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The A and B Terms of Magnetic Circular Dichroism Revisited

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The temperature-independent part of the magnetic circular dichroism spectrum is conventionally divided into the Faraday A and B terms, where the A term is nonzero only for systems with degenerate states. We propose that this separation is abandoned in favor of a unified temperature-independent term. This proposal is based on complex polarization propagator calculations on three structurally similar porphyrins. These calculations also suggest that the Soret band of Zn-porphyrin is determined by an isolated degenerate $2E_u$ state.

Since the seminal papers by Buckingham and Stephens,[1,2] which laid the theoretical foundation for magnetic circular dichroism (MCD), the contributions to an observed MCD spectrum have been conventionally divided into three terms,[3,4] (1) the A term associated with degenerate ground and excited states and a measure of the magnetic moments of the degenerate states, (2) the B term associated with the magnetic field perturbation of the electronic states of the molecule and occurring for all electronic states and molecules, and (3) the C term associated with an orbitally degenerate ground state and due to the different populations of the magnetic spin sublevels. Since the populations of the spin sublevels are temperature-dependent, the C term is temperature-dependent, whereas the A and B terms are temperature-independent.

This partitioning of the contributions to the MCD intensity into three terms stands in sharp contrast to most other birefringences,[5] which are normally divided into two terms only, a temperature-independent and a temperature-dependent part. We here propose that for closed-shell molecules, the historical separation into an A and a B term should be abandoned, being instead considered as a single temperature-independent contribution. We believe the artificial separation into A and B terms can lead to incorrect analyses of the nature of excited states in highly symmetric systems and complicate both the theoretical calculation and the analysis of experimental MCD data.

The artificial partitioning of the temperature-independent contribution into an A and a B term is perhaps most easily understood in terms of small geometrical distortions of a highly symmetric molecule, such as the D_{4h} metalloporphyrins studied in a recent work by Peralta et al.[6] In the fully symmetric D_{4h} porphyrin system, the dominating contributions will, in general, arise from the A term of the degenerate excited states. Small geometrical distortions of the porphyrin ring system, lowering the symmetry to C_{2v}, are not expected to lead to major changes in the MCD spectrum,[6] the latter being now, however, entirely determined by the B term. As the shape of the MCD spectrum still displays a derivative band shape instead of the absorption band shape normally associated with the B term, such a response is often referred to as a pseudo-A term.[3] However, the fact remains that the physical interaction mechanisms remain identical in these two systems, the difference in interpretation being due to the artificial partitioning of the temperature-independent contribution into the A and B terms.

We recently introduced a complex polarization propagator approach for the unified treatment of the A and B terms of MCD,[7,8] an approach which has also been developed independently by Krykunov et al. and applied to the calculation of the MCD B term.[9]By considering the magnetic field perturbation of a complex polarizability, in which the finite lifetimes of the excited states are taken explicitly into account, we showed that the complex polarization propagator contains both the A and the B terms and that the propagator describes the MCD response of closed-shell molecules for both degenerate and nondegenerate electronic excited states.

The complex polarization propagator that determines the MCD response is given by the equation

$$\langle\langle\mu_\alpha;\mu_\beta,m_\gamma\rangle\rangle_{\omega,0}=\frac{1}{\hbar^2}\sum_{n,k>0}$$

$$\left\{\begin{matrix} \dfrac{\langle 0|\mu_\alpha|n\rangle\langle n|\bar{\mu}_\beta|k\rangle\langle k|m_\gamma|0\rangle}{(\omega_{k0}-i\gamma_k)(\omega_{n0}-\omega-i\gamma_n)} & + & \dfrac{\langle 0|\mu_\alpha|n\rangle\langle n|\bar{m}_\gamma|k\rangle\langle k|\mu_\beta|0\rangle}{(\omega_{k0}-\omega-i\gamma_k)(\omega_{n0}-\omega-i\gamma_n)} \\ +\dfrac{\langle 0|m_\gamma|k\rangle\langle k|\bar{\mu}_\beta|n\rangle\langle n|\mu_\alpha|0\rangle}{(\omega_{k0}+i\gamma_k)(\omega_{n0}+\omega+i\gamma_n)} & + & \dfrac{\langle 0|\mu_\beta|k\rangle\langle k|\bar{m}_\gamma|n\rangle\langle n|\mu_\alpha|0\rangle}{(\omega_{k0}+\omega+i\gamma_k)(\omega_{n0}+\omega+i\gamma_n)} \\ +\dfrac{\langle 0|\mu_\beta|n\rangle\langle n|\bar{\mu}_\alpha|k\rangle\langle k|m_\gamma|0\rangle}{(\omega_{n0}+\omega+i\gamma_n)(\omega_{k0}-i\gamma_k)} & + & \dfrac{\langle 0|m_\gamma|n\rangle\langle n|\bar{\mu}_\alpha|k\rangle\langle k|\mu_\beta|0}{(\omega_{n0}+i\gamma_n)(\omega_{k0}-\omega-i\gamma_k)} \end{matrix}\right\} \quad (1)$$

