

# Computation of Magnetic Circular Dichroism by Sum-Over-States Summations

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Magnetic circular dichroism (MCD) spectroscopy has been established as a convenient method to study electronic structure, in particular for small symmetric organic molecules. Newer applications on more complex systems are additionally stimulated by the latest availability of precise quantumchemical techniques for the spectral simulations. In this work, a sum over states (SOS) summation is reexamined as an alternative to the derivative techniques for the MCD modeling. Unlike in previous works, the excited electronic states are calculated by the time-dependent density functional theory (TDDFT). A gradient formulation of the MCD intensities is also proposed, less dependent on the origin choice than the standard expressions. The dependencies of the results on the basis set, number of electronic states, and coordinate origin are tested on model examples, including large symmetric molecules with degenerate electronic states. The results suggest that the SOS/TDDFT approach is a viable and accurate technique for spectral simulation. It may even considerably reduce the computational time, if compared with the traditional MCD computational procedures based on the response theory. © 2013 Wiley Periodicals, Inc.

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# Introduction

Electronic circular dichroism (ECD) is a differential absorption of left and right circularly polarized visible or ultraviolet light. It provides enhanced information about electronic states and structure of chiral molecules: unlike absorption, it may be both positive and negative, and it is additionally sensitive to the transition magnetic moment.<sup>[1,2]</sup> For the magnetic circular dichroism (MCD), where the sample is put in a stationary magnetic field parallel with the direction of light propagation, the analogous information is available also for nonchiral systems.<sup>[3,4]</sup> In the past, MCD proved to be useful already for simple molecules.<sup>[4–9]</sup> Even larger potential is apparent for more complex systems, such as porphyrins and their complexes with metals or their conjugates encountered in living organisms.<sup>[8,10–18]</sup>

Although the theory of MCD was developed a long-time ago,<sup>[19–22]</sup> accurate quantum-chemical computational procedures are available only relatively recently.<sup>[12,14,15,18,23–28]</sup> In particular, the implementations within the density functional theory (DFT) and response theory (RT) calculus appear useful as bigger molecules can be calculated with sufficient precision relatively quickly.<sup>[14,26,27]</sup> A real time DFT approach was also tried for C<sub>60</sub>, where it brought a limited accuracy only.<sup>[29]</sup>

Within RT, one can use standard second-order RT or the magnetically-perturbed time-dependent density functional theory (TDDFT),<sup>[30–32]</sup> giving rise to the individual spectral intensities for each transition, similarly as one obtains dipole and rotatory strength. Alternative RT approach is the so-called complex polarization propagator (CPP) computation scheme using damped RT formalism.<sup>[26]</sup>

The origin dependence of the results can be removed by introduction of the gauge-including atomic orbitals (GIAO).<sup>[28]</sup> However, this is not always available. Within the coupled clus-

ters with single and double excitations (CCSD) theory, for example, a GIAO implementation<sup>[33]</sup> was reported for a program interfaced to Dalton, and within TDDFT, GIAO can be used in the LSDalton variant.<sup>[34]</sup> Within standard Dalton program, the origin is automatically placed at the center of mass and GIAOs are not used.

Practical DFT RT computations may still be problematic. They suffer from long computer time and significant memory requirements, often prohibitive for large systems. In case of CPP, it is particularly difficult to analyze the results in terms of individual electronic state contributions. Some other implementations of the RT are not suitable for molecules with degenerate states. These problems encouraged us to revisit the possibility to use the direct sum over state (SOS) summation as an alternative.

SOS computational methods have been used relatively extensively for MCD computations in the past and are generally believed to be inconvenient for routine computations as they involve lengthy configuration interaction procedures.<sup>[35]</sup> However, as shown below, this is not true for accurate excited states obtained from the TDDFT. On the contrary, MCD

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simulations can take advantage of the efficient TDDFT implementations available in most contemporary quantum chemical software. Once the excited states are obtained, the SOS summation required for MCD is much faster than the RT procedure. Yet the SOS approach may suffer from the origin-dependence of the results, similarly as RT, and an incomplete representation of the excited electronic state space. According to our knowledge, neither of these two aspects has been systematically studied before.

The SOS approach itself was used for MCD, for example, in studies of the benzene<sup>[5]</sup> or cyclopropane<sup>[36]</sup> molecules, mostly as a fast approach in connection with the semiempirical molecular orbital methods.<sup>[37]</sup> However, it also allowed for integration of the vibronic effects.<sup>[38]</sup> In particular, for highly correlated wavefunction methods, the SOS summation is easier to implement than for the RT techniques; the former was thus used for MCD of systems exhibiting spin-spin and spin-orbit coupling,<sup>[39]</sup> with the CASSCF/ MC-CASPT2<sup>[17]</sup> and CASSFC/MRCI<sup>[8]</sup> complete active space and multi-reference methods, and so on. TDDFT-SOS approach itself has been used relatively rarely, for example, for calculation of the specific rotation of small molecules.<sup>[40]</sup>

In this study, we briefly introduce the MCD theory and provide details about the TDDFT-SOS implementation including an alternate gradient formalism for the *B*-term. In Results section, the SOS results are compared to RT computation for the pyrrole,  $C_{60}$ , and  $C_{70}$  model molecules. The origin dependence and the dependence on the number of states are also tested. It turns out that the SOS computation can easily achieve the RT accuracy, mostly within a shorter computational time, and thus, the TDDFT/SOS approach may in many cases serves as a convenient alternative for MCD spectral interpretations.

## Method

#### Theory

For isotropic samples, such as solutions, we measure the MCD differential absorption index  $\Delta \varepsilon$ . Contribution from each transition  $n \rightarrow j$  is<sup>[3]</sup>

$$\Delta \varepsilon = -\frac{\mu_0 c I N B_z}{3\hbar} \left[ \frac{4\omega_{jn} \omega^2}{\hbar} f g A + \omega^2 g \left( B + \frac{C}{kT} \right) \right], \tag{1}$$

where  $\mu_0$  is the vacuum permeability (the magnetic constant), c is the concentration, I is the path length, N is the number of molecules per unit volume,  $B_z$  is the magnetic field intensity,  $\hbar$  is the reduced Planck constant,  $\omega$  is the light angular frequency,  $\omega_{jn}$  corresponds to the difference of state energies,  $\hbar\omega_{jn} = E_j - E_n = \hbar\omega_j - \hbar\omega_n$ , k is the Boltzmann constant, and T is the temperature.

