Density Functional Calculations

Sphere Currents of Buckminsterfullerene**

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The aromatic character of Buckminsterfullerene has been a matter of debate since the remark by Kroto et al.[1] that C_{60} "appears to be aromatic". Since then, various studies of the aromaticity of C_{60} have been reported. All studies on aromaticity are of course challenged by the elusive nature of the property; although age-old as a concept, a final, clear-cut definition of aromaticity has not emerged. However, aromatic systems tend to behave in a characteristic manner in a magnetic field. Traditional aromatic species, such as the arch-example benzene, contain rings and are more or less planar, two-dimensional molecules. Also, they usually follow the $4N+2$ Hückel rule for annulene aromaticity. Exposure of the molecules to a magnetic field perpendicular to the plane induces ring currents, with the electrons circling the rings or even larger areas. The magnetic view of aromaticity has usually been employed in the study of fullerene aromaticity, and more often than not the focus has been on local currents of, and shieldings near, the constituent rings. The endohedral magnetic shielding has also been used as a measure of the strength of the ring currents of the individual rings,[2] and ^{3}He NMR spectroscopy has been used to estimate the chemical shifts of the endohedral carbon atoms of fullerenes.[3,4]

The charge state is known to alter the electronic structure of fullerenes significantly, and thereby also their magnetic properties.[4–7] This strong dependence on charge was rationalized when Hirsch et al.[8] devised a rule for a three-dimensional (3D) form of aromaticity for fullerenes of icosahedral symmetry. Like 2D aromaticity, this spherical aromaticity depends on the number of delocalized π electrons present, but instead follows a $2(N+1)^2$ rule that corresponds to closed-shell configurations of pseudoatoms with spherical shell potentials.[9] Spherically aromatic fullerenes exhibit many of the usual characteristics of aromatic species, such as enhanced stability, bond-length equalization, and high diamagnetic shielding at the cage centers.

As discussed above, the magnetically induced currents can provide valuable information about potentially aromatic species such as fullerenes. Although it is a real physical effect, a method for direct experimental observation of these currents has yet to be devised. Quantum chemical calculations can, however, provide insight into the electronic pathways.[10–12] With the newly developed gauge-including magnetically induced currents (GIMIC) method,[13] it is possible to not only visualize these currents, but also to get a quantitative measure of their strength, a property previously unattainable. Herein, we investigate by using GIMIC the magnetic properties of both the neutral C_{60} and the spherically aromatic, though still unsynthesized, C_{60}^{10+} ion, which fulfills the $2(N+1)^2$ rule with $N=4$.

The currents induced by a magnetic field are visualized in Figures 1 and 2 by using vector plots of the current strength at various parts of the surfaces. Figure 1 shows a side view of the fullerenes, with the magnetic field oriented vertically from above, perpendicular to the pentagons positioned at the

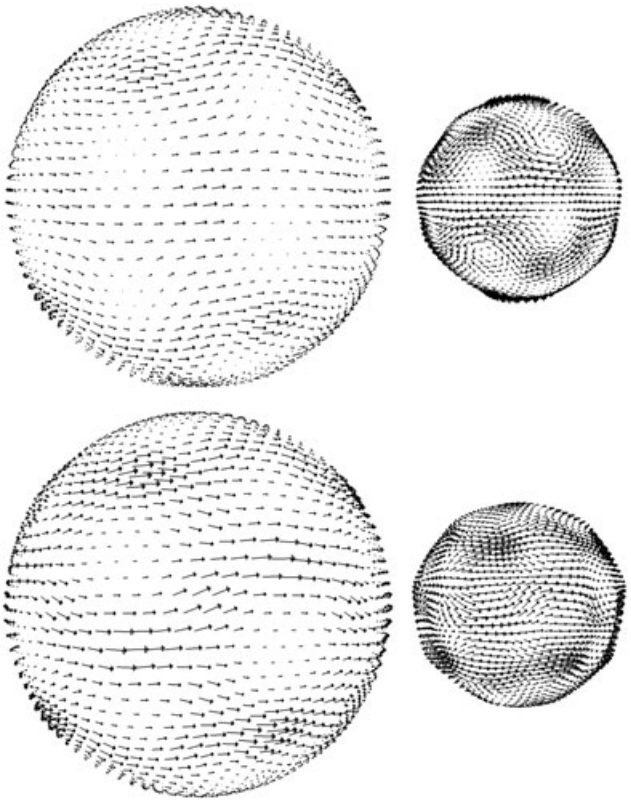

Figure 1. The induced currents in neutral (top) and +10 charged (bottom) fullerene 1 Å above (left) and below (right) the surface. The magnetic field is directed along the plane from top to bottom.