In this equation, we have introduced the dipole moment operator μ and the magnetic dipole operator m; $\hbar\omega_{n0}$ here represents the excitation energy from the ground to the nth excited state, ω is the frequency of the incident electromagnetic light, and γ_n is a measure of the relaxation of the nth excited state back to the

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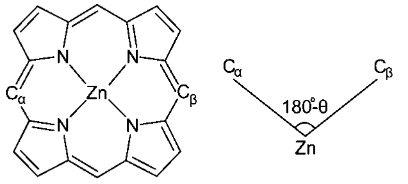

Figure 1. Illustration of the bending angle used in the calculations on the distorted porphyrins, obtained by bending the porphyrin backbone around the meso-carbon−metal−meso-carbon axis.

ground state and is, in our approach, an empirical parameter. The overline denotes fluctuation operators $\bar{\Omega} = \Omega - \langle 0|\Omega|0\rangle$. Equation 1 is the spectral resolution of the response function, and within the self-consistent field approximation (SCF), the sum-overstates expression will become a matrix equation (see ref 8).

The differential absorption of right and left circularly polarized light determined by the polarization propagator in eq 1 is related to the experimentally observed spectrum through

$$\mathrm{MCD}(\omega) = \chi\hbar\omega\frac{1}{3\mu_{\mathrm{B}}}\sum_{\alpha\beta\gamma}\varepsilon_{\alpha\beta\gamma}\mathrm{Re}\langle\langle\mu_\alpha;\mu_\beta, m_\gamma\rangle\rangle_{\omega,0} \qquad (2)$$

where μ_{B} is the Bohr magneton, $\varepsilon_{\alpha\beta\gamma}$ is the Levi−Civita antisymmetric tensor, and χ is a factor which depends on the quantity actually measured in experiment.[3]

In order to demonstrate computationally that the complex polarization propagator contains all of the necessary information about the MCD response of an orbitally nondegenerate ground state without the artificial separation into an A and a B term, we have calculated the MCD spectra of Mg-, Zn-, and Ni-porphyrin at the density functional level of theory using the complex polarization propagator approach.[7,8] For the MCD calculations, we have used the CAM-B3LYP[10,11] functional and the aug-cc-pVDZ[12−14] basis set. The lifetime broadening has been set to 1000 cm^{-1} for all excited states. The spectra have been determined on a grid of frequencies with a grid point separation of 0.001 hartree. All calculations have been carried out in the gas phase. The D_{4h} geometries have been optimized at the DFT/B3LYP level using the cc-pVTZ[14,15] basis set. Distorted geometries (vide infra) have not been reoptimized but have been obtained by bending the porphyrin ring by 10, 20, and 30° about the meso-carbon−metal−meso-carbon axis (see Figure 1). When discussing excitation energies, these have been obtained in a separate calculation from the poles of the linear response function. All calculations have been performed using a local version of the Dalton program.[16]

In Figure 2, we report the results of our complex polarization propagator calculations for Mg-, Zn-, and Ni-porphyrins in the frequency range observed experimentally.[17] The observed transitions at around 2.3−2.4 and 3.6 eV correspond to the Q and Soret bands, respectively. We note that the calculations produce very similar MCD spectra for these three molecules, in agreement with the observation that these bands originate almost exclusively from excitations on the ligand with little involvement of orbitals on the metal center.[6,18] Our results are also in good agreement with the experimentally observed MCD spectrum of the Zn-porphyrin, save the vibronic feature present in the Q-band in experiment, which is not included in our computational procedure. The complex polarization propagator contains all physical information needed to analyze and describe the electronic part of the experimental MCD spectrum. As these lowest-lying bands involve excitations to the two lowest excited states of E_u symmetry, these bands would conventionally be described as A terms.

