Software News and Updates
Update of the AIM2000-Program for Atoms in Molecules

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Abstract: The second version of the program package AIM2000 is presented. AIM2000 makes use of the well established theory of atoms in molecules. AIM2000 analyzes the molecular structure and calculates properties of atoms in molecules as well as properties of interatomic surfaces. The program has an interactive, context-sensitive help component and extensive 2D and 3D visualization components.

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Key words: atoms in molecules; atomic basins; interatomic surfaces; average properties; molecular topology

Introduction

In May 2000 the first version of the program AIM2000 was placed onto the internet for download. The response of the scientific community has been overwhelming: more than 1200 downloads were counted by November 2001.

There have also been numerous suggestions to extend and improve the program. Many of these suggestions have been incorporated into the second version of AIM2000, which will appear in January 2002.

It is hoped that the mathematically rigorous theory of atoms in molecules developed by Bader[1] has become more popular because an easy to use software package is now available that allows analysis, computation, and visualization of atoms in molecules under a single graphical user interface.

New Features of AIM2000, Version 2.0

While there has been extensive re-engineering of the code of AIM2000, the new version keeps nearly all features of the previous one, sometimes under an improved user interface. For a description of the numerical methods employed in AIM2000 see ref. 2, for an overview of the features of version 1, see ref. 3. Just as in version 1, the new version of AIM2000 runs under all Win32 operating systems (Windows 95/98/NT/ME/2000).

The new features of the program can be divided into three groups, which will be considered separately:

1. Improvements of user interface and runtime performance.
2. New calculation options for atoms in molecules.
3. New visualization options.

Major Improvements of User Interface and Runtime Performance

- 3D-View, where a three-dimensional visualization of the current density function can be displayed, now has its own window that can be resized, closed, opened (via View menu), maximized, and minimized independently.
- Screen-shots of 3D-View can be saved in a file.
- Multi-Threading has been introduced in order to give lengthy calculations their own low-priority thread. Other programs with normal priority (e.g., text processing) can be used parallel to an AIM2000 calculation.
- The AIM2000 main window can be minimized even during a calculation. To restore the window right-left-double-click on the icon in the task bar.
- The content of the Record View can be written to an ASCII-file (via File menu). From here the data can be copied into other documents.
- For a given point in space, the current density and other properties can be analyzed and written to the Record View (via Properties of Density Functions in the Calculation menu).

New Calculation Options for Atoms in Molecules

- As a new property, the orbital overlap matrix has been introduced. It is a symmetric matrix with n_{mo} rows and columns, where n_{mo} is the number of molecular orbitals in the molecule. The elements of the overlap matrix are defined as $S_{ij}(\boldsymbol{x}) = \phi_i\phi_j$, where $i,j = 1, \ldots, n_{\mathrm{mo}}$, and the ϕ_i are the molecular

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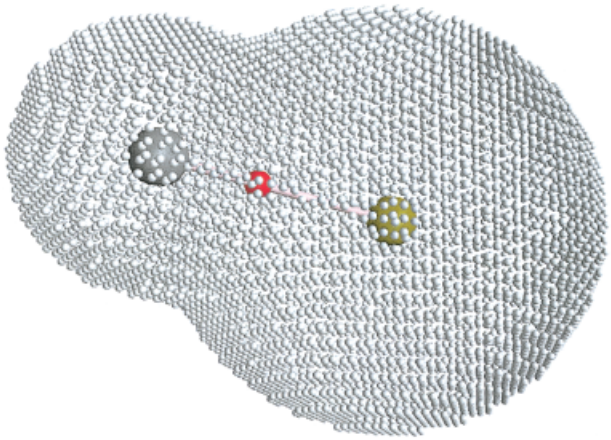

Figure 1. Electron density of LiF, 0.01 au isosurface. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

orbitals. The Record View output of a point in space contains the elements of the overlap matrix.

The overlap matrix can be integrated over an atomic basin Ω, which yields the atomic overlap matrix with elements $S_{ij} = \int_\Omega S_{ij}(\boldsymbol{x})\, d\boldsymbol{x}$. This matrix is part of the Record View output of an atom. Note that the effort to integrate the overlap matrix may become predominant in the case of many orbitals: $1/2 n_{\mathrm{mo}} \cdot (n_{\mathrm{mo}} + 1)$ different integrals have to be computed.

