COMMENTS

Comment on the Validity of the Atom Monopole−Dipole Interaction Model for Optical Activity

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A model that has proven useful in predicting polarizability tensors of conjugated molecules is the atom monopole−dipole interaction (AMDI) model of Olson and Sundberg.[1] The molecular response to an electric field is treated in terms of the local dipole polarizations of the atoms and the monopole polarizations associated with electron migration within the molecule. A transferable set of atom polarizability parameters has been found to give satisfactory tensors for planar aromatic hydrocarbons,[2] closed-cage fullerenes,[3] nitrogen heterocycles,[4] and linear polyenes.[5] The related electronic absorption spectrum of naphthalene has also been treated with partial success.[6] The model has the potential to predict properties of large systems with modest computational effort.

It would be of particular interest to know whether the AMDI model is valid for predicting optical activity of chiral conjugated molecules, as there are many important complex molecules of this type. Unfortunately, the answer to this question is negative, as an inherent feature of the model is a dependence of the molecular rotatory parameter β for an isotropic system on the choice of the origin of the molecular coordinate system, a physically impossible behavior. The purpose of this comment is to show how this origin dependence arises and to call attention to its limitation on the validity of the AMDI model.

The AMDI model consists of an array of N atoms in which atom i responds to the local electric potential ϕ_i by the induction of a charge $q_i = -\sigma_i\phi_i$ and responds to the local electric field $\mathbf{E}_i$ by the induction of a dipole moment $\boldsymbol{\mu}_i = \boldsymbol{\alpha}_i\cdot\mathbf{E}_i$, where σ_i and $\boldsymbol{\alpha}_i$ are the atom monopole and dipole polarizabilities, respectively.[1] The solution to the interaction problem is an expression of the column matrix M of atom monopoles and dipoles in terms of the column matrix $\mathcal{E}$ of potentials and fields in the form[2,7]

$$M = B\mathcal{E} \tag{1}$$

where B is the 4N-order matrix of relay polytensors. The molecular rotatory parameter β (whose real and imaginary parts give optical rotation and circular dichroism, respectively) has been derived for a general multipole interaction model,[7] and the expression for the AMDI model reduces to

$$\beta = \frac{1}{6}\epsilon\vdots\sum_{i,j}[\mathbf{r}_i\mathbf{B}_{ij}^{(0,1)}\mathbf{r}_j + \mathbf{B}_{ij}^{(1,1)}\mathbf{r}_j] \tag{2}$$

where ϵ is the third-rank permutation tensor, $\mathbf{r}_i$ is the position of atom i in the chosen molecular coordinate system, and the $\mathbf{B}_{ij}^{(m,n)}$ tensors are elements of the B matrix.

An insight into the behavior of the model is gained by transforming eq 2 into a sum over the "virtual" normal modes of the system.[8] There are 4N normal modes, of which the nth is described by an eigenvalue d_n and an eigenvector $\mathbf{k}_n$ of the B matrix. The elements of $\mathbf{k}_n$ are the atomic charge and electric dipole amplitudes $q_i^{(n)}$ and $\boldsymbol{\mu}_i^{(n)}$ for $i = 1, 2, ..., N$. From the expansion of B in terms of these modes[8] one finds

$$\mathbf{B}_{ij}^{(0,1)} = \sum_{n=1}^{4N} d_n q_i^{(n)}\boldsymbol{\mu}_j^{(n)} \tag{3}$$

$$\mathbf{B}_{ij}^{(1,1)} = \sum_{n=1}^{4N} d_n \boldsymbol{\mu}_i^{(n)}\boldsymbol{\mu}_j^{(n)} \tag{4}$$

Consider the following molecular moments of the nth normal mode.

$$\boldsymbol{\nu}^{(n)} = \sum_{i=1}^{N} q_i^{(n)}\mathbf{r}_i \tag{5}$$

$$\boldsymbol{\mu}^{(n)} = \sum_{i=1}^{N} \boldsymbol{\mu}_i^{(n)} \tag{6}$$

$$\mathbf{m}^{(n)} = \sum_{i=1}^{N} \mathbf{r}_i \times \boldsymbol{\mu}_i^{(n)} \tag{7}$$

Equation 2 is then transformed to

$$\beta = \frac{1}{6}\sum_{n=1}^{4N} d_n[\boldsymbol{\nu}^{(n)} + \boldsymbol{\mu}^{(n)}]\cdot\mathbf{m}^{(n)} \tag{8}$$

If the origin of the molecule-fixed coordinate system is shifted to a point $-\mathbf{R}$, then the atom coordinates are shifted to $\mathbf{r}_i + \mathbf{R}$. There is no change in B or its eigenvalues and eigenvectors, as the matrix is a function of differences between atom positions. From eq 8 one finds that β is shifted to a new value $\hat{\beta}$ given by

$$\hat{\beta} = \beta + \frac{1}{6}\sum_{n=1}^{4N} d_n\boldsymbol{\nu}^{(n)}\cdot\mathbf{R} \times \boldsymbol{\mu}^{(n)} \tag{9}$$

That is, β is origin-dependent whenever $\boldsymbol{\nu}^{(n)}$ and $\boldsymbol{\mu}^{(n)}$ are not parallel, as is generally the case.

The reason for the origin dependence is now evident. The electric dipole moment has contributions from both $q_i^{(n)}$ and $\boldsymbol{\mu}_i^{(n)}$, while the magnetic dipole moment represented by $\mathbf{m}^{(n)}$ contains only the latter. This is unrealistic for a molecule, as there should be currents associated with the oscillations in both $q_i^{(n)}$ and $\boldsymbol{\mu}_i^{(n)}$, and both should contribute to $\mathbf{m}^{(n)}$. A complete specification of the current distribution would necessarily give β independent of origin.

The predicted origin dependence is quite large in typical cases. Numerical calculations for some small, chiral aromatic hydrocarbons show shifts in β of 100% or more for origin shifts within the molecular dimensions.

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A special case of chiral molecular symmetry in which the origin dependence of the AMDI model vanishes is that of the D_2 point group. By the methods of group theory it can be shown that $\boldsymbol{\nu}^{(n)}$ and $\boldsymbol{\mu}^{(n)}$ are parallel for all normal modes in this case. However, this does not imply that the neglect of currents associated with charge migrations is valid even in this case. While the details of the current distributions are not defined for the AMDI model, the symmetry species of the current distribution in any normal mode must be the same as that of the atom dipole moments; hence, there must be a contribution from the currents to $\mathbf{m}^{(n)}$ in addition to the atom dipole contribution in eq 7.

It is worth noting that the origin dependence of optical activity in the AMDI model, which is based on classical electromagnetic theory, has a close analogy in the quantum mechanical theory of optical activity. Moffitt[9] showed that the rotational strength of an electronic transition is proportional to the scalar product of the linear momentum and angular momentum matrix elements and that there is no origin dependence when these matrix elements are calculated accurately. He showed, however, that an approximation in which the linear momentum and electric transition moment matrix elements are not parallel gives rise to origin dependence in a manner similar to that shown above for the AMDI model.

The origin dependence of optical activity in the AMDI model does not detract from the validity of previous applications of the model to calculations of polarizability tensors and absorption spectra. These properties are determined primarily by the local monopole and dipole polarization of atoms; the currents contribute only through the accumulation of charge on the atoms, and no origin dependence of the properties has been found in the theory.

References and Notes

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