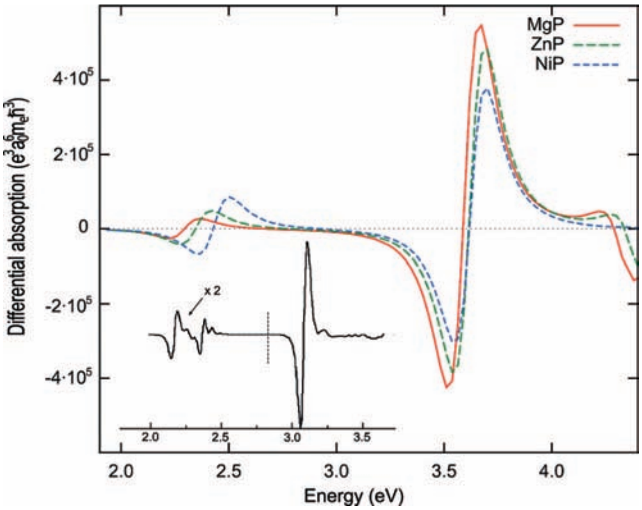

Figure 2. Calculated MCD spectra of Mg-, Zn-, and Ni-porphyrin obtained using the aug-cc-pVDZ basis set and the CAM-B3LYP functional. The inset shows the experimental spectrum of Zn-porphyrin taken from ref 17.

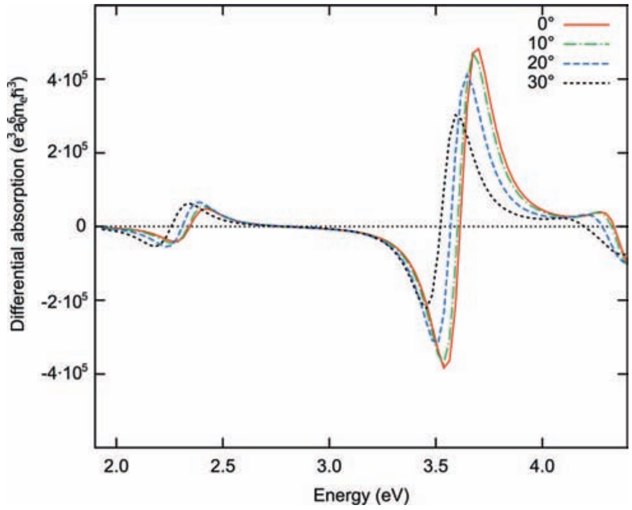

Figure 3. Calculated MCD of Zn-porphyrin bent about the meso-carbon−metal−meso-carbon axis obtained using the aug-cc-pVDZ basis set and the CAM-B3LYP functional.

For closed-shell molecules, the A term only appears for electronically degenerate excited states, which can only occur for highly symmetric molecules. Small, symmetry-breaking distortions, which may not significantly alter the nature of the electronic states, may thus lead to a complete reinterpretation of origin of the MCD signal, even though there are no significant changes in the electronic structure of the molecule. We illustrate this point in Figure 3, where we report the results of our MCD calculations for the Zn-porphyrin in which we, in addition to the D_{4h} porphyrin, also report the results obtained by bending the porphyrin by 10, 20, and 30° about the meso-carbon−metal−meso-carbon axis, as illustrated in Figure 1. It is worth noting that the degenerate excited state now becomes only weakly split, the energy separation being a modest 0.006 eV for the Soret band of the Zn-porphyrin bent by 10°.

We observe that even for the rather severe geometry distortion of 30°, the qualitative, and to a large extent also the quantitative, features of the MCD spectrum remain unchanged. The complex polarization propagator[7,8] thus allows the transition from the highly symmetrical porphyrin system to the lower-symmetry systems to be smoothly handled, without neither the need for a reevaluation of the physical origins of the effects nor the need to consider different computational methodologies[19−22] to handle the high-symmetry and lower-symmetry situations.

In modern textbooks on MCD, the close relationship between the A and the B terms is often emphasized[3] since the B term is noted to become large when two or more excited states are lying close in energy. If the excited states are separated in energy less than their band widths, the MCD response from these excited states may have the appearance of an A term, and this kind of MCD response is then referred to as a pseudo-A term. The MCD responses for the distorted porphyrins in Figure 2 are thus examples of such pseudo-A terms. However, the physical origin of the response is the same for both the D_{4h} and the distorted porphyrins, even though some of the excited states become electronically degenerate for the undistorted porphyrin. The physics in the response is properly recovered by the complex polarization propagator approach.