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"poles". The plots show the currents 1 Å above and below the surfaces. The currents are seen to move around the whole pseudosphere roughly perpendicularly to the magnetic field. The wavy nature[10] of the currents is quite pronounced. For the neutral fullerene, the currents on either side of the surface predominantly move in opposite directions: the current is diamagnetic on the outside, but paramagnetic on the inside. The diamagnetic outside current was noted already in the work by Zanasi and Fowler.[10] The field lines are diamagnetic throughout for C_{60}^{10+}. The currents in C_{60} and C_{60}^{10+} are, perhaps a bit surprisingly, nearly indistinguishable at the surface (see the Supporting Information). It can be noted that the currents of neutral fullerene, especially on the inside, are much more twisted and nonuniform than in C_{60}^{10+}. The ring currents under the pentagons can, in particular, be discerned. The π electrons also move quite freely over, and under, the entire surface in neutral C_{60}.

Figure 2 shows the currents, looking out from the centers of the fullerenes, along the magnetic field towards one of the pentagons. Again, plots 1 Å above and below the surfaces are shown. The currents for C_{60}^{10+} are seen to move in a clockwise, diamagnetic manner on both sides of the surface. A weak counterclockwise, paramagnetic current circulates the pentagon. The strength of this current 1 Å above the plane is, however, too weak to be seen from the figure. This is in stark contrast to the currents in neutral C_{60}; for this species, the outside current is again diamagnetic, with the exception of the area occupied by the pentagon. On the inside, however, the currents are mostly paramagnetic.

The vector plots reveal the main feature of the induced currents, that is, their large uniformity as they traverse the fullerene. This uniformity of the currents persists through the fullerenes, with the largest deviations seen just on the surface of the carbon framework. Here, the bond and ring currents of the individual pentagons and hexagons dominate the picture. However, these local currents are obscured just beyond the surface by the sphere currents of the fullerene. The global currents seem predominant, even in neutral C_{60}. The strengths of the currents decrease significantly when moving away from the atomic cage and fall to zero at the center (a view of the currents in a plane through the equator is available in the Supporting Information).

Although the pictures are descriptive and provide a qualitative view, they give no accurate information about the strengths of the currents. Quantitative measurement of the strengths were obtained by numerically integrating the current passing a plane from the central axis out through half the fullerene. The magnetic field can of course be directed at any angle with respect to the fullerene. Here, we chose two different orientations: perpendicular to a pentagon (along a C_5 axis) and perpendicular to a hexagon (C_3 axis). The total net current along with the diamagnetic and paramagnetic components are tabulated in Table 1. The net current for neutral C_{60} is actually paramagnetic when the field is directed through a pentagon and only very slightly diamagnetic with hexagons at the poles. This observation is in line with the previously noted strong paramagneticity of the pentagons.[6,7,14] The currents in C_{60} are thus somewhat sensitive to the orientation of the molecule in the magnetic field, but the net current is always small. The case of the spherically aromatic C_{60}^{10+} ion is very different: with the direction of the currents the same on both sides of the surface, the net current is significantly stronger than in the neutral counterpart. The currents show only a slight dependence on the direction of the magnetic field, thus indicating the much weaker paramagnetism of the pentagons.

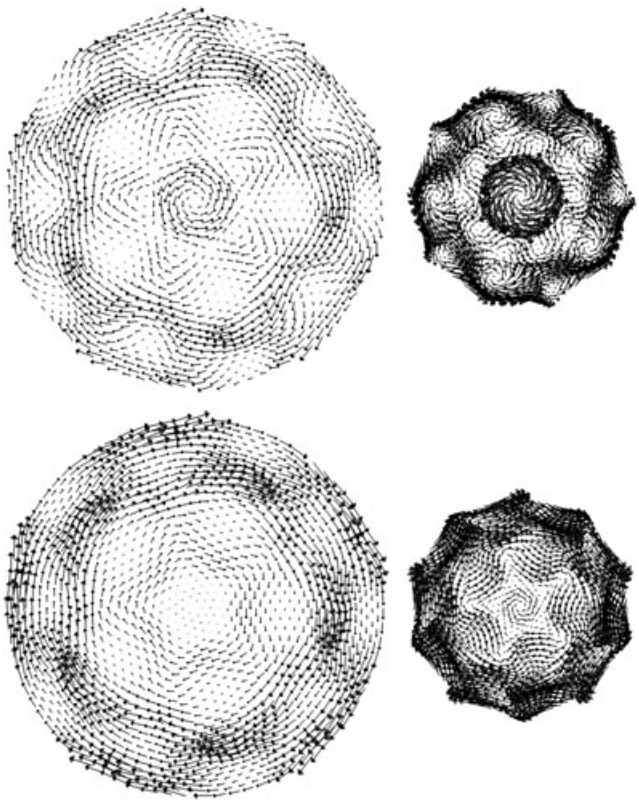

Figure 2. The induced currents in neutral (top) and +10 charged (bottom) fullerene 1 Å above (left) and below (right) the surface. The magnetic field is directed perpendicularly out of the plane.

