Quantum control of photoelectron circular dichroism

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(Dated: September 13, 2018)

We demonstrate coherent control over the photoelectron circular dichroism in randomly oriented chiral molecules, based on quantum interference between multiple photoionization pathways. To significantly enhance the chiral signature, we use a finite manifold of indistinguishable (1+1’) REMPI pathways interfering at a common photoelectron energy but probing different intermediate states. We show that this coherent control mechanism outperforms other schemes, including interference between opposite-parity pathways driven by bichromatic (ω, 2ω) fields as well as sequential pump-probe schemes, by maximizing the number of molecular states that constructively contribute to the dichroism at an optimal photoelectron energy.

Chiral molecules are non-superimposable mirror images of each other, referred to as enantiomers. Recent advances in measuring enantiomer-sensitive observables in gas phase table-top experiments [1–4] have brought chiral molecules into the spotlight of current AMO research. One of these observables is photoelectron circular dichroism (PECD), i.e., the differential photoelectron angular distribution obtained by ionizing randomly oriented molecules with left circularly and right circularly polarized light [1, 5–9]. PECD is a purely electric dipole effect, yielding much stronger signals than traditional absorption circular dichroism (CD), which involves also the electron momentum provides the second vector in PECD. More intuitively, two non-parallel vectors are needed to provide an orientation with which to probe the handedness of the molecular scaffold and create a pseudo-scalar observable. While in traditional CD these are the electric and magnetic dipole moment, the photoelectron momentum provides the second vector in PECD. This picture connects PECD with the general framework for electric–dipole-based chiral observables [11]. Perturbation theory can also explain the PECD observed in resonantly enhanced multi-photon ionization (REMPI) [1], in terms of the electronically excited intermediate state of the REMPI process [12]. Dependence of the chiral signal on excitation wavelength is then understood in terms of probing different intermediate states [13]. Whether PECD is amenable to coherent control by suitably shaping the ionizing pulses is an open question [14].

Here, we address this question by making use of optimal control theory and show that, for a chiral methane derivative, CHBrCIF, quantum interference between distinct two-photon ionization pathways significantly enhances PECD. To this end, we combine a many-body description of the electron dynamics, scattering theory to efficiently describe the photoelectron continuum [5–7], and second-order time-dependent perturbation theory with an optimization technique [18]. We use this approach to maximize the PECD for CHBrCIF while fully accounting for the chiral nature of the potential experienced by the photoelectron. We use CHBrCIF as one of the simplest chiral molecules that has featured prominently in recent experiments [3] but expect our findings to be relevant for larger molecules as well.

We first detail our methodology to calculate the photoelectron spectrum and PECD. Keeping the nuclei fixed and neglecting relativistic effects, the Schrödinger equation for the many electron system reads

$$i \frac{\partial}{\partial t} \Psi^N(t) = \left[ \mathcal{H}_0 + \mathcal{H}_1 - \mathcal{E}(t) \cdot \hat{\mathbf{r}} \right] \Psi^N(t),$$

where $\mathcal{H}_0$ and $\mathcal{H}_1$ refer to the mean-field Fock operator and the residual Coulomb interaction, respectively. Accounting for one-particle one-hole excitations only, the many-body wave function is described by the manifold [19]

$$|\Psi^N(t)\rangle = \alpha_0(t) e^{-i\mathcal{E}_0 t} |\Phi_0\rangle + \sum_{t,\omega} \alpha^\omega_i(t) e^{-i\mathcal{E}_i t} |\Phi^\omega_i\rangle + \sum_i \int d\mathbf{k} \alpha^\mathbf{k}_i(t) e^{-i\mathbf{k} \cdot \mathbf{r}_i} |\Phi^\mathbf{k}_i\rangle,$$

where $\alpha_0(t)$, $\alpha^\omega_i(t)$ and $\alpha^\mathbf{k}_i(t)$ are time-dependent coefficients, and $|\Phi_0\rangle$ refers to the Hartree-Fock ground state. $|\Phi^\omega_i\rangle = \mathbf{c}^\omega_i \mathbf{c}^\omega_i |\Phi_0\rangle$ and $|\Phi^\mathbf{k}_i\rangle$ describe one-particle one-hole excitations from an initially occupied orbital $i$ to a bound unoccupied orbital $a$ or a continuum state with energy $|\mathbf{k}|^2/2$. To model an ensemble of randomly oriented molecules, we average over all Euler angles $\gamma = (\alpha, \beta, \gamma)[22]$. The orientation-averaged photoelectron momentum distribution is obtained upon integration over $\gamma$ and incoherent summation over the

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Fock orbitals were obtained using the MOLPRO [10, 11] program package with the aug-cc-pVDZ basis set [25]. The scattering portion \( \varphi_k^-(r) \) of the total wave function is an eigenfunction of the scattering problem,

\[
\left[ -\frac{\nabla^2}{2} - \frac{1}{r} + \hat{V} - \frac{k^2}{2} \right] \varphi_k^-(r) = 0, \tag{5}
\]

where \( \hat{V}(r) \) is the short-range part of the electron-ion interaction. Equation (5) is solved using a locally modified version of the ePolyScat program package [5–7], see the supplemental material [22] for more detail. PECD is calculated by expanding Eq. (4) into Legendre polynomials \( P_k^m \),

\[
d^2\sigma^{(\pm)}(\pm) = \sum \beta_{l,m}^{(\pm)}(\epsilon_k) P_k^m(\cos \theta) e^{im\phi}, \tag{6}
\]

where \( \pm \) distinguishes the momentum distribution obtained with left (+) and right (−) circularly polarized light. The anisotropy parameters \( \beta_{l,m}^{(\pm)}(\epsilon_k) \) are decomposed into contributions from the one- and two-photon ionization pathways and their interference,

\[
\beta_{l,m}^{(\pm)}(\epsilon_k) = \rho_{l,m}^{(1)ph}(\epsilon_k) + \rho_{l,m}^{(2)ph}(\epsilon_k) + \rho_{l,m}^{(2)int}(\epsilon_k).
\]

PECD is the non-vanishing component that remains after subtracting Eq. (6) obtained with left and right circularly polarized light [1, 5–9] and reads [22], for \( \phi = \pi/2 \),

\[
\text{PECD}(\epsilon_k, \theta, \phi = \pi/2) = 2 \sum_{n,k} \beta_{2k+1,0}^{(2)ph}(\epsilon_k) P_{2k+1}^0(\cos \theta) + 6 \text{Im} \left[ \beta_{2,1}^{(2)int}(\epsilon_k) \right] \sin(2\theta). \tag{7}
\]

Anisotropy parameters and PECD are expressed in percentage of the peak photoelectron intensity. The driving electric field is parametrized,

\[
\epsilon(t) = \sum_{j=1}^\infty \epsilon_j e^{-(t-\tau_j)^2/2\tau_j^2} \cos(\omega_j(t-\tau_j) + \phi_j), \tag{8}
\]

with \( \epsilon_j, \omega_j, \phi_j \) the amplitude, frequency, and carrier envelope phase of the \( j \)th pulse with full width at half maximum FWHM = 2\sqrt{2}ln 2\tau_j and time delay \( \tau_j \), which are optimized following Ref. [18].

Figure 2(a) displays the PECD obtained with a reference \( (\omega, 2\omega) \)-bichromatic field with \( \omega = 108 \) nm, peak intensity \( I_0 = 5.1 \times 10^{10} \) W/cm² and flat spectral phase. The PECD corresponds to just 4% of the peak photoionization intensity, with a kinetic energy distribution centered around 11 eV. The red (blue) color in Fig. 2 denotes excess (deficit) of photoelectrons in a given direction. Optimizing the parameters in Eq. (8), starting from the reference field, obeying the constraint \( (\omega, 2\omega) \) for the frequencies and restricting the amplitudes to the two-photon regime, \( 1.0 \times 10^{12} \) W/cm², raises the PECD to about 20%, cf. Fig. 2(b). This is comparable to asymmetries predicted for \( (\omega, 2\omega) \) bichromatic fields, linearly polarized in two mutually-orthogonal directions employing
rotationally tailored laser pulses for control [26]. Optimization of all parameters in Eq. (8) without the \((\omega, 2\omega)\)-constraint, but keeping the spectral components within [30 nm, 950 nm], or [1.3 eV, 41.3 eV], results in a PECD of 68% (for a total ionization yield of 6%). The optimized field has a maximal peak intensity of \(3.5 \times 10^{10}\) W/cm\(^2\).

The different PECD values in Fig. 2 are explained by inspecting the individual contributions of the one- and two-photon ionization pathways and their interference, shown in Fig. 3. For the reference field, \(\beta_{1,0}^{(+)}\) and \(\beta_{1,0}^{(2)}\) have opposite sign in Fig. 3(a), i.e., the one-photon and two-photon pathways interfere destructively resulting in a small overall \(\beta_{1,0}^{(+)}\). The two-photon pathway captured in \(\beta_{2,0}^{(+)}\) also contributes with a negative sign at \(\theta = 0\) (maximum PECD), further decreasing the net PECD. It becomes clear that the relative contribution of each ionization pathway plays a key role for the improvements seen in Fig. 2(b) and (c).