The line shape functions are defined as  $fg = \frac{(\omega_{jn}^2 - \omega^2)\omega\Gamma_j}{[(\omega_{jn}^2 - \omega^2)^2 + \omega^2\Gamma_j^2]^2}$ and  $g = \frac{\omega\Gamma_j}{(\omega_{jn}^2 - \omega^2)^2 + \omega^2\Gamma_j^2}$ . The width  $\Gamma_j$  can be associated with the lifetime of the excited state j.<sup>[3]</sup> However, for a direct comparison between the experimental and calculated spectra, it is more convenient to set the width equal to the inhomogeneous broadening, significantly larger than  $\Gamma_j$ . Finally, *A*, *B*, and *C* are the Faraday's MCD terms, first introduced already in 1932,<sup>[41]</sup> and defined in terms of electronic molecular states as

$$A = \frac{\varepsilon_{\alpha\beta\gamma}}{2d_n} \sum_n \left( \langle j | m_\alpha | j \rangle - \langle n | m_\alpha | n \rangle \right) \operatorname{Im} \langle n | \mu_\beta | j \rangle \langle j | \mu_\gamma | n \rangle$$
(2a)

$$B = B_{r} = \frac{\varepsilon_{\alpha\beta\gamma}}{d_{n}} \sum_{n} \operatorname{Im} \left[ \sum_{k\neq n} \frac{\langle k|m_{\alpha}|n\rangle}{E_{k} - E_{n}} \langle n|\mu_{\beta}|j\rangle\langle j|\mu_{\gamma}|k\rangle + \sum_{k\neq i} \frac{\langle j|m_{\alpha}|k\rangle}{E_{k} - E_{j}} \langle n|\mu_{\beta}|j\rangle\langle k|\mu_{\gamma}|n\rangle \right]$$
(2b)

$$C = \frac{\varepsilon_{\alpha\beta\gamma}}{2d_n} \sum_n \langle n|m_\alpha|n\rangle \mathrm{Im}\langle n|\mu_\beta|j\rangle \langle j|\mu_\gamma|n\rangle, \qquad (2c)$$

where  $d_n$  is the ground-state degeneracy,  $\varepsilon_{\alpha\beta\gamma}$  is the Levi-Civita antisymmetric tensor, and m and  $\mu$  are the respective magnetic and electric dipole operators.

#### Implementation

The *C*-term is not relevant for closed-shell molecules,<sup>[11]</sup> and it is omitted in this study. It is also well-known that the *A*-terms can be expressed as a combination of *B*-terms.<sup>[4]</sup> An example of the equivalence between the *A*- and *B*-terms for a doubledegenerate state is given in Appendix A. We use this fact to formally eliminate the *A*-term also for highly symmetric molecules. For degenerate states, we introduce an arbitrary splitting, for example, three-times degenerate state *n* is split to three irreducible (real) components of energies  $E_n$ ,  $E_n+\Delta$ , and  $E_n+2\Delta$ , where  $\Delta$  is a small number. We have verified that the final spectral shape (of a broadening  $\Gamma >> \Delta$ ) is fairly independent on  $\Delta$ . Only for large  $\Delta$  ( $\geq$ 0.001 hartree), the spectra were somewhat distorted.  $\Delta = 0.0001$  hartree was used as the default.

For an alternate expression of the *B*-term, we can use the dipole–velocity transformation<sup>[42]</sup> valid for exact wavefunctions (from now on we use atomic units),  $\langle k | \bigtriangledown | g \rangle / E_{kg} = \langle k | \mathbf{r} | g \rangle$ . We need to separate permanent electric dipole moments, not expressible by gradients, and from eq. (2b) we obtain the gradient form of the *B*-term as

$$B_{\nabla} = \frac{\varepsilon_{\alpha\beta\gamma}}{d_g} \sum_{g} \operatorname{Im} \left[ \sum_{k \neq g, k \neq j} \left( \langle k | m_{\alpha} | g \rangle \langle g | \nabla_{\beta} | j \rangle \langle j | \nabla_{\gamma} | k \rangle \right. \\ \left. - \langle j | m_{\alpha} | k \rangle \langle g | \nabla_{\beta} | j \rangle \langle k | \nabla_{\gamma} | g \rangle \right) (E_{kg} E_{jg} E_{kj})^{-1} \\ \left. + E_{jg}^{-2} \langle j | m_{\alpha} | g \rangle \langle g | \nabla_{\beta} | j \rangle (\langle g | \mu_{\gamma} | g \rangle - \langle j | \mu_{\gamma} | j \rangle) \right]$$

$$(3)$$

Molecular absorption, given by the dipole strength (*D*), can be expressed either using the length or velocity/gradient formalism as well

$$D_r = \langle g | r_{\alpha} | j \rangle \langle j | r_{\alpha} | g \rangle$$
 (4a)

$$D_{\nabla} = E_{jq}^{-2} \langle g | \nabla_{\alpha} | j \rangle \langle j | \nabla_{\alpha} | g \rangle.$$
(4b)

Although for exact wavefunction or complete basis set limit  $B_{\nabla} = B_p$  practical computations, in general, provide different

values. One can easily verify that the *B*-term can be dependent on the origin unless, in addition to the dipole–velocity transformation, the wavefunctions obey the completeness relation,  $\sum_k |k\rangle \langle k| = 1$  (Appendix B). It turns out that the dependence on the choice of origin is mild around molecular center, and  $B_{\nabla}$  is more resistant to origin shifts than  $B_n$   $D_n$  and  $D_{\nabla}$  are always origin independent.

#### Ab initio computations

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The test molecules involved pyrrole, and the C<sub>60</sub> and C<sub>70</sub> fullerenes. Pyrrole was chosen as a convenient small system for benchmarking computations, and as a part of the porphyrin chromophore encountered in many MCD studies.<sup>[4]</sup> The performance of the simulations for sizable and symmetric systems is documented on the two fullerenes. Note that C<sub>60</sub> was also studied by the MCD technique previously.<sup>[9,29,43]</sup> Programs Turbomole (version 6.3.1)<sup>[44]</sup> and Gaussian (v. C01)<sup>[45]</sup> were used for the geometry optimizations.