The elements of the atomic overlap matrix determine the extent of overlap of each orbital or orbital pair within an atomic basin and the degree of localization of the electrons within the atomic basin and their delocalization into the basins of other atoms.[1,5] A diagonal element with indices "i,i" is the contribution of orbital "i" to the population of an atom from the electrons of either spin. One sees that in LiF (see below) the diagonal overlap for the lowest energy orbital is totally localized on the F atom as $S_{11}(\mathrm{F}) = 1$. The next orbital is localized on the Li atom as it is a core orbital of that atom and $S_{22}(\mathrm{Li}) = 1$. The sum of the diagonal elements for a given atom gives half the total population of electrons on that atom. Orbitals that are shared between two or more atoms have $S_{ii} < 1$. In a linear or a planar molecule, there is no overlap between the σ and π sets of orbitals, the corresponding overlap elements are all zero (see LiF below), and the matrix is blocked into contributions from σ and from π orbitals. This has an interesting physical consequence, as it shows that there is no exchange between the σ and π electrons in such molecules.

- The Record View output of an atom has been further extended. It now contains:
  - Bond distances (distance between bonded nuclei) and bond lengths (length of gradient path between two charge density maxima).
  - Bond angles and bond path angles.
  - The localization index of the atom: $\lambda(A) = 2 \cdot \sum_{i,j=1}^{n_{\mathrm{mo}}} S_{ij}^2(A)$.
  - The delocalization indices between pairs of atoms: $\delta(A,B) = 4 \cdot \sum_{ij=1}^{n_{\mathrm{mo}}} S_{ij}(A) \cdot S_{ij}(B)$.

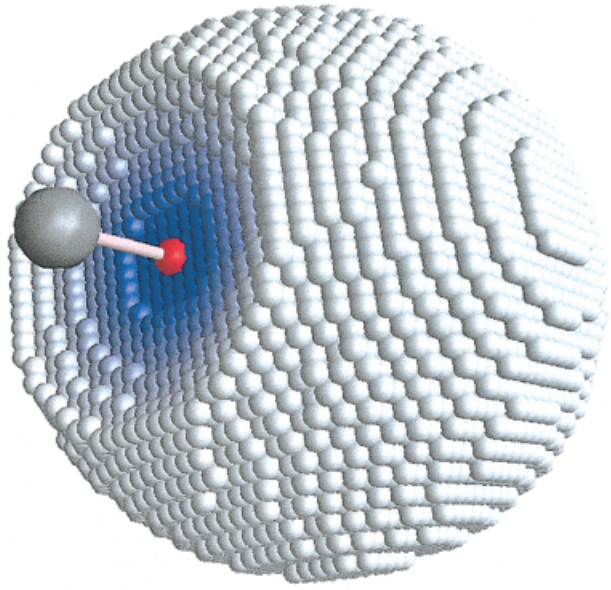

Figure 2. Electron density of F in LiF, 0.01 au isosurface and interatomic surface. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Localization and delocalization may be applied to wave functions at any level of theory. However, their calculation in AIM2000 is limited to closed-shell single determinant wave functions. AIM2000 can be used for a single determinant spin unrestricted wave function simply by inputting the orbital coefficients for the

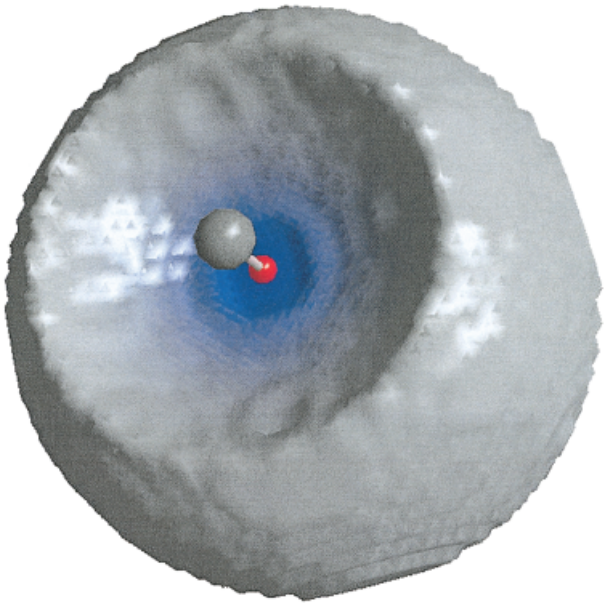

Figure 3. Electron density of F in LiF, 0.001 au isosurface and interatomic surface, triangulated envelope map. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

alpha spin and beta spin orbitals in two separate calculations of the atomic overlap matrix.