For the optimized bichromatic field, the largest part of PECD (17% out of the 20%) is due to constructive interference between opposite-parity pathways, given by the term proportional to \(\sin(2\theta)\) in Eq. (7). Interference between opposite-parity photoionization pathways is a general, well-documented control mechanism [20, 21, 27, 28], and bichromatic pulses have been suggested to realize this scenario for atoms using linearly [27] and circularly [28] polarized light. Anisotropy after bichromatic ionization is also predicted for randomly oriented chiral molecules [26]. Here, however, we find that allowing for a more general spectral shape than that of a bichromatic field yields a significantly more efficient control mechanism for maximizing PECD, cf. Fig. 2(c). As shown in Fig. 3(b), PECD in this case is characterized by a main peak at 6.50 eV and two satellites at 2.39 eV and 11 eV. In contrast to the bichromatic pulses, for which the contributions from the one-photon ionization and the interference term are relevant, these processes are absent for the frequency-unconstrained pulse. In fact, both \(\beta_{1,0}^{(+)}\) and \(\beta_{2,0}^{(+)}\) in Fig. 3(b) vanish over the entire energy domain. Furthermore, the one-photon ionization pathway is completely suppressed, even for the symmetric part, since \(\beta_{0,0}^{(+)} = 0\). Instead, the remarkable enhancement of the PECD is due to even-parity, i.e., two-photon, ionization pathways, because both \(\beta_{1,0}^{(2)}\) and \(\beta_{3,0}^{(2)}\) are non-zero.

Analyzing the spectrum of the frequency-unconstrained optimized field, shown in Fig. 3(c), we identify the interference between different two-photon ionization pathways that give rise to the control observed in Fig. 2(c). The spectrum contains peaks at \(\omega_1 = 7.24\) eV, \(\omega_2 = 10.70\) eV, and \(\omega_3 = 11.35\) eV and overlaps with transitions from the HOMO to the first unoccupied orbitals, namely, \(\omega_{10} = 7.07\) eV, \(\omega_{20} = 10.90\) eV, \(\omega_{30} = 11.06\) eV and \(\omega_{40} = 11.47\) eV, cf.
Fig. 3(c). The two-photon ionization pathway \( 2 \times \omega_{10} \) promotes the photoelectron to 2.27 eV and explains the small peak at 2.39 eV in Fig. 3(b). Conversely, the pathways \( 2 \times \omega_2, \omega_2 + \omega_3, \omega_2 + \omega_4, \ldots \), explain the small PECD at 11 eV. However, these pathways do not contribute much to PECD which is mainly due to the peak at 6.5 eV. The most important pathways leading to 6.5 eV, cf. Fig. 2(f), are \( \omega_{20} + (\omega_{10} + \delta\omega_1) \) and similarly \( (\omega_{10} + \delta\omega_1) + \omega_{20} \) with an offset of \( \delta\omega_1 = 0.4 \) eV as well as \( \omega_{30} + (\omega_{10} - \delta\omega) \) with \( \delta\omega = 0.12 \) eV. The latter probes the LUMO+3, whereas the former two probe the LUMO+1 and LUMO. The required offsets are available within the spectral bandwidth. The pathways \( \omega_{30} + \omega_{10} \) and \( \omega_{10} + \omega_{30} \), probing the LUMO+2, are also compatible with the pulse spectrum; however, the frequency \( \omega_{30} \) is suppressed, and removing the LUMO+2 decreases the PECD by only 0.4%. In other words, the high frequency components of the optimized field correspond to photon energies which resonantly excite the first LUMO + \( j \) orbitals \( (j = 1, 2, \ldots) \), while the peak centered at \( \omega_1 \) can either excite the LUMO from the ground state or ionize the LUMO+\( j \) population, cf. Fig. 2(f). Its bandwidth guarantees interference at a common photoelectron energy. Thus, the width and peak position at \( \omega_1 \) are key for the constructive interference among a finite manifold of two-photon ionization pathways at a common final photoelectron energy to significantly enhance PECD. Imposing \( \omega_1 \) to be exactly \( \omega_{10} \) while reducing its spectral bandwidth results in a smaller PECD (\( \approx 50\% \)). Conversely, allowing \( \omega_1 \) to be further blue-shifted with respect to \( \omega_{10} \) while increasing the spectral bandwidth such that it still overlaps with \( \omega_{10} \) results in a PECD of about 70%.

The coherent nature of the control mechanism is further confirmed by modifying the spectral phase of the optimized pulse while keeping the spectral amplitude unaffected, cf. dashed lines in Fig. 3(c). This corresponds to introducing a time delay between the high and low-frequency components of the pulse. Figure 4 shows the variation of the PECD, between 68% to 6%, as a function of this time delay. Positive (negative) delays correspond to the high-frequency components arriving before (after) the low-frequency components, as verified by inspecting the Wigner distribution function of the pulses. For negative time delays, highlighted in red in Figs. 2(f) and 4, only the LUMO is excited. PECD thus does not depend on the time delay and reflects the chiral signature of the LUMO only, which amounts to about 10%. For positive time delays, highlighted in blue in Figs. 2(f) and 4, the high-frequency components of the pulse prepare a superposition of higher excited states, such that the PECD depends on the time delay and contains the chiral fingerprints of the LUMO+\( j \) (\( j \geq 1 \)) with a maximum of 55%. These two scenarios correspond to pump-probe control [30, 31] where the pump pulse spectrum selects the manifold of intermediate states that contribute. PECD can be pushed to 62% by further optimization of time-separated pump and probe pulses for positive delays. However, the maximal value of PECD, 68%, is obtained when pump and probe overlap, as highlighted in yellow in Figs. 2(f) and 4. This can be rationalized by exploiting interference of all the pathways, including the two-photon ionization through the LUMO, depicted in Fig. 2(f).

In conclusion, we have identified constructive interference in two-photon photoionization to significantly enhance PECD of randomly oriented CHBrClF molecules. Control is achieved via various \((1+1')\) REMPI pathways leading to a common final photoelectron state but probing different intermediate states. Separating pump and probe photons in time slightly reduces the number of pathways that may interfere and thus the PECD. In this excitation scheme based on interference of same-parity pathways, we find significantly larger PECD than can be obtained with optimized bichromatic circularly polarized
FIG. 4. PECD as a function of the time delay between the $\omega_1$-component and the higher frequency components of the optimized pulse shown in Fig. 3(c). In regions $S_1$ and $S_2$, the sub-pulses are temporally separated (pump-probe scenario) with $S_1$ corresponding to ionization via the LUMO only (cf. right part of Fig. 2(f)) whereas in $S_2$, ionization proceeds via a superposition of different excited states without the LUMO (cf. left part of Fig. 2(f)). In $S_3$, pump and probe pulses overlap in time such that interference between all two-photon ionization pathways can be exploited. The spectral phases corresponding to the maximum and minimum PECD are shown in Fig. 3(c).

fields where opposite parity pathways are made to interfere constructively. While experimental realization of our control scenario assumes the capability to shape the spectral phase of XUV pulses, the requirements on pulse amplitude and spectral width are moderate and compatible with existing technology. It will be straightforward to extend this type of control to molecules other than CHBrClF, with only the central frequencies and spectral widths depending on the specific chiral molecule. Higher-order terms in the perturbation expansion, while requiring larger amplitudes, are likely to facilitate even more pathway interference and could also be used to drive photoionization with optical instead of XUV pulses. Whether an upper bound to PECD exists and what type of driving field would saturate it is yet unknown.

We would like to thank Thomas Baumert for helpful comments on the manuscript. The computing for this project was performed on the Beocat Research Cluster at Kansas State University, which is funded in part by NSF grants CNS-1006860, EPS-1006860, and EPS-0919443. CPK acknowledges financial support from the Deutsche Forschungsgemeinschaft (CRC 1319).

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Supplemental material for Quantum control of photoelectron circular dichroism

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(Dated: September 12, 2018)

For completeness, we provide here the details of the derivation of the orientation-averaged experimental observables, i.e., the anisotropy parameters and photoelectron circular dichroism (PECD), within the framework of second-order time-dependent perturbation approximation. Section I introduces the equations of motion for the electron dynamics and describes the perturbation treatment of the light-matter interaction. It also summarizes the operations needed to express the photoelectron momentum distribution in the laboratory frame of reference. Section II defines the orientation averaged laboratory-frame anisotropy parameters for the one- and two-photon ionization pathways and their interference. In Sec. III the symmetry properties of the different anisotropy parameters under polarization reversal are analyzed and the PECD is defined accordingly. Finally, sections IV and V contain the input file parameters for the electronic structure and scattering calculations, respectively.

