# Quantum Mechanical Polarizable Continuum Model Approach to the Kerr Effect of Pure Liquids

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A quantum mechanical methodology, working within the framework of the polarizable continuum model (PCM), yielding quantities directly comparable with data extracted from Kerr experiments of liquids, is presented. The procedure permits us to obtain the final molar property (specifically, the Kerr constant) in terms of effective molecular dipoles and (hyper)polarizabilities. The latter are obtained through an ab initio description of the molecule of interest when it is mutually interacting with the surrounding medium, which is represented by a continuum dielectric. Effects due to the liquid macroscopic polarization yielded by the output wave are also included. Numerical applications, and comparison with experiments, are presented for a selection of pure liquids.

## I. Introduction

The Kerr effect, i.e., the linear birefringence, which is observed when a (strong) electric field is applied perpendicular to the direction of propagation of linearly polarized light traversing an isotropic sample, plays an important role in the study and design of chromophores providing great enhancements of electrooptical response in amorphous organic materials, as discussed by R. Wortmann and co-workers.[1,2] Also, the electrooptic variant of the classical Kerr experiment, where weak and very low frequency electric fields are employed, has been used to monitor and affect the intramolecular motion in rotaxanes, with interesting implications in nanotechnology.[3] The time-resolved optical Kerr effect has been used to study the dynamical behavior of pure liquids, solutions, liquid, and plastic crystals.[4,5] More generally, the Kerr effect is a viable tool, when combined with other birefringences or other optical experiments, for the determination of the molecular permanent dipole moment, electric dipole polarizabilities, and first and second hyperpolarizabilities.[6−9]

The effect has been known since 1875, e.g., since the observation made by John Kerr,[10,11] who first measured the birefringence developing on glasses[10] and, subsequently, on liquids.[11] Today, liquids are still the preferred samples for the measurement of this effect.

The first attempts at a theoretical rationalization of the Kerr effect began in the early years of the last century, and the story behind the progress of knowledge of such an effect is well described in refs 12 and 13. An important contribution came fifty years ago due to Buckingham and Pople,[14] who derived an expression relating the observable quantity, the linear birefringence, to the microscopic molecular properties *in dilute (ideal) gases*. Buckingham discussed the frequency dependence of the effect[15] and that of pressure.[16] In the latter study, a statistical−mechanical theory of the Kerr effect which could also be applied to the condensed phase was presented.

In recent times, thanks to the fast progress in computational chemistry, there has been a renewed interest in studying the general phenomenon of birefringences,[17] a subject of great challenge for theory, computational science, and experiment. Most of the work has been centered on other processes involving mixed electric and magnetic fields, but attention has also been paid to the Kerr effect of species such as benzene,[18] hexafluorobenzene,[19] and very recently molecular oxygen,[20] all in the gas phase. Although the experiment in the gases requires a more elaborate setup than needed for studies in the condensed phase, the complications arising in the theoretical description of optical properties in liquids, as discussed in ref 16, make their ab initio calculation far more challenging.[21] For a discussion of some of the aspects of the optical Kerr effect in solutions and in pure liquids, the reader is also referred to refs 22 and 23.

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A theoretical understanding of optical properties for systems in the condensed phase can provide significant help in the rationalization of experiments and in the prediction of the response of experimentally impracticable molecular systems. The increasing efforts devoted to investigations of high-order properties of solvated molecules and liquids follow the success of modern quantum chemical tools in the prediction of the same properties for isolated systems. The approach, which is generally adopted in the modeling of solvated systems, consists of applying the same methodologies developed so far for the isolated systems, with the additional introduction of solvent-dependent peculiarities. Among them, we cite the fact that the presence of the solvating environment modifies the geometry and the electronic density of the molecule and modifies the electric field of the incident radiation, which has thus to be redefined. Also, nonequilibrium solvent effects in response to the external perturbation (connected to motions of solvent molecules around the solute) as well as, in some cases, specific aggregation effects can be relevant.

Among the various solvent-induced effects just mentioned, a key point is the definition of the relation between the molecular and the material properties, i.e., the distinction between the microscopic field at a molecule and the macroscopic field applied to the material. Obviously, the latter is determined by the experimental conditions, but a suitable theory is needed to define the microscopic field. The most common approach to this matter is the use of the Onsager−Lorentz model[24] which defines the different molecular properties for the systems in the condensed phase in terms of the corresponding gas-phase values multiplied by suitable "local field" factors.[6]

A more general framework to treat local field effects in linear and nonlinear optical processes in solution has been pioneered, among others,[25] by Wortmann and Bishop.[26] Still, by using a classical Onsager reaction field model, one can introduce the solvent effects in two steps. First, the solute polarizability is defined by taking into account all the effects caused by the static reaction field induced by the solute dipole. Secondly, an effective polarizability is defined to include the effects due to the difference between the local field acting on solute molecules and the macroscopic optical field (Maxwell field) in the medium. Note that the Lorentz correction for the local field can be viewed as a special case of the more general reaction field model.

The approach leading to effective polarizabilities has been reformulated within the quantum mechanical polarizable continuum model (PCM)[27] framework by some of the present authors.[28] Within this method, the effective properties are obtained by introducing into an ab initio response equation scheme the proper terms representing the interaction with both the solvent reaction field and the Maxwell field in the medium, thus leading to an ab initio evaluation of the corresponding macroscopic susceptibilities. This method has been applied to several linear and nonlinear optical processes[21,28,29] and spectroscopies[30−32] in the liquid phase, including the Cotton−Mouton magnetic field induced birefringence,[33] and is able to give calculated properties of solvated systems directly comparable with those of experimental counterparts.

Another aspect to be taken into account in the calculation of molecular properties in a condensed medium is the case of systems constituted by "identical chromophores", i.e., pure liquids. In a typical nonlinear optical experiment, the presence of a large number of chromophores perturbed by the optical radiation at a fixed (fundamental) frequency produces a macroscopic nonlinear polarization which, in turn, acts as a source of an additional perturbing field. As a result, the nonlinear response of each chromophore arises from both the nonlinear response to the fundamental field and the linear response to the perturbing field at the output frequency. The analysis of this effect, which is usually done in terms of classical local field factors, has been extended to the PCM calculation of the effective polarizabilities needed for the evaluation of macroscopic susceptibilities of pure liquids.[34] In the present paper, the same methodology is applied to the evaluation of the Kerr effect of a selected set of pure liquids.

