

Optical rotation studied by density-functional and coupled-cluster methods

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Abstract

We describe the implementation of a gauge-origin independent, time-dependent linear-response formalism for the calculation of optical rotation using London atomic orbitals and density-functional theory. We test the accuracy of density-functional methods for studying optical rotation on difficult systems by modeling the optical rotation as a function of the dihedral angle. We also report the first linear response coupled-cluster singles-and-doubles results of optical rotation. The B3LYP functional gives reliable results for the optical rotation, even for molecules with nearly degenerate excited electronic states of opposite polarization. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

The last few years have seen an increasing interest in the theoretical calculation of optical rotation [1–10]. Although the necessary linear-response tensor (the frequency-dependent mixed electric and magnetic dipole polarizability) has been available at the Hartree–Fock (HF) [6] and multiconfigurational self-consistent field (MCSCF) [7] levels for many years, the first *ab initio* calculations of optical rotation appeared only in 1997 [8]. One reason for this slow development can be traced to the fact that optical rotations are usually measured for rather large

molecules, which until recently have not been accessible to *ab initio* investigations.

Stephens and coworkers [4] recently presented the first gauge-origin independent implementation of optical rotation using density-functional theory (DFT). They have investigated the effects of basis-set and electron-correlation [4], dispersion [9], and solvents [10] on the optical rotation, concluding that basis sets of at least augmented correlation-consistent polarized valence double-zeta (aug-cc-pVDZ) quality are needed. There are also indications that zero-point vibrational corrections may be substantial [11].

A recent study strongly advocates the use of the Kohn–Sham (KS) method over the HF method for calculations of optical rotation when comparing with experiment [9], in particular in conjunction with the three-parameter hybrid Becke–Lee–

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Yang–Parr (B3LYP) functional [12]. While agreement with experiment is undoubtedly a useful criterion from an experimental point of view, we believe that the relative merits of different theoretical methods should also be examined by comparisons with higher-level calculations, where factors affecting the direct comparison with experiment are avoided.

It has recently been demonstrated that the optical rotation as a function of dihedral angle in small molecules such as H_2O_2 and H_2S_2 not only shows a strong dependence on the one-particle basis set but also is critically dependent on the quality of the many-particle description [5]. The reason for this can be traced to the accidental degeneracy of excited states of opposite polarizations that almost cancel at dihedral angles of about 90° [13]. This cancellation is difficult to achieve with for instance a HF wavefunction [5]. Since these molecules are small, they are ideal test systems. We here compare the performance of some common density functionals with the results of high-level ab initio techniques such as the MCSCF [7] and coupled-cluster singles-and-doubles (CCSD) linear-response methods [14].

2. Theory

A frequency-dependent DFT implementation of optical rotation using London atomic orbitals (LAOs) to ensure gauge-origin independence was recently described by Cheeseman et al. [4,9]. A similar approach has been presented by Grimme without LAOs [15]. We here only summarize the theory, focusing on some aspects of our implementation in DALTON [16].

The implementation of DFT for the calculation of optical rotation using LAOs requires only minor changes to the Dalton HF optical-rotation code. In particular, since a DFT LAO implementation of nuclear shieldings was recently presented [17], the new features required for optical rotation can be taken over from this implementation. Even though optical rotation (unlike shieldings) is a frequency-dependent property, our response solver is immediately capable of including dispersion in the adiabatic approximation

[18], when our HF equation solver [19] is modified for KS theory.

At the frequency of the sodium D-line ν_D (in cm^{-1}), the specific optical rotation $[\alpha]_D$ is given by the equation

$$[\alpha]_D = \frac{28800\pi^2 N_A \nu_D^2}{c^2 M} \beta, \quad (1)$$

where N_A is Avogadro's number and M is the molecular weight. Here, β is a scalar related to the trace of the mixed electric–magnetic dipole polarizability

$$\beta = -\omega_D^{-1} (G'_{xx} + G'_{yy} + G'_{zz}), \quad (2)$$

$$G'_{\alpha\beta} = -\omega_D \text{Im} \langle \langle \mu_\alpha; m_\beta \rangle \rangle_{\omega_D}, \quad (3)$$

where $\omega_D = 2\pi\nu_D$ (now in atomic units), and μ_α and m_β are components of the electric and the magnetic dipole operators, respectively. For the systems studied in this Letter, ν_D is well separated from any resonances. We also note that only the trace of the electric–magnetic polarizability is origin-independent; the individual components are gauge-origin dependent.

In extending our HF program to DFT, there are two key elements. First, we must remove (or scale) the exchange contributions to the various Fock-type matrices that appear in the coupled-perturbed HF/KS equations; second, we must include the contributions from the exchange–correlation functional.