The integration shows that neutral C_{60} is best described as globally non-aromatic. Thus, the "ambiguous character" of fullerene aromaticity[15,16] appears to be a mirage; local ring currents induce an association between them and the aromaticity of the annulene. However, when assessing the

Table 1: Integrated induced global currents for the icosahedral fullerenes C_{60} and C_{60}^{10+} [nAT^{-1}].[a]

	C_{60}		C_{60}^{10+}		chd		Benzene
	5R	6R	5R	6R	DB	SB	
total current	−15	3	57	60	−1	−1	12
positive part	36	42	78	81	10	7	17
negative part	−51	−39	−21	−21	−11	−8	−5

[a] Values with the magnetic field perpendicular to both a pentagon (5R) and a hexagon (6R) are shown. The results for cyclo-1,4-hexadiene (chd) and benzene are reported for comparison; for chd, currents over both the double (DB) and single (SB) bonds are shown. The positive (diamagnetic) and negative (paramagnetic) contributions are reported together with the total current.

aromaticity of three-dimensional pseudospherical molecules, such as fullerenes, one should primarily consider global currents, and only ascribe secondary importance to local currents. The one-dimensional bond currents are not decisive for traditional, two-dimensional aromaticity either. The difference between C_{60} and C_{60}^{10+} can be compared to that between non-aromatic cyclo-1,4-hexadiene and benzene. From Table 1 it can be seen that the total gross current, determined by adding together both the absolute diamagnetic and paramagnetic contributions, is of comparable magnitude for cyclohexadiene and benzene. The same is true for C_{60} and C_{60}^{10+}. Benzene and C_{60}^{10+} are aromatic because the global currents cancel only to a small extent, while cyclohexadiene and C_{60} are non-aromatic because the currents almost completely cancel. So, contrary to common belief, the reason for the global non-aromaticity of C_{60} is not directly related to the paramagnetism of the pentagons, although they do contribute to the decrease in net current. Instead, the main reason is the oppositely directed exterior and interior sphere currents of the π electrons. This finding is also consistent with the low magnetic susceptibility of C_{60}.

This view is corroborated by studying the equatorial region, where the currents are quite independent of the nature of the ring and sphere currents near the polar caps of the fullerenes. In this region, the oppositely directed sphere currents of C_{60} in effect cancel each other: integration of the net current through a slab 1 Å thick at the equator gives essentially a zero result. For the C_{60}^{10+} ion, with its concurrent sphere currents, the same integration yields a value of 9 and 13 nAT^{-1}, with the magnetic field perpendicular to a pentagon and hexagon, respectively. Over two thirds of this current is endohedral. The endohedral magnetic shielding originates from the induced currents in the surrounding carbon shell.[2,16,17] For a fullerene with a finite thickness of the carbon network, the magnetic shielding inside the molecule depends both on the current strengths and on the radius of the system.[18] A spherical, infinitely thin and magnetically susceptible shell is in effect a perfect magnetic Faraday cage; the magnetic shielding inside is constant. Whereas neutral fullerene has been found to behave as an electric Faraday cage,[19] spherical aromaticity indeed makes the fullerenes behave like miniature magnetic Faraday cages.[20] The magnetic shielding inside C_{60}^{10+} is quite constant, but much more irregular and weaker inside C_{60} (see the Supporting Information). It can be noted that the negative value at the origin corresponds to the nucleus-independent chemical shift (NICS) value[21] at the center of the fullerenes. As observed from the initial studies,[8] the shielding at the center of C_{60}^{10+} is high—ten times larger than in C_{60}.

In summary, we have described the extraordinary behavior of both neutral and spherically aromatic fullerene in a magnetic field. In both, the π electrons move uniformly around the fullerene on both sides of the surface. The currents mainly move in opposite directions in neutral C_{60}. However, the current is unidirectional in C_{60}^{10+} and leads to a strong induced electric current around the molecule as well as a remarkably homogeneous and large endohedral magnetic shielding. These truly three-dimensional sphere currents are, in our opinion, the defining feature of global aromaticity in fullerenes. While the currents of the 60 π electrons in neutral C_{60} compete in moderate discord, the 50 π electrons of the spherically aromatic fullerene are beautifully in accord.