The paper is organized as follows. In section II, after a brief introduction of the phenomenological descriptors of the Kerr effect in pure liquids, a theoretical scheme for the evaluation of the molar Kerr constant in terms of effective molecular polarizabilities is presented. The theory developed here is limited to the formulation of the electronic contributions to the effects, such that vibrational effects are completely neglected. Section III reports the application of the theory developed here to a few simple pure liquids, namely, $C_6H_6$ (benzene), $C_6H_5F$ (fluorobenzene), $C_5H_5N$ (pyridine), $C_3H_6O$ (acetone), $C_6H_5CN$ (benzonitrile), $C_6H_5NO_2$ (nitrobenzene), $CH_3CN$ (acetonitrile), and $CH_2\text{=}CH-CN$ (acrylonitrile), and to the comparison between calculated and experimental findings. Section IV closes the paper with a critical discussion of the numerical results and some conclusions.

## II. Theory: The Kerr Effect in Condensed Systems

In the Kerr effect, a birefringence arises when linearly polarized light traverses a sample in a direction perpendicular to an applied external electric field, $\mathbf{E}$. Let us indicate with $n_{\parallel}$ the refractive index for the polarization component parallel to the external field and indicate with $n_{\perp}$ the one for the polarization component perpendicular to the field. The Kerr constant, $B_K$, for systems in the condensed phase is defined as

$$B_K = \frac{n_{\parallel} - n_{\perp}}{n} \frac{1}{E^2} = \frac{\Delta n(\lambda)}{n} \frac{1}{E^2} \tag{1}$$

[6,35,36] The corresponding "molar" Kerr constant has been defined by Le Fèvre et al.[12] as

$$_mK = \frac{6nV_m}{(n^2 + 2)^2(\epsilon + 2)^2} \frac{\Delta n(\lambda)}{E^2} \tag{2}$$

In eqs 1 and 2, $n$ and $\epsilon$ are the refractive index and the static dielectric permittivity of the liquid, respectively, $V_m$ is the molar volume, and $E^2$ is the electric field strength in the liquid medium.

The molar Kerr constant $_mK$ in eq 2 is not a direct experimental quantity in that it accounts, with a modelistic approximation, for the fact that the "local" static ($\mathbf{E}^{loc}$) and optical ($\mathbf{E}_{\omega}{}^{loc}$) electric fields acting on molecules in the liquid phase differ from the corresponding Maxwell fields, $\mathbf{E}$ and $\mathbf{E}_{\omega}$, in the medium. In particular, it is assumed that[6]

$$\mathbf{E}_{\omega}{}^{loc} = \frac{n^2 + 2}{3}\mathbf{E}_{\omega} \qquad \mathbf{E}^{loc} = \frac{\epsilon + 2}{3}\mathbf{E} \tag{3}$$

where the factors have been introduced within the Onsager's (Lorentz) theory of electric polarization (a polarizable point dipole in a spherical cavity in a continuum dielectric). This approximation is motivated by the attempt to relate the macroscopic molar Kerr constant of the liquid with the microscopic electric response properties of its constituents in the gas phase.

As already mentioned in the Introduction, still keeping a continuum solvation approach,[37,38] we have proposed a general

formulation of the local field problem by introducing the concept of "effective" molecular response properties, which directly describe the response of the molecular solutes to the Maxwell field in the liquid, both static $\mathbf{E}$ and dynamic $\mathbf{E}_\omega$.[28−30]

The definition of the effective polarizabilities comes from the expansion of the molecular dipole in terms of the Maxwell field in the medium[29]

$$\tilde{\mu}_a(\omega) = \tilde{\alpha}_{ab}(-\omega;\omega)E_b^\omega + \tilde{\beta}_{abc}(-\omega;\omega, 0)E_b^\omega E_c + \frac{1}{2}\tilde{\gamma}_{abcd}(-\omega;\omega, 0, 0)E_b^\omega E_c E_d + ... \quad (4)$$

where we indicate with $\tilde{\mu}(\omega)$ the Fourier component of the dipole moment induced by the optical field $\mathbf{E}_\omega$. A protocol for the evaluation of such effective molecular response properties within the framework of the PCM with application to several spectroscopic and linear and nonlinear optical processes has recently been developed.[28−33] In particular, in refs 29 and 33, the evaluation of the molar contribution to the refractive index and to nonlinear optical susceptibilities is reported. In the following, the extension of such an approach to the Kerr effect is described.

To show how to formulate the Kerr birefringence within the effective polarizability scheme, it is convenient to remove the local field factor from the Kerr molar constant of eq 2 and define a "modified" molar Kerr constant $_m\tilde{K}(\lambda, T)$

$$_m\tilde{K}(\lambda, T) = {}_mK\frac{(n^2 + 2)^2}{9}\frac{(\epsilon + 2)^2}{9} \quad (5)$$

Following Buckingham and Pople,[14] the molar Kerr constant is defined as

$$_mK = \lim_{\mathbf{E}\to 0}\frac{2n\Delta n V_m}{27E^2} \quad (6)$$

In Kerr experiments, the refractive indexes of the liquid at the frequency $\omega$ for the light polarization component $\delta$ parallel and perpendicular to the applied field $n_\delta^\omega$ are related to the first-order susceptibility $\chi^{(1)}(-\omega;\omega)$ and the Kerr susceptibility $\chi_{ZZXX}^{(3)}(-\omega;\omega, 0, 0)$ (the Cartesian indexes refer to an arbitrary chosen laboratory frame)

$$(n_\delta^\omega)^2 - 1 = Re\chi^{(1)}(-\omega;\omega) + 3\chi_{ZZ\delta\delta}^{(3)}(-\omega;\omega, 0, 0)\mathbf{E}_\delta^0\,\mathbf{E}_\delta^0 \quad (7)$$

The refractive index anisotropy induced by the static field is then given by

$$\frac{\Delta n(\omega)}{E^2} = \frac{3[\chi_{ZZZZ}^{(3)}(-\omega;\omega, 0, 0) - \chi_{ZZXX}^{(3)}(-\omega;\omega, 0, 0)]}{2n} \quad (8)$$