For the gradient and length SOS computations of the B-term, excited electronic energies and wavefunctions were obtained by TDDFT. Within the adiabatic approximation, TDDFT yields only single excitations,<sup>[46]</sup> although TDDFT extension to multiple-excitations is possible.<sup>[47,48]</sup> Thus, the atomic and molecular orbital integrals required in the above expressions can be readily obtained from the Slater's rules. For this purpose, we used our own software interfaced to Gaussian. The wavefunction for excited state *j* was taken as  $\varphi_i$  =  $\sum_{i} c_{i}^{J} \Delta_{a, \rightarrow bi}$ , where  $\Delta_{a, \rightarrow bi}$  is the Slater determinant with an electron moved from orbital  $a_i$  to orbital  $b_i$ , and the expansion coefficients  $c_i^{\prime}$  were taken from the Gaussian output. For a closed shells and a singlet transition from the ground state, for example,  $\langle g | r_{\alpha} | j \rangle = \sqrt{2} \sum_{i} c_{i}^{i} \langle a_{i} | r_{\alpha} | b_{i} \rangle$ . Detailed discussion of this approach can be found elsewhere.<sup>[49,50]</sup> Note that we strictly use the exact TDDFT energies, i.e. not the orbital energies also encountered in SOS approaches.<sup>[49,50]</sup>

The standard 6-31G, 6-31G<sup>\*\*</sup>, 6-31++G<sup>\*\*</sup>, 6-311++G<sup>\*\*</sup>, augcc-pVTZ, and aug-cc-pVQZ basis sets and the B3LYP<sup>[51]</sup> DFT functional were used as specified below. The BP86<sup>[52]</sup>/def-TZVP method was used to optimize the fullerene geometries in Turbomole, and for pyrrole, we used the B3LYP/6-311++G<sup>\*\*</sup> optimized geometry by Gaussian. By other tests, we found that the MCD spectra are not particularly sensitive to geometry optimization.

For comparison, the SOS MCD intensities were compared to those obtained by the RT method  $^{[18,25-27]}$  as implemented in the Dalton  $^{[53]}$  program, version "2011."

Simulated MCD spectra are normalized to the unit magnetic field, obtained from the *B*-term contributions as<sup>[54]</sup>

$$\Delta \varepsilon(\lambda) \ [L \text{ mol}^{-1} \text{ cm}^{-1} \text{ T}^{-1}] = -5.98442 \times 10^{-3} p(\lambda) B \ [a.u.], \ (5)$$

where  $p(\lambda)$ ,  $\int p(\lambda)/\lambda d\lambda = 1$ , is a shape function. The MCD and absorption spectra were simulated using Gaussian bands, by default 10 nm broad (full width at half height). For absorption, we used<sup>[1]</sup>

$$\varepsilon(\lambda) \quad [L \text{ mol}^{-1} \text{ cm}^{-1}] = 108.9p(\lambda)D \quad [\text{debye}]. \tag{6}$$

### **Results and Discussion**

## Length vs. gradient MCD intensities

For pyrrole, the *B*-terms and dipole strengths calculated by the gradient and length formalism for six basis sets (6-31G,  $6-31G^{**}$ ,  $6-31++G^{**}$ ,  $6-311++G^{**}$ , aug-cc-pVTZ, and aug-cc-pVQZ, with 55, 100, 125, 145, 345, and 800 basis functions, respectively) and the B3LYP functional are compared in Table 1. As can be expected, smaller basis sets, such as 6-31G, provide

<b>Table 1.</b> The correlation ( <i>cc</i> ) and the regression <i>b</i> (e.g., $B_{\nabla} = b \times B_r$ )
coefficients between the length and gradient absorption and MCD
intensities, calculated for 500 lowest energy pyrrole states and the B3LYP
functional.

	Absorption	MCD	Absorption	MCD
Basis set	сс	сс	b	b
6-31G	0.946	0.994	0.794	0.826
6-31G**	0.981	0.998	0.969	0.998
6-31++G**	0.992	0.972	0.963	1.097
6-311++G**	0.996	0.804	0.975	0.683
aug-cc-pVTZ	1.000	0.936	0.993	1.069
aug-cc-pVQZ	1.000	0.993	0.994	0.998

in general larger deviations between the two formalisms; however, the correlation coefficient is always rather large, cc > 0.80.

At 6-31G, both the dipole strengths and the *B*-terms are significantly underestimated when calculated within the gradient formalism, reaching 79.4 and 82.6% of the length values, respectively. Larger basis sets quickly improve the agreement, with the exception of  $6-311++G^{**}$ , where on average only 68.3% length *B*-term magnitudes are recovered by the gradient computation. However, the statistics in this case is strongly biased by an accidental degeneracy of electronic levels at a single wavelength (75 nm), perhaps causing an instability in the excited state computation; if this value is removed, both the correlation coefficient and the fitting coefficient are close to one, as for the other cases.

Finally, we note that the convergence of the gradient and length values to each other with increasing basis set size are smoother and more monotonic for the absorption than for MCD. This is given by the complicated *B*-term formula containing the gradient operator within the magnetic dipole. A similar dependence was also observed for the ECD.<sup>[55,56]</sup>

In general, the gradient and length values of spectroscopic properties appear reasonably close and can be considered equivalent in practical computations.

#### The origin dependence

Strictly speaking, the origin dependence makes the computation not meaningful. Within the SOS scheme, a usage of the GIAO<sup>[57,58]</sup> that make the procedure origin independent is not known to us. Fortunately, stabilized results can be obtained if the origin is placed reasonably close to the center of mass, similarly as for the RT method or other magnetic properties



Figure 1. Dependence of the *B*-terms for two selected transitions in pyrrole (203.7 and 166.1 nm, polarized in the *y*- and *z*-direction, respectively) on the shift of coordinate origin with respect to the center of mass, as calculated at the B3LYP/SOS/6-311++G<sup>\*\*</sup> level. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

including nuclear magnetic resonance shielding,<sup>[57]</sup> Raman optical activity,<sup>[59]</sup> or electronic<sup>[58]</sup> and vibrational<sup>[60]</sup> circular dichroism.

For pyrrole, the origin dependence of MCD intensities calculated at the B3LYP/SOS/6-311++G\*\* level is documented for two transitions in Figure 1. Within the length approach, the *B*-terms change very mildly for origin shifts smaller than 1 Å. However, for larger translations significantly different values are obtained than for the molecule placed at the origin center. For the terms obtained with the gradient approach, the dependence is much less steep, and the 'stable' region where the MCD intensity changes with a few percents only allows for two to three times larger shifts than for the length formalism.