New Visualization Options

- The 2D plot component has been re-engineered:
  - Models can be rotated around three axes.
  - Plots can be copied into the clipboard for transfer into other documents.
  - All plots will be completely saved into .aim files (no recalculation necessary after reload).
  - Molecular graph plots can be labeled automatically and the symbols can be edited.
  - Contour plot: Dialog has been reorganized to give better overview of the different features.
- The three-dimensional display in 3D-View can be configured according to the needs of the user: nuclei, different kinds of critical points, gradient paths, and coordinate axes can be switched on and off. Changing to a different density function triggers the display of the new density function in 3D-View.
- Envelope maps can be generated: After calculating a grid of points covering a region of the molecule, these points can be displayed in 3D-View. By manipulating the display, different envelope maps are produced:
  - The display can be restricted to points in certain atomic basins.
  - The display can be restricted to points where the current density function has values in a certain interval.
  - The points can be displayed as spheres of different sizes.
  - Alternatively, a triangulation of the cloud of points can be generated.

The first version of AIM2000 could be obtained freely via the internet. However, because changes, improvements, and extensions implied a lot of programming work but hardly any scientific challenge, there is a charge for the second release of AIM2000.

Example Molecules

We demonstrate the new features of AIM2000 by presenting selected results of three molecules. For a full list of properties certify refs. 2 and 3. Atomic units are used throughout.

Wave functions were calculated with the program GAUSSIAN98,[6] but any other program package for the calculation of wave functions with Gaussian basis sets can be used alternatively (e.g., GAMESS[7]), provided a file in wfn-format is produced.

Lithium Floride

First we consider the simple diatomic molecule lithium floride. The wave function has six molecular orbitals. Integrating over atomic basins we obtain the following results.

For Li:

$\int_\Omega \rho(x)\, dx = 2.05991333$, Charge = 0.94008667
$\int_\Omega -1/4\nabla^2 \rho(x)\, dx = -0.00002157$

Atomic overlap matrix

0.000000					
0.000005	0.987989				
0.000004	−0.045924	0.005906			
−0.000008	0.045193	−0.010830	0.022826		
−0.000000	0.000000	−0.000000	0.000000	0.006618	
0.000000	0.000000	0.000000	−0.000000	0.000000	0.006618

Localization index of Li: 1.97060568
Delocalization index of Li and F: 0.17861989

For F:

$\int_\Omega \rho(x)\, dx = 9.93990778$ Charge = −0.93990778
$\int_\Omega -1/4\nabla^2 \rho(x)\, dx = -0.00013919$

Atomic overlap matrix

1.000000					
−0.000005	0.012014				
−0.000004	0.045926	0.994090			
0.000009	−0.045199	0.010839	0.977131		
0.000000	0.000000	0.000000	−0.000000	0.993359	
−0.000000	0.000000	0.000000	−0.000000	0.000001	0.993359

Localization index of F: 9.85041792

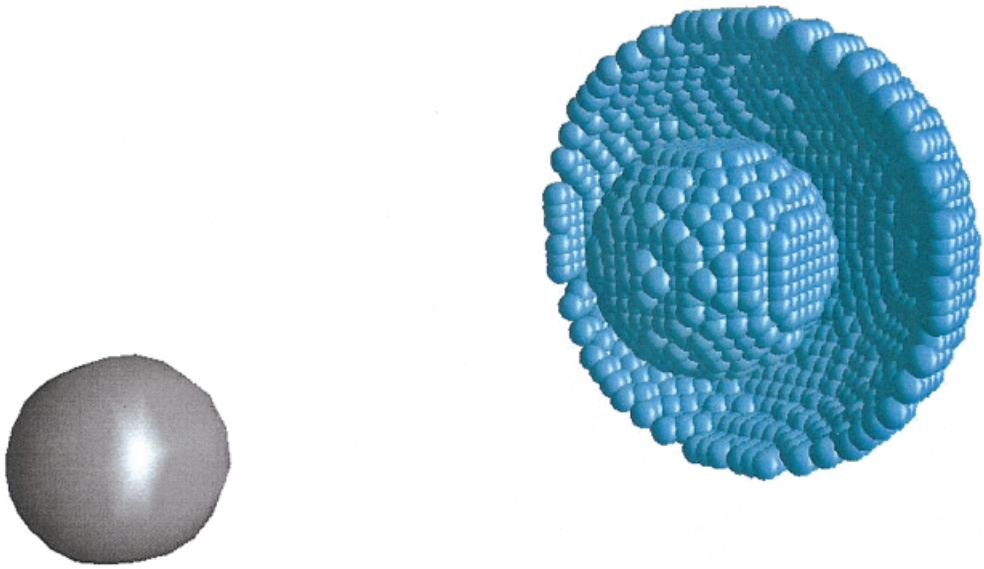

Figure 4. Laplace density of LiF, −0.3 au isosurface. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figures 1–4 show different envelope maps of LiF.

