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Relationes

On the Application of the Geometric Approximation to the Calculation of Ring-Current Properties

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Burrows' formula giving an upper bound for the error in the geometric approximation is applied to the calculation of the ring-current contribution to the diamagnetic anisotropies of conjugated molecules. It is also emphasized that this approximation is easily applied in practice.

Key words: Diamagnetic anisotropies of conjugated molecules – Ring-current properties – Geometric approximation

Introduction

Given a Hartree-Fock ground-state wavefunction the second-order change in the energy due to a perturbation of the form $\sum_i z(i)$ can be found by applying what has become known as coupled Hartree-Fock perturbation theory [1–5]. In an attempt to simplify such a calculation and, in particular, to avoid the use of the iterative procedure inherent in a coupled approach, it was suggested that second-order properties could be estimated using the uncoupled version of the perturbation theory [6–11] as long as certain correction terms, calculated by means of the geometric approximation [12–16] were included.

In a recent paper Burrows [17] derived an upper bound for the error, e, arising from such an approximation. We shall apply this formula to the calculation of the bound for the ring-current contributions to the anisotropies of a selection of conjugated molecules within a semi-empirical pi-electron framework. We show that, having regard to the accuracy normally associated with such a model, e is very small and that, therefore, there is a negligible difference between the coupled results and those given by corrected uncoupled theory.

In its original formulation, application of the geometric approximation necessarily involved a summation over four indices in order to calculate the first correction term. It is thought possible that this point would have deterred workers from using the uncoupled method, especially for large systems, if it was believed that long periods of computing time would be involved. It has recently [21, 22] been suggested, in fact, that the coupled method compares favourably from this viewpoint.

We show that this is not the case for the calculation of diamagnetic anisotropies, and that the special nature of the wavefunction in the presence of a magnetic field leads to certain simplifying features, resulting in a formula for the correction which can be readily and rapidly evaluated. We note, in an appendix, that this is also true when using the test-dipole method to calculate the ring-current contribution to the chemical shift.

Basic Equations and Formulae

In the presence of a magnetic field $\boldsymbol{H}$, perpendicular to the plane of the molecule, the single-particle Hamiltonian F may be written, in the usual notation, as [15]

$$F = \frac{1}{2m}\left(\boldsymbol{p} + \frac{e}{c}A\right)^2 + V,$$

where $A = A^H = \frac{1}{2}\boldsymbol{H} \wedge \tilde{\boldsymbol{r}}$, a tilde denoting that the origin of coordinates is chosen arbitrarily. In terms of the so-called gauge-invariant orbitals $\{\chi_s\}$ where

$$\chi_s = \omega_s \exp(-i\alpha A_s \cdot \tilde{\boldsymbol{r}}), \qquad (A_s = \tfrac{1}{2}\boldsymbol{H} \wedge \tilde{\boldsymbol{R}}_s),$$

the new orbitals will be

$$\phi_i = \Sigma\, c_{is} \chi_s .$$

Application of the uncoupled procedure using the zero transition dipole and quadrupole moments approximation [15] gives

$$F_{st} = H^0_{st} \exp(i\alpha H \tilde{S}_{st}) + F^0_{st} - H^0_{st},$$

where H^0 is that part of the field-free Hamiltonian matrix F^0 which arises from one-electron terms only, and $H\tilde{S}_{st} = \frac{1}{2}\boldsymbol{H} \cdot (\tilde{\boldsymbol{R}}_s \wedge \tilde{\boldsymbol{R}}_t)$.

Since the magnetic susceptibility is a second-order property in the field we expand F_{st} and c_{is} in orders of magnitude of H i.e.

$$F_{st} = F^0_{st} + i\alpha H F'_{st} + \alpha^2 H^2 F''_{st} + \cdots$$

$$c_{is} = c^0_{is} + i\alpha H c'_{is} + \alpha^2 H^2 c''_{is} + \cdots .$$

After some manipulation the second-order energy can then be shown to be

$$E_{02} = E^d_{02} + E^p_2,$$

where

$$E^d_{02} = -2\alpha^2 \sum_i^{\text{occ}} \langle \phi^0_i | F' | \phi'_i \rangle$$

and

$$E^p_2 = 2\alpha^2 \sum_i^{\text{occ}} \langle \phi^0_i | F'' | \phi^0_i \rangle$$

where

$$\phi^0_i = \sum_i c^0_{is}\omega_s, \qquad \phi'_i = \sum_i c'_{is}\omega_s,$$

and the first-order orbital coefficients satisfy the equations

$$\sum_t (F^0_{st} - \varepsilon^0_i \delta_{st})\, c'_{it} = -\sum_t F'_{st} c^0_{st} .$$

We define a first-order bond-order matrix $\tilde{P}'$ such that

$$\tilde{P}'_{st} = 2 \sum_{i}^{\text{occ}} (c'_{is} c^0_{it} - c^0_{is} c'_{it}) \, .$$

Then, in terms of these matrix elements,

$$E^d_{02} = -\alpha^2 \sum_{s<t} P'_{st} \tilde{S}_{st} H^0_{st} \quad \text{and} \quad E^p_2 = -\alpha^2 \sum_{s<t} P^0_{st} \tilde{S}^2_{st} H^0_{st} \, .$$