The effective molar Kerr constant may be expressed in terms of the Kerr susceptibilities as (see also ref 2)

$$_m\tilde{K} = \frac{V_m}{9}[\chi_{ZZZZ}^{(3)}(-\omega;\omega, 0, 0) - \chi_{ZZXX}^{(3)}(-\omega;\omega, 0, 0)] \quad (9)$$

where $\chi_{a\alpha\beta\gamma}^{(3)}(-\omega;\omega, 0, 0)$ can be derived from a Boltzmann average of the Fourier component of the molecular dipole

moment (eq 4), namely

$$\chi_{a\alpha\beta\gamma}^{(3)}(-\omega;\omega, 0, 0) = \frac{N_A}{3}\frac{\partial^3}{\partial E_\alpha^\omega \partial E_\beta^0 \partial E_\gamma^0}\langle w\tilde{\mu}_a(\omega)\rangle \quad (10)$$

$N_A$ is the Avogadro number and $\langle\ \rangle$ denotes a statistical−mechanical average over the orientations. The canonical distribution function describing the molecular orientation is

$$w = \frac{\exp(-W/kT)}{\langle\exp(-W/kT)\rangle}$$

where $W$ represents the energy of a molecule with respect to the orientation of the static component of the Maxwell field, i.e., up to the second order

$$W = -\mu*\mathbf{E}^0 - \frac{1}{2}\alpha*\mathbf{E}^0\mathbf{E}^0 + ... \quad (11)$$

The "star" quantities are defined as

$$\mu_a^* = \frac{\partial G}{\partial E_a} \quad (12)$$

$$\alpha_{ab}^* = \frac{\partial^2 G}{\partial E_a \partial E_b} \quad (13)$$

where $G$ is the electrostatic free energy.

Following the treatment usually adopted in the gas phase (see, for example, ref 6 in combination with eq 11), the effective molar Kerr constant $_m\tilde{K}$ defined in eq 5 can now be determined in terms of the effective (hyper)polarizabilities as

$$_m\tilde{K}(\lambda, T) = A + B + C + D$$

$$A = \frac{N_A}{54\epsilon_0}\tilde{\gamma}_K(\omega)$$

$$B = \frac{N_A}{54\epsilon_0}\left[\frac{\sum_a\sum_b\tilde{\alpha}_{ab}(\omega)\alpha_{ab}^* - 3\tilde{\alpha}_{iso}(\omega)\alpha_{iso}^*}{5kT}\right]$$

$$C = \frac{N_A}{54\epsilon_0}\left[\frac{4\sum_a\sum_b\mu_a^*\tilde{\beta}(\omega, 0)_{abb}}{15kT}\right]$$

$$D = \frac{N_A}{54\epsilon_0}\left[\frac{\sum_a\sum_b\tilde{\alpha}_{ab}(\omega)\mu_a^*\mu_b^* - \tilde{\alpha}_{iso}(\omega)|\mu^*|^2}{5(kT)^2}\right] \quad (14)$$

with

$$\tilde{\alpha}_{iso}(\omega) = \frac{\sum_a\tilde{\alpha}_{aa}(\omega)}{3} \quad (15)$$

$$\tilde{\gamma}_K = \sum_{a,b,c,d}\tilde{\gamma}_{abcd}(\omega, 0, 0)\frac{(-2\delta_{ab}\delta_{cd} + 3\delta_{ac}\delta_{bd} + 3\delta_{ad}\delta_{bc})}{30} \quad (16)$$

Note that eq 14 is formally identical to the expression which applies to the case of dilute gases,[6] where all the tildes and stars are taken away, i.e., where the properties assume their usual

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gas-phase expression. In eq 14, the Kerr constant has explicitly been divided into four terms on the basis of their dependence on the temperature. In particular, $A$, which is independent of $T$, is connected to the molecular electronic reorganization as a response to the external field, whereas the other terms (all dependent on $T$) represent the orientational response at the various orders to the external static field.

In the following section, a summary of the protocol for the quantum mechanical evaluation of the effective molecular response properties entering eq 14 in the PCM framework is presented.

**A. Quantum Mechanical Formulation of the Kerr Effect in the Condensed Phase.** Within the framework of dielectric continuum models (as PCM), the effective field experienced by the molecule in the cavity can be seen as the sum of a reaction field term and a cavity field term. The reaction field is connected to the response (polarization) of the dielectric to the solute charge distribution, whereas the cavity field depends on the polarization of the dielectric induced by the applied field once the cavity has been created.

In the PCM, reaction field effects are introduced by adding suitable operators to the Fock operator of the isolated molecule.[39] In a matrix formalism, employing a suitable expansion basis set, we represent such operators by the matrices $\mathbf{j}$ and $\mathbf{X}(\mathbf{R})$. These are constructed in terms of a discretized charge distribution spread on the cavity surface, which accounts for solute−solvent mutual polarization effects. The general expression of the Fock matrix for a solute in a solvent is given by

$$\mathbf{F} = \mathbf{h}^0 + \mathbf{j} + \mathbf{G}^0(\mathbf{R}) + \mathbf{X}(\mathbf{R}) \qquad (17)$$

where $\mathbf{h}^0$ and $\mathbf{G}^0(\mathbf{R})$ are the usual one- and two-electron matrices for the solute in vacuo and $\mathbf{R}$ is the solute density matrix.

By analogy with the Onsager's theory of electric polarization, we can assume that the response of the molecule to an external probing field can be expressed in terms of an "external dipole moment" sum of the molecular dipole moment and the dipole moment arising from the molecule-induced dielectric polarization. Following refs 28 and 30, the latter is

$$\tilde{\mu}_a^{\mathrm{sol}} = -\mathrm{tr}[\mathbf{R}\tilde{\mathbf{m}}_a] + \tilde{\mu}_{N,a}^{\mathrm{sol}} \qquad (18)$$

where $\tilde{\mu}_{N,a}^{\mathrm{sol}}$ indicates the nuclear contribution to the $a$th component of $\tilde{\mu}^{\mathrm{sol}}$.[30] The $\tilde{\mathbf{m}}_a$ matrix in eq 18 is defined starting from an additional charge distribution spread on the cavity surface (the external charge). Using the standard boundary element method, we discretize this charge into a set of pointlike charges, $q^{\mathrm{ex}}$, placed on representative points, $\mathbf{s}_l$, on the cavity surface. Within this formalism

$$\tilde{\mathbf{m}}_a = -\left(\sum_l \mathbf{V}(\mathbf{s}_l)\frac{\partial q_l^{\mathrm{ex}}}{\partial E_a}\right) \qquad (19)$$

where $\mathbf{V}(\mathbf{s}_l)$ are potential integrals evaluated at the point $\mathbf{s}_l$.

