A Unified Strategy for the Chemically Intuitive Interpretation of Molecular Optical Response Properties

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ABSTRACT: Interpreting response properties such as the polarizability, optical rotation (OR), or hyperpolarizabilities is a complex task for which a uniform strategy would be desirable. We propose a response analysis procedure called the RespA approach with two interrelated schemes to describe molecular optical response properties in terms of natural response orbitals (NROs) and chemical fragment response for convenient elucidation of structure–(optical)property relationships. These quantities can be easily extracted from the frequency-dependent perturbed one-electron transition/current density matrix obtained from any quantum mechanical response function calculation. NROs provide the most compact representation of the virtual excitations occurring in the (hyper)scattering process. It is



decomposed in hole and electron NRO pairs providing a simple exciton picture. For a chemist, it is natural to interpret a property by decomposing it into functional groups or fragment contributions. In this spirit, the response is partitioned into on-site and between-site fragment responses, allowing a property mapping into real space. The new RespA procedure was implemented and tested at the simplified time-dependent density functional theory (sTD-DFT) level enabling calculations for large systems. The RespA strategy is a method-independent route for the understanding of a wide variety of response properties. We showcase how the chemically intuitive RespA approach extracts easily structure—property relationships for the particularly difficult case of OR. As examples, we demonstrate how to enhance the OR of [5]helicene and norbornenone, provide an analysis of the change of the OR observed for camphor and fenchone, and finally investigate the case of a (P,P)-bis-helicenic 2,2'-bipyridine chiroptical switch.

■ INTRODUCTION

No unified theoretical scheme exists for the interpretation of linear and nonlinear response properties such as optical rotation (OR), polarizabilities, or hyperpolarizabilities. These scattering or hyperscattering effects can be understood as virtual excitation processes for which their sum-over-state (SOS) representations¹ are rather slowly convergent. Computationally efficient ways to calculate such properties imply response functions¹ that allow one to directly determine the property without resorting to intermediate excited states. While response functions are computationally convenient, they miss an easy picture for the chemical understanding and a deep analysis of the related phenomenon. However, the linear or nonlinear response vector that is determined to compute such properties is a frequency-dependent perturbed one-electron transition/current density matrix (ω PDM) that links the tensor observable to the many-electron wave function in a virtual exciton picture. (Note that, in the following, we drop most of the time the term "virtual" making it implicit when considering response properties.) The ω PDM is full of information that could be extracted by rotating basis sets from molecular orbitals (MOs) to the newly introduced natural response orbitals (NROs) or atomic orbitals (AOs).

We propose a unified, complete, and chemically intuitive route to analyze response properties, the so-called RespA procedure, with two complementary schemes. The first one is based on a virtual exciton picture for which we derive the so-called natural response orbitals. The second one is a fragment-based decomposition into chemically intuitive contributions. The key quantity in these approaches is the frequency-dependent perturbed one-electron transition/current density matrix also called the response vector or the response density matrix that we rotate in two different orbital spaces.

Very recently, Krylov² stressed again the importance of MOs as a central concept in chemistry. However, MOs usually obtained from Hartree–Fock or Kohn–Sham ground-state treatments suffer from their delocalized and unspecific characters. A great deal of work has been provided to show

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that proper orbitals can also be constructed from reduced quantities like (transition)density matrices that link the manyelectron wave functions to observables. In her recent perspective, she discussed the role of natural transition orbitals²⁻⁹ (NTOs) as key quantities to interpret spectroscopic data that imply excited states. As the first analysis tool for the RespA approach, we introduce the concept of natural response orbitals, which are NTOs of the response density matrix. They will be used for a quantum chemical method-independent description of electronic virtual excitations to interpret linear and nonlinear response properties. In the NRO representation, the ω PDM becomes diagonal and should be the most compact representation of the excitation process. The global response is then decomposed into hole and electron NRO pair contributions, allowing a clear identification of important largely weighted transitions. For NRO pairs, numerical descriptors are also introduced.

It is very natural for chemists to decompose a molecular property into contributions from groups of atoms or fragments of a molecule. This is why Plasser and co-workers.^{6–8,10,11} proposed to rotate the one-electron transition density matrix into the AO space to describe the amount of charge transfer between excited state fragments. As a second analysis tool for the RespA procedure, we propose to transform the ω PDM in the AO space. By collecting AO responses into fragments and between fragments contributions, we shall be able to map any response property into real space, providing a chemically intuitive description of the phenomenon. On-site and between-site contributions are numerical descriptors, and thus, no cumbersome visual inspection of orbitals is needed.

To showcase how the RespA approach eases the interpretation of response properties, we start our journey by considering the molecular OR phenomenon. There is no need to recall the extensive role that plays chirality in living organisms and their biochemistry.¹² The oldest way to probe the optical activity of a molecule is the measurement of its specific rotation $[\alpha]_{\omega}$. In 1929, Rosenfeld¹³ laid the theoretical foundation of OR also known as the optical birefringence. He used time-dependent perturbation theory to show that the variation of the electric dipole moment of a molecule induced by a frequency-dependent electromagnetic field reads

$$\vec{\mu}_{\text{ind.}}(t) = \vec{\alpha}(-\omega;\,\omega) \cdot \vec{E} + \vec{G}(-\omega;\,\omega) \cdot \frac{\partial B}{\partial t} + \dots \tag{1}$$

where $\vec{\alpha}$ ($-\omega; \omega$) is the electric dipole polarizability tensor, and \vec{G} ($-\omega; \omega$) is the electric dipole-magnetic dipole polarizability. The OR is proportional to the trace of \vec{G} ($-\omega; \omega$). Since this groundbreaking work, a plethora of quantum chemistry methods was developed for OR computations, e.g., in the frameworks of the coupled-cluster theory (CC) or the density-functional theory (DFT).^{14–30} To treat large systems or screen large sets of compounds, we have recently extended the well-known simplified TD-DFT (sTD-DFT) method^{31–37} to the evaluation of the OR.³⁸

