Software News and Updates

AIM2000—A Program to Analyze and Visualize Atoms in Molecules

Introduction

About 20 years ago, Bader et al. formulated the theory of atoms in molecules.[1] It has since proven to be a valuable tool for the qualitative and quantitative analysis of molecular structure and properties. Soon after, in 1979–1982, a program package (AIMPAC[2, 4]) was developed that utilized the rigorous mathematics of the theory. AIMPAC consists of 11 different programs, which were developed in Fortran. Different tasks performed by these programs are: (a) calculation of critical points of the charge density and other density functions; (b) calculation of gradient paths, especially bond paths; (c) plotting of the charge density and other functions: gradient path plots, relief plots, and contour maps; and (d) calculation of properties of atoms in molecules. This procedure integrates a function f over the basin Ω of a given atom in a molecule:

$$F(\Omega) = \int_{\Omega} f(x) \, dx$$

The last procedure is very time consuming, and sometimes supplies unsatisfactory results. Therefore, alternative numerical methods have been developed that overcome the computational and numerical difficulties.[3] This led to a reimplementation and extension of AIMPAC called AIM2000.[5]

This article describes the objectives and features of AIM2000. A set of examples is given that demonstrates the components of AIM2000 and their capabilities: (a) analysis of the topological structure of density functions; (b) calculation of properties of atoms and interatomic surfaces in molecules; and (c) two- and three-dimensional visualizations of density functions.

AIM2000—Overview

The main intentions in the development of AIM2000 were:

1. All components run under a single windows- and graphics-oriented user interface.
2. Most parts of the program can be operated intuitively. An on-line help component supplies necessary explanations.
3. The topological structure of a molecule is displayed in three dimensions as soon as it is calculated. The user immediately gets an overview of the molecular structure.
4. Two-dimensional plots can be generated and manipulated onscreen, and viewed on the screen before printing out a hardcopy ("wysiwyg").
5. The algorithms to calculate properties of atoms in molecules by integrating over atomic basins have been improved and numerical difficulties removed.
6. A component to integrate functions over interatomic surfaces in a molecule has been added.
7. As input, a standard wave function file (extension wfn) is needed.

AIM2000 has been implemented under Windows NT 4.0 using Visual C++ version 6.0 and Microsoft Foundation Classes. AIM2000 runs under the operating systems Windows 95/98 and NT.

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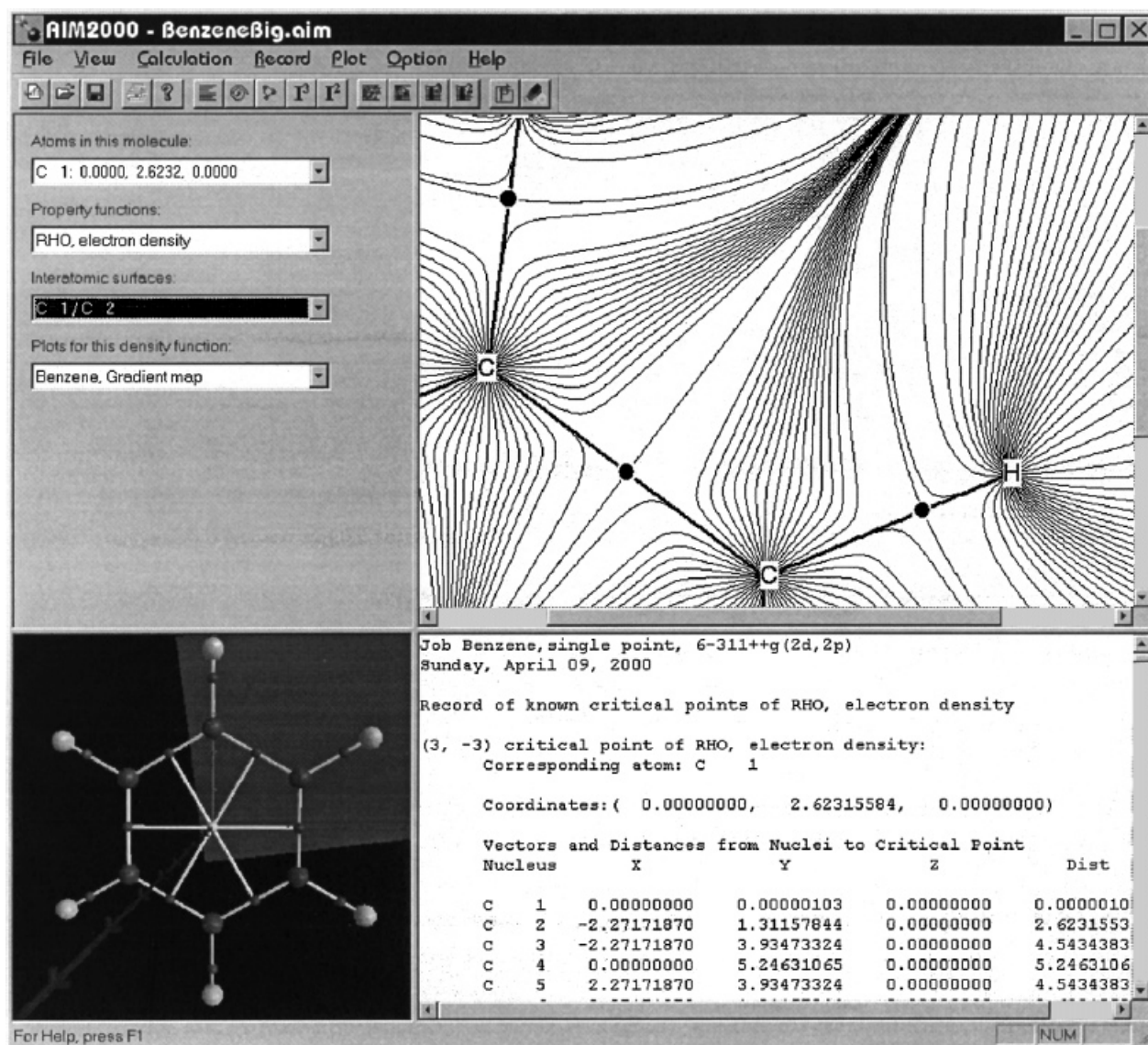
FIGURE 1.