The effective electric properties, which include the cavity field contribution and directly represent the "in situ" response of the solute to variations in the Maxwell fields in the medium, are calculated by exploiting a coupled perturbed (CP) scheme.[40]

$$\tilde{\alpha}_{ab}(-\omega;\omega) = -\mathrm{tr}[\mathbf{m}_a\mathbf{R}^b(\omega)]$$

$$\tilde{\beta}_{abc}(-\omega_\sigma;\omega_1, \omega_2) = -\mathrm{tr}[\mathbf{m}_a\mathbf{R}^{bc}(\omega_1, \omega_2)] \qquad (20)$$

$$\tilde{\gamma}_{abcd}(-\omega_\sigma;\omega_1, \omega_2, \omega_3) = -\mathrm{tr}[\mathbf{m}_a\mathbf{R}^{bcd}(\omega_1, \omega_2, \omega_3)]$$

where $\omega_\sigma = \sum_i \omega_i$ and, in the present study, $\omega_1 = \omega$ and $\omega_2 = \omega_3 = 0$. The trace operation is on the dipole integrals matrix $\mathbf{m}$; the derivatives of the solute density matrix are $\mathbf{R}^b$, $\mathbf{R}^{bc}$, and $\mathbf{R}^{bcd}$ with respect to the applied field obtained as solutions of the CP equations with an effective Fock matrix, which includes an explicit term due to the presence of the field given by

$$\tilde{\mathbf{F}} = \mathbf{F}(0) + \sum_a [\mathbf{m}_a + \tilde{\mathbf{m}}_a](\omega)E_a(e^{i\omega t} + e^{-i\omega t}) \qquad (21)$$

**B. Kerr Effect of Pure Liquids: Contribution of the Output Wave.** The extension of the concept of effective polarizabilities to pure liquids introduces further issues. In fact, an optical radiation at frequency $\omega$ produces, in the liquid, a macroscopic nonlinear polarization density at the same frequency $(\mathbf{P}^\omega)^{\mathrm{NL}}$, which acts as a source of an additional perturbing field. The response of each molecule of the liquid to such a field can be represented in terms of the effective polarizability $\ddot{\alpha}(-\omega;\omega)$.[34] The induced effective dipole previously introduced in eq 4 thus becomes

$$\tilde{\mu}_a(\omega) = \ddot{\alpha}_{ab}(-\omega;\omega)(P_b^\omega)^{\mathrm{NL}} + \tilde{\alpha}_{ab}(-\omega;\omega)E_b^\omega +$$
$$\tilde{\beta}_{abc}(-\omega;\omega, 0)E_b^\omega E_c +$$
$$\frac{1}{2}\tilde{\gamma}_{abcd}(-\omega;\omega, 0, 0)E_b^\omega E_c E_d + \dots \quad (22)$$

In eq 22, the effective quantities indicated with a tilde have the same meaning as those in the previous section. $(\mathbf{P}^\omega)^{\mathrm{NL}}$ can be obtained by[34]

$$(P_a^\omega)^{\mathrm{NL}} = 3\chi_{abcd}^{(3)}(-\omega;\omega, 0, 0)E_b^\omega E_c E_d \qquad (23)$$

By using eq 22 in the derivation of eq 14 and by using standard orientational averaging methods, we obtain the following expression of the effective molar Kerr constant for pure liquids.

$$_m\tilde{K}^{\mathrm{pl}}(\lambda, T) = \frac{_m\tilde{K}(\lambda, T)}{1 - \rho\ddot{\alpha}_{\mathrm{iso}}(-\omega;\omega)} \qquad (24)$$

where $_m\tilde{K}(\lambda, T)$ indicates the effective molecular response to the applied Maxwell field given in eq 14.

The denominator of eq 24 represents the effect of the polarization density as a source field, and it depends on the number density of the liquid $\rho$ and on the effective polarizability $\ddot{\alpha}(-\omega;\omega)$ through its average value, defined as one-third of the trace of the corresponding tensor. Such a polarizability represents the response of the medium to the field generated by $(\mathbf{P}^\omega)^{\mathrm{NL}}$. This effect is analogous to the so-called "cascade effect"[25,41−43] at a frequency equal to that of the fundamental field.

To obtain $\ddot{\alpha}(-\omega;\omega)$, a scheme similar to that described in the previous section can be used: an additional set of apparent surface charges, $\ddot{q}_\omega^{\mathrm{ex}}$, is introduced, and they correspond to the apparent charges representing the electrostatic potential produced by the polarization density $(\mathbf{P}^\omega)^{\mathrm{NL}}$. If we consider a fictitious electric field, $\mathbf{F}^\omega$, associated with $(\mathbf{P}^\omega)^{\mathrm{NL}}$ through the susceptibility $\chi^{(1)}(\omega) = (n^2 - 1)/4\pi$, namely,

$$F_\alpha^\omega = [\chi^{(1)}(\omega)]^{-1}(P_a^\omega)^{\mathrm{NL}} \qquad (25)$$

then the apparent surface charges $\ddot{q}_\omega^{\mathrm{ex}}$ can be obtained in terms of such a fictitious field by using the standard PCM relation,

exploiting the normal component of the field at the cavity surface

$$\mathbf{D}\ddot{q}_\omega^{ex} = -\mathbf{F}^\omega \cdot \mathbf{n} \qquad (26)$$

where $\mathbf{D}$ is the PCM square matrix collecting the electric field operators between apparent charges, and $\mathbf{n}$ is the outward-pointing vector at the cavity surface.[39]

As done before to calculate $\tilde{\alpha}(-\omega;\omega)$, here, we also have to define the proper term to be inserted in the perturbed Fock matrix; by analogy with eq 19, we can define such a term through the matrix $\ddot{\mathbf{m}}_a$

$$\ddot{\mathbf{m}}_a = -\sum_l \mathbf{V}(\mathbf{s}_l)\frac{\partial \ddot{q}_\omega^{ex}(\mathbf{s}_l)}{\partial P_a^\omega} = -\sum_k \mathbf{V}(\mathbf{s}_l)\frac{\partial \ddot{q}_\omega^{ex}(\mathbf{s}_l)\partial E_a^\omega}{\partial E_a^\omega \ \partial P_a^\omega} =$$
$$-[\chi^{(1)}(\omega)]^{-1}\tilde{\mathbf{m}}_a \qquad (27)$$

We note that the effects of $\ddot{q}_\omega^{ex}$ in the limit of a spherical cavity coincide with those of the Lorentz approximation for the evaluation of the electric field produced inside a spherical cavity by a uniform polarization density.[6]

### III. Numerical Results

In this section, calculated Kerr constants obtained by exploiting the theory outlined in the previous section are reported. Eight pure liquids were considered: a nondipolar system, $C_6H_6$ (benzene), and seven polar liquids, namely, $C_6H_5F$ (fluorobenzene), $C_5H_5N$ (pyridine), $C_3H_6O$ (acetone), $C_6H_5CN$ (benzonitrile), $C_6H_5NO_2$ (nitrobenzene), $CH_3CN$ (acetonitrile), and $CH_2=CH-CN$ (acrylonitrile), were chosen for their structural properties and the wide range of values taken by their measured Kerr linear birefringence.