I. PERTURBATION EXPANSION

A. Equations of motion

Equations (1) and (2) of the main text introduce the time-dependent many-electron Schrödinger equation and the expansion of the many-electron state |ΨN(t)⟩ into the Hartree-Fock (HF) ground state and one-particle-one-hole excitations, |Φi⟩. The Slater determinant describing the HF ground-state is constructed from an anti-symmetric product of one-electron spin-orbitals φi,

$$\Phi_0 = A \prod_{i=1}^{N} \varphi_i(r_i) \quad (1)$$

such that $$\hat{H}_0|\varphi_p⟩ = \epsilon_p|\varphi_p⟩$$ where $\epsilon_p$ are the orbital energies. Expanding the many-electron Hamiltonian into the basis of HF ground state and one-particle-one-hole excitations, defining

$$\epsilon_0 = \langle \Phi_0 | \hat{H}_0 | \Phi_0 \rangle ,$$

$$\epsilon_i^a = \langle \Phi_i^a | \hat{H}_0 | \Phi_i^a \rangle$$

$$= \epsilon_0 + \epsilon_a - \epsilon_i , \quad (2)$$

and applying Brillouin’s theorem [1],

$$\langle \Phi_0 | \hat{H}_1 | \Phi_i^a \rangle = 0 \quad (3)$$

we arrive at a set of coupled equations for the expansion coefficients,

$$\dot{\alpha}_0(t) = i\mathcal{E}(t) \left[ \langle \Phi_0 | \hat{H} | \Phi_0 \rangle \alpha_0(t) \right. \right.$$  

$$\left. + \sum_{i,a} \langle \Phi_0 | \hat{H}_i^a | \Phi_0 \rangle e^{-i(\epsilon_i^a - \epsilon_0)t} \alpha_i^a(t) \right]$$  

$$\dot{\alpha}_i^a(t) = i\mathcal{E}(t) \left[ \langle \Phi_i^a | \hat{H} | \Phi_0 \rangle e^{-i(\epsilon_0 - \epsilon_i^a)t} \alpha_0(t) \right. \right.$$  

$$\left. + \sum_{j,b} \langle \Phi_i^a | \hat{H}_j^b | \Phi_j^b \rangle e^{-i(\epsilon_j^b - \epsilon_i^a)t} \alpha_j^b(t) \right]$$  

$$\left. - i \sum_{j,b} \langle \Phi_i^a | \hat{H}_1 | \Phi_j^b \rangle \alpha_j^b(t) e^{-i(\epsilon_j^b - \epsilon_i^a)t}. \right.$$  

In particular, for $$a = k$$, the coefficients $$\alpha_k^i(t)$$ describe the transition amplitude from an initially occupied orbital $$i$$ to a continuum state with energy $$\epsilon_k = |k|^2/2$$ in the direction $$k/|k|$$ with respect to the molecular frame of reference, $$R_k$$. Similarly, $$\alpha_k^i(t)$$ describe this transition in the laboratory frame, $$\mathcal{R}_k$$.

B. Orientation-averaged momentum distribution

The orientation-averaged momentum distribution of photoelectrons with energy $$\epsilon_k$$ emitted within a solid angle $$d\Omega_k$$ measured in the laboratory frame is given by Eq. (3) of the main text. In order to account for first- and second-order processes and their interference, we solve the equation of motion for the amplitudes $$\alpha_k^i(t; \gamma_k)$$ using second-order time-dependent perturbation theory which results in Eq. (4) of the main text. We limit the calculations to the single-channel approximation with $$i_0$$ labeling the HOMO orbital. The angle and energy resolved photoelectron distribution can then be written in terms of the contributions from one- and two-photon ionization processes and their interference,

$$\frac{d^2\sigma^{(\mu_0)}}{d\epsilon_k d\Omega_k'} = \frac{d^2\sigma^{(\mu_0)1ph}}{d\epsilon_k d\Omega_k'} + \frac{d^2\sigma^{(\mu_0)2ph}}{d\epsilon_k d\Omega_k'} + \frac{d^2\sigma^{(\mu_0)int}}{d\epsilon_k d\Omega_k'} , \quad (5)$$

where $$\mu_0 = (\pm 1, 0)$$ defines the spherical unit vector components of the polarization direction $$\epsilon_{\mu_0}$$ in $$\mathcal{R}_k$$. It has been introduced to distinguish the photoelectron distribution obtained with left ($$\mu_0 = +1$$) and right ($$\mu_0 = -1$$) circularly polarized light or with linear ($$\mu_0 = 0$$) polarization. The contribution from one-photon processes in
Eq. (5) becomes
\[ \frac{d^2 \sigma^{(\mu_0)1ph}}{d \epsilon_k \, d \Omega_{k'}} = \int \alpha^{(1)k'}_{\mu_0}(t; \gamma \gamma) \alpha^{s(1)k'}_{\mu_0}(t; \gamma \gamma) d^3 \gamma \gamma \]  
(6)
\[ = \sum_{L,M} \beta_{L,M}^{(\mu_0)1ph}(\epsilon_k) P_L^M (\cos \theta_{k'}) e^{iM \phi_{k'}} , \]
where in the second line we have invoked an expansion into associated Legendre polynomials, \(P_L^M(\cdot)\). Similarly, contributions to the photoelectron momentum distribution originating from second-order process reads
\[ \frac{d^2 \sigma^{(\mu_0)2ph}}{d \epsilon_k \, d \Omega_{k'}} = \int \alpha^{(2)k'}_{\mu_0}(t; \gamma \gamma) \alpha^{s(2)k'}_{\mu_0}(t; \gamma \gamma) d^3 \gamma \gamma \]  
(7)
\[ = \sum_{L,M} \beta_{L,M}^{(\mu_0)2ph}(\epsilon_k) P_L^M (\cos \theta_{k'}) e^{iM \phi_{k'}} . \]

For the interference terms between one- and two-photon ionization pathways in Eq. (4) of the main text, we define
\[ \beta_{L,M}^{(\mu_0)int} = \int \alpha^{(1)k'}_{\mu_0}(\gamma \gamma) \alpha^{s(2)k'}_{\mu_0}(\gamma \gamma) d^3 \gamma \gamma . \]  
(8)

Using Eq. (8), the contribution from the interfering pathways to the photoelectron spectrum reads
\[ \frac{d^2 \sigma^{(\mu_0)int}}{d \epsilon_k \, d \Omega_{k'}} = \int \left( \epsilon^{(1)k'}_{\mu_0}(t; \gamma \gamma) \epsilon^{s(2)k'}_{\mu_0}(t; \gamma \gamma) + c.c. \right) d^3 \gamma \gamma \]  
\[ = \sum_{L,M} \beta_{L,M}^{(\mu_0)int}(\epsilon_k) e^{iM \phi_{k'}} + c.c. P_L^M (\cos \theta_{k'}) , \]
or, equivalently,
\[ \frac{d^2 \sigma^{(\mu_0)int}}{d \epsilon_k \, d \Omega_{k'}} = 2 \sum_{L,M} \left[ \text{Re} \left( \beta_{L,M}^{(\mu_0)int}(\epsilon_k) \right) \cos(M \phi_{k'}) \right] P_L^M (\cos \theta_{k'}) , \]  
\[ - \text{Im} \left( \beta_{L,M}^{(\mu_0)int}(\epsilon_k) \right) \sin(M \phi_{k'}) P_L^M (\cos \theta_{k'}) , \]
where the possible values of \(L\) and \(M\) are determined by \(\mu_0\) as well as the symmetry properties after the orientation averaging. The portion of the photoelectron spectrum due to the interference term is sensitive to the relative phase between one- and two-photon processes. In particular, measurements on the \((z', y')\)-plane \((\phi_{k'} = \pi/2)\) and \((z', x')\)-plane \((\phi_{k'} = 0)\) may allow reconstruction of the phase.