CH_3SH

We report some results for the C- and S-atoms in this molecule.

Results for C:

Atoms bonded to C1 (with distance and bond path length in atomic units):

S2 (3.44, 3.44)
H3 (2.04, 2.01)
H4 (2.04, 2.00)
H5 (2.04, 2.00)

Bond angles and bond path angles (in degrees):
H3 ⟨C1⟩ S2: 106.29°, 105.68°
H4 ⟨C1⟩ S2: 110.96°, 108.46°
H4 ⟨C1⟩ H3: 109.02°, 110.82°

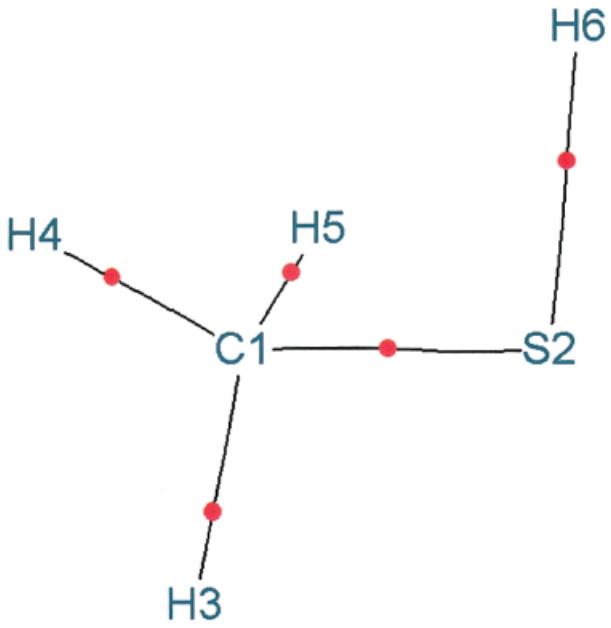

Figure 5. Molecular graph of CH_3SH. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

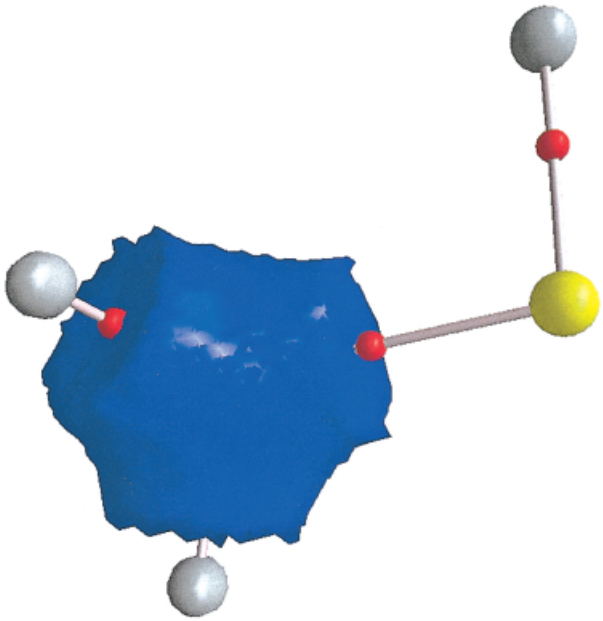

Figure 6. Charge density of C in CH_3SH, 0.1 au isosurface and interatomic surfaces. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