The SOS scheme thus does lead to reliable MCD intensities, providing that the origin is placed close to the center of the molecule. In addition, the gradient formalism is significantly less sensitive to origin variations than the length-based approach.

#### Number of states dependence

Another limit of the SOS approach that has been often discussed in the past is the dependence of the MCD spectra on the number of electronic states involved in the computations.<sup>[7,35]</sup> The TDDFT computations typically provide a predefined number of electronic excited states, starting from the lowest energy (highest wavelength) one.<sup>[61]</sup> As follows directly from the equations, even states with energies outside the measured region contribute to the signal. This is documented in Figure 2, where the pyrrole MCD and absorption spectra are simulated with 10–400 states involved, using the B3LYP/  $6-311++G^{**}$  level of approximation.

As expected, the absorption spectrum (lower part of Fig. 2) can be built state by state, higher energy states influencing the lower frequency ones only via the finite band widths. On the contrary, MCD spectra (upper part, Fig. 2) even in the higher wavelength region (e.g., within the experimentally most accessible interval of about 170–250 nm) are still influenced by the involvement of more distant states. Fortunately, as apparent from the figure, the influence is also limited. For



example, within the 170–250 nm interval only the spectra obtained with 10 and 50 states are significantly different from a converged curve, and even for 10 states the principle spectral features are already well-reproduced.

This is in a qualitative agreement with a previous TDDFT-SOS study of the specific rotation,<sup>[40]</sup> where, however, the convergence was less monotonic. This may reflect the different nature of MCD, given by the polarizability perturbed by magnetic field, where the excited states are only coupled to the states of the observed transition

[cf. eq. (2b)]. For the rotation, all states contribute directly.<sup>[3,40]</sup> Thus, while the sensitivity to the number of states should always be tested, it does not appear to be prohibitive for reliable SOS MCD computations, similarly as for the origin dependence.

#### Comparison to RT computation

In Figure 3, the RT MCD spectra of pyrrole as obtained by Dalton at the HF/6-31G and B3LYP/6-311++G\*\* levels are



Figure 2. Dependence of the simulated (B3LYP/SOS/6-311++G\*\*) pyrrole MCD (top) and absorption (bottom) spectra on the number of states involved. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]





Figure 3. Comparison of the RT and SOS MCD simulations for pyrrole for the HF/6-31G and B3LYP/6-311++G<sup>\*\*</sup> computations. The spectra are simulated with a narrow width of 1 nm so that individual transitions are visible. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

compared to the corresponding SOS computations including 300 states. The RT and SOS results exhibit minor differences in relative peak intensities; however, the overall sign patterns are identical. Especially, the length-based SOS results are virtually indistinguishable from RT. For RT, 15 states were involved only as computations with more states were not numerically stable. We may speculate that the RT instability is caused by nearly degenerate excited electronic states causing divergences in the *B*-term expression for the MCD intensity.



**Figure 4.** Comparison of approximate CPU times (recalculated to one 3.5 GHz Intel X5690 processor) for MCD pyrrole computations with the SOS and RT methods and the B3LYP functional. The 15 state computations were done in Dalton, without explicit symmetry use, the 300 state SOS computation is from Gaussian and with the  $C_{2\nu}$  symmetry switched on. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As can be seen in Figure 4, where the computational times with the B3LYP functional are compared for six basis sets, the SOS computations are significantly faster than RT. The 15-state computations were performed in Dalton, the 300-state SOS computation was done in Gaussian because our version of Dalton does not allow for too many states. However, our tests for the excited state computation suggest that the performances of both programs are approximately the same (unlike for ground-state computations). The example well illustrates that the reduction of the computational time with the SOS method is possible. For example, with the aug-cc-pVTZ basis set, the MCD RT computation with 15 states took about 38 h, as compared to the 19 h of the SOS approach with 300 states, and so on. The latter calculation can further be reduced to 1.3 h if only 12 states are calculated.

To put in perspective the variance of the MCD spectra simulated by different theoretical approaches, we plot pyrrole absorption (length formalism) and length and gradient MCD spectra as obtained at the B3LYP approximation level with the six basis sets in Figure 5. Clearly, the basis set variation has a dramatic effect on the spectra, mostly larger than, for example, the length  $\rightarrow$  gradient formalism change. The absorption threshold changes from  ${\sim}190$  to  ${\sim}230$  nm if the basis is changed from 6-31G to aug-cc-pVQZ. The most profound change occurs when the diffuse functions (++) are added to the basis set; for larger bases sets, the basic features in the absorption and MCD spectra seem to be stabilized. The MCD curve varies slightly more than the absorption. In particular, the gradient MCD simulation (right-hand side in Fig. 5) changes still notably even between the very large aug-cc-pVTZ and aug-cc-pVQZ basis sets.

#### **Fullerene simulations**

Although the C<sub>60</sub> and C<sub>70</sub> molecules are much larger and more symmetric than pyrrole, the MCD/SOS simulations behave consistently. For example, the curves agree with the benchmark RT computations, and the length and gradient intensities are strongly correlated (Fig. 6). The RT curves were obtained using Dalton using a point-by-point simulation with a finite bandwidth,[26] as the A-terms are not implemented directly within the current RT implementation in Dalton. The high-frequency (low wavelength) parts appear less reliable since the gradient and length intensities significantly differ in this region. This inconvenience is not unique for the SOS method; also, the RT computations exhibited a convergence slowdown therein. The RT computations (~200 and 540 days of normalized CPU time for C<sub>60</sub> and C<sub>70</sub>) were again significantly more demanding than for the SOS method (from 4 to 40 days for both molecules, according to the number of electronic states involved; note, however, that computations the RT and SOS were performed with different programs, Dalton and Gaussian).

The arbitrary degeneracy breaking of the electronic levels in the fullerenes (of  $I_h$  and  $D_{5h}$  symmetry for  $C_{60}$  and  $C_{70}$ , respectively) does not seem to pose significant problem for the computations. The stability of the simulated MCD spectra with respect to the variation of the arbitrary splitting of degenerate electronic levels is explored in Figure 7 for  $C_{70}$ . Except for the largest values ( $10^{-2}$  to  $10^{-3}$  hartree), all the other splittings ( $10^{-4}$  to  $10^{-6}$  hartree) provide indistinguishable spectral profiles. Under the limited resolution given by the inhomogeneous broadening of spectral lines in the condensed phase, the replacement of the A-terms by the arbitrarily degenerate *B*contributions thus appears sufficient.