**A. Computational Details.** All the calculations were performed using the density functional theory (DFT) with the B3LYP[44−46] functional and the Dunning's correlation consistent basis set aug-cc-pVDZ.[47] The quality of such a combination of a DFT functional and a basis set in the prediction of high-order molecular properties has been assessed in recent studies by some of the present authors.[19,33,48]

In all the calculations, in both the gas and condensed phases, the experimental geometries of the gas phase were used: all the geometrical parameters were taken from ref 49, except those of nitrobenzene which were taken from ref 50. Calculations in the condensed phase were done by exploiting the IEF version[51−53] of the PCM. The molecular cavities were obtained in terms of interlocking spheres having the following radii: 1.9 Å for aromatic CH groups, 1.47 Å for fluorine, 1.55 Å for nitrogen, 1.52 Å for oxygen, 2.0 Å for methyl and methylene groups, and 1.7 Å for carbonyl and nitryl carbon atoms. Such values were multiplied by a cavity-size factor, $f_R$, equal to 1.2.[37]

The static and frequency dependent polarizabilities $\alpha(0)$, $\alpha(-\omega;\omega)$, $\tilde{\alpha}(-\omega;\omega)$, and $\breve{\alpha}(-\omega;\omega)$ were computed analytically. Numerical differentiation yielded $\beta(\omega, 0)$, $\tilde{\beta}(\omega, 0)$, $\gamma_k(\omega)$, and $\tilde{\gamma}_k(\omega)$. Nonequilibrium solvent effects were taken into account,[54] whereas vibrational contributions on the properties were neglected. All the calculations were performed using a locally modified version of the Gaussian 03 package.[55]

**B. Molar Kerr Constant in the Gas Phase.** In Table 1, calculated Kerr constants, $_mK(\lambda, T)$, for the eight molecules in the gas phase are reported, together with the four contributions, $A$, $B$, $C$, and $D$, of eq 14, computed by employing gas-phase molecular properties. In the case of benzene, the only system among those selected in this study not having a dipolar character

**TABLE 1: Kerr Constant, $_mK(\omega, T)$, in the Gas Phase[a]**

| | B | C | D | $10^2 A$ | $_mK^{vac}$ | exptl[b] |
|---|---|---|---|---|---|---|
| benzene[c] | 1.62 | | | 6.54 | 1.69 | 1.53[c] |
| F-benzene | 1.73 | 0.202 | 9.98 | 9.80 | 12.0 | |
| pyridine[d] | 1.03 | 0.039 | 7.08 | 15.1 | 8.30 | 7.24[d] |
| acetone | 0.19 | 0.395 | 11.8 | 15.6 | 12.5 | |
| benzonitrile | 4.84 | −0.197 | 248. | 17.6 | 253. | |
| acrylonitrile | 1.24 | 0.373 | 92.1 | 3.64 | 93.7 | |
| nitrobenzene[e] | 2.58 | −1.130 | 65.8 | 12.0 | 67.4 | 49.8[e] |
| acetonitrile | 0.32 | −0.037 | 53.1 | 2.05 | 53.4 | |

[a] $T = 298.15$ K, except where specified otherwise. Ab initio B3LYP/aug-cc-pVDZ. SI units of $10^{-26} \times V^{-2}$ $m^5$ $mol^{-1}$. All values at 632.8 nm. Experimental geometries taken from the gas phase are assumed. [b] Reference 6. [c] $T = 27$ °C. [d] $T = 146.3$ °C. [e] $T = 235.5$ °C.

(thus, terms $C$ and $D$ are null), $_mK(\lambda, T)$ is dominated by the contribution due to the polarizability, the term $B$ in eq 14, the $A$ term being 2 orders of magnitude smaller. For the remaining (polar) systems, the dominating term in all cases is $D$, generally followed by $B$, whose contribution, $\approx 4−8\%$ of the total for pyridine and fluorobenzene, lowers to $\approx 1−3\%$ for the remaining systems. The $C$ contribution is smaller than both the $B$ and $D$ terms, with the exception of acetone, where it is roughly twice that of $B$ but still far lower than the $D$ contribution. $A$ yields $\approx 1−2\%$ of the total contribution for pyridine, florobenzene, and acetone. The percentage lowers to parts per thousand for nitrobenzene, and it decreases by another order of magnitude for the nitriles. The $_mK(\lambda, T)$ value, $1.69 \times 10^{-26}$ $V^{-2}$ $m^5$ $mol^{-1}$, in the case of benzene, increases by more than 6 times when moving to fluorobenzene because of the contribution of the dipole-moment-dependent terms $C$ and $D$, whereas the $B$ contribution remains essentially unchanged.

The comparison of calculated and available experimental values, the latter taken from ref 6, shows a slight overestimation of experimental values in the case of benzene (10%) and pyridine (15%), whereas the value of nitrobenzene is overestimated by around 35%. In view of the small contribution of the $B$ term, the disagreement may be assigned to the overestimation of the nitrobenzene dipole moment (4.8917 vs 4.22[6] D).

**C. Refractive Index and Dielectric Constant.** A preliminary analysis on the performance of our approach in calculating the effective properties can be done by estimating the dielectric constant and the refractive index of the liquid and comparing their values with experimental values. The dielectric constant and refractive index can be obtained from the following expressions obtained by generalizing to PCM effective properties of the usual standard definition.[6,56] In particular, by rewriting eq 7 in the absence of any static field, it follows that

$$(n^\omega)^2 - 1 = Re\chi^{(1)}(-\omega;\omega)$$
$$= 1 + \frac{N_A d}{\epsilon_0 M_w}\tilde{\alpha}_{iso}(\omega) \qquad (28)$$

The same formalism can be applied also to formulate the static dielectric constant $\epsilon$ as[29,56]

$$\epsilon = 1 + \frac{N_A d}{\epsilon_0 M_w}\left(\frac{\mu^*\mu}{3kT} + \tilde{\alpha}_{iso}(0)\right) \qquad (29)$$

Above $\mu$ is the molecular dipole moment in the liquid, $d$ is the liquid density, $M_w$ is its molecular mass, and $\epsilon_0$ is the vacuum permittivity.