In addition to the above-mentioned functionality, the usual standard properties of Windows programs are supplied:

1. Saving and loading data of a session ("serialization").
2. Output of a window content to a printer.
3. Print preview.
4. Menubar with pull-down menus. Each function of AIM2000 can be triggered via a menu entry.

5. Toolbar with icons for the most frequent tasks.
6. Statusbar to indicate important information.

The working area of AIM2000 consists of four parts ("views," see Fig. 1):

7. Control View (top left), where the user chooses the objects to work with, such as density functions, atoms, interatomic surfaces, and plots.

8. Record View (bottom right). A record of all calculations can be displayed in this view. Control View and Record Menu define the output into the Record View. Examples: (a) for the density function chosen in Control View a list of critical points with their properties can be listed; (b) for an atom chosen in Control View a list of all atomic properties calculated so far can be displayed; (c) the content of Record View is formatted for printout. An on-line preview can be generated.

9. 3D-View (bottom left). To get an impression of the spatial structure of the molecule, it is displayed in 3D-View, including all critical points and gradient paths calculated so far. The look of 3D-View can be manipulated via a context menu. The view can be rotated, translated, and zoomed (see help component).

10. 2D-View (top right). This view can display two-dimensional plots of the chosen density function. These plots can be defined and modified via Plot Menu and screen dialogs. They can also be translated, rotated, and zoomed interactively. There are implemented: (a) molecular graph plot which displays the molecule with its atoms, critical points, bond paths, and other gradient paths connecting critical points. The appearance of the different items can be chosen in the definition dialog. (b) Relief map. This is a three-dimensional plot. The first two dimensions define the plane of a cross-section of the molecule. The third dimension displays the values of a density function in this plane. A shaded display is used for this "mountain." The plane of cross-section, colors, and perspective can be defined in a screen dialog. (c) Contour map. Similar to the relief map, the plane of a cross-section of the molecule is defined, the values of a density function are displayed using contour lines. The user can choose interactively value, style, and color of each contour line. (d) Gradient path map. This map can be combined with a contour map into one plot. It displays a number of gradient paths originating or terminating at a chosen critical point. Gradient path sources as well as line style, line color, and number of gradient paths can be adjusted in the plot definition dialog.

Calculation of Molecular Structure and Atomic Properties

Both Calculation Menu and toolbar contain entries to trigger the calculations of AIM2000.