Finally, we can note that the simulated absorption and MCD  $C_{60}$  spectra are consistent with available experimental





Figure 5. (Left) absorption in the length formalism and (middle and right) MCD calculated in the length and gradient formalisms for pyrrole with the B3LYP/SOS model and six different basis sets.

data.<sup>[9,43]</sup> For example, the "- +" couplet calculated at 321 nm is clearly visible both in argon matrix<sup>[9]</sup> and a solution.<sup>[36]</sup> The signal around 367 nm is experimentally less pronounced,

appearing as a shoulder of the 321 nm signal. The predominantly negative MCD around 250 nm can also be observed, with a similar relative intensity.



**Figure 6.** Simulated RT (0.05 eV bandwidths, see Ref. <sup>[26]</sup>) and SOS MCD ( $\Delta \varepsilon$ ) spectra of C<sub>60</sub> and C<sub>70</sub>; in the absorption ( $\varepsilon$ ) positions and of the electronic transitions are indicated as the red lines. For the SOS MCD and absorption spectra obtained both by the length and gradient formalisms are plotted, the B3LYP/6-31G\*\* theory is used.





Figure 7. MCD spectra of C\_{70} simulated with different splitting ( $\Delta$ , in hartrees) of the degenerate levels.

# Conclusions

We have explored the TDDFT/SOS computations of MCD intensities as an alternative to the RT approaches. The A-terms encountered in symmetric molecules could be included as well. Although the SOS procedure can be dependent on the chosen origin and number of states involved, the results suggest that these obstacles are not prohibitive to reliable simulations of molecular spectra. The origin dependence could be avoided by placing the molecule to its center and/or by usage of the gradient formula for MCD. The influence of high-energy electronic states on the lower energy MCD intensities was found to be quite limited. The SOS computations very well agreed with the RT benchmark, and for the tested systems it provided significant savings of computer time.

# Appendix A: On the Replacement of the A Term by B

In order to provide insight into the algebra involved, we investigate MCD contribution of a double-degenerate ground state, that is,  $d_n = 2$ . For simplicity, the state *j* is not degenerate. Typically, the two ground-state wavefunctions  $g_+$  and  $g_-$  are complex, and can be reduced to real functions  $g_1$  and  $g_2$ ,

$$|g_{\pm}\rangle = (|g_1\rangle \pm i|g_2\rangle)/\sqrt{2}.$$
 (A1)

From the definition of the line shape functions and for  $\Gamma_j \ll \omega_{jn}$  we obtain  $fg \cong \frac{1}{4\omega} \frac{\partial g}{\partial \omega'}$  and hence from eq. (1)

$$\Delta \varepsilon \simeq -\frac{\mu_0 cINB_z \omega^2}{3\hbar} \left[ A \frac{1}{\hbar} \frac{\partial g}{\partial \omega} + gB \right]. \tag{A2}$$

From eq. (2a), we obtain directly

$$A = A_+ + A_-, \tag{A3}$$

where

$$\begin{aligned} A_{+} &= -\frac{\varepsilon_{\alpha\beta\gamma}}{4} \langle g_{+} | m_{\alpha} | g_{+} \rangle \mathrm{Im} \langle g_{+} | \mu_{\beta} | j \rangle \langle j | \mu_{\gamma} | g_{+} \rangle \\ &= \frac{i \varepsilon_{\alpha\beta\gamma}}{4} \langle g_{2} | m_{\alpha} | g_{1} \rangle (\langle g_{1} | \mu_{\beta} | j \rangle \langle j | \mu_{\gamma} | g_{2} \rangle \end{aligned} \tag{A4a}$$

and

$$A_{-} = -\frac{\varepsilon_{\alpha\beta\gamma}}{4} \langle g_{-} | m_{\alpha} | g_{-} \rangle \mathrm{Im} \langle g_{-} | \mu_{\beta} | j \rangle \langle j | \mu_{\gamma} | g_{-} \rangle = A_{+}.$$
 (A4b)

Therefore,

$$\Delta \varepsilon = -\frac{\mu_0 c I N B_z \omega^2}{3\hbar} \frac{2A_+}{\hbar} \frac{\partial g}{\partial \omega}.$$
 (A5)

Alternatively, we can introduce a small split of the groundstate energy levels, so that the energy of  $|g_2\rangle$  is larger than that of  $|g_1\rangle$  by  $\Delta$ . Then, in eq. (2b) for the transition  $g_1 \rightarrow j$  at frequency  $\omega_{j1}$  we get just one dominant term,

$$B_{1} = \frac{\varepsilon_{\alpha\beta\gamma}}{2} \operatorname{Im} \frac{\langle g_{2} | m_{\alpha} | g_{1} \rangle}{\Delta} \langle g_{1} | \mu_{\beta} | j \rangle \langle j | \mu_{\gamma} | g_{2} \rangle.$$
 (A6a)

Similarly for the  $g_2 \rightarrow j$  transition at frequency  $\omega_{j1} - \Delta/\hbar$ , we get

$$B_{2} = -\frac{\varepsilon_{\alpha\beta\gamma}}{2} \operatorname{Im} \frac{\langle g_{1} | m_{\alpha} | g_{2} \rangle}{\Delta} \langle g_{2} | \mu_{\beta} | j \rangle \langle j | \mu_{\gamma} | g_{1} \rangle.$$
 (A6B)

Using  $\langle g_1 | m_{\alpha} | g_2 \rangle = - \langle g_2 | m_{\alpha} | g_1 \rangle$ ,  $\text{Im} \langle g_2 | m_{\alpha} | g_1 \rangle = -i \langle g_2 | m_{\alpha} | g_1 \rangle$ , properties of the Levi-Civita tensor, and by comparison to eq. (A4a) we see that

$$B_1 = -B_2 = -\frac{2}{\Delta}A_+.$$
 (A7)

Realizing that  $\frac{\partial g}{\partial \omega} \cong -\frac{\partial g}{\partial \omega_{jn}} = \lim_{\Delta \to 0} [g(\omega_{jn}) - g(\omega_{jn} - \Delta)]/\Delta$ , we can transform the spectral contribution of the *B*-terms to the same expression as eq. (A5),

$$\Delta \varepsilon = -\frac{\mu_0 cINB_z \omega^2}{3\hbar} B_1[g(\omega_{j1}) - g(\omega_{j1} - \Delta/\hbar)]$$
  
=  $-\frac{\mu_0 cINB_z \omega^2}{3\hbar} (\frac{-2A_+}{\hbar}) \frac{g(\omega_{j1}) - g(\omega_{j1} - \Delta/\hbar)}{(\Delta/\hbar)}$  (A8)  
$$\cong -\frac{\mu_0 cINB_z \omega^2}{3\hbar} \frac{2A_+}{\hbar} \frac{\partial g}{\partial \omega}.$$

For two close energy levels, the MCD signal can be thus obtained alternatively by the two *B*-terms or by the *A*-term. See also Ref.<sup>[4]</sup> for the definition of the pseudo *A*-term for accidental degeneracy and other details.