**C. First-order corrections**

The first order correction of \(\alpha_0(t)\) in Eq. (4a) reads
\[ \alpha_0^{(1)}(t) = i \langle \Phi_0 | \hat{r} | \Phi_0 \rangle \int_{-\infty}^{t} \epsilon(t') \alpha_0^{(0)}(t') dt' \]  
(10)
\[ + i \sum_{j,a} \langle \Phi_0 | \hat{r} | \alpha_j^{(a)} \rangle \int_{-\infty}^{t} e^{-i(\epsilon_j - \epsilon_0)t'} \alpha_j^{(a)}(t') \epsilon(t') dt' , \]
where \(j\) in \(\alpha_j^{(j)}(t)\) and \(\alpha_j^{(a)}(t)\) indicates the perturbation order. For convenience, both one-particle one-hole excitations to virtual bound and scattering states are contained in the index \(a\) in Eq. (10). Using the zeroth order approximations \(\alpha_0^{(0)}(t) \approx 1\) and \(\alpha_j^{(a)}(t) \approx 0\), Eq. (10) becomes
\[ \alpha_0^{(1)}(t) = i \langle \Phi_0 | \hat{r} | \Phi_0 \rangle \int_{-\infty}^{t} \epsilon(t') dt' . \]  
(11)
The first order correction for the one-particle one-hole excitations reads
\[ \alpha_i^{(1)}(t) = i \langle \Phi_i | \hat{r} | \Phi_0 \rangle \int_{-\infty}^{t} \alpha_i^{(0)}(t') e^{-i(\epsilon_0 - \epsilon_i)t'} \epsilon(t') dt' \]  
(12)
\[ + i \sum_{j,b} \langle \Phi_i | \hat{r} | \Phi_j \rangle \int_{-\infty}^{t} \alpha_j^{(b)}(t') e^{-i(\epsilon_j - \epsilon_i)t'} \epsilon(t') dt' \]
\[ - i \sum_{j,b} \langle \Phi_i | \hat{H}_1 | \Phi_j \rangle \int_{-\infty}^{t} e^{-i(\epsilon_j - \epsilon_i)t'} \alpha_j^{(b)}(t') dt' . \]
Using \(\alpha_0^{(0)}(t) \approx 1\) and \(\alpha_j^{(a)}(t) \approx 0\), Eq. (12) reduces to
\[ \alpha_i^{(1)}(t) = i \langle \Phi_i | \hat{r} | \Phi_0 \rangle \int_{-\infty}^{t} e^{-i(\epsilon_0 - \epsilon_i)^t' \epsilon(t') dt' , \]  
(13)
where the two determinants differ only by one spin-orbital. Application of the Slater-Condon rules for one-electron operators \(\mathcal{O}\) [2],
\[ \langle \Phi_0 | \hat{O} | \Phi_0 \rangle = \sum_i \langle \varphi_i | \hat{O} | \varphi_i \rangle , \]
\[ \langle \Phi_0 | \hat{O} | \Phi_0 \rangle = \langle \varphi_i | \hat{O} | \varphi_i \rangle , \]  
(14)
to Eq. (13) allows us to write the matrix elements in terms of the HF one-electron spin-orbitals,
\[ \alpha_i^{(1)}(t) = i \langle \varphi_i | \hat{r} | \varphi_i \rangle \int_{-\infty}^{t} e^{-i(\epsilon_0 - \epsilon_i)^t' \epsilon(t') dt' , \]  
(15)
with \(\varphi_s\) the sth occupied or unoccupied spin-orbital, cf. Eq. (1). In particular, the first-order correction for the quantity of interest, namely \(\alpha_0^{(0)}(t)\), reads
\[ \alpha_i^{(1)}(t) = i \langle \Phi_i | \hat{r} | \Phi_0 \rangle \int_{-\infty}^{t} e^{-i(\epsilon_0 - \epsilon_i)^t' \epsilon(t') dt' , \]  
(16)
Assuming no relaxation of the contributing orbitals, the total wave function \(\Phi_i^k(r_N)\) can be defined, for any \(i \in occ\), as an antisymmetrized product,
\[ \Phi_i^k(r_1, \ldots , r_N) = A_N [ \varphi_k^- (r_N); \Phi_i (r_1, \ldots , r_{N-1}) ] , \]  
(17)
where \(\varphi_k^- (r_N)\) is the scattering portion of the wave function and \(\Phi_i (r_1, \ldots , r_{N-1})\) the \(N - 1\) electron final state after ionization. We obtain \(\varphi_k^- (r)\) by solving the scattering problem
\[ \left[ \nabla^2 - \frac{1}{r} + \hat{V} - \frac{k^2}{2} \right] \varphi_k^- (r) = 0 , \]  
(18)
with scattering boundary conditions [3, 4] for the outgoing wave \(\varphi_k^- (r)\) at large distances \(r \rightarrow \infty\), and where
\( \mathbf{V}(r) \) describes the short-range part of the electron-ion interaction. Equation (18) including its matrix and tensor elements are computed using a locally modified version of the ePolyScat program package [5–7]. The orthogonality between the Hartree-Fock orbitals and scattering states obtained from the scattering calculations have been numerically verified within the tolerance range.

### D. Second-order corrections

The second order correction of \( \alpha_i^k(t) \) for \( i \in \text{occ} \) is, according to Eq. (4b),

\[
\alpha_i^{k(2)}(t) = i \langle \Phi_k^{(0)} | \hat{\mathbf{r}} | \Phi_0 \rangle \int_{-\infty}^{t} e^{i(\epsilon_i^k - \epsilon_0)t'} \mathbf{E}(t') \alpha_0^{(1)}(t') dt' \tag{19}
\]

\[
+ i \sum_{j,b} \langle \Phi_i^{(0)} | \hat{\mathbf{r}}_b | \Phi_j \rangle \int_{-\infty}^{t} e^{i(\epsilon_i^k - \epsilon_j)'} \mathbf{E}(t') \alpha_j^{(1)}(t') dt' \\
- i \sum_{j,b} \langle \Phi_i^{(0)} | \hat{\mathbf{r}}_b | \Phi_j \rangle \int_{-\infty}^{t} e^{i(\epsilon_i^k - \epsilon_j)'} \mathbf{E}(t') \alpha_j^{(1)}(t') dt'.
\]

The electron-correlation effects described by \( \hat{\mathbf{H}}_0 \) will be neglected. However, the exchange and Coulomb operator in \( \hat{\mathbf{H}}_0 \) ensure the excited electron to still experience a (chiral) Coulomb attraction to the residual cation \([8]\). To verify the chiral origin of PECD when \( \hat{\mathbf{H}}_1 \) is ignored, we have performed the same calculations using the achiral CH and N2 molecules, for which no PECD was observed (below machine precision).

Matrix elements are obtained using the rules for one-electron operators (14) together with

\[
\langle \Phi_i^{(0)} | \hat{\mathbf{r}} | \Phi_j \rangle = \delta_{a,b} (1 - \delta_{i,j}) \langle \varphi_a | \hat{\mathbf{r}} | \varphi_b \rangle \\
+ \delta_{i,j} (1 - \delta_{a,b}) \langle \varphi_j | \hat{\mathbf{r}} | \varphi_i \rangle \\
+ \delta_{i,j} \delta_{a,b} \sum_{r \in \left\{ m^a \right\}} \langle \varphi_i | \hat{\mathbf{r}} | \varphi_r \rangle,
\]

with \( \left\{ m^a \right\} = \{1, \ldots, i - 1, a, i + 1, \ldots, N\} \). We restrict ourselves to the frozen-core approximation as well as the single-channel approximation for the photoionization processes, allowing only the HOMO orbital, \( \varphi_{i0} \), to contribute to the photoionization via direct (first order) or two-photon (second order) ionization probing different unoccupied orbitals \( \varphi_a \).

Inserting the first order corrections \( \alpha_i^{(0)}(t) \) and \( \alpha_i^{(1)}(t) \) defined in Eqs. (11) and (13) into Eq. (19) gives

\[
\alpha_i^{k(2)}(t) = - \langle \Phi_i^{(0)} | \hat{\mathbf{r}} | \Phi_0 \rangle \langle \Phi_0 | \hat{\mathbf{r}}_0 | \Phi_0 \rangle \\
\times \int_{-\infty}^{t} e^{i(\epsilon_i^0 - \epsilon_0)t'} \mathbf{E}(t') \int_{-\infty}^{t'} \mathbf{E}(t'') dt'' dt' \\
- \sum_{k \in \text{occ}} \sum_{j \in \text{occ}} \langle \Phi_i^{(0)} | \hat{\mathbf{r}}_b | \Phi_j \rangle \langle \varphi_k | \varphi_b | \varphi_j \rangle \int_{-\infty}^{t} e^{i(\epsilon_i - \epsilon_j)'} \mathbf{E}(t') \\
\times \int_{-\infty}^{t'} e^{i(\epsilon_j^b - \epsilon_0)'} \mathbf{E}(t'') dt'' dt'.
\]

### E. Orientation-dependent momentum distribution

Two steps are still required to compute the laboratory frame quantities \( \alpha_{i0}^{k(1)}(t; \gamma_R) \) and \( \alpha_{i0}^{k(2)}(t; \gamma_R) \). First, if \( \mathbf{E}(t) = \mathbf{E}_{\mu_0}(t) \) is known in \( R' \), the component \( \mathbf{E}_{\mu_0}(t) \) must be projected into the molecular frame in order to evaluate all tensor elements. The orientation of \( R \) with respect to \( R' \) is defined by the Euler angles \( \gamma_R = (\alpha, \beta, \gamma) \). The second step involves rotation of the photoelectron direction of emission from \( R \) to \( R' \), which is performed using the inverse of the transformation used in step 1.

In \( R' \), the electric field is decomposed into the spherical unit vectors \( \epsilon_{\mu} \), with \( \mu = \pm 1, 0 \),

\[
\mathbf{E}(t) = \sum_{\mu} \mathbf{E}_{\mu} \epsilon_{\mu}^* = \sum_{\mu} (-1)^\mu \mathbf{E}_{\mu} \epsilon_{-\mu},
\]

such that \( \mathbf{E}(t) \cdot \epsilon_{\mu_0} = \mathbf{E}_{\mu_0}(t) \). We recall that \( \mu_0 = \pm 1, 0 \) defines the left (+1), right (−1) or linear (0) polarization direction of the field. The spherical unit vector \( \epsilon_{\mu_0} \) can be written in terms of its molecular-frame counterparts, \( \epsilon_{\mu} \),

\[
\epsilon_{\mu_0} = \sum_{\mu = \pm 1, 0} D^{\mu}_{\mu_0} (\gamma_R) \epsilon_{\mu},
\]

where \( D^{\mu}_{\mu_0} (\gamma_R) \) are the components of the Wigner rotation matrix. Rotations between the two coordinate systems, \( R \) and \( R' \), are performed following the convention for the Wigner rotation matrices of Ref. [9]. The tensor operator \( \hat{\mathbf{r}} \) is also projected into the spherical unit vectors in \( R' \),

\[
\hat{\mathbf{r}} = \sum_{\mu} (-1)^\mu \hat{r}_{\mu} \epsilon_{-\mu},
\]

such that \( \hat{\mathbf{r}} \cdot \epsilon_{\mu_0} = \hat{r}_{\mu_0} \). Finally, in the molecular frame, the dipole interaction reads

\[
\mathbf{E}(t) \cdot \hat{\mathbf{r}} = \mathbf{E}_{\mu_0}(t) \sum_{\mu} D^{\mu}_{\mu_0} (\gamma_R) \hat{r}_{\mu},
\]

with \( \mu = \pm 1, 0 \) and the matrix elements of the interaction become

\[
\mathbf{E}_{\mu_0}(t) \langle \varphi_p | \epsilon_{\mu_0}^* \cdot \hat{\mathbf{r}} | \varphi_q \rangle = \mathbf{E}_{\mu_0}(t) \sum_{\mu} D^{\mu}_{\mu_0} (\gamma_R) \langle \varphi_p | \hat{r}_{\mu} | \varphi_q \rangle,
\]

where \( \epsilon_{\mu_0} \) and \( \varphi_q \) symbolize two arbitrary spin-orbitals, and Eq. (23) is also valid for scattering states. Here, the \( z' > 0 \) axis is defined by the propagation direction of the laser beam, normal to the \( (x', y') \)-plane (polarization plane for \( \mu_0 = \pm 1 \)).