CALCULATION OF CRITICAL POINTS

To calculate critical points of the chosen density function, Newton's method is used to find zeros of its gradient. Taking the charge density $\rho(x)$ as the density function, the following equation describes one step of the iteration

$$x^{i+1} = x^i - \sigma \cdot H(\rho(x^i))^{-1} \cdot \rho(x^i)$$

where $H(\rho(x^i))$ is the Hessian matrix of second partial derivatives of ρ, and σ the Newton stepsize. With $\sigma = 1$, the classical Newton's method is employed. This stepsize together with desired accuracy and maximal number of iterations can be set in the options dialog for critical points.

In general, Newton's method converges rapidly, and supplies accurate results. However, success is highly dependent on the choice of starting values. The calculation dialog for critical points presents several choices of starting values:

1. Starting values at nuclear positions. This is recommended for the charge density to find the density maxima near the nuclear positions.
2. Starting values at mean values of density maxima pairs. When applied to the charge density this usually computes the $(3, -1)$-bond critical points. Sometimes it is necessary to reduce the Newton stepsize σ to 0.5 to prevent the iteration from leaving the considered area.
3. Starting values at mean values of three density maxima. When applied to the charge density this procedure looks for ring- and cage-critical points.
4. Single starting values: the user can choose arbitrary starting values or compose a set of starting values from nuclear positions and already calculated critical points.
5. Grid search for critical points: a cube can be defined and a grid of starting values inside the cube to search for critical points systematically. This option is useful for other density functions like $L = -\frac{1}{4}\nabla^2\rho$, which can have a great number of critical points.

CALCULATION OF MOLECULAR GRAPH

The molecular graph of a molecule consists of all gradient paths of the charge density that connect critical points uniquely:

1. A bond path connects a $(3, -1)$-critical point x_b with a charge density maximum x_m. These paths can be calculated going uphill from x_b in the direction of the eigenvector of the positive eigenvalue of the Hessian matrix of x_b.

2. A unique path connects a $(3, +1)$-critical point x_r with a $(3, -1)$-critical point x_b, which lies in the ring plane. Unfortunately, no unique direction defines this path. There is a two-dimensional set of paths going uphill from x_r as well as a two-dimensional set of paths going downhill from x_b. The common path has to be calculated iteratively. A bisection iteration to find the uphill direction from x_r is employed. This method can be time consuming, especially in cases where the gradient paths strongly bend.

3. A unique path connects a charge density minimum x_c with a $(3, +1)$-critical point x_r, which belongs to the cage. These paths can be calculated going downhill from x_r in the direction of the eigenvector of the negative eigenvalue of the Hessian matrix of x_r.

To calculate points along a gradient path the following initial value problem is solved:

$$g(x_m) = \left\{ x(l) \in \mathbb{R}^3 \ \middle| \ \frac{dx(l)}{dl} = -\frac{\nabla \rho(x(l), X)}{\|\nabla \rho(x(l), X)\|_2}; \right.$$
$$\left. x(0) = x_m \right\}$$

where l is the arclength of the gradient path. This representation ensures an equal distribution of points along a gradient path. Following the path uphill means $l < 0$, downhill means $l > 0$.

CALCULATION OF PROPERTIES OF ATOMS AND INTERATOMIC SURFACES

After choosing an atom in Control View and clicking *Integration over atomic basin* in the Calculation Menu, a dialog appears that controls the calculation of atomic properties. The integration is done in a polar atomic coordinate system, which has its origin at the nuclear position, and which is rotated such that molecular symmetry can be used. This coordinate system is displayed in 3D-View. A list of the coordinates of all nuclei and critical points in the atomic coordinate system is displayed. The user can set the borders of the φ-integration, which usually runs from 0 to 360 degrees. If the integration borders are equal, rotational symmetry is assumed. According to the integration intervall in φ, a symmetry factor is displayed. All integration results are multiplied by this factor. In case of rotational symmetry, this factor would be 2π. The user can overwrite this factor.

The user can choose between two integration methods. The first algorithm uses radial coordinates to integrate inside a sphere with radius β and "natural coordinates" ouside. It is described in ref. 3. This algorithm does not involve calculation of interatomic surfaces, and is usually the faster one. The other algorithm integrates the whole basin in radial coordinates and computes the intersections of a ray defined by the angles θ and φ and the interatomic surface using a bisection method. A basic form of this algorithm has already been part of AIMPAC.