The LAOs are defined as [20]

$$\zeta_\alpha = \exp\left(-\frac{1}{2} \mathbf{iB} \times \mathbf{R}_{\text{AO}} \cdot \mathbf{r}\right) \chi_\alpha(\mathbf{r}_A), \quad (4)$$

where $\chi_\alpha(\mathbf{r}_A)$ is a Gaussian basis function and \mathbf{R}_{AO} the position of nucleus A relative to the gauge origin \mathbf{O} . Because of the explicit dependence of the LAOs on \mathbf{B} , the electron density also depends explicitly on \mathbf{B} :

$$\rho(\mathbf{r}, \mathbf{B}) = \sum_{\alpha, \beta} D_{\alpha\beta} \exp\left(\frac{1}{2} \mathbf{B} \times \mathbf{R}_{\text{AB}} \cdot \mathbf{r}\right) \times \chi_\alpha(\mathbf{r}_A) \chi_\beta(\mathbf{r}_B). \quad (5)$$

Here the summation runs over all AOs, and $D_{\alpha\beta}$ is the density matrix in the AO basis. However, the first derivative of the electron density with respect

to \mathbf{B} at $\mathbf{B} = \mathbf{0}$ vanishes; the only explicit corrections come from the derivative KS matrices in the coupled-perturbed KS equations.

Because of the explicit dependence of the LAOs on \mathbf{B} , the first derivative of the exchange–correlation potential F^{xc} does not vanish [17] but is instead given by the expression

$$\begin{aligned} \left. \frac{\partial F_{\alpha\beta}^{\text{xc}}}{\partial \mathbf{B}} \right|_{\mathbf{B}=\mathbf{0}} &= \frac{i}{2} \int (\mathbf{R}_{\text{AB}} \times \mathbf{r}) \frac{\partial F}{\partial \rho} \chi_{\alpha}(\mathbf{r}_{\text{A}}) \chi_{\beta}(\mathbf{r}_{\text{B}}) \, \text{d}\mathbf{r} \\ &+ \frac{i}{2} \int (\mathbf{R}_{\text{AB}} \times \mathbf{r}) \frac{\partial F}{\partial \zeta} \zeta^{-1} \nabla \rho \\ &\cdot \nabla [\chi_{\alpha}(\mathbf{r}_{\text{A}}) \chi_{\beta}(\mathbf{r}_{\text{B}})] \, \text{d}\mathbf{r} + \frac{i}{2} \int (\mathbf{R}_{\text{AB}} \\ &\times \zeta^{-1} \nabla \rho) \frac{\partial F}{\partial \zeta} \chi_{\alpha}(\mathbf{r}_{\text{A}}) \chi_{\beta}(\mathbf{r}_{\text{B}}) \, \text{d}\mathbf{r}, \quad (6) \end{aligned}$$

where ζ is the norm of the density gradient $\zeta = |\nabla \rho|$. This integral is evaluated by numerical quadrature. The routines for generating abscissas and weights for the density quadrature and for the functionals themselves are as in the CADPAC program [21]. Our implementation includes the local density approximation (LDA) [22,23], Becke–Lee–Yang–Parr (BLYP) [24,25], and three-parameter hybrid BLYP (B3LYP) [12,26] functionals.

3. Computational details

Stephens and coworkers [4,9] have recently examined the computational requirements for the accurate calculation of optical rotations using the HF and KS methods, demonstrating that diffuse functions are needed for results close to the basis-set limit. The aug-cc-pVTZ basis is here used for H_2O_2 and H_2S_2 to ensure near gauge-origin independence in the non-LAO coupled-cluster calculations [27]. A comparison at the HF and KS levels shows that for this basis set the LAO and non-LAO results for H_2O_2 differ by not more than a couple of degrees; we assume that a similar close agreement holds at the coupled-cluster level. For biphenyl we have used the aug-cc-pVDZ basis set, while we have used the same basis as [5] for allene. For H_2O_2 , H_2S_2 , and C_3H_4 , we have used the geometries of [5]. For biphenyl, the geometries have

been obtained by an initial HF/aug-cc-pVDZ geometry optimization, followed by a rigid rotation about the phenyl-group linkage. For all calculations, we have used a local version of the DALTON program [16].