The second type of rotation involves projection of the direction of photoelectron emission from the molecular to the laboratory frame. In the molecular frame, the direction of photoelectron emission is obtained by expanding the scattering wave function into spherical harmonics,

\[
\varphi_k^-(r) = \sum_{\ell, m} \varphi_{k\ell, m}^-(r) Y_{\ell m}(\theta_k, \phi_k),
\]

(24)
where \( \theta_k \) and \( \phi_k \) correspond to the polar and azimuthal angles in the molecular frame. To obtain the anisotropy parameters, evaluation of the product of two spherical harmonics, \( Y^L_m(\theta_k, \phi_k)Y^L_{m'}(\theta_k, \phi_k) \), is required. This can be done using the well known expression [2]

\[
Y^L_m(\theta_k, \phi_k)Y^L_{m'}(\theta_k, \phi_k) = (-1)^m \sum_{L, M} \tilde{\gamma}^{L}_{L', \ell'} \ Y^L_{m-m'}(\theta_k, \phi_k) \begin{pmatrix} \ell & \ell' & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & \ell' & L \\ m & -m' & m' - m \end{pmatrix}.
\] (25)

where

\[ \tilde{\gamma}(\ell, \ell', L) = \sqrt{\frac{(2L+1)}{4\pi}}(2\ell + 1)(2\ell' + 1). \]

The last step consists in writing the direction of photoelectron emission — determined by \( Y^L_{m-m'}(\theta_k, \phi_k) \) appearing in the rhs of Eq. (25) — with respect to the laboratory frame. This is achieved using the inverse of the transformation (22),

\[
Y^L_{m-m'}(\theta_k, \phi_k) = \mathcal{D}^{-1}(\gamma_R) \sum_{M'} (-1)^{m-m'-M} \mathcal{D}^L_{m',m,-M}(\gamma_R) \ Y^L_{M}(\theta_k', \phi_k'),
\] (26)

which allows us to write Eq. (25) as a function of the polar and azimuthal angles \( \theta_k' \) and \( \phi_k' \) in the laboratory frame. The reason for rotating the product of two spherical harmonics instead of evaluating the product of two rotated harmonics is two-fold: first, it results in a more straightforward analysis of the properties of the Wigner 3j symbols appearing in the anisotropy parameters under polarization reversal which is of interest when evaluating the PECD.

Finally, applying Eq. (26) to the spherical harmonics in the rhs of Eq. (25) gives

\[
Y^L_m(\theta_k, \phi_k)Y^{*L}_{m'}(\theta_k, \phi_k) = (-1)^m \sum_{L, M} \tilde{\gamma}^{L}_{L', \ell'} \ Y^L_{m-m'}(\theta_k, \phi_k) \begin{pmatrix} \ell & \ell' & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & \ell' & L \\ m & -m' & m' - m \end{pmatrix} (-1)^{-M} \mathcal{D}^L_{m',m,-M}(\gamma_R) \ Y^L_{M}(\theta_k', \phi_k'),
\] (27)

where \( P^M_L(\cdot) \) denotes the associate Legendre polynomials and

\[
\tilde{\gamma}^{L,M}_{L', \ell'} = \sqrt{\frac{(2L+1)(2\ell + 1)(L-M)!}{(L+M)!}}. \] (28)

The orientation-averaged laboratory-frame anisotropy parameters associated to the one- and two-photon ionization pathways and their interference defined in Sec. 1B are evaluated in the following.

## II. LABORATORY-FRAME ANISOTROPY PARAMETERS

### A. Anisotropy parameters \( \beta^{(\ell_0\ell)}_{L,M} \)

Using Eq. (23), the molecular-frame Eq. (16) becomes

\[
\alpha^{(1)}_{\ell_0}(t; \gamma_R) = \sum_{\mu} \langle \Phi_{\ell_0} | \Phi_{\mu} \rangle \mathcal{D}^{(1)}_{\mu,\ell_0}(\gamma_R) \times \int_{-\infty}^{t} e^{-i(t'-t_{\ell_0})} E_{\mu_0}(t') \ dt'.
\] (29)
Inserting the partial wave expansion (24), we find

\[ \alpha_{i\nu_0}^{k(1)}(t; \gamma_R) = i \sum_{\mu, \ell, m} \mathcal{M}_{k, \ell, m}^{(1)} D_{\mu, \nu_0}^{* (1)}(\gamma_R) \]

\[ \times Y_{m}^{\ell}(\theta_{k}, \phi_{k}) \int_{-\infty}^{t} e^{-i(\epsilon_{k_0} - \epsilon_{t}) t'} \mathcal{E}_{\mu_0}(t') dt', \]

where \( \mathcal{M}_{k, \ell, m}^{(1)} \equiv \langle \Phi_{i\nu_0}^{k, \ell, m} | \mathcal{E}_{\mu_0} \rangle \) is the partial wave decomposition of the matrix elements in Eq. (29). Making use of Eq. (27) and evaluating \( \alpha_{i\nu_0}^{k}(t; \gamma_R) \alpha_{i\nu_0}^{* k}(t; \gamma_R) \) results in

\[ \alpha_{i\nu_0}^{k(1)}(\gamma_R) \alpha_{i\nu_0}^{* k(1)}(\gamma_R) = (-1)^{-\mu_0} \sum_{\mu, \ell, m} \mathcal{M}_{k, \ell, m}^{(1)} \mathcal{M}_{k, \ell', m'}^{* (1)} \int_{-\infty}^{t} e^{i(\epsilon_{k_0} - \epsilon_{t}) t'} \mathcal{E}_{\mu_0}(t') dt' \int_{-\infty}^{t} e^{-i(\epsilon_{k_0} - \epsilon_{t}) t'} \mathcal{E}_{\mu_0}^{*}(t') dt' \]

\[ \times \sum_{L, M}^{L, M} \mathcal{D}_{\mu, \nu_0}^{L, M}(\gamma_R) \mathcal{D}_{\mu, \nu_0}^{L, M}(\gamma_R) \mathcal{D}_{m, -M}^{0, -M}(\gamma_R). \]

(31)

We recall that \( \mu_0 = \pm 1, 0 \) defines the light polarization direction in the laboratory frame. Following Eq. (6), integrating Eq. (31) over the Euler angles leads to the contribution of the one-photon pathway to the momentum distribution. Integrating a product of three Wigner 3j–symbols over the Euler angles can be evaluated according to [9]

\[ \int \mathcal{D}_{m_1, m_1'}^{(\ell_1)}(\gamma_R) \mathcal{D}_{m_2, m_2'}^{(\ell_2)}(\gamma_R) \mathcal{D}_{m_3, m_3'}^{(\ell_3)}(\gamma_R) \frac{d^3 \gamma_R}{8\pi^2} = \left( \begin{array}{ccc} \ell_1 & \ell_2 & \ell_3 \\ m_1 & m_2 & m_3 \end{array} \right) \left( \begin{array}{ccc} \ell_1 & \ell_2 & \ell_3 \\ m_1' & m_2' & m_3' \end{array} \right). \]

(32)

Another useful property concerns the product of two Wigner rotation matrices given by [9]

\[ \mathcal{D}_{m_1, m_1'}^{(\ell_1)}(\gamma_R) \mathcal{D}_{m_2, m_2'}^{(\ell_2)}(\gamma_R) = \sum_{\ell} (2\ell + 1) \mathcal{D}_{-m_1, -m_1'}^{(\ell)}(\gamma_R) \times \left( \begin{array}{ccc} \ell_1 & \ell_2 & \ell \\ m_1 & m_2 & -m_1' \end{array} \right) \left( \begin{array}{ccc} m_1' & m_2' & -m_1'' \end{array} \right), \]

(33)

with \( m_{12} = m_1 + m_2 \) and \( m_{12}' = m_1' + m_2' \). Upon integration of Eq. (31) over the Euler angles using Eq. (32) and equating the result with Eq. (6), the contribution from the one-photon ionization pathway to the orientation-averaged anisotropy parameters is obtained,

\[ \beta_{L, M}^{1ph}(\epsilon_k) = 2\pi (2L + 1) \sqrt{(2\ell + 1)(2\ell' + 1)} (-1)^{-\mu_0} \]

\[ \times \sum_{\mu, \ell, m} \mathcal{M}_{k, \ell, m}^{(1)} \mathcal{M}_{k, \ell', m'}^{* (1)} \int_{-\infty}^{t} e^{i(\epsilon_{k_0} - \epsilon_{t}) t'} \mathcal{E}_{\mu_0}(t') dt' \int_{-\infty}^{t} e^{-i(\epsilon_{k_0} - \epsilon_{t}) t'} \mathcal{E}_{\mu_0}^{*}(t') dt' \]

\[ \times (-1)^{-m' + \mu} \left( \begin{array}{ccc} \ell & \ell' & L \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} \ell & \ell' & L \\ m & -m' & m' - m \end{array} \right) \left( \begin{array}{ccc} 1 & 1 & L \\ -\mu & \mu' & m' - m \end{array} \right) \delta_{M, 0}. \]