We select the OR response as an illustrative case because it is well-known that interpreting OR data and assigning the magnitude and sign of the response of a chiral molecule to structural aspects is particularly difficult. Providing design guidelines for new enhanced chirooptical dyes is also particularly challenging. Many attempts to provide tools to estimate OR structure–property relationships were proposed with more or less success over the years. Already sixty years ago, Djerassi et al.^{39,40} formulated the famous octant rule that

was designed to determine the absolute configuration of saturated carbonyl compounds. In 1968, Schellman⁴¹ proposed symmetry rules for OR. He restricted the discussion to the OR resulting from a single-dominating electronic transition, avoiding the complexity of the OR signal at a specific wavelength for which a large amount of excited states contribute. For model systems with no more than two excited states, he proposed three mechanisms of OR, distinguishing magnetic and electric transitions. First, the one-electron or Condon, Altar, and Eyring mechanism for which both excited states are located on the same chromophore while one is magnetically accessible and the other on dipole electrically. What remains from the molecule behaves like "a perturbing field which partially breaks down the symmetry of the chromophore and mixes the two transitions". Second, the molecule includes two chromophoric groups where each of them has one excited state electronically accessible. In the Kuhn-Kirkwood model, their coupling induces a magnetic moment. If both groups are identical, this is called "the exciton modification of Moffit". Third, in the $\mu - m$ mechanism, the molecule has also two chromophoric groups but one has an excited state electronically accessible while the other one is only magnetically active. The OR originates from the coupling between both of them. These simple rules are difficult to apply to real systems for which the OR response is recorded at the sodium D-line (589.3 nm). In 1998, at a time when ab initio OR calculations were only possible by the coupled-perturbed Hartree-Fock method, Kondru et al.⁴¹⁻⁴⁴ proposed to partition the OR response into atomic contributions in analogy to the Mulliken population analysis. A few examples were given for small molecules such as substituted oxiranes, substituted bicyclic orthoesters, and 2-fluorohexane in different conformations, showing how the response is modulated with respect to the change of substituents or conformation.⁴² They also investigated a marine natural product called hennoxazole⁴³ and the absolute configuration of indoline, azetidine, menthols, and menthones.⁴⁴ Another atomic decomposition of the OR response was also proposed by Ferraro and co-workers⁴⁵⁻⁴ who focused on rather small molecules such as hydrogen peroxide,⁴⁵ hydrazine isomers,⁴⁶ and methylhydroperoxide.⁴⁷ Following this, Autschbach and coworkers^{48,49} proposed to analyze the OR with localized molecular orbitals (i.e., bond and lone-pair MOs). They were particularly interested in the large OR of norbornenone,⁴⁹ showing that one OR tensor component was enhanced by the coupling between the C=Cdouble bond and C=O oxygen lone pair. Norbornenone has attracted a lot of attention in the past, see, e.g., refs 50 and 51. The first paper investigated the large solvation effect while the second one provided a deep analysis of the origin of its large OR with a focus on electric and magnetic transition moments of the first excited state. Kahr and co-workers^{52,53} analyzed the OR with a Hückel theory decomposition scheme to determine if only accounting for $\pi \rightarrow \pi^*$ rotatory strengths is sufficient for a proper description. Caricato^{54,55} decomposes the OR into MO contributions for (1S,4S)-norbornenone, (P)-2,3-pentadiene, (S)-(+)-2-carene, and (R)-3-methylcyclopentanone in an approach termed the \tilde{S}_{μ} method. In their analysis of a few helicenes, Aharon and Caricato⁵⁶ showed that the OR may be decomposed into three types of excitation classes for which the magnetic moment could be parallel, orthogonal, or tilted with respect to the helical axis. The transitions with the magnetic moment parallel to the helical axis present the largest contribution and are mainly responsible for the sign and

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magnitude of the response. They also tried to apply localized MO schemes as proposed by Autschbach and co-workers^{48,49} but they concluded that they are probably more suited for compounds with smaller chromophores. As one may note, no global or unified strategy as the RespA procedure already exists for the interpretation of OR. In principle, RespA could be used with any quantum chemical response method and for basically any property, but we restrict ourselves here initially to the probably most interesting chiral case.

The new RespA procedure is tested for four case studies, namely, [5]helicene, norbornenone, the modulation of the response between camphor and fenchone, and the amplification of the OR when (P,P)-bis-helicenic 2,2'-bipyridine⁵⁷ is bonded to Zn(OAc)₂.

The article is organized as follows: The next section presents the theoretical background. Then, we provide the computational details, discuss the results, and draw some conclusions.

THEORETICAL BACKGROUND

In this section, we introduce the general formulation of the RespA approach for linear response functions. To extend this to nonlinear response properties, one needs to account for intermediate states also. For example, the first hyperpolarizability can be seen as a virtual two-photon process with one frequency-dependent intermediate state. As usual, p, q, r, s indices refer to general molecular orbitals (MOs), i, j, k, l to occupied, and a, b, c, d to unoccupied ones. ω represents the frequency of the perturbation, and ζ and η refer to Cartesian components. A and B represent arbitrary operators. Any linear response properties can be defined by their sum-over-state expression¹

$$\langle\langle A_{\zeta}; B_{\eta} \rangle\rangle_{\omega} = \sum_{n} \left[\frac{\langle 0|A_{\zeta}|n\rangle\langle n|B_{\eta}|0\rangle}{\omega - \omega_{n}} - \frac{\langle 0|B_{\eta}|n\rangle\langle n|A_{\zeta}|0\rangle}{\omega + \omega_{n}} \right]$$
(2)

In the case of $A = B = \mu$, the response function $\langle \langle \mu_{\zeta}; \mu_{\eta} \rangle \rangle_{\omega}$ is related to the polarizability. If A = m and $B = \mu$, the response function $\Im \langle \langle m_{\zeta}; \mu_{\eta} \rangle \rangle_{\omega}$ is directly proportional to the electric dipole-magnetic dipole polarizability tensor element.