In Table 2, the calculated values are collected together with the experimental values. Densities are taken from ref 57, and they are given in Table 5 below. For benzene, fluorobenzene,

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**TABLE 2: B3LYP/aug-cc-pVDZ and Experimental Dielectric Constant and Refractive Index[a]**

|  | $n_{calcd}$ | $n_{exptl}$ | $\epsilon_{calcd}$ | $\epsilon_{exptl}$ |
|---|---|---|---|---|
| benzene | 1.500 | 1.498 | 2.200 | 2.247 |
| *F*-benzene | 1.469 | 1.463 | 5.423 | 5.42 |
| pyridine | 1.504 | 1.507 | 12.90 | 12.978 |
| acetone | 1.359 | 1.357 | 20.14 | 20.3244 |
| benzonitrile | 1.541 | 1.523 | 30.57 | 25.286 |
| acrylonitrile | 1.409 | 1.388 | 34.04 | 33.0904 |
| nitrobenzene | 1.560 | 1.503 | 30.96 | 34.809 |
| acetonitrile | 1.350 | 1.344 | 40.60 | 36.64 |

[a] Experimental geometries taken from the gas phase are assumed. $T = 298.15$ K.

**TABLE 3: Kerr Constant, $_m\tilde{K}(\omega, T)$, for Pure Liquids[a]**

|  | B | C | D | $10^2 A$ | $_m\tilde{K}$ |
|---|---|---|---|---|---|
| benzene | 2.5 |  |  | 21.5 | 2.71 |
| *F*-benzene[b] | 2.29 | 0.996 | 26.8 | 44.7 | 30.5 |
| pyridine | 2.03 | −0.024 | 68.6 | 48.8 | 71.1 |
| acetone | 0.379 | 0.77 | 54.1 | 37.7 | 55.6 |
| benzonitrile | 4.9 | −1.7 | 737 | 67.4 | 741 |
| acrylonitrile | 1.4 | 0.327 | 271 | 10.3 | 273 |
| nitrobenzene | 4.49 | −13.7 | 671 | 75.9 | 662 |
| acetonitrile | 0.16 | −0.576 | 145 | 5.05 | 145 |

[a] $T = 298.15$ K, except where specified otherwise. Ab initio B3LYP/aug-cc-pVDZ. SI units of $10^{-26} \times$ V$^{-2}$ m$^5$ mol$^{-1}$. All values at 632.8 nm. Experimental geometries taken from the gas phase are assumed. [b] $T = 20$ °C.

pyridine, and acetone, the calculated results are in nice agreement with reference data for both $n$ and $\epsilon$, whereas for the other systems, deviations are observed. The largest differences for $n$ are shown by nitrobenzene, followed by benzonitrile and acrylonitrile. For $\epsilon$, the worst agreement is seen for benzonitrile, which, for this property, behaves very similarly to acetonitrile; the agreement improves slightly for nitrobenzene. By combining the results for $n$ and $\epsilon$, we conclude that both nitriles and nitrobenzene are apparently not accurately described by a continuum model. The behavior of nitrobenzene, however, is not unexpected: in fact, experimental evidence has been given[6] suggesting strong aggregation in liquid nitrobenzene, for example, on the basis of anomalous (positive) saturation effects. Our results agree with this picture.

**D. Molar Kerr Constant in the Condensed Phase.** *1. Reaction and Cavity Field Effects.* In Table 3, the values of the effective Kerr constant, with the individual contributions, calculated for the pure liquids by using eq 14 are reported. Note that these values include both reaction and cavity field effects but not those due to the output wave. For this reason, the comparison with experiments will be postponed to the next section, where all the terms will be accounted for. Also, the geometry of the molecules was taken, as for the case of calculations in the gas phase, from experimental data. This choice allows a direct comparison between values calculated in vacuo and in the condensed phase because any indirect solvent effect (causing a change in the molecular geometry) is neglected. Anyway, later in this section, an estimate of the role of such effects will be given.

The comparison of the data reported in Table 3 with those for the isolated systems (Table 1) shows in all cases a huge increase of the values due to reaction and cavity field effects. The percentage of variation depends on the system: ≈60% for benzene and increasing up to more than 880% for nitrobenzene.

In the liquid model, the polarizability anisotropy term $B$ shows a variety of behaviors, hugely increasing, with respect to the gas phase, in benzene (around 50%), nitrobenzene (around 70%),

**TABLE 4: Differential Gas-to-Liquid (in percentage) Molecular Dipole Moment and Static and Frequency-Dependent (at 632.8 nm) Isotropic Polarizabilities[a]**

|  | $\Delta\mu$ | $\Delta\alpha(0)$ | $\Delta\alpha(\omega)$ |
|---|---|---|---|
| benzene |  | 65 | 38 |
| *F*-benzene | 51 | 122 | 35 |
| pyridine | 89 | 157 | 37 |
| acetone | 78 | 158 | 25 |
| benzonitrile | 55 | 170 | 38 |
| acrylonitrile | 59 | 157 | 27 |
| nitrobenzene | 71 | 184 | 43 |
| acetonitrile | 56 | 155 | 24 |

[a] Ab initio B3LYP/aug-cc-pVDZ. Experimental geometries taken from the gas phase are assumed.

and pyridine (around 90%). By contrast, changes are small for acetone and benzo-, acrylo-, and acetonitrile.

The effect is even larger on the dominating $D$ term whose behavior determines that of the Kerr constant and which increases by almost an order of magnitude in pyridine and nitrobenzene. The $C$ contribution increases remarkably with respect to the gas phase (by more than an order of magnitude) for nitrobenzene and acetonitrile, and it almost doubles for acetone. It becomes roughly 4 and 8 times as large for fluorobenzene and benzonitrile, respectively, whereas it changes its sign for acrylonitrile and pyridine. As noted above for the calculations in vacuo, the $A$ term is smaller than the others (with acetone being the only notable exception), although its value is far larger in the condensed phase than in gases.