4. Results

In a recent study, the applicability of two empirical models for the calculation of optical rotation was investigated [5]. For H_2O_2 and H_2S_2 , the two models – the dihedral $\sin \theta$ model [28] and Kirkwood’s polarizability model [29] – are reduced to simple $\sin \theta$ and $\sin 2\theta$ dependencies on the dihedral angle, respectively. It would seem a simple task to establish by ab initio calculations which prediction is the correct one. However, whereas the HF approximation supports a $\sin \theta$ dependence, the large MCSCF calculations favor a $\sin 2\theta$ dependence. This discrepancy arises from the existence of accidentally degenerate states at a dihedral angle of about 90° [13,5], where the contributions to the optical rotation from the degenerate states have opposite signs and almost cancel. The single-configuration random-phase approximation is unable to describe this cancellation properly, giving the incorrect $\sin \theta$ dependence.

These calculations also highlighted the limitations of the empirical formulas for the prediction of optical rotation: Even though Kirkwood’s polarizability model agrees with the MCSCF results, the special electronic structure of H_2O_2 makes this agreement accidental rather than intrinsic. The functional dependence of the optical rotation on the dihedral angle may therefore serve as a critical test of the performance of different methods for the calculation of optical rotation.

4.1. Optical rotation of H_2O_2

In Table 1, we have collected our DFT results for the optical rotation of H_2O_2 as a function of the dihedral angle; we have also included HF and MCSCF results [5] and non-LAO coupled-cluster results. The resulting curves are plotted in Fig. 1. The HF method is the only method incapable of reproducing the $\sin 2\theta$ dependence of the optical

Table 1

A comparison of the calculated optical rotation of H_2O_2 as a function of the dihedral angle

Dihedral angle	HF	MCSCF	LDA	BLYP	B3LYP	CCSD
-10	-16	-52	-60	-61	-37	-35
-20	-31	-99	-118	-121	-72	-68
-30	-45	-134	-168	-175	-105	-97
-40	-56	-150	-205	-214	-129	-117
-50	-64	-153	-222	-233	-143	-128
-60	-67	-142	-217	-227	-143	-126
-70	-66	-122	-191	-197	-129	-113
-80	-61	-90	-146	-145	-101	-90
-90	-52	-52	-89	-79	-64	-59
-100	-41	-10	-26	-7	-23	-25
-110	-28	33	34	64	19	10
-120	-16	73	86	124	55	39
-130	-5	105	123	165	80	60
-140	3	124	140	183	92	70
-150	7	126	133	173	89	68
-160	7	108	104	134	70	53
-170	4	64	57	74	28	29

The HF and MCSCF results are taken from [5].

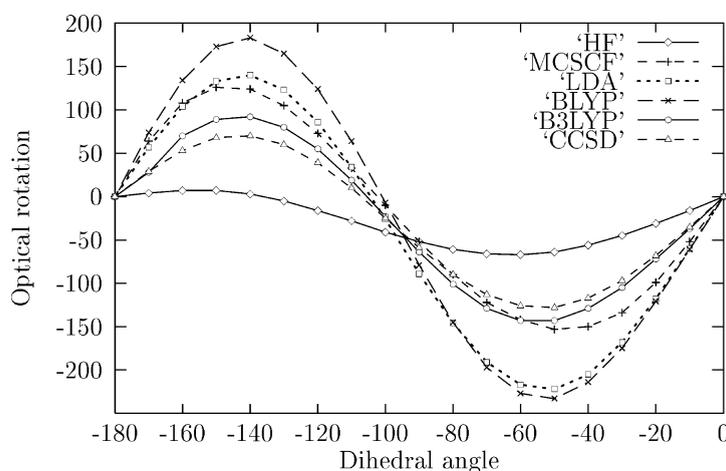


Fig. 1. The specific optical rotation of H_2O_2 (in degrees) as a function of dihedral angle for the different computational methods used in this Letter.

rotation; even the simple LDA model gives a qualitatively correct curve.

The B3LYP and CCSD calculations agree for all dihedral angles, with B3LYP giving a slightly larger rotation. Whereas MCSCF theory is well suited to near-degeneracy situations, it recovers only a small proportion of dynamical correlation, which may be substantial. The difference between CCSD and MCSCF may therefore arise from a better description of dynamical correlation at the

CCSD level. The non-hybrid BLYP and LDA methods overestimate the optical rotation significantly but give the correct $\sin 2\theta$ dependence.