The linear response function can be reformulated in terms of the symmetric or antisymmetric ω PDM

$$\langle\langle A_{\zeta}; \, \mu_{\eta} \rangle\rangle_{\omega} = \left(2 \sum_{pq} A_{pq,\zeta} \gamma_{\eta,pq}^{(+)\mathrm{or}(-)}(\omega)\right) \tag{3}$$

In the density-based linear-response time-dependent density functional theory (TD-DFT) formalism, ^{58–64} the symmetric or anti-symmetric ω PDM is expressed in terms of a linear combination of linear (electric dipole) response vectors $\mathbf{X}_{\eta}(\omega)$ and $\mathbf{Y}_{\eta}(\omega)$ that reads

$$\begin{cases} \gamma_{\eta,ia}^{(+)}(\omega) = X_{\eta,ai}(\omega) + Y_{\eta,ai}(\omega) \\ \gamma_{\eta,ia}^{(-)}(\omega) = X_{\eta,ai}(\omega) - Y_{\eta,ai}(\omega) \end{cases}$$
(4)

The $X_{\eta}(\omega)$ and $Y_{\eta}(\omega)$ vectors cast virtual (electric dipole) excitations and de-excitations, respectively, present in the scattering process. Alternatively for the OR, the response function (eq 3) could be defined in terms of the magnetic dipole ω PDM.

The first scheme proposed in the RespA approach concerns the NRO representation of the ω PDM. We follow the

approach developed by Nanda and Krylov⁹ for the description of virtual intermediate states in two-photon absorption processes where they recast the response equation in terms of ω PDM but here applied to pure response properties. As for the determination of NTOs, ω PDM is transformed in the most compact way by a singular value decomposition

$$\Lambda^{\eta}(\omega) = \mathbf{U}^{1}(\gamma_{\eta}(\omega))\mathbf{V}$$
⁽⁵⁾

such that the excitation is described by the minimum number of MO pairs. The diagonal matrix $\Lambda^{\eta}(\omega)$ contains all the information about the electric dipole excitation process but on the basis of NTOs of the response density matrix that we term natural response orbitals (NROs). The virtual exciton can be represent by pairs of hole and electron NROs

$$\begin{cases} \psi_{i,\eta}^{\text{virt.hole}}(\vec{r}) = \sum_{p} U_{pi}\phi_{p}(\vec{r}) \\ \psi_{i,\eta}^{\text{virt.elec.}}(\vec{r}) = \sum_{p} V_{pi}\phi_{p}(\vec{r}) \end{cases}$$
(6)

The same basis set rotation can be applied to any other operators

$$\boldsymbol{\Upsilon}^{\boldsymbol{\zeta}} = \boldsymbol{U}^{T}(\boldsymbol{A}^{\boldsymbol{\zeta}})\boldsymbol{V}$$
(7)

which allows one to redefine the response function in the compact NRO representation

$$\langle\langle A_{\zeta}; \, \mu_{\eta} \rangle\rangle_{\omega} = \left(2\sum_{i}^{\text{occ}} \Upsilon_{i}^{\zeta} \Lambda_{i}^{\eta}(\omega)\right) = \Im\left(\sum_{i}^{\text{occ}} \beta_{\zeta\eta}^{i}(\omega)\right) \tag{8}$$

This expression can be regarded as a sum of NRO contributions $\beta^i_{\zeta\eta}(\omega)$. The NRO representation for the description of responses is method independent and attenuates the usual dependence on the basis set. Note that the maximum number of contributions corresponds to the number of occupied MOs. Each contribution has a weight in the excitation process defined as

$$w_i(\omega) = \frac{|\beta_{\zeta\eta}^i(\omega)|}{\sum_i |\beta_{\zeta\eta}^i(\omega)|}$$
(9)

The number of nonnegligible hole–electron pairs contributing to the response is defined by the following participation ratio

$$PR_{NRO}(\omega) = \frac{\left(\sum_{i} w_{i}(\omega)\right)^{2}}{\sum_{i} w_{i}(\omega)^{2}}$$
(10)

Note that hole and electron densities signed and weighted by the response can also be defined as

$$\begin{cases} \rho_{\text{virt.hole}}^{+}(\vec{r}) = \sum_{i}^{+} w_{i}^{+}(\omega) |\psi_{i,\eta}^{\text{virt.hole}}(\vec{r})|^{2} \\ \rho_{\text{virt.hole}}^{-}(\vec{r}) = \sum_{i}^{-} w_{i}^{-}(\omega) |\psi_{i,\eta}^{\text{virt.hole}}(\vec{r})|^{2} \end{cases}$$
(11)

and

1



Figure 1. Molecule coordinate system for [5]helicene as well as hole and electron NRO pairs for the two largely weighted contributions to each diagonal components of the OR tensor at the sodium D-line (589.3 nm). The weights as defined in eq 9 are provided above the arrows, while the

$$\begin{cases} \rho_{\text{virt.elec.}}^{+}(\vec{r}) = \sum_{i}^{+} w_{i}^{+}(\omega) |\psi_{i,\eta}^{\text{virt.elec}}(\vec{r})|^{2} \\ \rho_{\text{virt.elec.}}^{-}(\vec{r}) = \sum_{i}^{-} w_{i}^{-}(\omega) |\psi_{i,\eta}^{\text{virt.elec.}}(\vec{r})|^{2} \end{cases}$$
(12)

responses of NRO pairs are shown below.

These allow a compact representation of the excitation process.

The second scheme of the RespA approach is based on another manipulation of the ω PDM for which instead of taking its SVD, we apply a Löwdin orthogonalization

$$\tilde{\boldsymbol{\Lambda}}^{\eta}(\boldsymbol{\omega}) = (\boldsymbol{P}\boldsymbol{Q}^{T})(\boldsymbol{\gamma}_{\eta}(\boldsymbol{\omega}))(\boldsymbol{P}\boldsymbol{Q}^{T})^{T}$$
(13)

where P and Q are left and right singular vectors of the MOcoefficient matrix C. Plasser and co-workers^{6-8,10,11} quantified charge transfer in excited states by applying a Löwdin orthogonalization to the one-electron transition density matrix. Here, we perform the same transformation on the response density matrix that is rotated into the AO space. Note that Plasser and co-workers^{6-8,10,11} showed for excited states that the Löwdin orthogonalization procedure to analyze the transition density matrix is "computationally more efficient and in most cases numerically more stable" than a Mulliken one. The same rotation can be applied to any other operators

$$\tilde{\boldsymbol{\Upsilon}}^{\zeta} = (\boldsymbol{P}\boldsymbol{Q}^{T})(\boldsymbol{A}^{\zeta})(\boldsymbol{P}\boldsymbol{Q}^{T})^{T}$$
(14)

