

On the use of the ring current concept

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The concept of ring currents is commonly used to interpret and calculate the magnetic susceptibility and the N.M.R. spectra of conjugated hydrocarbons. Controversy over the theoretical soundness of its use has led both theoretical and experimental chemists working in the field to the rather uneasy situation of frequently using a concept suspected of being totally unnecessary and non-physical.

The idea that an external magnetic field might induce a ring current in a molecule like benzene was introduced in a classical context by Ehrenfest [1] and Pauling [2]. However, the extensive use of ring current ideas originated from London's [3] approximate quantum mechanical method of calculation of the magnetic susceptibility, in which a basis set of field dependent orbitals, the so-called gauge invariant atomic orbitals (GIAO), was used. Later, methods of calculating magnetic susceptibilities and N.M.R. chemical shifts were developed [4-6] which still made use in different ways of those early ideas. In these and modified theories, the concept of ring current plays an important, more or less explicit, role; it has been a very useful instrument in the understanding of the magnetic properties of conjugated molecules.

A major criticism of the use of the ring current concept was put forward by Musher [7] who argued that the supposed ring current contribution to the magnetic susceptibility could equally well be ascribed to the sum of the susceptibilities of electrons localized in non-overlapping segments of the ring. It is claimed [8] that localized anisotropic contributions and ring current contributions are one and the same.

Although many authors have given attention to Musher's argument in favour of localized models, the most pertinent comments so far appear to be those of Gaidis and West [9] together with the subsequent reply [10]. These do not seem to have fully answered the difficulties and most authors keep to their traditional use of ring current but with a non-committal note of cation. Calculations by Nowakowski [11] on several polycyclic conjugated hydrocarbons point towards the use of ring currents as a more effective tool than the concept of increments. However, in a recent series of papers, Blustin [12, 13] uses a localized model with great success to calculate both the magnetic susceptibilities and the chemical shifts of a variety of benzenoid hydrocarbons.

It is the purpose of this note to help in clarifying this problem by showing that Musher's [7] comparison between localized and delocalized models is fallacious and that a model making use of local (atom or bond, say) magnetic susceptibility anisotropies cannot give a full description of the magnetic properties of the molecule. Since general theoretical arguments lead to the prediction of a

non-zero, appropriately defined, ring current, the conclusion is reached that the use of ring currents as an intuitive simple way of describing some of the effects of a magnetic field on monocyclic or polycyclic conjugated molecules, is quite appropriate.

Musher [7] compared two related model wavefunctions for a cylindrically symmetric problem. The first (a) (figure 1) may be thought of as a torus-like distribution of probability amplitude while in the second (b) (figure 1) a probability amplitude similar to the previous one is given to each of the four quadrants, one electron being attributed to each.

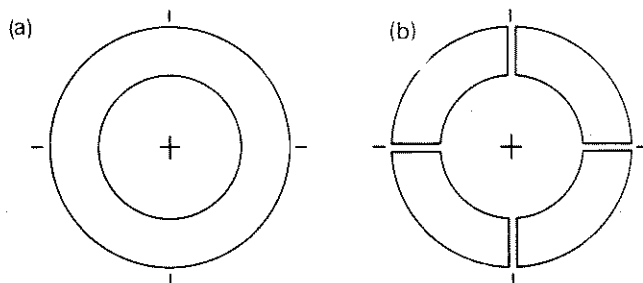


Figure 1. Model wavefunctions for the delocalized (a) and localized (b) models of Musher.

For a model wavefunction to make sense, there must be some physical model, in the present case of one-electron functions, a one-electron potential, which can be associated with it. It is easy to think of physically acceptable constraints which will result in a wavefunction of type (a). Some more care is needed with (b). Considering each of the quadrants individually, there must exist an infinite barrier forcing the electron to stay in that quadrant. If the potential barrier is assumed to be continuous, it defines the third model (c) (figure 2). When this potential is taken to the limit of an infinite square well (within each quadrant) the wavefunction will satisfy the boundary conditions postulated in (b).

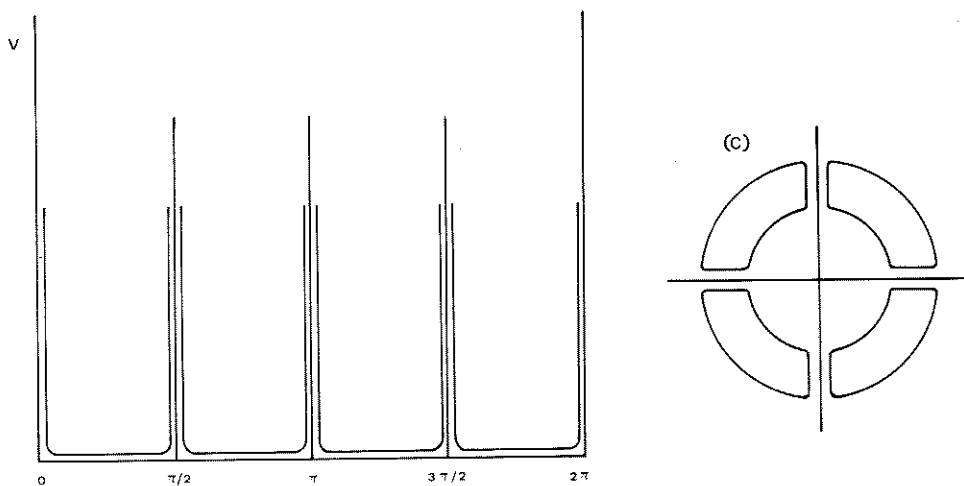


Figure 2. Model for a potential function which is continuous inside each quadrant and of the wavefunction associated with it.