Accuracy requirements and default values can be set in an option dialog. Computer time consumption is high for the integration procedures, and very sensitive to changes in accuracy requirements.

Choosing an interatomic surface in Control View and clicking *Integration over interatomic surface* in the Calculation Menu brings up a dialog that controls calculation of properties of interatomic surfaces. Similar to the calculation of atomic properties, symmetry can be used to accelerate the integration over interatomic surfaces. The method of integration also uses a natural coordinate system, and is described in ref. 3.

The functions that are integrated in the integration procedures can be selected using two option dialogs: *Functions for Basin Integration* and *Functions for Surface Integrations*. By default, all functions are selected.

Help Component

The help component of AIM2000 is implemented in HTML. It is available stand alone via the Internet[5] and as on-line help during a program run. Typing F1 displays the main page, while Shift-F1 is a context-sensitive help component and displays information about the current program part or dialog.

TABLE I.
Definitions of Atomic Properties for Basin Integration.

Name of Atomic Property	Definition of Property for Atom A with Basin Ω
Number of electrons	$N(A) = \int_\Omega d\mathbf{x}\, \rho(\mathbf{x}) = \int_\Omega d\mathbf{x}(N \int d\tau'\, \psi^*\psi)$
Laplacian of atom	$L(A) = \int_\Omega d\mathbf{x}\, L(\mathbf{x}) = \int_\Omega d\mathbf{x}(-\frac{1}{4}\nabla^2\rho)$
Lagrangian kinetic energy	$G(A) = \int_\Omega d\mathbf{x}\, G(\mathbf{x}) = \int_\Omega d\mathbf{x}\,((\hbar^2/2m)N \int d\tau'\, \nabla\psi^* \cdot \nabla\psi)$
Hamiltonian kinetic energy	$K(A) = \int_\Omega d\mathbf{x}\, K(\mathbf{x}) = \int_\Omega d\mathbf{x}\,((\hbar^2/2m)N \int d\tau'\, \psi \cdot \nabla^2\psi^* + \nabla^2\psi \cdot \psi)$
Virial field	$V(A) = \int_\Omega d\mathbf{x}\,(-\mathbf{x} \cdot \nabla \cdot \sigma(\mathbf{x}) + \nabla \cdot (\mathbf{x} \cdot \sigma(\mathbf{x})))$
Energy of atom	$E(A) = \int_\Omega d\mathbf{x}\,(K(\mathbf{x}) \cdot (1-R))$
Missing information	$I(A) = \int_\Omega d\mathbf{x}\,(-(\rho/N) \cdot \ln(\rho/N))$
Atomic average of $1/r$	$R_{-1}(A) = \int_\Omega d\mathbf{x}\,(\rho/r_A)$
Atomic average of r	$R_1(A) = \int_\Omega d\mathbf{x}\,(\rho \cdot r_A)$
Atomic average of r^2	$R_2(A) = \int_\Omega d\mathbf{x}\,(\rho \cdot r_A^2)$
Atomic average of r^4	$R_4(A) = \int_\Omega d\mathbf{x}\,(\rho \cdot r_A^4)$
Atomic average of $\nabla\rho \cdot \mathbf{x}/r_A$	$GR_{-1}(A) = \int_\Omega d\mathbf{x}\,(\nabla\rho \cdot \mathbf{x}/r_A)$
Atomic average of $\nabla\rho \cdot \mathbf{x}$	$GR_0(A) = \int_\Omega d\mathbf{x}\,(\nabla\rho \cdot \mathbf{x})$
Atomic average of $\nabla\rho \cdot \mathbf{x} \cdot r_A$	$GR_1(A) = \int_\Omega d\mathbf{x}\,(\nabla\rho \cdot \mathbf{x} \cdot r_A)$
Atomic average of $\nabla\rho \cdot \mathbf{x} \cdot r_A^2$	$GR_2(A) = \int_\Omega d\mathbf{x}\,(\nabla\rho \cdot \mathbf{x} \cdot r_A^2)$
Electric dipole (x) Electric dipole (y) Electric dipole (z)	$\begin{pmatrix} M_x(A) \\ M_y(A) \\ M_z(A) \end{pmatrix} = \int_\Omega d\mathbf{x}\,(\rho \cdot \mathbf{d}_A)$
Attraction of density A by nucleus A	$V_{ne}^0(A) = \int_\Omega d\mathbf{x}\,(-Z_A\rho(\mathbf{x})/r_A)$
Attraction of density A by nucleus A (corr.)	$VC_{ne}^0(A) = \frac{-2(1-R)}{R}V_{ne}^0(A)$
Attraction of density A by all nuclei	$V_{ne}(A) = \int_\Omega d\mathbf{x}\,(-\sum_B Z_B\rho(\mathbf{x})/r_B)$
Attraction of density A by all nuclei (corr.)	$VC_{ne}(A) = \frac{-2(1-R)}{R}V_{ne}(A)$
Electron–electron repulsion contribution to energy of atom A	$V_{ee}(A) = \int_\Omega d\mathbf{x}\, V_{ee}(\mathbf{x})$
Electron–electron repulsion contribution to energy of atom A (corr.)	$VC_{ee}(A) = \frac{-2(1-R)}{R}V_{ee}(A)$
Potential energy of repulsion (corr.)	$V_{rep}(A) = 2E(A) - VC_{ne}(A)$
Total potential energy of atom	$V_{tot}(A) = VC_{ne}(A) + V_{rep}(A)$
Atomic quadrupole (xx) Atomic quadrupole (xy) Atomic quadrupole (xz) Atomic quadrupole (yy) Atomic quadrupole (yz) Atomic quadrupole (zz)	$\begin{pmatrix} Q_{xx}(A) & Q_{xy}(A) & Q_{xz}(A) \\ Q_{xy}(A) & Q_{yy}(A) & Q_{yz}(A) \\ Q_{xz}(A) & Q_{yz}(A) & Q_{zz}(A) \end{pmatrix}$ $= \int_\Omega d\mathbf{x}\,(-3\rho \cdot \mathbf{d}_A \cdot \mathbf{d}_A^T + \rho \cdot \mathbf{d}_A^T \cdot \mathbf{d}_A \cdot \mathbf{E})$
Force exerted on nucleus A by density of A (x) Force exerted on nucleus A by density of A (y) Force exerted on nucleus A by density of A (z)	$\begin{pmatrix} F_{Ax}(A) \\ F_{Ay}(A) \\ F_{Az}(A) \end{pmatrix} = \int_\Omega d\mathbf{x}\,(\rho \cdot Z_A \cdot \mathbf{d}_A/r_A^3)$
Force exerted on all other nuclei by density of A (x) Force exerted on all other nuclei by density of A (y) Force exerted on all other nuclei by density of A (z)	$\begin{pmatrix} F_{Bx}(A) \\ F_{By}(A) \\ F_{Bz}(A) \end{pmatrix} = \int_\Omega d\mathbf{x}\,(\sum_B \rho \cdot Z_B \cdot \mathbf{d}_B/r_B^3)$