This allows a redefinition of the response function in the AO space

$$\langle\langle A_{\zeta}; \, \mu_{\eta} \rangle\rangle_{\omega} = \left(2 \sum_{\mu\nu} \tilde{\Upsilon}^{\zeta}_{\mu\nu} \tilde{\Lambda}^{\eta}_{\mu\nu}(\omega) \right) = \Im \left(\sum_{\mu\nu} \tilde{\beta}^{\zeta\eta}_{\mu\nu}(\omega) \right)$$
(15)

The AO contributions to the response can be grouped into fragments (A, B,...) where the response is decomposed in onsite (AA) and between fragments (AB) items

$$\Omega^{\omega}_{\zeta\eta}(AB) = \left(2\sum_{\mu\in A}\sum_{\nu\in B}\tilde{\Upsilon}^{\zeta}_{\mu\nu}\tilde{\Lambda}^{\eta}_{\mu\nu}(\omega)\right)$$
(16)

This fragment response scheme presents some advantages with respect to NROs because it yields numerical values and avoids cumbersome manual inspection of orbitals. Nevertheless, both approaches of the RespA procedure seem complementary in the description of responses. Here, we provide a methodindependent approach where fragments are defined by our chemical intuition.

In the illustrative case of the OR, at a perturbing frequency ω , one needs to take the orientation average

$$\beta(\omega) = -Tr \frac{\Im\langle\langle m_{\zeta}; \mu_{\zeta} \rangle\rangle_{\omega}}{3\omega}$$
(17)

of the electric dipole-magnetic dipole polarizability tensor

$$G_{\zeta\zeta}(\omega) = -\omega^{-1} \Im\langle\langle m_{\zeta}; \mu_{\zeta} \rangle\rangle_{\omega}$$
(18)

where $\Im\langle\langle m_{\zeta}; \mu_{\zeta} \rangle\rangle_{\omega}$ is the imaginary part of the electric dipole-magnetic dipole linear response function. For each of these particular orientations, the photon-electron scattering process can be seen as a virtual excitation mechanism where a few NRO transitions are contributing. This raises the importance of the definition of the molecule coordinate system. Previously,^{54,55} it was suggested to waive this by directly considering rotatory strengths redefining the SOS expression in those terms instead of using tensorial components of the response function. We will see in the following that a cunning definition of the Cartesian frame can be quite important for fine-tuning or designing the OR response. Note that the formula for the often quoted specific rotation reads

$$[\alpha]_{\omega} = 1.343 \times 10^{-4} \frac{\tilde{\nu}^2 \beta(\omega)}{M} \gamma_s \tag{19}$$

where γ_s is the Lorentz solvent correction factor ($\gamma_s = (n^2 + 2)/3$) assumed to be unity throughout.

COMPUTATIONAL DETAILS

The RespA procedure that uses NROs and fragment response to analyze response properties was implemented in a development version of stda program.⁶⁵ Geometries of

[5] helicene, norbornenone, camphor, and fenchone were taken from ref 66 and their experimental molar rotations at the sodium D-line while (P,P)-bis-helicenic 2,2'-bipyridine and its $Zn(OAc)_2$ complex are from ref 57. Extra model systems were optimized at the B3LYP/6-311G** level of theory with Q-Chem 5.1⁶⁷ to obtain structures, which are consistent to those from ref 66. All OR calculations were performed using the velocity representation at the sTD-DFT level of theory³⁸ that we recently implemented in stda program.⁶⁵ To obtain Kohn-Sham orbitals and energies prior to the sTD-DFT calculation, we used Q-Chem 5.1⁶⁷ for the SCF step at the B3LYP/6-31+G(d) level for [5]helicene, norbornenone, camphor, and fenchone and CAM-B3LYP/aug-cc-pVDZ for the (P,P)-bishelicenic 2,2'-bipyridine systems. In the sTD-DFT procedure, a configuration selection energy threshold of 50 eV was used for norbornenone, camphor, and fenchone, 20 eV for [5]helicene and 15 eV for the (P,P)-bis-helicenic 2,2'bipyridines. Note that solvent effects are neglected all along in this work. Our main purpose is not to provide a direct comparison with experimental data but how we may conveniently analyze the OR of typical molecules. It should be noted, however, that our computed OR values are in most of the cases relatively close to experiment.

All specific OR values $[\alpha]_{\omega}$ are given in ° $[dm(g/cm^3)]^{-1}$ and molar rotations in °cm²dmol⁻¹ units. In the following, we use s"functional name" as the short notation that refers to a sTD-DFT calculation made with this functional (e.g., sB3LYP is the short notation for a sTD-DFT/B3LYP calculation). If not stated otherwise, all reported results refer to a perturbing wavelength of 589.3 nm (sodium D-line).

RESULTS

To assess the applicability of the RespA procedure, we use the OR as an illustrative response property for which the first case

Table 1. Nonnegligible NRO Contributions to each Diagonal Components of the OR Tensor for [5]Helicene. Magnetic and Electric Field Orientations, Weights, Magnetic and Frequency-Dependent Electric Dipole NRO Contributions to the Response, and the Response of NRO Pairs Are Listed

ζζ	w _i	M_i^ζ	Λ_i^{ζ} (589.3 nm)	$\beta_i^{\zeta\zeta}$ (589.3 nm)
xx	0.38	-0.168	17.107	-5.743
xx	0.26	-0.134	14.206	-3.812
xx	0.03	0.146	1.567	0.458
xx	0.04	0.319	0.841	0.536
уу	0.24	-1.176	3.595	-8.457
уу	0.16	-1.013	2.846	-5.764
уу	0.11	-0.677	2.748	-3.718
уу	0.03	-0.230	2.434	-1.118
уу	0.04	0.456	1.401	1.278
уу	0.04	0.774	0.977	1.513
уу	0.04	0.771	0.853	1.316
уу	0.04	-1.590	0.471	-1.497
уу	0.05	-2.036	0.456	-1.856
zz	0.25	0.320	11.303	7.237
zz	0.21	0.305	10.114	6.170
zz	0.11	0.342	4.700	3.212
zz	0.09	0.282	4.570	2.573
zz	0.04	0.677	0.767	1.038
zz	0.03	-1.283	0.375	-0.961



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Figure 2. Fragment definitions for [5]helicene as well as on-site (red) and between-site response (green for A < B and blue for A > B) for each component of the OR response tensor.