(34)

Next, we analyze the symmetry properties of \( \beta_{L, m}^{1ph} \) under polarization reversal, i.e., \( \mu_0 \rightarrow -\mu_0 \), which is of interest in view of defining the PECD in Sec. III. We start by considering the fourth 3j Wigner symbol in Eq. (34),

which is the only polarization dependent term in Eq. (34), and denote it by \( S_{1ph}(\mu_0) \). Under polarization reversal,
\[ \mu_0 \rightarrow -\mu_0, \beta_{L, 0}^{(\mu_0) 1ph} \text{ transforms to } \beta_{L, 0}^{(-\mu_0) 1ph}, \text{ and} \]
\[ S_{1ph}(-\mu_0) = \begin{pmatrix} 1 & 1 & L \\ \mu_0 & -\mu_0 & 0 \end{pmatrix} = (-1)^{2+L} \begin{pmatrix} 1 & 1 & L \\ -\mu_0 & \mu_0 & 0 \end{pmatrix}, \]
\[ = (-1)^L S(+\mu_0), \] (35)
due to the symmetry property for the Wigner 3j symbols,
\[ \left( \begin{array}{ccc} j_1 & j_2 & j \\ m_1 & m_2 & m \end{array} \right) = (-1)^{j_1+j_2+j} \left( \begin{array}{ccc} j_1 & j_2 & j \\ -m_1 & -m_2 & -m \end{array} \right). \] (36)

Since no other term depends on \( \mu_0 \), Eq. (35) implies
\[ \beta_{L, 0}^{(+\mu_0) 1ph} = (-1)^L \beta_{L, 0}^{(-\mu_0) 1ph}. \] (37)

For \( \mu_0 = 0 \) (linear polarization), \( S(\mu_0 = 0) \) allows for only even numbers \( k + L \) to be non-zero. Therefore \( \beta_{L=1, M=0}^{(0) 1ph} = 0 \). Furthermore, for \( \mu_0 = \pm 1, L = 1 \) is the only contributing term (up to second order), as it should be, since both the third and fourth Wigner 3j symbol in Eq. (34) are non-zero only for \( 0 \leq L \leq 2 \). This implies \( \beta_{L=0}^{(\mu_0) 1ph} = 0 \). Finally, using Eq. (37), Eq. (6) becomes, under the exchange \( \mu_0 \rightarrow -\mu_0 \),
\[ \frac{d^2 \sigma^{(-\mu_0) 1ph}}{d\epsilon_k d\Omega_K} = \sum_{L=0}^{2} \beta_{L, 0}^{(-\mu_0) 1ph} \mathcal{P}_L^0(\cos \theta_K) \]
\[ = \sum_{L=0}^{2} (-1)^L \beta_{L, 0}^{(\mu_0) 1ph} \mathcal{P}_L^0(\cos \theta_K). \] (38)

B. Anisotropy parameters \( \beta_{L, M}^{(\mu_0) 2ph} \)

Rotating all tensor elements of the dipole interaction in Eq. (21) into the molecular frame leads to

\[
\alpha_{\nu_0}^{k(2)}(t; \gamma_R) = - \sum_{\mu, \mu'} D_{\mu, \mu_0}(\gamma_R) D^{*(\mu)}_{\mu', \mu_0}(\gamma_R) \left[ \langle \Phi_k | \hat{\Phi}_\mu | \Phi_0 \rangle \langle \Phi_0 | \hat{\Phi}_{\mu'} | \Phi_0 \rangle \int_{-\infty}^{t} e^{i (\epsilon_0 - \epsilon_0) t'} \mathcal{E}_{\mu_0}(t') \int_{-\infty}^{t'} \mathcal{E}_{\mu_0}(t'') d t'' d t' \right. \]
\[ + \sum_{\nu \in \text{occ}} \sum_{\gamma \in \text{occ}} \left. \langle \Phi_k | \hat{\Phi}_\mu | \Phi_k \rangle \langle \Phi_k | \hat{\Phi}_{\mu'} | \Phi_k \rangle \int_{-\infty}^{t} e^{i (\epsilon_0 - \epsilon_0) t'} \mathcal{E}_{\mu_0}(t') \int_{-\infty}^{t'} e^{i (\epsilon_0 - \epsilon_0) \mathcal{E}_{\mu_0}(t'')} d t'' d t' \right]. \] (39)

In order to write the final expression as a product of three Wigner rotation matrices — for easy integration over the Euler angles — it is convenient to apply Eq. (33) to the two Wigner rotation matrices in Eq. (39). Defining two-photon tensor matrix elements,
\[ T_{\mu, \mu'}^{(i_0, r)}(k, l, m) = \left\{ \begin{array}{ll} \langle \varphi_{k, \ell, m} | \hat{\Phi}_\mu | \varphi_{i_0} \rangle \langle \Phi_0 | \hat{\Phi}_{\mu'} | \Phi_0 \rangle, & \text{if } r = i_0 \\
\langle \varphi_{k, \ell, m} | \hat{\Phi}_\mu | \varphi_{i_0} \rangle, & \text{if } r > i_0 \end{array} \right. \]
together with the control-dependent quantity
\[ \zeta_{\mu_0}^{(i_0, r)}(t; k) = \left\{ \begin{array}{ll} \int_{-\infty}^{t} e^{i (\epsilon_0 - \epsilon_0) t'} \mathcal{E}_{\mu_0}(t') \int_{-\infty}^{t'} \mathcal{E}_{\mu_0}(t'') d t'' d t', & \text{if } r = i_0 \\
\int_{-\infty}^{t} e^{i (\epsilon_0 - \epsilon_0) t'} \mathcal{E}_{\mu_0}(t') \int_{-\infty}^{t'} e^{i (\epsilon_0 - \epsilon_0) \mathcal{E}_{\mu_0}(t'')} d t'' d t', & \text{if } r > i_0 \end{array} \right. \] (40)

Eq. (39) becomes
\[ \alpha_{\mu_0}^{k(2)}(t; \gamma_R) = - \sum_{\mu, \mu'} \sum_{\ell, m} \sum_{r \geq i_0} T_{\mu, \mu'}^{(i_0, r)}(k, \ell, m) \zeta_{\mu_0}^{(i_0, r)}(t; k) \sum_{Q_1=0}^{2} \mathcal{D}_{\mu, \mu'}^{(Q_1)}(\mu_0) \mathcal{D}_{-\mu, -\mu'}^{(Q_1)}(\gamma_R) Y_{\ell m}(\Omega_k) \] (41)

where
\[ \mathcal{D}_{\mu, \mu'}^{(Q_1)}(\mu_0) \equiv (2Q_1 + 1) \begin{pmatrix} 1 & 1 & Q_1 \\ \mu & \mu' & -\mu - \mu' \end{pmatrix} \begin{pmatrix} 1 & 1 & Q_1 \\ \mu_0 & -\mu_0 & -2\mu_0 \end{pmatrix}. \]

Analogously to the first-order correction, multiplication of Eq. (41) with its complex conjugate, followed by rewriting the product \( Y_{\ell m}^*(\Omega_k) Y_{\ell m'}^*(\Omega_k) \) using Eq. (27), we find
\[ |\alpha_{i_0}^{(2)}(t; \gamma_R)|^2 = \sum_{\mu,\mu'} \sum_{\ell, m \neq i_0} T^{i_{\ell_{\mu'}}}_{\mu,\mu'}(k, \ell, m) c^{\dagger i_{\mu'}}_{\mu_0}(t; k) \sum_{Q_1=0}^2 g_{\mu,\mu'}^{(Q_1)}(\mu_0) \times \sum_{\nu,\nu'} \sum_{\ell', m' \neq i_0} T^{i_{\ell_{\nu'}}}_{\nu,\nu'}(k, \ell', m') c^{\dagger i_{\nu'}}_{\mu_0}(t; k) \sum_{Q_2=0}^2 g_{\nu,\nu'}^{(Q_2)}(\mu_0) \times (-1)^{-m'-\nu'} \sqrt{(2\ell+1)(2\ell'+1)} \sum_{L,M} \left( \begin{array}{ccc} \ell & \ell' & L \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} \ell & \ell' & L \\ m & -m' & m'-m \end{array} \right) \frac{(2L+1)}{4\pi} \sqrt{(L-M)!} \left( \begin{array}{ccc} Q_1 & Q_2 & L \\ -2\mu_0 & 2\mu_0 & -M \end{array} \right) \delta_{M,0} \right). \]

Using Eq. (32), integration of Eq. (42) over the Euler angles gives the anisotropy parameters \(\beta_{L,M}^{(\mu_0)2\text{ph}}\), associated with the two-photon ionization process,

\[ \beta_{L,M}^{(\mu_0)2\text{ph}}(\epsilon_k) = (2\pi)(2L+1) \sum_{\mu,\mu'} \sum_{\ell, m \neq i_0} T^{i_{\ell_{\mu'}}}_{\mu,\mu'}(k, \ell, m) c^{\dagger i_{\mu'}}_{\mu_0}(t; k) \sum_{Q_1=0}^2 g_{\mu,\mu'}^{(Q_1)}(\mu_0) \times \sum_{\nu,\nu'} \sum_{\ell', m' \neq i_0} T^{i_{\ell_{\nu'}}}_{\nu,\nu'}(k, \ell', m') c^{\dagger i_{\nu'}}_{\mu_0}(t; k) \sum_{Q_2=0}^2 g_{\nu,\nu'}^{(Q_2)}(\mu_0) \times (-1)^{-m'-\nu'} \sqrt{(2\ell+1)(2\ell'+1)} \times \left( \begin{array}{ccc} \ell & \ell' & L \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} \ell & \ell' & L \\ m & -m' & m'-m \end{array} \right) \frac{(2L+1)}{4\pi} \sqrt{(L-M)!} \left( \begin{array}{ccc} Q_1 & Q_2 & L \\ -2\mu_0 & 2\mu_0 & -M \end{array} \right) \delta_{M,0} \right) \]

with \(\mu_0 = \pm 1, 0\). Since the last Wigner 3j symbol in Eq. (43) is non-zero only if \(-2\mu_0 + 2\mu_0 - M = 0\), non-vanishing Legendre coefficients are possible only for \(M = 0\). This translates into a symmetry of the photoelectron probability distribution around the \(z'\) axis.

