\in\mathfrak{D}_f}\Big\{\Big(\tilde{\xi}^{m_\gamma}R^{\mu_\alpha}_{f'}(-\omega_f)\Big)\cdot T^{\mu_\beta}_{f'0}$$
$$+\Big(\tilde{\xi}^{\mu_\alpha}(-\omega_f)^{\perp}R^{m_\gamma}_{f'}\Big)\cdot T^{\mu_\beta}_{f'0}$$
$$+\Big(\Big[\mathbf{F}^{m_\gamma}t^{\mu_\alpha}(-\omega_f)+\mathbf{F}^{\mu_\alpha}t^{m_\gamma}+\mathbf{G}t^{\mu_\alpha}(-\omega_f)t^{m_\gamma}\Big]R_{f'}\Big)\cdot T^{\mu_\beta}_{f'0}$$
$$+M_{f'}\Big[\mathbf{A}^{\mu_\alpha}t^{m_\gamma}+\mathbf{A}^{m_\gamma}t^{\mu_\alpha}(-\omega_f)+\mathbf{B}t^{m_\gamma}t^{\mu_\alpha}(-\omega_f)\Big]\cdot T^{\mu_\beta}_{f'0}$$
$$+T^{\mu_\alpha}_{0f'}\cdot\Big(L_{f'}\mathbf{A}^{\mu_\beta}t^{m_\gamma}+{}^{\perp}L^{m_\gamma}_{f'}\xi^{\mu_\beta}\Big)\Big\}\quad\text{(A6)}$$

$$=\frac{1}{2}\mathscr{P}^{\alpha\beta}\sum_{f'\in\mathfrak{D}_f}\left\{\frac{dT^{\mu_\alpha}_{0f'}}{d\varepsilon_\gamma}T^{\mu_\beta}_{f'0}+T^{\mu_\alpha}_{0f'}\cdot\frac{dT^{\mu_\beta}_{f'0}}{d\varepsilon_\gamma}\right\}.\quad\text{(A7)}$$

Only one contribution to the derivative of the damped linear response function, $\tilde{t}^{\mu_\alpha}(-\omega-i\bar{\omega})[\mathbf{A}^{m_\gamma}+\mathbf{B}t^{m_\gamma}]t^{\mu_\beta}(\omega+i\bar{\omega})$, contains two vectors that become singular for $\omega\to\omega_f$ and contributes to the second-order residue

$$\lim_{\omega+i\bar{\omega}\to\omega_f}(\omega+i\bar{\omega}-\omega_f)^2\frac{d\langle\langle\mu_\alpha;\mu_\beta\rangle\rangle_{\omega+i\bar{\omega}}}{d\varepsilon_\gamma}\quad\text{(A8)}$$

$$=\frac{1}{2}\mathscr{P}^{\alpha\beta}\sum_{f,f'\in\mathfrak{D}_f}T^{\mu_\alpha}_{0f'}\cdot\Big(L_{f'}\Big[\mathbf{A}^{m_\gamma}+\mathbf{B}t^{m_\gamma}\Big]R_f\Big)T^{\mu_\beta}_{f0}$$
$$=\mathscr{P}^{\alpha\beta}\sum_{f<f'\in\mathfrak{D}_f}T^{\mu_\alpha}_{0f'}\cdot T^{m_\gamma}_{f'f}\cdot T^{\mu_\beta}_{f0}.\quad\text{(A9)}$$

If we include the Levi-Civita tensor and the negative sign from Eq. (43), the results agree with the definition of the $\mathscr{B}$ and $\mathscr{A}$ terms in Eqs. (28) and (40).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

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