Figure 3. Three [5]helicene derivatives and their specific rotations at the sodium d-line.



Figure 4. Molecule coordinate system for norbornenone as well as hole and electron NRO pair for the largely weighted contribution to the β_{zz} component of the OR tensor. The weight as defined in eq 11 is provided above the arrows, while the response of NRO pairs is shown below. Fragment definitions for norbornenone as well as important on-site (red) and between-site response (green for A < B and blue for A > B) for the β_{zz} component of the OR response tensor are also shown.

study concerns [5]helicene. Figure 1 presents the molecule coordinate system as well as hole and electron NRO pairs for

Table 2. Nonnegligible NRO Contributions to the β_{zz} Component of the OR Tensor for Norbornenone. Magnetic and Electric Field Orientations, Weights, Magnetic and Frequency-Dependent Electric Dipole NRO Contributions to the Response, and of NRO Pairs Are Listed

w _i	M_i^ζ	Λ_i^{ζ} (589.3 nm)	$\beta_{i}^{\zeta\zeta}$ (589.3 nm)
0.52	-0.469	3.090	-2.900
0.07	0.158	1.209	0.382
0.12	0.466	0.696	0.649
0.09	-0.413	0.588	-0.485
0.08	-0.639	0.346	-0.443
0.04	-0.357	0.307	-0.219

the two largely weighted contributions to each diagonal components of the OR tensor. For nonnegligible NRO contributions, Table 1 provides details about NRO descriptors such as weights (w_i) , magnetic (M_i^{ζ}) and frequency-dependent electric dipole (Λ_i^{ζ}) NRO contributions to the response, and $\beta_i^{\zeta\zeta}$. Note that M_i^{ζ} is simply the magnetic moment rotated in the NRO basis. For each component of the OR response tensor, Figure 2 depicts the definitions of the three fragments for [5]helicene as well as on-site $\Omega_{\zeta\zeta}(AA)$ and between-site $\Omega_{\zeta\zeta}(AB)$ fragment response. The sB3LYP/6-31+G(d) molar rotation of -6087 °cm²dmol⁻¹ is very close to the experimental value of -6012 °cm²dmol⁻¹. The theoretical value results from the orientation mean of the three diagonal components $\beta_{\zeta\zeta} = \Im\langle\langle m_{\zeta}; \mu_{\zeta} \rangle\rangle_{\omega}$ of the response tensor, giving an overall negative value where the positive β_{zz} contribution is counter-balanced by both negative β_{xx} and β_{yy} components (see Figure 1). Obtaining a compact representation of the OR response is difficult because it depends of the full excited state manifold. From a sum-over-state expression with a few states, only a truncated view of the process can be extracted. In our NRO approach, the first scheme of the RespA strategy, the SVD step extracts from the ω PDM the most compact representation of the OR response. Each diagonal $\beta_{\zeta\zeta}$ component is decomposed in an exciton picture where a few hole/electron pairs describe the OR scattering phenomenon. For [5]helicene, we obtained participation ratios of 5.6, 11.6, and 7.3 for β_{xx} , β_{yy} , and β_{zz} components, respectively. This descriptor provides the number of nonnegligible NRO pairs, although some of them have very small contribution to the response (see Table 1). These small OR contributions illustrate the complexity of the OR phenomenon that needs to be regarded as a multi-virtual-excitation process. As illustrated in Figure 1, the most contributing NRO pairs are composed of $\pi \rightarrow \pi^*$ transitions. Smaller contributions also



Figure 6. Axis and fragment definitions for 1(R)-campbor and 1(R)-fenchone as well as on-site (red) and between-site response (green for A < B and blue for A > B) for each components of the OR tensor.

include $\sigma \rightarrow \sigma^*$ excitations from C–H bonds with very limited impact on the response. In comparison to MOs, NROs are transformed in a way that some AO contributions are decreased because they are not contributing to the respective component. This is particularly evident for the two NRO pairs shown for the β_{yy} component where the middle (flat) part of the molecule shows little orbital contributions.

From the NRO decomposition of the β_{xx} component, the two largely weighted NRO pairs capture most of the response. The visual inspection of both hole and electron NROs shows larger orbital contributions for the middle flat part of the molecule, which is not distorted along the x-axis. This is further confirmed by the fragment response decomposition that shows that fragment 2 and between fragment 2 and others capture most of the response while on-site contributions for 1 and 3 are of only -0.33 a.u. The magnetic part of the response along



Figure 5. Molecule coordinate system for tricyclo[6.2.1.02,7]undeca-2(7),5-dien-9-one as well as its fragment definitions and important on-site (red) and between-site response (green for A < B and blue for A > B) for the β_{zz} component of the OR tensor.



Figure 7. Axis and fragment definitions for (1S,3S,7S)-1,3,7-trimethylbicyclo[2.2.1]heptan-2-one as well as onsite (red) and between-site response (green for A < B and blue for A > B) for each component of the OR response tensor.