We now evaluate the behavior of \(\beta_{L,0}^{(\mu_0)2\text{ph}}\) under helicity exchange \(\mu_0 \rightarrow -\mu_0\). To this end, we define the fourth Wigner 3j symbol in Eq. (43) by \(S_{2\text{ph}}^{(\mu_0)}(\mu_0)\). Under helicity reversal, it transforms according to

\[ S_{2\text{ph}}^{(-\mu_0)}(\mu_0) = \begin{pmatrix} Q_1 & Q_2 & L \\ +2\mu_0 & -2\mu_0 & 0 \end{pmatrix} = (-1)^{Q_1+Q_2+L} \begin{pmatrix} Q_1 & Q_2 & L \\ -2\mu_0 & +2\mu_0 & 0 \end{pmatrix} = (-1)^{Q_1+Q_2+L} S_{2\text{ph}}^{(+\mu_0)}(\mu_0). \]

Additional \(\mu_0\)-dependent quantities in Eq. (43) are \(g_{\mu,\mu'}^{(Q_1)}(\mu_0)\) and \(g_{\nu,\nu'}^{(Q_2)}(\mu_0)\), both transforming according to

\[ g_{\mu,\mu'}^{(Q_1)}(-\mu_0) = (-1)^{Q_1} g_{\mu,\mu'}^{(Q_1)}(\mu_0), \]
\[ g_{\nu,\nu'}^{(Q_2)}(-\mu_0) = (-1)^{Q_2} g_{\nu,\nu'}^{(Q_2)}(\mu_0). \]

We thus find

\[ S_{2\text{ph}}^{(-\mu_0)} g_{\mu,\mu'}^{(Q_1)}(-\mu_0) = (-1)^L S_{2\text{ph}}^{(+\mu_0)} \times g_{\mu,\mu'}^{(Q_1)}(+\mu_0) \times g_{\nu,\nu'}^{(Q_2)}(+\mu_0), \]

which implies

\[ \beta_{L,M}^{(-\mu_0)2\text{ph}}(\epsilon_k) = \begin{pmatrix} -1 \end{pmatrix} L \beta_{L,M}^{(\mu_0)2\text{ph}}(\epsilon_k). \]

Analogously to \(\beta_{L,0}^{(\mu_0)1\text{ph}}\) and as expected, \(\beta_{L,0}^{(\mu_0)2\text{ph}}\) also changes sign only for odd \(L\) and remains unchanged for even \(L\) when \(\mu_0 \rightarrow -\mu_0\). However, in contrast to \(\beta_{L,0}^{(\mu_0)1\text{ph}}\), for which the only odd contributing order was found to be \(L = 1\), both \(L = 1\) and \(L = 3\) are allowed for \(\beta_{L,M}^{(\mu_0)2\text{ph}}\). In fact, since \(|Q_1 - Q_2| \leq L \leq Q_1 + Q_2\), cf. the fourth Wigner 3j symbol in Eq. (43), and because \(0 \leq Q_1 \leq 2\) and \(0 \leq Q_2 \leq 2\), the possible values for \(L\) are \(0 \leq L \leq 4\). Finally, under polarization reversal, Eq. (9) becomes

\[ \frac{d^2 \sigma^{(\mu_0)2\text{ph}}}{d\epsilon_k d\Omega_{k'}} = \sum_{L=0}^{4} \beta_{L,0}^{(-\mu_0)2\text{ph}}(\epsilon_k) P_L^0(\cos \theta_{k'}) \]
\[ = \sum_{L=0}^{4} \begin{pmatrix} -1 \end{pmatrix} L \beta_{L,0}^{(+\mu_0)2\text{ph}}(\epsilon_k) P_L^0(\cos \theta_{k'}). \]

C. Anisotropy parameters \(\beta_{L,M}^{(\mu_0)\text{int}}\)

Using Eq. (30) and Eq. (41) for the first and second order corrections, respectively, we obtain, after rotation of the product \(Y_{\ell_{\mu}}^m(\Omega_k) Y_{\ell_{\nu}}^{m'}(\Omega_k)\) from the molecular to the laboratory frame, according to Eq. (27),
\[ a_{t_0}^{(1)}(t; \gamma) a_{t_0}^{(2)}(t; \gamma) = -\frac{i}{4\pi} (-1)^{-\mu_0} \sum_\mu \sum_{\ell, m} M^\mu_{\ell, m} \int_{-\infty}^t e^{-i(k R - \omega_0) t'} c_{\mu_0}(t') \ dt' \]

\[ \times \sum_{\nu, \nu', \ell, m, \ell', m'} \sum_{r \geq 0} 2 T^{\nu, \nu', r}_{\ell, \ell'}(k, \ell', m') c^{\nu, \nu', r}_{\mu_0}(t; k) g^{(Q)}_{\nu', \nu'}(\mu_0) \]

\[ \times (-1)^{-\mu' - \nu - \nu'} \sqrt{(2\ell + 1)(2\ell' + 1)} \left( \frac{\ell}{0} \frac{\ell'}{0} \right) \left( \frac{L}{m} \frac{L}{m'} \right) (-\mu' + \nu' + m' - m) \]

\[ \times \sum_{M = -L}^L \frac{(L - M)!}{(L + M)!} \left[ D^{(1)}_{-\mu, -\mu_0} (\gamma_R) D^{(Q)}_{\nu + \nu', 2\mu_0} (\gamma_R) D^{(L)}_{m - m', -M} (\gamma_R) \right] \times P^M_L (\cos \theta_k') e^{iM \phi_k'} \]

Integrating Eq. (48) over the Euler angles gives the (complex) anisotropy parameters associated with the interference term, as defined in Eq. (8). Orientation averaging determines the possible values of \( M \) in Eq. (9). In fact, using the equality

\[ \int \frac{d^3 \gamma_R}{8\pi^2} \left( \begin{array}{cccc} 1 & Q & L & \mu_0 \nu' - \nu \mu \phi \gamma \\ -\mu & \nu' + \nu & m' - m & 2\mu_0 - M \end{array} \right) = \delta_{M, M_0} \]

i.e., \( M = \mu_0 \). Therefore, Eq. (9) is reduced to

\[ \frac{d^2 \sigma^{(\mu_0)_{int}}}{d\ell_k d\Omega_{k'}} = \sum_{L=0}^3 \left[ \beta^{(\mu_0)_{int}}_{L, \mu_0} (\epsilon_k) e^{i\mu_0 \phi_k'} + \beta^{(\mu_0)_{int}}_{L, \mu_0} (\epsilon_k) e^{-i\mu_0 \phi_k'} \right] P^\mu_L (\cos \theta_k') \]

From Eq. (51), it is apparent that for \( \mu_0 = \pm 1 \), the portion of the momentum distribution due to the interference between one-photon and two-photon ionization pathways breaks the azimuthal symmetry of photoelectron emission around the light propagation direction \( z' \). This is in contrast to the contributions from \( \beta^{(\mu_0)_{1ph}}_{L, 0} \) and \( \beta^{(\mu_0)_{2ph}}_{L, 0} \) which we found to be symmetric around \( z' \). The anisotropy parameter due to interference is obtained upon the integration of Eq. (48) over the Euler angles using Eq. (49) and reads

\[ \beta^{(\mu_0)_{int}}_{L, \mu_0} (\epsilon_k) = -2i\pi (2L + 1) \sum_{\mu} \sum_{\ell, m} M^\mu_{\ell, m} \int_{-\infty}^t e^{-i(k R - \omega_0) t'} c_{\mu_0}(t') \ dt' \times \sum_{\nu, \nu', \ell', m'} \sum_{r \geq 0} 2 T^{\nu, \nu', r}_{\ell, \ell'}(k, \ell', m') c^{\nu, \nu', r}_{\mu_0}(t; k) \]

\[ \times (-1)^{-\mu' - \nu + \nu'} \sqrt{(2\ell + 1)(2\ell' + 1)} \left( \frac{\ell}{0} \frac{\ell'}{0} \right) \left( \frac{L}{m} \frac{L}{m'} \right) (-\mu' + \nu' + m' - m) \]

\[ \times \sum_{M = -L}^L \frac{(L - M)!}{(L + M)!} \left[ D^{(1)}_{-\mu, -\mu_0} (\gamma_R) D^{(Q)}_{\nu + \nu', 2\mu_0} (\gamma_R) D^{(L)}_{m - m', -M} (\gamma_R) \right] \times P^M_L (\cos \theta_k') \]

Since \( Q = 0, 1, 2 \), it is apparent from the fourth Wigner 3j symbol in Eq. (52) that \( L = 4 \) cannot contribute. Furthermore, if \( \mu_0 = \pm 1 \), it also the \( L = 0 \) term vanishes, and the allowed values are \( L = 1, 2, 3 \) for circularly polarized light, which explains the upper limit in the summation over \( Q \) in Eq. (51).