# Appendix B: Origin Dependence of the B-Term

We want to know which conditions need to be met to satisfy origin independence of the *B*-term. Realizing that in atomic units  $\mathbf{m} = -\mathbf{r} \times \nabla/2$  and  $\mu = -\mathbf{r}$ , from eq. (2b) we get

$$B = -\frac{1}{2d_n} \sum_{n} \operatorname{Im} \left[ \sum_{k \neq n} \frac{\langle k | \mathbf{r} \times \nabla | n \rangle}{E_k - E_n} \cdot \langle n | \mathbf{r} | j \rangle \times \langle j | \mathbf{r} | k \rangle \right. \\ \left. + \sum_{k \neq j} \frac{\langle j | \mathbf{r} \times \nabla | k \rangle}{E_k - E_j} \cdot \langle n | \mathbf{r} | j \rangle \times \langle k | \mathbf{r} | n \rangle \right]$$
(B1)

A shift of coordinates  $\mathbf{r} \rightarrow \mathbf{r} + \mathbf{T}$  causes a change in  $B, B \rightarrow B$ - X, where



$$X = \frac{1}{2d_n} \sum_{n} \operatorname{Im} \left[ \sum_{k \neq n} \mathbf{T} \times \frac{\langle k | \nabla | n \rangle}{E_k - E_n} \cdot \langle n | \mathbf{r} | j \rangle \times \langle j | \mathbf{r} | k \rangle + \sum_{k \neq j} \mathbf{T} \times \frac{\langle j | \nabla | k \rangle}{E_k - E_j} \cdot \langle n | \mathbf{r} | j \rangle \times \langle k | \mathbf{r} | n \rangle \right]$$

$$+ \frac{\langle j | \mathbf{r} \times \nabla | n \rangle}{E_j - E_n} \cdot \langle n | \mathbf{r} | j \rangle \times \mathbf{T} + \frac{\langle j | \mathbf{r} \times \nabla | n \rangle}{E_n - E_j} \cdot \langle n | \mathbf{r} | j \rangle \times \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_j - E_n} \cdot \langle n | \mathbf{r} | j \rangle \times \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_n - E_j} \cdot \langle n | \mathbf{r} | j \rangle \times \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_n - E_j} \cdot \langle n | \mathbf{r} | j \rangle \times \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_n - E_j} \cdot \langle n | \mathbf{r} | j \rangle \times \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_n - E_j} \cdot \langle n | \mathbf{r} | j \rangle \times \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_n - E_j} \cdot \langle n | \mathbf{r} | j \rangle \times \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_n - E_j} \cdot \langle n | \mathbf{r} | j \rangle \times \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_n - E_j} \cdot \langle n | \mathbf{r} | j \rangle \times \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_n - E_j} \cdot \langle n | \mathbf{r} | j \rangle \times \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_n - E_j} \cdot \langle n | \mathbf{r} | j \rangle \times \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_n - E_j} \cdot \langle n | \mathbf{r} | j \rangle \times \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_n - E_j} \cdot \langle n | \mathbf{r} | j \rangle \times \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_n - E_j} \cdot \langle n | \mathbf{r} | j \rangle \times \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_n - E_j} \cdot \langle n | \mathbf{r} | j \rangle \times \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_n - E_j} \cdot \langle n | \mathbf{r} | j \rangle \times \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_n - E_j} \cdot \langle n | \mathbf{r} | j \rangle \times \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_n - E_j} \cdot \langle n | \mathbf{r} | j \rangle \times \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_n - E_j} \cdot \langle n | \mathbf{r} | j \rangle \times \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_n - E_j} \cdot \langle n | \mathbf{r} | j \rangle \times \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_n - E_j} \cdot \langle n | \mathbf{r} | j \rangle \times \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_n - E_j} \cdot \langle n | \mathbf{r} | j \rangle \times \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_n - E_j} \cdot \langle n | \mathbf{r} | j \rangle \times \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_n - E_j} \cdot \langle n | \mathbf{r} | j \rangle \times \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_n - E_j} \cdot (\mathbf{T} + \mathbf{T} \times \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_n - E_j} \cdot \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_n - E_j} \cdot \mathbf{T} + \mathbf{T} \times \frac{\langle j | \nabla | n \rangle}{E_n - E_j} \cdot \mathbf{T} + \mathbf{T} \times \mathbf{T} + \mathbf{$$

The last four terms in the previous expression add to zero. For exact wavefunctions, we can use the "dipole-velocity" transformation, so that the remaining part is

$$X = \frac{1}{2d_n} \sum_{n} \operatorname{Im}(\sum_{k \neq n} \mathbf{T} \times \langle k | \mathbf{r} | n \rangle \cdot \langle n | \mathbf{r} | j \rangle \times \langle j | \mathbf{r} | k \rangle$$
$$- \sum_{k \neq j} \mathbf{T} \times \langle j | \mathbf{r} | k \rangle \cdot \langle n | \mathbf{r} | j \rangle \times \langle k | \mathbf{r} | n \rangle).$$
(B3)