We attempt to understand solvent effects on the dominating $D$ and $B$ terms by looking at the single effective properties. In Table 4, the percentage of variation of the dipole moment and the static and frequency-dependent polarizabilities moving from the gas phase to a liquid is reported. For the liquid, the quantities used are $\mu^*$, $\alpha^*_{iso}$, and $\tilde{\alpha}_{iso}(\omega)$.

It is interesting to note that the large variation in the static polarizability, which is observed for the more polar liquids, is not reflected in the trend of the $B$ term. In fact, the minimum variation is found in benzene, where a great increase of $B$ occurs. The opposite behavior is shown by benzonitrile, where a large increase in $\alpha(0)$ but a small variation in $B$ is obtained. Instead, moving to the $D$ term, a direct correlation with the increase in the dipole moment is found. In fact, the two liquids with the largest increase in $D$ (pyridine and nitrobenzene) show the largest variation in the dipole.

The discussion above evidences the complexity of the Kerr constant and the difficulty in correlating it with the behavior of the molecular properties entering its definition.

*2. Effect of the Output Wave.* In Table 5, calculated values obtained by accounting for the macroscopic solvent polarization arising from the output wave are reported. A general increase in the Kerr constant is observed. This is not surprising: within Onsager's theory,[24] such an effect would be represented by a factor depending on the liquid refractive index, $f^{pl}_{classic}$, multiplying $_m\tilde{K}$

$$f^{pl}_{classic} = \frac{n^2 + 2}{3} \tag{30}$$

The comparison of $f^{pl}_{classic}$ with the PCM equivalent (which can be obtained by $_m\tilde{K}^{pl}/_m\tilde{K}$) shows a general similarity between the two, with PCM values always being slightly lower (in any case, less than 10%).

In Table 5, an overall good agreement between our values and experimental values is observed. More quantitatively, PCM

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**TABLE 5: Effect of the Macroscopic Nonlinear Polarization Due to the Output Wave for the Kerr Constant of Pure Liquids**[a]

| | density (mg/mL)[b] | $\tilde{\alpha}_{iso}$ | $_m\tilde{K}^{pl}$ | $_mK^{exptl}$ |
|---|---|---|---|---|
| benzene | 0.874 | 250.64 | 3.61 | $2.68 \pm 0.04^c$ |
| F-benzene[d] | 1.024 | 251.75 | 35 | $44.1^e$ |
| pyridine | 0.978 | 226.77 | 91 | $125^e$ |
| acetone | 0.791 | 164.33 | 69 | $79 \pm 2^f$ |
| | | | | $80^g$ |
| | | | | $77^h$ |
| | | | | $99 \pm 5^i$ |
| benzonitrile | 1.01 | 297.01 | 1001 | $2020^f$ |
| acrylonitrile | 0.806 | 157.00 | 347 | $440^f$ |
| nitrobenzene | 1.196 | 314.12 | 910 | $2364 \pm 142^j$ |
| | | | | $2546 \pm 51^f$ |
| ' | | | | $2549^h$ |
| | | | | $2576^g$ |
| | | | | $2676^k$ |
| acetonitrile | 0.786 | 111.57 | 182 | $277^f$ |
| | | | | $146^l$ |

[a] $T = 298.15$ K, except where specified otherwise. Ab initio B3LYP/aug-cc-pVDZ. SI units of $10^{-26} \times V^{-2} m^5 mol^{-1}$. All values at 632.8 nm. Experimental geometries taken from the gas phase are assumed. [b] Reference 57. [c] Reference 12. [d] $T = 20$ °C. [e] Reference 6. [f] Reference 61. [g] Reference 62. [h] Reference 63. [i] Reference 64. [j] Reference 65. [k] Reference 66. [l] $\lambda = 538$ nm. See ref 6.

**TABLE 6: PCM and Classic Factors for the Kerr Constant of Pure Liquids**[a]

| | PCM | $f_{classic}$ |
|---|---|---|
| benzene | 1.410 | 2.270 |
| F-benzene | 1.710 | 2.862 |
| pyridine | 2.684 | 3.310 |
| acetone | 2.657 | 3.068 |
| benzonitrile | 1.864 | 3.487 |
| acrylonitrile | 1.855 | 3.204 |
| nitrobenzene | 2.092 | 3.480 |
| acetonitrile | 1.833 | 3.115 |

[a] Ab initio B3LYP/aug-cc-pVDZ. $T = 298.15$ K.

values underestimate experimental values for polar systems, whereas for benzene, the opposite is observed. For the polar liquids, the difference between calculated and experimental values is in the range 20−35%, with the notable exceptions of benzonitrile (around 50%) and nitrobenzene (around 65%). As a result of this large discrepancy, the calculated value for nitrobenzene is not the largest in the series, as observed experimentally. Also, in view of the results reported in section III-C for the refractive index and the dielectric constant, we suggest that such a discrepancy is due to aggregation effects in the liquid phase, which are not taken into account by our purely dielectric model. The role of aggregation effects on the Kerr constant has been demonstrated on the basis of Kirkwood correlation factor data largely deviating from the unity.[6]

*3. Comparison with Classical Factors.* To evaluate the differences in the description of cavity field and output wave effects between the PCM formulation and classical theories, in Table 6 the PCM factor is compared with the classical analogue $f_{classic}$. The former is obtained as

$$f_{PCM} = \frac{_m\tilde{K}^{pl}}{_mK^{sol}} \quad (31)$$

where $_mK^{sol}$ is the analogue of $_m\tilde{K}$ but is computed by accounting only for reaction field contributions, i.e., where all the tilde and star quantities in eq 14 are taken away and the properties are

**TABLE 7: Liquid Nitrobenzene, Calculations with Two Different Cavity-Scale Factors, $f_R$, and at Different Geometries with $f_R = 1.20$**[a]

| | B | C | D | $10^2 A$ | $_m\tilde{K}^b$ | $_m\tilde{K}^{pl}$ [c] |
|---|---|---|---|---|---|---|
| $f_R = 1.10$ | 5.50 | −14.6 | 695 | 75.9 | 686 | 943 |
| $f_R = 1.15$ | 4.74 | −14.0 | 679 | 75.9 | 670 | 921 |
| optimized in gas | 4.82 | −15.2 | 741 | 75.9 | 732 | 1010 |
| optimized in liquid | 5.03 | −16.2 | 800 | 75.9 | 790 | 1092 |

[a] $\gamma_K$ with $f_R = 1.20$ at an optimized geometry in liquid. SI units of $10^{-26} \times V^{-2} m^5 mol^{-1}$. $\lambda = 632.8$ nm. Experimental geometries taken from the gas phase are assumed. All data include the contribution of the macroscopic nonlinear polarization due to the output wave. [b] Cf. value with $f_R = 1.2$, experimental geometry, from Table 3: $_m\tilde{K} = 662$ au. [c] Cf. value with $f_R = 1.2$, experimental geometry, from Table 5: $_m\tilde{K}^{pl} = 910$ au.

calculated for the system in solution by considering only direct reaction field effects.