Let us now consider the pattern of currents induced by a perpendicular magnetic field. Models (a) and (c) satisfy the general conditions under which a current density can be properly defined [14]; this current density satisfies the continuity equation. Figure 3 suggests the sort of pattern of currents to be expected. When model (c) is taken to the limit to generate model (b), the continuity equation will be satisfied by allowing for surface currents in the planes dividing the quadrants. Allowing now for the cancellation of these surface currents in the planes shared between quadrants, we get a pattern of currents as drawn in figure 3 (b). Patterns (a) and (b) are different, showing the fundamental difference between the two models. The patterns of electronic currents shown in figure 3 are indicative of the sort of current fields allowed by fundamental principles, and these must be satisfied whatever the details of the model systems are. Working with non-physical wavefunctions [7] may lead to non-physical conclusions which should be discarded if we are interested in understanding the behaviour of actual physical systems.

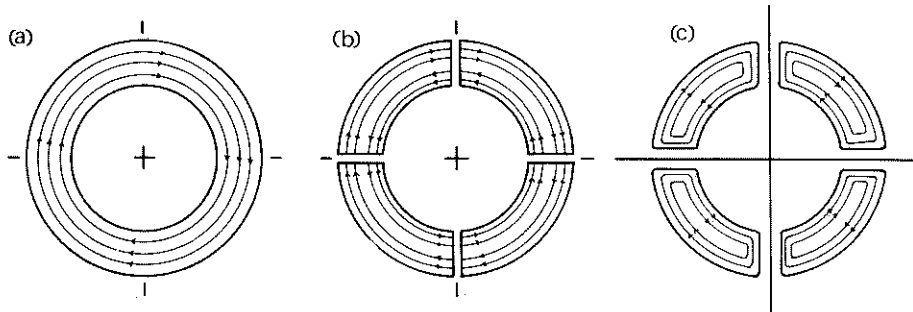


Figure 3. Pattern of currents induced by an external magnetic field in models (a), (b) and (c).

On the strength of the argument produced above, it cannot be claimed that localized or delocalized models lead to the same predictions. No net current is predicted to flow around the ring in (b) in contrast with the prediction for (a).

For our discussion, we shall consider the ring current to be measured by the net flow of the electronic current around a ring. This is computed by the flux of the current density vector across a semi-infinite plane from the axis of the molecule. This definition is independent of the methods or approximations which in the past have been used to estimate ring currents. For polycyclic molecules more care is needed in defining the surface across which the current density flux is measured, but the situation is not fundamentally different. Classically, a current is expected to flow in a non-resistive ring of radius R under the effect of a perpendicular magnetic field B , provided no potential barrier higher than $(e^2 B^2 R^2/8m)$ is introduced. Quantum mechanically the problem is not so simple as the calculations by Baer *et al.* [15], on a one-dimensional ring model show. For our purposes here, the important new feature is that the condition on the potential barrier must be relaxed; any finite potential will, in principle, allow a current to flow. In an actual molecule the current density field is, of course, very complex and the ring current as defined above measures only one of its aspects. As no lower bound has been given for this ring current,

it is not possible to give, in general terms, an estimate of the importance of its contribution to the molecular properties. However, it should be realized that its effects cannot be completely described by any model of local susceptibilities for, at short distances from the ring, the ring current secondary field cannot be simulated by a dipolar field.

Discussion of the numerical results available in the literature is not easy as no good *ab initio* calculations are available, even for a relatively small system such as benzene. Estimates of the π electron ring current as defined above, with the conventional GIAO basis functions [14] or the related integrated currents [16], correlate well with the more conventional ring currents as calculated by the Hückel-London-Pople-McWeeny method [3-6, 17].

Musher [7] uses magnetic susceptibility increments which depend on whether or not a carbon atom is shared. When application of this method is restricted to the magnetic susceptibilities of benzenoid hydrocarbons, it allows for an even distribution of the eventual ring currents effects among the six carbon atoms in each ring. This is suggested by the values actually used, with $\chi^{\parallel}(C)$, χ^{\perp} (unshared C) and χ^{\perp} (shared C) increasing by steps of about $0.11 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$; in fact one-sixth of the π electron magnetic susceptibility χ^{\perp} was estimated [16] to be $0.10 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$. A similar comment may be made about the increments used by Blustin [12]; the difference between the internal and external bond anisotropies is $0.12 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$. But the crucial test cannot be made with the magnetic susceptibility which samples equally the entire molecule. N.M.R. chemical shifts, sampling the magnetic field locally, can, in principle, measure the importance of ring currents against the local currents described by susceptibility anisotropies. The results reported by Blustin [13], however impressive, cannot alone be taken as conclusive of the irrelevance of the ring current effects. One has to consider that only benzenoid hydrocarbons were used in the test and it is in non-benzenoid molecules that more disparate ring currents have been predicted. Moreover, one great success of the ring current concept has been in explaining the down- (up-) field shifts observed for outer (inner) protons of $[4n+2]$ -annulenes and reverse effects in $[4n]$ -annulenes [18]. It seems unlikely that Blustin's local anisotropy model will perform equally well in these cases. From the general arguments given earlier, it should also be clear that the *ab initio* localized orbital theory [19], which suggested the localized models of Blustin [12, 13], does not preclude the existence of a ring current. Estimates of it have not been published however.

From the discussion above the conclusion may be drawn that a magnetic ring current is expected to exist in cyclic molecules and the description of the magnetic effects cannot be complete in terms of local susceptibilities alone. With the currently available data, there are no reasons to believe that semi-empirical conventional estimates of ring currents are not representative of their actual sizes and it is therefore correct to use them in interpreting or predicting magnetic properties. Doubts that may remain about the magnitude of the ring current contributions can only be answered when reliable *ab initio* calculations become available and this, for benzene say, should be feasible using modern facilities.

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