We rearrange the summations

$$X = \frac{1}{2d_n} \sum_{n} \operatorname{Im} \left[ \sum_{k} \left( \mathbf{T} \times \langle k | \mathbf{r} | n \rangle \cdot \langle n | \mathbf{r} | j \rangle \times \langle j | \mathbf{r} | k \rangle - \mathbf{T} \right] \\ \times \langle j | \mathbf{r} | k \rangle \cdot \langle n | \mathbf{r} | j \rangle \times \langle k | \mathbf{r} | n \rangle). - .\mathbf{T} \times \langle n | \mathbf{r} | n \rangle \cdot \langle n | \mathbf{r} | j \rangle \\ \times \langle j | \mathbf{r} | n \rangle + \mathbf{T} \times \langle j | \mathbf{r} | j \rangle \cdot \langle n | \mathbf{r} | j \rangle \times \langle j | \mathbf{r} | n \rangle],$$
(B4)

where again the last two terms containing  $\langle n|\mathbf{r}|j\rangle \times \langle j|\mathbf{r}|n\rangle = 0$  vanish. With some vector algebra, we get

$$X = \frac{1}{2d_n} \sum_{n} \operatorname{Im} \left[ \sum_{k} (\langle k | \mathbf{r} | n \rangle \times (\langle n | \mathbf{r} | j \rangle \times \langle j | \mathbf{r} | k \rangle) \cdot \mathbf{T} - \langle j | \mathbf{r} | k \rangle \right]$$

$$\times (\langle n | \mathbf{r} | j \rangle \times \langle k | \mathbf{r} | n \rangle) \cdot \mathbf{T} \right]$$

$$= \frac{1}{2d_n} \sum_{n} \operatorname{Im} \left[ \sum_{k} (\langle n | \mathbf{r} | j \rangle \cdot \mathbf{T} \langle k | \mathbf{r} | n \rangle \cdot \langle j | \mathbf{r} | k \rangle - \langle k | \mathbf{r} | n \rangle \right]$$

$$\cdot \langle n | \mathbf{r} | j \rangle \langle j | \mathbf{r} | k \rangle \cdot \mathbf{T} - \langle n | \mathbf{r} | j \rangle \cdot \mathbf{T} \langle j | \mathbf{r} | k \rangle \cdot \langle k | \mathbf{r} | n \rangle + \langle j | \mathbf{r} | k \rangle$$

$$\cdot \langle n | \mathbf{r} | j \rangle \langle k | \mathbf{r} | n \rangle \cdot \mathbf{T} \right]$$

$$= \frac{1}{2d_n} \sum_{n} \operatorname{Im} \sum_{k} (\langle n | \mathbf{r} | k \rangle \langle k | \mathbf{r} | j \rangle \cdot \langle n | \mathbf{r} | j \rangle - \langle j | \mathbf{r} | k \rangle \langle k | \mathbf{r} | n \rangle$$

$$\cdot \langle n | \mathbf{r} | j \rangle) \cdot \mathbf{T}.$$
(B5)

Finally, using the completeness property of exact wavefunctions,  $\sum |k\rangle \langle k| = 1$ ,

$$X = \frac{1}{2d_n} \sum_{n} \operatorname{Im}(\langle n | \mathbf{r} \mathbf{r} | j \rangle \cdot \langle n | \mathbf{r} | j \rangle - \langle j | \mathbf{r} \mathbf{r} | n \rangle \cdot \langle n | \mathbf{r} | j \rangle) \cdot \mathbf{T} = 0.$$
(B6)

In summary, in order to be completely origin independent, *B* must be calculated with complete wavefunctions (at least without the GIAO orbitals) and satisfying the dipole–velocity transformation.

**Keywords:** time-dependent  $\cdot$  density functional theory  $\cdot$  sum over states  $\cdot$  spectroscopy  $\cdot$  magnetic circular dichroism  $\cdot$  origin dependence

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- E. Charney, The Molecular Basis of Optical Activity; Wiley-Interscience: New York, 1979.
- [2] T. A. Keiderling, In Circular Dichroism: Principles and Applications; N. Berova, K. Nakanishi, R. W. Woody, Eds.; Wiley: New York, **2000**; p. 621.
- [3] L. D. Barron, Molecular Light Scattering and Optical Activity; Cambridge University Press: Cambridge, 2004.
- [4] W. R. Mason, A Practical Guide to Magnetic Circular Dichroism Spectroscopy; Wiley-Interscience: Portland, 2007.
- [5] D. W. Miles, H. Eyring, Proc. Natl. Acad. Sci. USA. 1973, 70, 3754.
- [6] T. A. Keiderling, J. Chem. Phys. 1981, 75, 3639.
- [7] J. Michl, Tetrahedron 1984, 40, 3845.
- [8] J. O. Jensen, G. F. Adams, C. F. Chabalowski, J. Chem. Phys. 1991, 94, 1332.
- [9] Z. Gasyna, P. N. Schatz, J. P. Hare, T. J. Dennis, H. W. Kroto, R. Taylor, D. R. M. Walton, *Chem. Phys. Lett.* **1991**, *183*, 283.
- [10] A. M. Bracete, S. Kadkhodayan, M. Sono, A. M. Huff, C. F. Zhuang, D. K. Cooper, K. M. Smith, C. K. Chang, J. H. Dawson, *Inorg. Chem.* **1994**, *33*, 5042.
- [11] M. Seth, T. Ziegler, J. Chem. Phys. 2006, 124, 144105.
- [12] G. A. Peralta, M. Seth, H. Zhekova, T. Ziegler, *Inorg. Chem.* 2008, 47, 4185.
- [13] E. H. Marin, M. Seth, T. Ziegler, Inorg. Chem. 2010, 49, 6066.
- [14] M. Seth, T. Ziegler. In Advances in Inorganic Chemistry; R. VanEldik, J. Harley, Eds.; Elsevier Academic Press, Inc.: CA, 2010, p. 41.
- [15] P. Štěpánek, V. Andrushchenko, K. Ruud, P. Bouř, J. Phys. Chem. A 2012, 116, 778.
- [16] J. R. Sabin, O. A. Varzatskii, Y. Z. Voloshin, Z. A. Starikova, V. V. Novikov, V. N. Nemykin, *Inorg. Chem.* 2012, *51*, 8362.
- [17] H. Bolvin, Inorg. Chem. 2007, 46, 417.
- [18] H. Solheim, K. Kornobis, K. Ruud, P. M. Kozlowski, J. Phys. Chem. B 2011, 115, 737.
- [19] L. Rosenfeld, Z. Phys. 1930, 57, 835.
- [20] P. J. Stephens, J. Chem. Phys. 1970, 52, 3489.
- [21] D. J. Shieh, S. H. Lin, H. Eyring, J. Phys. Chem. 1972, 76, 1844.
- [22] P. J. Stephens, Adv. Chem. Phys. 1976, 35, 197.
- [23] M. Seth, T. Ziegler, J. Autschbach, J. Chem. Phys. 2005, 122, 094112.
- [24] M. Seth, J. Autschbach, T. Ziegler, J. Chem. Theory Comput. 2007, 3,
- 434.
  [25] H. Solheim, K. Ruud, S. Coriani, P. Norman, J. Phys. Chem. A 2008, 112, 9615.
- [26] H. Solheim, K. Ruud, S. Coriani, P. Norman, J. Chem. Phys. 2008, 128, 094103.
- [27] T. Kjaergaard, S. Coriani, K. Ruud, Wiley Interdiscip. Rev. Comput. Mol. Sci. 2012, 2, 443.
- [28] T. Kjærgaard, B. Jansík, P. Jørgensen, J. Phys. Chem. A 2007, 111, 11278.
- [29] K. M. Lee, K. Yabana, G. F. Bertsch, J. Chem. Phys. 2011, 134, 144106.
- [30] M. Seth, M. Krykunov, T. Ziegler, J. Autschbach, J. Chem. Phys. 2008, 128, 234102.
- [31] M. Seth, M. Krykunov, T. Ziegler, J. Autschbach, A. Banerjee, J. Chem. Phys. 2008, 128, 144105.
- [32] M. Seth, T. Ziegler, J. Chem. Phys. 2007, 127, 134108.
- [33] S. Coriani, C. Hättig, P. Jørgensen, J. Chem. Phys. 2000, 113, 3561.
- [34] T. Kjærgaard, P. Jørgensen, A. J. Thorvaldsen, P. Sałek, S. Coriani, J. Chem. Theory Comput. 2009, 5, 1997.
- [35] Y. Honda, M. Hada, J. Chem. Phys. 2005, 123, 164113.
- [36] E. Goldstein, S. Vijaya, G. A. Segal, J. Am. Chem. Soc. 1980, 102, 6198.