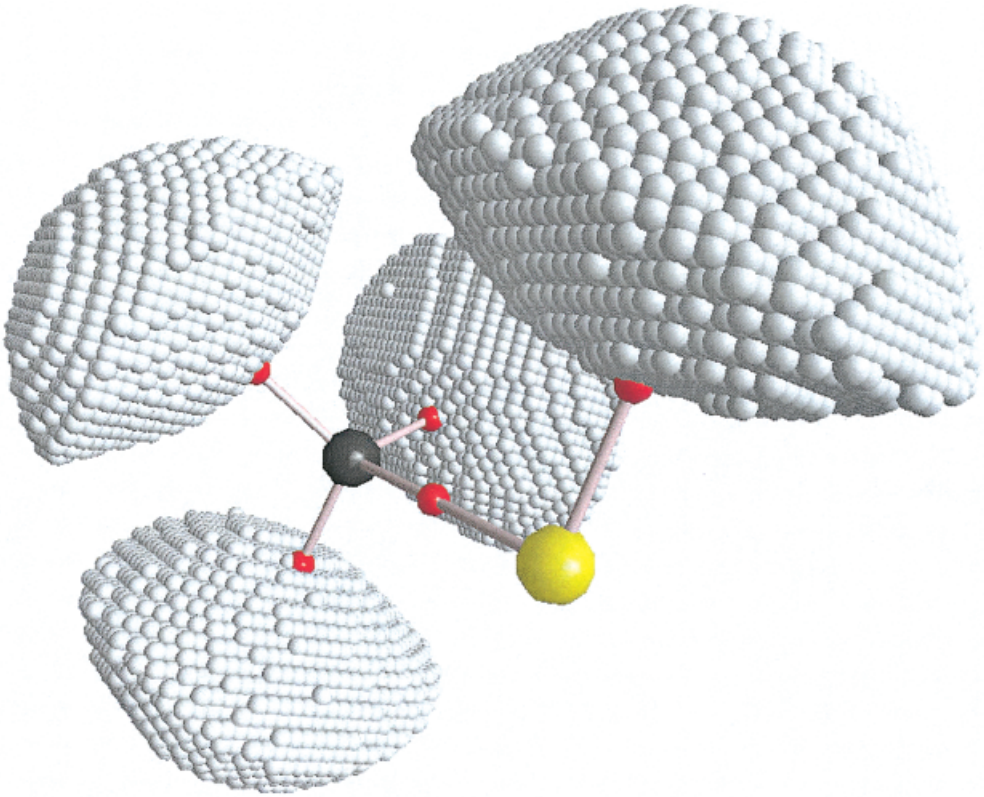

Figure 7. Charge density envelope map of H atoms in CH_3SH, 0.01 au isosurfaces. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

H5 ⟨C1⟩ S2: 110.96°, 108.46°
H5 ⟨C1⟩ H3: 109.02°, 110.82°
H5 ⟨C1⟩ H4: 110.48°, 112.33°
$\int_\Omega \rho(x)\, dx = 5.95256207$ Charge = 0.04743793
$\int_\Omega -\frac{1}{4}\nabla^2 \rho(x)\, dx = 0.00019169$
Localization index of C1: 3.93080626
Delocalization index of C1 and S2: 1.09555658
Delocalization index of C1 and H3: 0.96706801
Delocalization index of C1 and H4: 0.96600559
Delocalization index of C1 and H6: 0.04762040

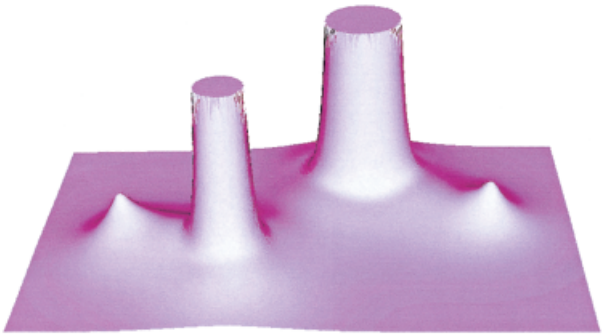

Figure 8. Relief map of CH_3SH in the plane of C, S, and two H atoms. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

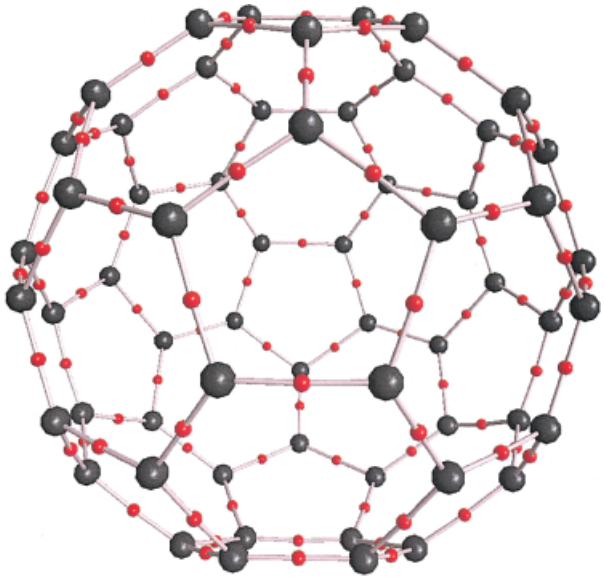

Figure 9. 3D-View of C_{60}. Black: nuclei, Red: bond critical points. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