TABLE I.
(Continued)

Name of Atomic Property	Definition of Property for Atom A with Basin Ω
Total integrated volume (0.001 au isosurface)	$VOL_1(A) = \int_\Omega d\mathbf{x}\,(1,\text{ if }\rho(\mathbf{x}) \geq 0.001,\text{ else } 0)$
Total integrated volume (0.002 au isosurface)	$VOL_2(A) = \int_\Omega d\mathbf{x}\,(1,\text{ if }\rho(\mathbf{x}) \geq 0.002,\text{ else } 0)$
Electron density over integrated volume (0.001 au isosurface)	$NVOL_1(A) = \int_\Omega d\mathbf{x}\,(\rho(\mathbf{x}),\text{ if }\rho(\mathbf{x}) \geq 0.001,\text{ else } 0)$
Electron density over integrated volume (0.002 au isosurface)	$NVOL_2(A) = \int_\Omega d\mathbf{x}\,(\rho(\mathbf{x}),\text{ if }\rho(\mathbf{x}) \geq 0.002,\text{ else } 0)$
Basin virial	$V_{BAS}(A) = \int_\Omega d\mathbf{x}\,(-\mathbf{x} \cdot \nabla \cdot \sigma(\mathbf{x}))$
Surface virial	$V_{SURF}(A) = -2K(A) - V_{BAS}(A)$
Ehrenfest force (x)	
Ehrenfest force (y)	$\begin{pmatrix} EF_x(A) \\ EF_y(A) \\ EF_z(A) \end{pmatrix} = \int_\Omega d\mathbf{x}\,(-\nabla \cdot \sigma(\mathbf{x}))$
Ehrenfest force (z)	

TABLE II.
Definition of Properties for Surface Integration.