From Tuan *et al.* [8] we may then express the first-order correction to E^d_{02} as

$$E^d_{12} = -2 \sum_{ij}^{\text{occ}} \{(i'j' | j^0 i^0) + (i' j^0 | j' i^0)\} \tag{1}$$

where $i^0 \equiv \phi^0_i$ and i' is the first-order change in the wavefunction *viz.*

$$i' = i\alpha \phi'_i - i\alpha \sum_s \boldsymbol{A}_s \cdot \boldsymbol{r} c^0_{is} \omega_s \, .$$

We note that the equation for E^d_{12} is simpler than the corresponding equation for real wavefunctions as used, for example, in calculations of polarizability [11] where the correction takes the form

$$2 \sum_{ij}^{\text{occ}} \{4(i'j' | i^0 j^0) - (i'j' | j^0 i^0) - (i' j^0 | j' i^0)\} \, .$$

This simplification arises because i' is pure imaginary. Evaluation of (1) using the usual approximations yields a sum over 4 indices

$$E^d_{12} = 2 \sum_{st} \gamma_{st} \sum_{ij}^{\text{occ}} (c'_{it} c'_{js} c^0_{jt} c^0_{is} - c'_{it} c'_{jt} c^0_{is} c^0_{js}) \, ,$$

which may be simply written[1] as

$$E^d_{12} = -\tfrac{1}{2} \sum_{s<t} \gamma_{st} (\tilde{P}'_{st})^2 \, . \tag{2}$$

Thus, since $\tilde{P}'_{st}$ has already been found in the process of calculating E^d_{02}, the extra work involved in finding the first-order correction is minimal.

The total second-order energy is then given by

$$E_2 = E^p_2 + \mu E^d_{02} \, ,$$

where

$$\mu = \left(1 - \frac{E^d_{12}}{E^d_{02}}\right)^{-1}$$

from which the pi-electron contribution to the susceptibility ΔK_π is found by $\Delta K_\pi = -2 A E_2$, where A is Avogadro's number.

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[1] A similar equation for the correction in a test-dipole calculation of the chemical shift is given in the appendix.

Table 1. Susceptibilities and error bounds (units of 10^{-6} cgs emu)

Molecule[a]	Susceptibility	Bound
Benzene	− 31.2	0.0
Naphthalene	− 66.3	−0.1
Azulene	− 70.9	−0.3
Triphenylene	−125.8	−0.6
Phenanthrene	− 98.7	−0.3
Chrysene	−136.0	−1.3
Fluoranthene	− 88.9	−0.9
11-12-Benzofluoranthene	−126.1	−2.6

[a] Regular geometry assumed. Semi-empirical parameters as in [15].

Error Bound

We apply the formula given by Burrows' [17] to the calculation of an upper bound to the magnitude of the error e in the evaluation of the magnetic susceptibility. As in the calculation of E_{12}^{d} the imaginary nature of the first-order change in the wavefunction results in a simplification of the formula and it can be shown that, applying the usual approximations,

$$0 \geqq e \geqq -\frac{4A\alpha^2}{\Delta E} \sum_{l}^{\text{unocc}} \sum_{m}^{\text{occ}} \left(\sum_{st} c_{ls}^{0} c_{mt}^{0} ((\mu-1) H_{st}^{0} \tilde{S}_{st} + \frac{\mu}{2} \gamma_{st} \tilde{P}'_{st}) \right)^2,$$

where ΔE is the difference between the energies of the lowest unoccupied and highest occupied orbitals. In Table 1 values of this bound are listed for a variety of conjugated hydrocarbons along with the corresponding total susceptibilities as found by applying the uncoupled procedure detailed above, fixing[2] the origin of coordinates at the centre of charge [15]. We may deduce that the error, relative to a coupled calculation, is insignificant at the level of approximation inherent in a semi-empirical calculation.

Appendix

An analysis similar to that given above may be applied to the calculation of the ring-current contribution to the chemical shift, using the test-dipole method [16] for which the vector potential takes the form

$$\boldsymbol{A} = \boldsymbol{A}^{H} + \boldsymbol{A}^{m} = \tfrac{1}{2}\boldsymbol{H} \wedge \tilde{\boldsymbol{r}} + \frac{\boldsymbol{m} \wedge \boldsymbol{r}}{r^3},$$

where the test-dipole has moment $\boldsymbol{m}$, perpendicular to the molecular plane. The origin of $\boldsymbol{r}$ in $\boldsymbol{A}^{m}$ is fixed at the proton in question. If the energy is expanded as a

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[2] As to be expected, the error bound varies with choice of origin so that in naphthalene, for example, the magnitude of the bound increases along the major axis reaching −0.25 at a distance of 2 a.u. from the centre of the molecule (compare with the variation in the susceptibility itself [15]).

power series in H and m the chemical shift may then be picked out as a multiple of the coefficient, E_{11}, of Hm. In the notation of [16]

$$E^a_{011} = 4\alpha^2 \sum_{s<t} \tilde{P}'_{st} S_{st} K_{st} H^0_{st} = 2\alpha^2 \sum_{s<t} P'_{st} \tilde{S}_{st} H^0_{st},$$

and

$$E^b_{11} = 4\alpha^2 \sum_{s<t} P^0_{st} \tilde{S}_{st} S_{st} K_{st} H^0_{st}$$

where P' is the first-order bond-order matrix with respect to the test-dipole perturbation, and K_{st} is a geometric factor discussed in detail elsewhere [18–20].

The equation for E^a_{111} may be written in the simplified form [c.f. Eq. (2)]

$$E^a_{111} = -\alpha^2 \sum_{s<t} P'_{st} \tilde{P}'_{st} \gamma_{st},$$

which, compared with the original summation over four indices [16], represents a considerable time saving in evaluation.

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