Table 3. Nonnegligible NRO Contributions to β_{xx} and β_{yy} Components of the OR Tensor for (P,P)-Bis-helicenic 2,2'-Bipyridine. Magnetic and Electric Field Orientations, Weights, Magnetic and Frequency-Dependent Electric Dipole NRO Contributions to the Response, and of NRO Pairs Are Listed

ζζ	w _i	M_i^ζ	Λ_i^{ζ} (589.3 nm)	$\beta_i^{\zeta\zeta}$ (589.3 nm)
xx	0.17	2.082	11.735	48.859
xx	0.20	2.531	11.182	56.592
xx	0.15	2.102	10.474	44.026
xx	0.20	2.732	10.293	56.248
уу	0.23	-1.472	17.177	-50.555
уу	0.18	-1.371	14.363	-39.391
уу	0.14	-1.083	13.729	-29.741
уу	0.19	-1.629	12.703	-41.380

Table 4. Nonnegligible NRO Contributions to β_{xx} and β_{yy} Components of the OR Tensor for (P,P)-Bis-helicenic 2,2'-Bipyridine Coordinated to $Zn(OAc)_2$. Magnetic and Electric Field Orientations, Weights, Magnetic and Frequency-Dependent Electric Dipole NRO Contributions to the Response, and of NRO Pairs Are Listed

ζζ	w_i	M_i^ζ	Λ_i^{ζ} (589.3 nm)	$\beta_i^{\zeta\zeta}$ (589.3 nm)
xx	0.24	4.061	16.695	135.599
xx	0.22	5.18	12.039	124.749
xx	0.17	-4.701	10.327	-97.095
xx	0.03	1.988	4.496	17.880
xx	0.04	3.616	3.085	22.307
уу	0.04	0.395	17.023	13.464
уу	0.20	-2.633	13.001	-68.458
уу	0.04	0.478	12.413	11.865
уу	0.25	-4.002	10.740	-85.956
уу	0.04	-2.818	2.124	-11.971
уу	0.04	-8.565	0.819	-14.029

the x-axis depends on the distortion of the molecule with respect to the *xz*-plan, here represented by fragments 1 and 3. We can conclude that the response is electric dipole dominated

because it does not depend much on fragments 1 and 3, out of the xz-plane. This is further confirmed looking at both magnetic and frequency-dependent electric dipole parts of the two first few NRO entries in Table 1.

Along the y-axis, most of the response results from the outer, more distorted parts of the molecule that is represented by fragment 1 and 3 where most of the NROs are located. With respect to the β_{xx} component, in Table 1, we observe that magnetic parts of the β_{yy} response are enhanced while the frequency-dependent electric dipole contributions are quite diminished. Thus, the β_{yy} component is magnetically dominated. This suggests that increasing the distortion along the y-axis may enhanced the overall OR value.

For the β_{zz} component, the four first couples of NROs are $\pi \rightarrow \pi^*$ transitions involving a full π -conjugated pathway with large Λ_i^z contributions, while both last NRO pairs are more Rydberg dominated contributions with larger magnetic component because electron NROs are located on fragments 1 and 3. Nevertheless, these last two contributions make only 7% of the β_{zz} component. The fragment analysis further confirms this because large positive contributions are observed for all fragments. The on-site value of fragment 2 is perhaps small but the cumulated coupling with fragments 1 and 3 is far to be negligible. To enhance frequency-dependent electric dipole (Λ_i^z) contributions, a simple extension of the π -conjugated pathway seems a feasible way, although this should decrease the overall OR because the β_{zz} contribution is positive.

Figure 3 presents three [5]helicene derivatives where we tested simple design guidelines to modify the [5]helicene OR $[\alpha]_D = -2187^{\circ} [dm(g/cm^3)]^{-1}$. We assume that the sTD-DFT method performs as well as for [5]helicene than for these very similar compounds. The first compound has its π -conjugated pathway increased along the z-axis without affecting the outer of *xz*-plane distortion. As expected, the OR value is decreases with respect to [5]helicene because the positive β_{zz} contribution is enhanced. For the next two model molecules, we increase the [5]helicene distortion by adding bulky groups inside the helix. The added isobutyl groups do not increase the

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Figure 8. Molecule coordinate system for (P,P)-bis-helicenic 2,2'-bipyridine as well as hole and electron NRO pairs for the four largely weighted contributions to β_{xx} and β_{yy} components of the OR tensor. The weights as defined in eq 9 are provided above the arrows while the response of NRO pairs are shown below.



Figure 9. Molecule coordinate system for (P_1P) -bis-helicenic 2,2'-bipyridine coordinated to $Zn(OAc)_2$ as well as hole and electron NRO pairs for the largely weighted contributions to β_{xx} and β_{yy} components of the OR tensor. The weights as defined in eq 9 are provided above the arrows, while the response of NRO pairs are shown below.

distortion angle but push both connecting atoms out of both ring planes, lowering the OR value. In the second attempt, we use bulkier groups (although purely hypothetical) to illustrate the point. With an OR value of $-2388 \,^{\circ}[dm(g/cm^3)]^{-1}$ and as expected, increasing the helix distortion enhances the β_{yy} component to a value of -26 a.u. and thus the overall OR response with respect to parent molecule [5]helicene.

The second case study concerns an understanding of the longstanding problem of the large OR of norbornenone.^{49–51} In the OR45 benchmark set,⁶⁶ the reported value of $[\alpha]_D = -1146^{\circ} \text{cm}^2 \text{dmol}^{-1}$ was originally measured in hexane.⁶⁸ More recently, Crawford and co-workers⁵⁰ provided an experimental value for the (1R,4R)-norbornenone enantiomer of 755 $^{\circ} \text{cm}^2 \text{dmol}^{-1}$ in vapor as well as 950 and 981 $^{\circ} \text{cm}^2 \text{dmol}^{-1}$ in CH₃CN and hexane solutions, respectively. Our sB3LYP/6-31+G(d) value of $-700 \,^{\circ} \text{cm}^2 \text{dmol}^{-1}$ for the (1S,4S)-norbornenone enantiomer is close to the gas phase value reported by Crawford and co-workers⁵⁰ for the other enantiomer.