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- [37] A. R. Meier, H. Wagniere, Chem. Phys. 1987, 113, 287.
- [38] G. Marconi, Chem. Phys. Lett. **1988**, 146, 259.
- [39] D. Ganyushin, F. Neese, J. Chem. Phys. 2008, 128, 114117.
- [40] K. B. Wiberg, Y. Wang, S. M. Wilson, P. H. Vaccaro, J. R. Cheeseman, J. Phys. Chem. A 2006, 110, 13995.
- [41] R. Serber, Phys. Rev. 1932, 41, 489.
- [42] A. Szabo, N. S. Ostlund, Modern Quantum Chemistry. Introduction to Advanced Electronic Structure Theory; Dover: New York, 1989.
- [43] M. Pilch, M. Pawlikowski, O. S. Mortensen, Chem. Phys. 1993, 172, 277.
- [44] R. Ahlrichs, M. Bar, H.-P. Baron, R. Bauernschmitt, S. Bocker, M. Ehrig, K. Eichkorn, S. Elliot, F. Furche, F. Haase, M. Haser, H. Horn, C. Huber, U. Huniar, M. Kattannek, C. Kolmel, M. Koolwitz, K. May, C. Ochsenfeld, H. Ohm, A. Schafer, U. Schneider, O. Treutler, M. von Arnim, F. Weigend, P. Weis, H. Weiss, Quantum Chemistry Group; University of Karlsruhe: Karlsruhe, **1998**.
- [45] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc.: Wallingford, CT, **2009**.
- [46] N. T. Maitra, F. Zhang, R. J. Cave, K. Burke, J. Chem. Phys. 2004, 120, 5932.
- [47] P. Elliott, S. Goldson, C. Canahui, N. T. Maitra, Chem. Phys. 2011, 391, 110.
- [48] F. Furche, R. Ahlrichs, J. Chem. Phys. 2002, 116, 7433.

- [49] V. G. Malkin, O. L. Makina, M. E. Casida, D. R. Salabub, J. Am. Chem. Soc. 1994, 116, 5898.
- [50] P. Bouř, Chem. Phys. Lett. 1998, 288, 363.
- [51] A. D. Becke, J. Chem. Phys. 1993, 98, 5648.
- [52] J. P. Perdew, Phys. Rev. B 1986, 33, 8822.
- [53] C. Angeli, K. L. Bak, V. Bakken, O. Christiansen, R. Cimiraglia, S. Coriani, P. Dahle, E. K. Dalskov, T. Enevoldsen, B. Fernandez, C. Haettig, K. Hald, A. Halkier, H. Heiberg, T. Helgaker, H. Hettema, H. J. A. Jensen, D. Jonsson, P. Joergensen, S. Kirpekar, W. Klopper, R. Kobayashi, H. Koch, O. B. Lutnaes, K. V. Mikkelsen, P. Norman, J. Olsen, M. J. Packer, T. B. Pedersen, Z. Rinkevicius, E. Rudberg, T. A. Ruden, K. Ruud, P. Salek, A. Sanchez de Meras, T. Saue, S. P. A. Sauer, B. Schimmelpfennig, K. O. Sylvester-Hvid, P. R. Taylor, O. Vahtras, D. J. Wilson, H. Agren; University of Oslo: Oslo, **2005**.
- [54] A. Rizzo, S. Coriani, K. Ruud, In Computational Strategies for Spectroscopy: From Small Molecules to Nano Systems; V. Barone, Ed.; Wiley: New Jersey, 2012, p. 77.
- [55] A. Rizzo, O. Vahtras, J. Chem. Phys. 2011, 134, 244109.
- [56] M. Pecul, K. Ruud, In Advances in Quantum Chemistry: Response Theory and Molecular Properties; J. R. Sabin, E. Brändas, H. Jorgen, A. Jensen, Eds.; Elsevier, Academic Press: London, **2005**, p. 185.
- [57] R. Ditchfield, Mol. Phys. 1974, 27, 789.
- [58] K. L. Bak, A. E. Hansen, K. Ruud, T. Helgaker, J. Olsen, P. Jørgensen, *Theor. Chim. Acta* **1995**, *90*, 441.
- [59] P. L. Polavarapu, L. Hecht, L. D. Barron, J. Phys. Chem. 1993, 97, 1793.
- [60] R. D. Amos, N. C. Handy, K. J. Jalkanen, P. J. Stephens, Chem. Phys. Lett. 1987, 133, 21.
- [61] F. Furche, R. Ahlrichs, C. Wachsmann, E. Weber, A. Sobanski, F. Vögtle, S. Grimme, J. Am. Chem. Soc. 2000, 122, 1717.

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