Name of Surface Property	Definition of Property for Surface S between Atoms A and B
Surface integral of electron density	$N(S) = \int_S d\mathbf{x}\,\rho(\mathbf{x})$
Surface integral of Laplacian density	$L(S) = \int_S d\mathbf{x}\,L(\mathbf{x})$
Lagrangian kinetic energy	$G(S) = \int_S d\mathbf{x}\,G(\mathbf{x})$
Hamiltonian kinetic energy	$K(S) = \int_S d\mathbf{x}\,K(\mathbf{x})$
Surface integral of $\nabla\rho \cdot \mathbf{n}(\mathbf{x})$	$GRN(S) = \int_S d\mathbf{x}\,(\nabla\rho \cdot \mathbf{n}(\mathbf{x}))$
Hypervirial gradient ($n = -1$), atom A	$VR_{-1,A}(S) = \int_S d\mathbf{x}\,(\rho \mathbf{d}_A^T \cdot \mathbf{n}(\mathbf{x})/r_A)$
Hypervirial gradient ($n = -1$), atom B	$VR_{-1,B}(S) = \int_S d\mathbf{x}\,(-\rho \mathbf{d}_B^T \cdot \mathbf{n}(\mathbf{x})/r_B)$
Hypervirial gradient ($n = 0$), atom A	$VR_{0,A}(S) = \int_S d\mathbf{x}\,(\rho \mathbf{d}_A^T \cdot \mathbf{n}(\mathbf{x}))$
Hypervirial gradient ($n = 0$), atom B	$VR_{0,B}(S) = \int_S d\mathbf{x}\,(-\rho \mathbf{d}_B^T \cdot \mathbf{n}(\mathbf{x}))$
Hypervirial gradient ($n = 1$), atom A	$VR_{1,A}(S) = \int_S d\mathbf{x}\,(\rho \mathbf{d}_A^T \cdot \mathbf{n}(\mathbf{x})r_A)$
Hypervirial gradient ($n = 1$), atom B	$VR_{1,B}(S) = \int_S d\mathbf{x}\,(-\rho \mathbf{d}_B^T \cdot \mathbf{n}(\mathbf{x})r_B)$
Hypervirial gradient ($n = 2$), atom A	$VR_{2,A}(S) = \int_S d\mathbf{x}\,(\rho \mathbf{d}_A^T \cdot \mathbf{n}(\mathbf{x})r_A^2)$
Hypervirial gradient ($n = 2$), atom B	$VR_{2,B}(S) = \int_S d\mathbf{x}\,(-\rho \mathbf{d}_B^T \cdot \mathbf{n}(\mathbf{x})r_B^2)$
Hypervirial gradient ($n = -1$), total	$VR_{-1} = VR_{-1,A} + VR_{-1,B}$
Hypervirial gradient ($n = 0$), total	$VR_0 = VR_{0,A} + VR_{0,B}$
Hypervirial gradient ($n = 1$), total	$VR_1 = VR_{1,A} + VR_{1,B}$
Hypervirial gradient ($n = 2$), total	$VR_2 = VR_{2,A} + VR_{2,B}$
Virial of force exerted on surface of A	$V_A(S) = \int_S d\mathbf{x}\,(-\mathbf{d}_A^T \cdot \sigma \cdot \mathbf{n}(\mathbf{x}))$
Virial of force exerted on surface of B	$V_B(S) = \int_S d\mathbf{x}\,(\mathbf{d}_B^T \cdot \sigma \cdot \mathbf{n}(\mathbf{x}))$
Total virial of force exerted on surface	$V(S) = V_A(S) + V_B(S)$
Total force exerted on electrons of atom A (x)	
Total force exerted on electrons of atom A (y)	$\begin{pmatrix} SGN_x(S) \\ SGN_y(S) \\ SGN_z(S) \end{pmatrix} = \int_S d\mathbf{x}\,(-\sigma \cdot \mathbf{n}(\mathbf{x}))$
Total force exerted on electrons of atom A (z)	
Gradient of force exerted on electrons of atom A	$SGN(S) = \int_S d\mathbf{x}\,(\text{div}(\sigma) \cdot \mathbf{n}(\mathbf{x}))$
Total integrated area (0.001 au isosurface)	$AREA(S) = \int_S d\mathbf{x}\,(1,\text{ if }\rho \geq 0.001,\text{ else } 0)$