Figure 4 shows the molecule coordinate system for (1S,4S)norbornenone, the hole and electron natural response orbital pair for the largely weighted contribution to the β_{zz} component of the OR tensor, fragment definitions, and important on-site and between-site fragment responses. Table 2 shows NRO descriptors for nonnegligible contributions to the β_{zz} component. The z-axis is oriented along the C=O bond, while the bond from fragment 1 to 2 is in the yz plane. In this Cartesian frame, the β_{zz} component dominates the OR response composed mainly of one NRO transition with a contribution of -2.9 a.u. for a weight of 0.52. As already shown in literature, $^{49-51}$ this transition results from the coupling of the $n \rightarrow \pi^*$ state of the C=O group with the $\pi \rightarrow \pi^*$ from the C=C bond. This is particularly well-captured by the largely weighted NRO pair (Figure 4) for which the response is dominated by a large frequency-dependent electric dipole contribution (see Table 2). Others lower-weighted contributions involve Rydberg transitions resulting from $\sigma \rightarrow \sigma^*$ excitations from C-H bonds with low response. The fragment decomposition further confirms this analysis. The three fragments 1,6, and 5 have nonnegligible on-site $\Omega_{zz}^{589.3 \text{ nm}}(AA)$ contributions. For fragment 5, this results from $\sigma \rightarrow \sigma^*$ excitations. As expected, the C=O (fragment 1) and C=C bonds (fragment 6) are coupled by a cumulated value of -0.41a.u. which are both also coupled to its neighbor fragment 2. Thus, it seems likely that extending the π -conjugated pathway of the double bond should enhance the overall OR response.

Figure 5 shows the first model system where we extended the π -conjugated pathway by adding an extra double and a

third ring to rigidify the structure. Axes and fragments definition are also depicted as well as important on-site and between-site response for the β_{zz} component of the OR tensor. As for the previous case study, because these compounds are structurally very similar, we assume that the sTD-DFT scheme is performing well for them. We obtain a value of $[\alpha]_D = -$ 752° cm² dmol⁻¹ corresponding to a 7% enhancement of the OR with respect to norbornenone. Because of the third ring, the extra C = C bond has more or less the same orientation as the other one with respect to the C=O bond. The fragment decomposition shows that not only fragment 7 has a nonnegligible contribution to the β_{zz} component but also fragment 8 that presents a Rydberg contribution. We propose a second model system where we cut the bond between fragment 8 and 9 and optimize the geometry. Between both C=C double bonds, we obtained a dihedral angle of 50° . This further enhances the OR value to $-774 \,^{\circ} \text{cm}^2 \text{dmol}^{-1}$.

The next case study is a particularly difficult. It involves the modulation of the OR response by the change of position for two CH_3 groups in 1(R)-camphor and 1(R)-fenchone. Giorgio et al.⁶⁹ measured in *n*-hexane solution $[\alpha]_D$ values of 59 and -44 $^{\circ}$ cm² dmol⁻¹ for 1(*R*)-camphor and 1(*R*)-fenchone, respectively. These values are very similar to our calculated sB3LYP/6-31+G(d) ones of 57 and -49 °cm²dmol⁻¹. Tables S1 and S2 present nonnegligible NRO contributions to each diagonal components of the OR tensor at the sodium D-line (589.3 nm) for the two systems. With cumulated participation ratios of 29.1 and 30.0 for camphor and fenchone to describe one unique OR value, the visual inspection of NROs is laborious. As shown in Tables S1 and S2, most contributions are low weighted and none is dominating. They have mostly Rydberg character and present many different combinations of $\sigma \rightarrow \sigma^*$ excitations. Thus, for these systems without welldefined chromophoric groups, extracting a simple picture from the NRO analysis is almost impossible.

From the RespA procedure, the alternative approach is to use the chemical fragment response for the analysis. Figure 6 depicts fragment definitions for 1(R)-camphor and 1(R)fenchone as well as on-site and between-site response for each component of the OR tensor. We subdivided each molecule in three fragments. This is the chemically most sensible decomposition scheme we found to provide a relevant and easy interpretation with a minimum number of fragments and without losing too many details. We tried also seven fragments in the same way as for norbornenone, but the resulting picture was difficult to interpret. For both molecules, fragment 1 is mainly in the *yz*-plane with the *z*-axis along the C=O bond. Fragment 2 presents two groups pointing out of the yz-plane in the -x direction and fragment 3 points out in the +x direction. From camphor to fenchone, the change of sign of the OR at 589.3 nm is mainly attributed to the modulation of the three β_{ii} components, i.e., β_{xx} and β_{yy} decrease while β_{zz} changes from 0.10 to -0.19 a.u. For the β_{xx} the decrease observed from camphor to fenchone results mainly from the reduction by -0.12 a.u. of the on-site response of fragment 3 and by -0.14a.u. for the cumulated response between fragments 1 and 2. Considering the β_{yy} component, the shifting of positions for both CH₃ groups decreased $\Omega_{yy}(22)$ by -0.19 a.u. but increased the cumulated response between fragments 1 and 2 by 0.22 a.u., compensating each other. Thus, it is the sum of $\Omega_{yy}(23)$ and $\Omega_{yy}(32)$ values that represents the main change with an increase of 0.43 a.u. For the β_{zz} component, most changes of fragment responses between camphor and fenchone

are compensating each other, except the large drop of -0.24a.u from the cumulated fragment responses between 2 and 3. For both β_{vv} and β_{zz} components, the coupling between fragment 2 and 3 seems to be the key to the change of the OR between camphor and fenchone while others are canceling each other. To verify this, we consider an intermediate structure where only one CH₃ is moved from fragment 2 to 1 with respect to camphor. Figure 7 presents fragment response results for this intermediate structure. We obtained a $[\alpha]_D$ value of -26 °cm²dmol⁻¹, intermediate between camphor and fenchone. The reduction of the β_{xx} component is smaller for this model structure than for fenchone with respect to camphor. The on-site fragment 3 contribution decreases by -0.11 a.u., while the reduction of the cumulated contribution between fragments 1 and 2 is only -0.03 a.u. The interaction of the CH₃ group has a strong impact on the fragment 3 response. The addition of the second CH₃ to fragment 1 causes a further reduction of the response for fenchone due to in-between fragment 1 and 2 contributions along the x-axis. For the β_{vv} component, the sum of $\Omega_{vv}(23)$ and $\Omega_{vv}(32)$ values presents an increase of 0.35 a.u. for this intermediate structure with respect to camphor. This is further enhanced by shifting of the second CH₃ group as already observed for fenchone. Finally, considering the OR along the z-axis, the shifting of the first CH₃ from camphor to the intermediate structure does not impact much of the cumulated contributions between fragments 2 and 3, showing the importance to switch the position for the second one also to get the larger reduction observed for fenchone with respect to camphor. Interestingly, the fragment 1 response decreases by -0.36 a.u. with respect to camphor, diminishing the β_{zz} value. Adding the second CH₃ to fragment 1 results in a strong cancellation of this value between camphor and fenchone. The interpretation of the OR of camphor and fenchone is nontrivial but the fragment decomposition analysis sheds light on the effect of moving CH₃ groups. To provide a deeper understanding, other model structures should be considered.