Experimental Section

The molecular structures were optimized at the density functional theory (DFT) level,[22,23] using the hybrid, semilocal gradient-corrected density functional B3LYP.[24,25] The calculations were performed with the Turbomole program suite,[26] version 5.6, modified to provide the perturbed densities required for the calculation of the induced currents. Turbomole's standard doubly polarized basis sets of triple-zeta quality (TZVPP)[27,28] was used for the geometries, while the magnetic calculations were performed using the smaller polarized split-valence basis set (SVP).[29] This has been shown to be adequate for organic aromatic systems.[13] Turbomole's standard m4 grid was used.

A quantitative measure of the induced ring current can be obtained by using the newly developed GIMIC method.[13] The various components of the magnetically induced current-density tensor are calculated using gauge-including atomic orbitals (GIAO). The current-density tensor is independent of the direction of the magnetic field. The tensor is contracted with an explicit magnetic field, thus making the induced current density direction-dependent. The magnetically induced current density was obtained at selected points in space. A scheme for obtaining quantitative values for induced currents by numerical integration over the current flow was developed. The net current flow through a plane could be determined by defining suitable cut planes.

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[1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **1985**, *318*, 162 – 163.
[2] M. Bühl, *Chem. Eur. J.* **1998**, *4*, 734 – 739.
[3] M. Saunders, H. A. Jiménez-Vázquez, R. J. Cross, S. Mroczkowski, D. I. Freedberg, F. A. L. Anet, *Nature* **1994**, *367*, 256 – 258.
[4] E. Shabtai, A. Weitz, R. C. Haddon, R. E. Hoffman, M. Rabinovitz, A. Khong, E. J. Cross, M. Saunders, P.-C. Cheng, L. T. Scott, *J. Am. Chem. Soc.* **1998**, *120*, 6389 – 6393.
[5] V. Elser, R. C. Haddon, *Nature* **1987**, *325*, 792 – 794.
[6] A. Pasquarello, M. Schlüter, R. C. Haddon, *Science* **1992**, *257*, 1660 – 1661.
[7] A. Pasquarello, M. Schlüter, R. C. Haddon, *Phys. Rev. A* **1993**, *47*, 1783 – 1789.
[8] A. Hirsch, Z. Chen, H. Jiao, *Angew. Chem.* **2000**, *112*, 4079 – 4081; *Angew. Chem. Int. Ed.* **2000**, *39*, 3915 – 3917; .
[9] M. Reiher, A. Hirsch, *Chem. Eur. J.* **2003**, *9*, 5442 – 5452.
[10] R. Zanasi, P. W. Fowler, *Chem. Phys. Lett.* **1995**, *238*, 270 – 280.
[11] P. Lazzeretti, *Prog. Nucl. Magn. Reson. Spectrosc.* **2000**, *36*, 1 – 88.
[12] J. A. N. F. Gomes, R. B. Mallion, *Chem. Rev.* **2001**, *101*, 1349 – 1383.
[13] J. Jusélius, D. Sundholm, J. Gauss, *J. Chem. Phys.* **2004**, *121*, 3952 – 3963.
[14] M. Prato, T. Suzuki, F. Wudl, V. Lucchini, M. Maggini, *J. Am. Chem. Soc.* **1993**, *115*, 7876 – 7877.
[15] R. C. Haddon, *Science* **1993**, *261*, 1545 – 1550.
[16] M. Bühl, A. Hirsch, *Chem. Rev.* **2001**, *101*, 1153 – 1183.
[17] M. Bühl, W. Thiel, H. Jiao, P. von R. Schleyer, F. A. L. Anet, *J. Am. Chem. Soc.* **1994**, *116*, 6005 – 6006.
[18] J. Lounila, M. Ala-Korpela, J. Jokisaari, M. J. Savolainen, Y. A. Kesäniemi, *Phys. Rev. Lett.* **1994**, *72*, 4049 – 4052.

[19] P. Delaney, J. C. Greer, *Appl. Phys. Lett.* **2004**, *84*, 431 – 433.
[20] M. P. Johansson, D. Sundholm, J. Vaara, *Angew. Chem.* **2004**, *116*, 2732 – 2735; *Angew. Chem. Int. Ed.* **2004**, *43*, 2678 – 2681; .
[21] P. von R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317 – 6318.
[22] P. Hohenberg, W. Kohn, *Phys. Rev.* **1964**, *136*, B864 – B871.
[23] W. Kohn, L. J. Sham, *Phys. Rev.* **1965**, *140*, A1133 – A1138.
[24] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648 – 5652.
[25] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785 – 789.
[26] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165 – 169.
[27] A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829 – 5835.
[28] T. H. Dunning, Jr., *J. Chem. Phys.* **1989**, *90*, 1007 – 1023.
[29] A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571 – 2577.