Example Sessions with AIM2000

The results of example sessions for three molecules are presented: benzene, diborane, and tryptophan. The wave functions have been calculated using the program package Gaussian.[6]

The definitions of calculated properties (refer to Tables I and II) are based on the following notations: X_A is the nuclear position of atom A, $d_A = x - X_A$, $r_A = \|d_A\|_2$; Z_A is the nuclear charge of atom A; $R = -V/T$ is the virial ratio of the molecule. For a molecule in an equilibrium geometry, R should equal 2 if the virial theorem is satisfied; ψ is the wave function of the molecule; $\int d\tau'$ is the summation over all spin and integration over all electronic coordinates but one; $V_{ee}(x)$ is the electron–electron repulsion energy density; $\sigma(x)$ is the quantum stress tensor; $n(x)$ is the normal to an interatomic surface between atoms A and B at a point x pointing outward from atom A; and E is the 3×3 unit matrix.

BENZENE

We used a 6-311++g(2d,2p) basis set for the Gaussian[6] calculation of the wave function. To examine the benzene molecule with AIM2000, the following steps have been carried out:

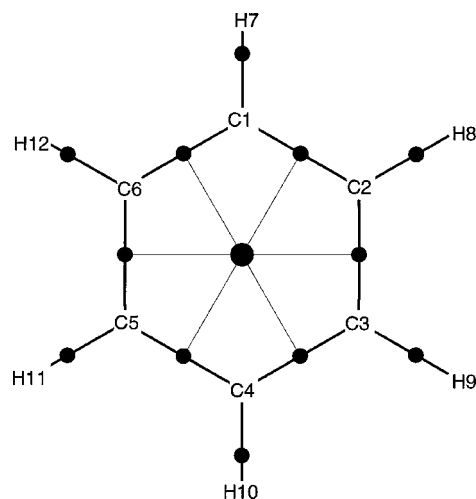1. Load the wave function using the entry in the file menu.

FIGURE 2.

2. Call the dialog for the calculation of critical points from the Calculation Menu. All critical points are determined successfully with default settings by using nuclear positions and mean values of density maxima pairs as starting values.
3. Call the dialog for the calculation of gradient paths of the molecular graph. With default settings there is no problem calculating bond and ring paths. View the results in 3D-View.

TABLE III.

Integrated Properties of Atoms in Benzene (Total Calculated Energy: -230.769094545203, Virial $R = -V/T = 2.00075285$).

Property	Results for Atom C1	Results for Atom H7
N	5.9830404197e+000	1.0156066265e+000
L	2.5183347861e−004	4.8882029469e−005
G	3.7798492684e+001	6.3320930006e−001
K	3.7798744518e+001	6.3325818209e−001
V	−7.5597237202e+001	−1.2664674821e+000
E	−3.7827201303e+001	−6.3373493051e−001
I	6.4307280415e−001	1.6114365003e−001
R_{-1}	1.4949653752e+001	1.3035968140e+000
R_1	6.1544559570e+000	1.1257716923e+000
R_2	9.6959117609e+000	1.6540791938e+000
R_4	4.6821363599e+001	7.1840929549e+000
GR_{-1}	−2.7077505869e+001	−1.8719611975e+000
GR_0	−1.3099327563e+001	−2.1793844089e+000
GR_1	−1.5771465438e+001	−3.3235768794e+000
GR_2	−3.1050068914e+001	−6.3444175448e+000

TABLE III.

(Continued)