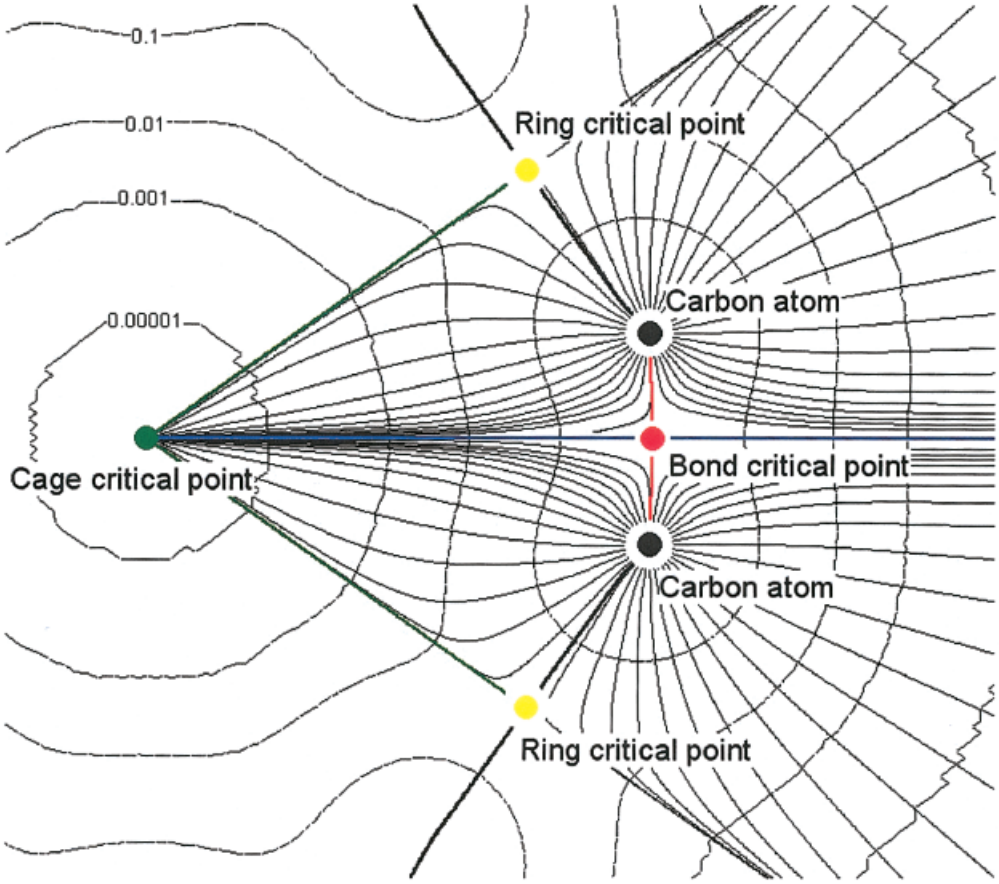

Figure 10. Line plot of C_{60}, plane of two carbon atoms, and Cage critical point. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Results for S:

Atoms bonded to S2 (with distance and bond path length):
C1 (3.44, 3.44)
H6 (2.50, 2.47)
Bond angles and bond path angles (in degrees):
H6 ⟨S2⟩ C1: 98.10°, 100.10°
$\int_\Omega \rho(x)\, dx = 15.84701182$ Charge $= 0.15298818$
$\int_\Omega -\frac{1}{4}\nabla^2 \rho(x)\, dx = -0.00225828$
Localization index of S2: 14.63956882
Delocalization index of S2 and C1: 1.09555658
Delocalization index of S2 and H3: 0.05330854
Delocalization index of S2 and H4: 0.06381057
Delocalization index of S2 and H6: 1.13497142

Figures 5–8 show different visualizations of CH_3SH.

C_{60}

This big molecule with 180 molecular orbitals forms a regular sphere with a very deep minimum of the charge density in the middle. We show two visualizations of the molecule: figure 9 shows a 3D-view of the molecule, and figure 10 shows a gradient paths map.

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