The last example concerns a recent chiroptical switch where two aza[6]helicenes are linked together resulting in a bipyridine core.⁵⁷ Its chiroptical activity is switched when (un)coordinated to a metallic ion. Uncoordinated, (P,P)-bishelicenic 2,2'-bipyridine ((P,P)-1) is in a trans conformations where the two nitrogen atoms are pointing in opposite directions, while both helical structures are in the -x direction from the yz-plane. Experimentally, a molar rotation of 17 300 °cm²dmol⁻¹ in dichloromethane was measured.⁵⁷ Coordinated to $Zn(OAc)_2$ (Zn-(P,P)-1), it adopts a cis conformation with only one helix pointing on the +x direction. With respect to its uncoordinated form, the molar rotation is enhanced to a value of 28 400 °cm²dmol⁻¹.⁵⁷ At the CAM-sB3LYP/aug-cc-pVDZ, we obtain 24 087 and 30 817 °cm²dmol⁻¹, respectively, for the two forms, overestimating the experimental values. Including solvent effects may close the gap between theory and experiment.

Tables 3 and 4 present nonnegligible NRO contributions to β_{xx} and β_{yy} components of the OR at the sodium D-line (589.3 nm) for (*P*,*P*)-bis-helicenic 2,2'-bipyridine and the coordinated Zn-complex. Figures 8 and 9 display the corresponding molecule coordinate system as well as hole and electron NRO pairs for the largely weighted contributions to β_{xx} and β_{yy} components. In both cases, β_{zz} components are small with respect to other components with 2 a.u. for (*P*,*P*)-bis-helicenic 2,2'-bipyridine and -27 a.u. when coordinated to Zn(OAc)₂.

As shown for [5]-helicene, the hole and electron NROs have $\pi \rightarrow \pi^*$ contributions in helix parts that have their π -conjugated pathway oriented along the component direction. For the β_{xx} component of (P,P)-bis-helicenic 2,2'-bipyridine, both helix ends pointing to -x are contributing to the positive response. In the case $Zn(OAc)_2$ coordinates species, NRO pairs that have contributions on the part pointing to -x contribute to the positive response, while pointing to +x gives a negative sign. Overall, the β_{xx} component remains very similar for both structures. From (P,P)-1 to Zn-(P,P)-1, the NRO pair that has a weight of 0.20 decreases to 0.03. Although at the larger wavelength of 1900 nm, it has still a weight of 0.10. At the shorter wavelength, orbital contributions to the NRO pairs are no more located at the end of the helix but delocalized all over the molecule decreasing its response, while other largely weighted contributions are frequency-enhanced. A deeper analysis could be an interesting prospect to understand the complex mechanism of frequency dependence. For the $\beta_{\nu\nu}$ component of (P,P)-1, nonnegligible NRO pairs yield contributions mostly from middle parts of each helix. NRO pairs with weights of 0.23 and 0.18 have almost identical $\pi \rightarrow$ π^* transitions but with different mixing between both helices. The same observation holds for the pairs with weights of 0.14 and 0.19. In the cis conformation of the bipyridine core in Zn-(P,P)-1, the remaining largely weighted NRO pairs do not have the same mixing as in (P,P)-1, and thus, the β_{yy} response is decreased. This explains why the overall response of Zn-(P,P)-1 is larger than for (P,P)-1.

CONCLUSIONS

In this contribution, we introduced the theoretical background for the interpretation of response properties in the so-called RespA procedure by means of newly introduced natural response orbitals (NROs) and chemical fragment response. These quantities are obtained by AO/MO/NRO basis set transformation of the frequency-dependent perturbed oneelectron transition/current density matrix. The RespA approach can be used in conjunction with any quantum chemical response calculations, providing a method-independent analysis tool. With its virtual exciton picture, NROs provide the most compact representation of the photonelectron scattering effect, which can be described as a multiexcitation process. On the other hand, the fragment response decomposition scheme allows to partition the response into on-site and between-site fragment contributions where functional groups or groups of atoms are defined according to chemical intuition. Both schemes seem to be complementary for a chemically intuitive description of response properties. The RespA approach was applied to the particularly difficult interpretation of optical rotation phenomena, as an illustrative case, and gave unprecedented detailed descriptions.

With the RespA strategy, we were able to identify particular components of the OR tensor mostly relevant for property design. For [5]helicene, we showed that increasing the distortion along the y-axis results in an enhancement of the response, while extending the π -conjugated pathway along the z-axis decreases it. For norbornenone, the analysis suggests the π -conjugated pathway of the C==C double bond as the most relevant OR enhancing factor. With the fragment response scheme, we analyzed the change of OR between 1(*R*)-camphor and 1(*R*)-fenchone and identified how the shift of the CH₃ groups drastically effects nearby fragments. In the case of the (P,P)-bis-helicenic 2,2'-bipyridine molecular switch, we showed that the trans-cis conformational change as induced by $Zn(OAc)_2$ complexation results in a different mixing between both helix $\pi \rightarrow \pi^*$ transitions in their NROs. These results are very promising and may lead in future works to design principles for new helicene molecules and related systems. Furthermore, application of the RespA approach to other response properties is currently carried in our laboratory.

ASSOCIATED CONTENT

③ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jctc.0c00990.

Nonnegligible NRO contributions to each diagonal components of the OR tensor at the sodium D-line (589.3 nm) for 1(R)-camphor and 1(R)-fenchone (Tables S1 and S2) (PDF)

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Notes

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