It is here worthwhile to revisit the results of Peralta et al.[6] By combining their A and B contributions to the MCD intensity, their Mg- and Zn-porphyrins have a ratio between the MCD signal of the Soret band and that of the Q-band of almost a factor of 400, whereas this ratio is approximately 5−10 in the case of the Ni-porphyrin. This latter ratio is in good agreement with our results for all three porphyrins and also in reasonable agreement with the experimental ratio for the Soret and Q bands of Zn-porphyrin.[17] The reason for the very large ratios between the Soret and Q bands of Mg- and Zn-porphyrin in ref 6 can be traced to the very large B term contribution for these two molecules, which arises because the Soret band in these calculations is composed of two sets of degenerate excited states ($2E_u$ and $3E_u$), being separated by only 0.07 eV. This is in marked contrast to the origin of our Soret band, which is a well-separated $2E_u$ state with a gap of 0.7 eV to the $3E_u$ state. When comparing these two theoretical results to the experimental spectrum of Zn-porphyrin, it would appear that the Soret band corresponds to an isolated $2E_u$ state and that the results of Peralta et al.[6] are due to the appearance of the $3E_u$ state too close in energy to the $2E_u$ state, leading to an unphysical divergence in their expression for the B term of this band. Our results thus suggest that the SAOP functional, as well as the BHLYP functional,[23] give an incorrect description of the $3E_u$ state, whereas the energy separation between the $2E_u$ and $3E_u$ states is well reproduced by our CAM-B3LYP functional. Our results are furthermore corroborated by SAC-CI calculations[24] as well as, to some extent, by MRCI/DFT[25] calculations. However, even though our energy separation between the $2E_u$ and $3E_u$ states appears to agree well with the experimental finding and thus that the Soret band corresponds to a single, degenerate excited state, our calculated excitation energy is about 0.5 eV too high compared to that of experiment.

An analysis of the response vectors obtained in the complex polarization propagator calculations shows that the character of the $1E_u$ state for the Mg-porphyrin is in quite good agreement with the analysis of Peralta et al.,[6] having largely a $4a_{2u} \rightarrow 4e_g$ and $1a_{1u} \rightarrow 2e_g$ character of almost equal weight (a ratio of 0.96, compared to the ratio of 1.21 in ref 6), denoting the orbitals according to their increasing energy in the D_{4h} point group. For the $2E_u$ state, however, the situation is very different. In our calculations, the same orbital characters dominate this transition with an approximately equal, but inverse, ratio (with some additional $3a_{2u} \rightarrow 4e_g$ character), whereas the $2E_u$ state in the work of Peralta et al. largely has $2b_{2u} \rightarrow 4e_g$ character). Indeed, our $2E_u$ state, to some extent, resembles more strongly the $3E_u$ state obtained in ref 6. Thus, the nature of the excited states appears to be very different in the work of Peralta et al. using the SAOP functional compared to that from our CAM-B3LYP results. Further studies into these low-lying states of the Mg-, Ni-, and Zn-porphyrins in order to elucidate which states actually enter into the Soret band of these molecules appear necessary, though we note that our computed MCD spectrum, when compared with the experimental spectrum for Zn-porphyrin, seems to indicate that the Soret band is governed by an isolated $2E_u$ state.

Returning now to the partitioning of the temperature-independent contribution of the MCD intensity into an A and a B term, we note that it may be argued that the fact that A and B terms experimentally are often associated with different band shapes is an argument in favor of splitting the temperature-independent contribution to the MCD response into two contributions. However, the fact that the same physical interaction mechanism may lead to two different experimental band shapes does not necessitate an artificial separation of the interaction mechanism. Indeed, the discussion of pseudo-A terms arising from nearly degenerate excited states in the expression for the B term illustrates that this partitioning is unphysical and unnecessary and, to some extent, even misleading, as illustrated for the distorted porphyrins. Little additional information about the nature of the excited states is obtained by trying to deconvolute the physical interactions present in a molecule in a MCD experiment into A, pseudo-A, and B terms.

Stephens has utilized the simple expression for the A term to devise a scheme in which the excited-state magnetic moments can be estimated from a knowledge of the MCD differential absorption of the left and rightcircularly polarized light and the total absorption for the transition to the degenerate excited states.[26] We emphasize that our reinterpretation of the temperature-independent contribution to the MCD signal does not preclude such an experimental means of obtaining the excited-state magnetic moment, as this situation is fully contained in the complex polarization propagator. Indeed, we see that we can, within the approximations employed by Stephens,[26] generalize this approach also to close-lying excited states which exhibit a pseudo-A term and, in this manner, obtain an effective excited-state magnetic moment for the energetically close-lying excited states. Thus, for the MCD spectra in Figure 2, such a generalization would allow us to obtain not only the magnetic moment of the degenerate excited states for the undistorted porphyrin but also an effective magnetic moment for the nearly degenerate excited states of the distorted structures.

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