The corresponding classical factor is

$$f_{classic} = \left(\frac{n^2 + 2}{3}\right)\left(\frac{3\epsilon}{2\epsilon + 1}\right)^2\left(\frac{3n^2}{2n^2 + 1}\right) \quad (32)$$

The PCM factors are, in all cases, smaller than the classical ones, with the differences ranging from around 13% to more than 45% (benzonitrile). The smallest differences are obtained for acetone and pyridine; this is not unexpected as, for these molecules, the PCM cavity is more similar to a sphere. More substantial differences appear in the cases of the quasi-linear systems (acetonitrile and acrylonitrile) and the aromatic systems. Also, in the case of benzene, the difference between the PCM and the classical description is large (around 38%).

*4. Dependence on the Choice of the Parameters of the PCM Calculation.* In the PCM, the only adjustable parameter is the size of the spheres used to generate the molecular-shaped cavity. To estimate the dependence of the results on the choice of such a parameter, calculated values obtained with two cavity-size factors, $f_R$, are reported in Table 7 for nitrobenzene, the most challenging system investigated here. An increase in the calculated Kerr constant of around 1% and 4% is observed if the radius of the spheres is decreased by 4% and 8%, respectively. These values can be taken as a measure of the uncertainty connected to the solvation method.

As a further test of the validity of the results shown in the previous sections, the calculations were repeated on optimized geometries, both in vacuo and in the pure liquid. Once again, the analysis is restricted to the case of nitrobenzene, where calculated results show the largest deviations from experimental values.

As can be seen from Table 7, an increase in the calculated value of the Kerr constant is obtained by using the optimized geometry in vacuo (around 11%), which is even more marked if the molecular geometry is optimized in the liquid phase. In this case, in fact, the calculated value increases by around 20%, thus contributing to reduce the discrepancy with the experimental value.

**IV. Summary and Conclusions**

We presented and discussed a quantum mechanical approach to the ab initio determination of the Kerr effect of systems in the condensed phase, in particular, pure liquids, relying on the use of a polarizable continuum model. The method is an extension of the one developed and employed in a previous work for the study of another linear birefringence, the Cotton−Mouton effect,[33] and is based on the introduction of effective molecular

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properties, dipole moments, polarizabilities, and hyperpolarizabilities, which include the changes in molecular polarization due to the external applied static electric field. The contribution of the macroscopic nonlinear polarization density generated by the probe beam is also properly accounted for through the introduction of an additional induced effective frequency-dependent polarizability.

The Kerr constant, directly related to the observable quantity (the anisotropy of the refractive index) is thus written in a form formally analogous to that usually associated with the effect in the gas phase.[6,14] In particular, it is written with the combination of contributions involving effective electric dipole (hyper)-polarizabilities, which are directly comparable with the properties measured in the experiment, and with the appearance of a multiplicative prefactor, which is due to the contribution of the output wave and involves the number density of the liquid and the additional frequency-dependent electric dipole polarizability.

The expression developed in this work has been employed to compute the Kerr constant of a series of eight pure liquids: a nondipolar system (benzene) and seven polar substances. The polar compounds were chosen for their structural properties and the wide range of values taken by their measured Kerr linear birefringence: two substituted benzenes (fluoro- and nitrobenzene), pyridine, acetone, and three nitriles (benzo-, acrylo-, and acetonitrile). In all cases, the Kerr constant has been computed, both in vacuo and in the liquid phase, using a density functional theory wave function model with a B3LYP functional and a correlation consistent basis set of augmented double-$\zeta$ quality, employing experimental gas-phase geometries. The effect of the output wave, that of the cavity size, and that of a change of geometry following optimization in both gas and liquid phases have been investigated, as was the use of classic factors vs the corresponding ones associated with the polarizable continuum model.

The results show that the approach is able to properly describe most of the effects affecting the comparison between the gas-phase and liquid-phase observable values. The enhancement of the Kerr effect seen in pure liquids, in some cases dramatic, is both qualitatively and quantitatively well reproduced, the latter in most cases where specific aggregation effects do not appear to be important. A clear hierarchy is established among the various contributions to the Kerr constant, with the term involving the square of the effective permanent dipole moment (vanishing in the case of benzene) yielding by far the most important contribution. At the other extreme, the contribution involving the effective second electric dipole hyperpolarizability $\tilde{\gamma}_K(\omega)$ is almost always negligible and does certainly not influence in the ultimate comparison between computed and experimental constants. The effect of the macroscopic optical polarization due to the output wave is noticeable and always enhances the effect, consistently contributing to improve the agreement (or decrease the disagreement) between theory and experiment. A change in the cavity size, the only external adjustable parameter of our model (besides the usual basis set, geometry, and wave function model), leads to a rather modest further enhancement of the Kerr constant, which is also affected to a certain extent (10−20% increase) by the change in the geometry, whether optimization in the gas or liquid phase is performed.

The ultimate comparison between computed and measured Kerr constants is affected, as indicated above, by the presence of specific aggregation effects (not accounted for in our scheme) in some cases (nitrobenzene) and also by the neglect of vibrational effects. It is a fact that molecular vibrations have

been found to be important, for example, in studies of natural optical activity,[58] Cotton−Mouton effects in polyatomic molecules, electric field gradient induced birefringence, and other cases.[17] A study of zero-point vibrational corrections on the optical rotation in methyloxirane[58] shows, for instance, that they can contribute as much as 20−30% of the electronic counterpart. Similar effects are likely to be responsible for the residual large disagreement between theory and experiment in liquid-phase studies of magnetochiral birefringence.[59,60]

Despite these residual deficiencies, whose critical importance might be mitigated by the fact that some of the experimental data with which we are comparing are quite dated and only scant information is available on the error bar associated with the experimental data, the performance of the approach developed and discussed here remains quite satisfactory and yields great promises for the further understanding of the phenomena arising from the interactions of radiation and external fields with condensed matter.

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