4.2. Optical rotation of H_2S_2

For H_2S_2 , we have, in Table 2, collected the optical rotations calculated using the LDA, BLYP, and B3LYP functionals. For comparison, we have included the MCSCF results of [5] but

Table 2
A comparison of the calculated optical rotation of H₂S₂ as a function of dihedral angle

Dihedral angle	MCSCF	LDA	BLYP	B3LYP
-10	-61	-74	-108	-96
-20	-177	-161	-224	-194
-30	-245	-255	-339	-287
-40	-289	-339	-433	-361
-50	-309	-393	-484	-403
-60	-304	-405	-483	-404
-70	-265	-371	-428	-364
-80	-251	-297	-328	-288
-90	-152	-194	-196	-187
-100	-88	-77	-48	-72
-110	317	39	99	42
-120	297	140	229	143
-130	267	214	325	218
-140	141	251	375	257
-150	138	245	366	252
-160	116	196	294	202
-170	70	109	164	112

The MCSCF results are taken from [5].

omitted the HF results, which again display an incorrect $\sin \theta$ dependence.

From the non-smoothness of the MCSCF optical rotation at dihedral angles around -130° in Table 2, we conclude that the MCSCF method does not properly represent the electronic structure at all geometries; no such deficiency is observed for DFT. However, it appears that DFT also for this molecule exaggerates the optical rotation, with BLYP giving the largest rotation and B3LYP and LDA being similar. This observation is corroborated by a CCSD calculation at a dihedral angle of -50° , giving an optical rotation of -333° – in reasonable agreement with MCSCF but smaller than for DFT.

Concerning the overestimation of optical rotation by DFT relative to MCSCF, we note that DFT predicts too low excitation energies in calculations of the circular dichroism of H₂S₂ [30]. As these energies appear in the denominator of the linear-response function Eq. 3, they may give too large contributions to the optical rotation. Moreover, since the nearly degenerate excited states partially cancel their contributions to the optical rotation, failure to provide a balanced description of such pairs may be part of the reason for the overestimation of the optical rotation.

4.3. Optical rotation of allene

We now turn to a system where the ground state rather than the excited states is degenerate. In Table 3, we report the optical rotation of allene as a function of dihedral angle. When the methylene units are perpendicular to each other, the ground state has two degenerate configurations. This situation is not properly described by a single-configuration method, although the optical rotation for all methods vanishes at 90° due to symmetry.

In Table 3, we have listed our HF and DFT results together with the MCSCF results of [5]. As for H₂S₂, the MCSCF wavefunction is incapable of describing the electronic structure of the molecule at all dihedral angles, although the main features are preserved. The DFT results are in good agreement with MCSCF for dihedral angles 100 – 150° . For larger angles the multiconfigurational character of the reference wavefunction becomes too prominent and the single-configuration KS method fails.

4.4. Optical rotation of biphenyl

Finally, we consider a problem that is difficult to treat quantitatively at the MCSCF level – the

Table 3

A comparison of the calculated optical rotation of C₃H₄ as a function of dihedral angle

Dihedral angle	HF	MCSCF	LDA	BLYP	B3LYP
100	-187	-164	-168	-149	-159
110	-380	-331	-343	-304	-325
120	-585	-503	-531	-474	-504
130	-809	-685	-742	-664	-704
140	-1055	-875	-982	-885	-933
150	-1325	-1068	-1260	-1145	-1199
160	-1599	-832	-1575	-1445	-1501
170	-1771	-955	-1877	-1755	-1798

The MCSCF results are taken from [5].

Table 4

A comparison of the calculated optical rotation of biphenyl as a function of dihedral angle

Dihedral angle	LDA	BLYP	B3LYP
10	133	134	132
20	207	210	210
30	174	179	194
40	61	66	105
50	-75	-69	-7
60	-171	-167	-92
70	-189	-184	-118
80	-122	-118	-79

atropisomerism of biphenyls, an important characteristic in organic stereochemistry [31]. The effect is illustrated by calculations of the optical rotation as a function of the dihedral angle of the phenyl rings, see Table 4. Whereas the three DFT methods agree for positive optical rotations, LDA and BLYP overestimate the effect for negative rotations. The behavior of the functionals for small molecules thus carries over to larger systems.

5. Concluding remarks

We have described the implementation of KS theory for the calculation of optical rotation in Dalton. The implementation employs LAOs to ensure gauge-origin independence of the results; in addition, the frequency-dependence of the rotation is accounted for. We have applied this implementation to the optical rotation of systems with chirality induced around a single bond (atropisomerism). For selected molecules, we have

compared the performance of DFT with correlated ab initio methods such as MCSCF and CCSD.

Unlike the HF method, the KS method correctly describes the $\sin 2\theta$ dependence of the optical rotation on the dihedral angle in H₂O₂ and H₂S₂. Even though some overestimation of the optical rotation occurs at the KS level as a result of a general underestimation of excitation energies (perhaps exacerbated by an unbalanced treatment of large, opposite contributions from nearly degenerate excited states), the performance for these difficult systems is good compared with MCSCF and CCSD.

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