The symmetry properties of \( \beta^{(\mu_0)_{int}}_{L, \mu_0} \) under polarization reversal are analyzed using the same technique as for the one-photon and two-photon terms. It is worth pointing out, however, that evaluation of symmetry properties of Eq. (51) under polarization reversal also requires evaluation of the angular functions under \( \mu_0 \rightarrow -\mu_0 \) if \( \mu_0 = \pm 1 \). As previously discussed, the term \( g^{(Q)}_{\nu', \nu'}(\mu_0) \) in the rhs of
Eq. (52) transforms according to
\[
g_{\nu,\nu'}^{(Q)}(-\mu_0) = (-1)^Q g_{\nu,\nu'}^{(Q)}(+\mu_0). \tag{53a}
\]
Analogously, the fourth Wigner 3j symbol in Eq. (52), denoted by \( S_{int}(\mu_0) \), changes, under \( \mu_0 \to -\mu_0 \), as
\[
S_{int}(-\mu_0) = (-1)^{1+Q+L} \begin{pmatrix} 1 & Q & L \\ +\mu_0 & -2\mu_0 & +\mu_0 \end{pmatrix} = (-1)^{1+Q+L} S(\mu_0). \tag{53b}
\]
Finally, defining
\[
B(\mu_0) = \sqrt{(L - \mu_0)! / (L + \mu_0)!},
\]
it is straightforward to show that
\[
B(-\mu_0) = B(+\mu_0) \times \frac{(L + \mu_0)!}{(L - \mu_0)!}. \tag{53c}
\]
Using Eqs. (53)(a)-(c), the anisotropy parameter \( \beta^{(-\mu_0)int}(\epsilon) \) behaves as
\[
\beta^{(-\mu_0)int}_{-L,-\mu_0} = (-1)^{1+L} \frac{(L - \mu_0)!}{(L + \mu_0)!} \times \beta^{(+\mu_0)int}_{L,+\mu_0} \tag{54}
\]
For the azimuthal dependency of Eq. (51), the transformation under helicity exchange is trivial. As for the associated Legendre polynomials \( P_L^M(\cdot) \), we use the well-known property
\[
P_L^{-M}(X) = (-1)^{-M} \frac{(L - M)!}{(L + M)!} \times P_L^M(X), \tag{55}
\]
which, together with Eq. (54), allows us to write the transformed Eq. (51), for \( \mu_0 = \pm 1 \),
\[
\frac{d^2\sigma^{(-\mu_0)int}}{d\epsilon_k d\Omega_k'} = 2 \sum_{L=0}^{3} (-1)^L \left[ \cos(\mu_0 \phi_{k'}) \text{Re} \left[ \beta^{(+\mu_0)int}_{L,+\mu_0} \right] \right] P_{L+\mu_0}^+(\cos \theta_{k'}) \tag{56}
\]
\begin{align*}
\text{III. PHOTOELECTRON CIRCULAR DICHROISM} \nonumber
\end{align*}

The PECD is defined as the non-vanishing component of the differential photoelectron signal obtained with left and right circularly polarized light,
\[
\text{PECD}(\epsilon_k, \theta_{k'}, \phi_{k'}) = \frac{d^2\sigma^{(+\mu_0)}_{\mu_0}}{d\epsilon_k d\Omega_k'} - \frac{d^2\sigma^{(-\mu_0)}_{\mu_0}}{d\epsilon_k d\Omega_k'}. \tag{57}
\]
Both terms on the rhs of Eq. (57) contain the contributions defined in Eq. (5), i.e., contributions from the one-photon and two-photon ionization pathways and their interference. Therefore, we can analyze the PECD associated with each of these pathways. In particular,
\[
\frac{d^2\sigma^{(+\mu_0)1ph}}{d\epsilon_k d\Omega_k'} - \frac{d^2\sigma^{(-\mu_0)1ph}}{d\epsilon_k d\Omega_k'} = \sum_{j} 2\beta_{2j+1,+\mu_0}^{(\mu_0)1ph} P_{2j+1}^0 \cos(\theta_{k'}) \nonumber
\]}
\begin{align*}
\text{gives the contribution of the one-photon ionization pathways to the PECD. The contribution from the two-photon ionization pathways is obtained as}
\end{align*}
\[
\frac{d^2\sigma^{(+\mu_0)2ph}}{d\epsilon_k d\Omega_k'} - \frac{d^2\sigma^{(-\mu_0)2ph}}{d\epsilon_k d\Omega_k'} = 2\beta_{1,0}^{(+\mu_0)2ph} P_{1,0}^0 \cos(\theta_{k'}) + 2\beta_{3,0}^{(+\mu_0)2ph} P_{3,0}^0 \cos(\theta_{k'}). \tag{58b}
\]
Finally, the contribution of the interference between one-photon and two-photon ionization pathways reads
\[
\frac{d^2\sigma^{(+\mu_0)int}}{d\epsilon_k d\Omega_k'} - \frac{d^2\sigma^{(-\mu_0)int}}{d\epsilon_k d\Omega_k'} = 4 \cos(\mu_0 \phi_{k'}) \sum_{j} \text{Re} \left[ \beta_{2j+1,+\mu_0}^{(+\mu_0)int} P_{2j+1}^{+\mu_0}(\cos \theta_{k'}) \right] - 4 \sin(\mu_0 \phi_{k'}) \sum_{j} \text{Im} \left[ \beta_{2j,+\mu_0}^{(+\mu_0)int} P_{2j}^{+\mu_0}(\cos \theta_{k'}) \right]. \tag{58c}
\]
Equation (58c) implies that, in the \((z', y')\)-plane, i.e., for \( \phi_{k'} = \pi/2 \), PECD due to the interference term depends on the associate Legendre polynomials of even order. PECD thus changes sign in the forward and backward direction defined by the intervals \( \theta_k \in [0, \pi/2] \) and \( \theta_k \in [-\pi/2, \pi] \), respectively. Conversely, projection of Eq. (58c) into the \((z', x')\)-plane leads to an odd-order dependency, which does not change sign between forward and backward directions. In fact, the associate Legendre polynomials are either even or odd according to
\[
P_L^M(-X) = (-1)^{L+M} P_L^M(X) \tag{58d}
\]
with \( M \equiv \mu_0 \) and where \( X \equiv \cos(\theta_{k'}) \) changes sign in the forward and backward directions. Choosing \( \phi_{k'} = \pi/2 \) and accounting for the fact that \( L = 2 \) is the possible even order for non-vanishing \( \beta^{(\mu_0)int}_{L,+\mu_0} \) for \( \mu_0 = \pm 1 \) as discussed in Section IIIC, Eq. (58c) becomes
\[
\frac{d^2\sigma^{(\mu_0)int}}{d\epsilon_k d\Omega_k'} |_{\phi_{k'}=\pi/2} = 6 \text{Im} \left[ \beta_{2,+1}^{(\mu_0)int} \right] \sin(2\theta_{k'}), \tag{58e}
\]
where we have used \( P_2^1(\cos \theta) = -3 \cos(\theta) \sin(\theta) \) together with the trigonometric identity \( \sin(2\theta) = 2 \cos(\theta) \sin(\theta) \).

Finally, accounting for the contributions from one-photon and two-photon ionization pathways and their interference, given by Eqs. (58a), (58b) and (58e), Eq. (57) becomes
\[
\text{PECD}(e_k, \theta_{k'}, \phi_{k'}) = \pi/2 = 2 \left[ \beta_{1,0}^{(1+1)ph}(e_k) + \beta_{1,0}^{(1+2)ph}(e_k) \right] P_1^0(\cos \theta_{k'}) + 2 \beta_{0,1}^{(2+1)ph}(e_k) P_3^0(\cos \theta_{k'}) + 6 \text{Im} \left[ \beta_{2,1}^{(1+int)(e_k)} \right] \sin(2\theta_{k'}) .
\] (59)

IV. INPUT FILE PARAMETERS FOR MOLPRO

```
# MOLPRO Program package [10, 11] input file
***,CHFClBr gs
RCH = 1.8 ANG
TANG = 109.471220634491 DEGREES
RCCl = 2.4 ANG
RCBr = 2.5 ANG
RCF = 2.5 ANG
cartesian geometry={
  C1; H1,C1,RCH; Cl2,C1,RCCl,H1,TANG;
  Br3,C1,RCBr,H1,TANG,C12,TANG,1;
  F4,C1,RCF,H1,TANG,C12,TANG,-1;
}
basis=avdz
{ rhf;
  wf,68,1,0;}
put, molden, chfclbr.molden;
optg;
```
Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, D. P. O’Neill, P. Palmieri, D. Peng, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, and M. Wang, “Molpro, version 2012.1, a package of ab initio programs,”.

[11] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, and M. Schtz, Wiley Interdisciplinary Reviews: Computational Molecular Science 2, 242 (2012).