Property	Results for Atom C1	Results for Atom H7
M_x	1.9729632176e−006	2.9425537273e−007
M_y	5.2223158481e−002	1.1988216649e−001
M_z	3.4612873009e−005	5.7207975436e−006
V_{ne}^0	−8.9697922510e+001	−1.3035968140e+000
VC_{ne}^0	−8.9731674346e+001	−1.3040873358e+000
V_{ne}	−1.4724279847e+002	−1.0425437205e+001
VC_{ne}	−1.4729820349e+002	−1.0429360124e+001
V_{ee}	4.2124297686e+001	4.5647708861e+000
VC_{ee}	4.2140148358e+001	4.5664885334e+000
V_{rep}	7.1632703325e+001	9.1601617402e+000
V_{tot}	−7.5665500163e+001	−1.2691983838e+000
Q_{xx}	1.8548650917e+000	−1.4133164458e−001
Q_{xy}	1.8412957890e−004	−1.1097481745e−005
Q_{xz}	1.7379950836e−004	2.5267563228e−005
Q_{yy}	1.6479168406e+000	5.0143892420e−001
Q_{yz}	9.3339043898e−005	1.1647766754e−005
Q_{zz}	−3.5027819324e+000	−3.6010727962e−001
F_{Ax}	4.6528251227e−004	−1.0116564073e−005
F_{Ay}	−2.7002749490e−001	−2.2076064572e−001
F_{Az}	−5.1963854693e−004	1.9822745194e−005
F_{Bx}	−5.2461905170e−005	−1.2239485993e−006
F_{By}	8.1784552399e+000	2.2415281255e+000
F_{Bz}	−2.7795674655e−005	1.2187364828e−005
VOL_1	8.3230752472e+001	4.9379654052e+001
VOL_2	7.0782453725e+001	3.7121284413e+001
$NVOL_1$	5.9632763188e+000	9.9237355348e−001
$NVOL_2$	5.9453895243e+000	9.7483921719e−001
V_{BAS}	−7.5331435647e+001	−1.1620346392e+000
V_{SURF}	−2.6580155560e−001	−1.0443284290e−001
EF_x	−3.4210324811e−004	9.2911642225e−006
EF_y	−2.4512599750e−002	−6.5749013942e−002
EF_z	5.9522957178e−004	−1.8411686352e−005

4. In Plot Menu choose a new plot and molecular graph to display the molecular graph of benzene in 2D-View (see Fig. 2).

5. After analyzing the molecular structure, properties of atoms in molecules can be calculated. After choosing an atom in Control View, call the dialog for integration over atomic basins. To get better results, relative and absolute accuracy are both set to 10^{-5} in the options dialog. Integration in natural coordinaates needs 3228167 wave function evaluations to integrate atom C1 and 474888 wave function evaluations to integrate atom H7. For results, see Table III. To get correct dipole and quadrupole moments, no symmetry was used. Results for other atoms follow by symmetry.

6. After choosing an interatomic surface in Control View, call the dialog for integration over interatomic surfaces from the calculation menu. Using defaul settings, integration is carried out for the surfaces between C1 and C2, and between C1 and H7. For results see Table IV. Results for other surfaces follow by symmetry.

7. After calculating these values, integration accuracy can be examined using Gauss'

TABLE IV.
Integrated Properties of Interatomic Surfaces in Benzene.

Property	Results for Surface between $A = C1$ and $B = C2$	Results for Surface between $A = C1$ and $B = H7$
N	1.435488	0.996293
L	−0.343893	−0.108499
G	0.934137	0.544816
K	0.590245	0.436317
GRN	0.000000	−0.000000
$VR_{-1,A}$	1.081951	0.657707
$VR_{-1,B}$	1.081951	0.735505
$VR_{0,A}$	1.882754	1.084239
$VR_{0,B}$	1.882754	0.867596
$VR_{1,A}$	3.490877	1.862423
$VR_{1,B}$	3.490878	1.178076
$VR_{2,A}$	7.029438	3.344751
$VR_{2,B}$	7.029439	1.913162
VR_{-1}	2.163901	1.393212
VR_0	3.765508	1.951835
VR_1	6.981755	3.040500
VR_2	14.058877	5.257912
V_A	−0.118583	−0.028916
V_B	−0.118583	−0.104887
V'	−0.237166	−0.133803
SGN_x	−0.078299	−0.000002
SGN_y	0.045206	−0.065824
SGN_z	0.000000	0.000011
SGN	0.000000	0.208372
$AREA$	39.208610	32.480316

FIGURE 3.

theorem.[3] With exact calculation, we have for volume integrals:

$$\int_{\Omega} L(x)\, dx = 0.$$

For surface integrals we have:

$$\int_{S} \nabla \rho(x)^T \cdot n(x)\, dx = 0.$$

Gauss' theorem connects both integral types:

$$g(A) \equiv 3 \cdot \int_{\Omega_A} \rho(x)\, dx + \int_{\Omega_A} \nabla \rho(x)^T \cdot x\, dx$$
$$- \sum_{S_A} \int_{S_A} \rho(x) \big(d_A(x)^T \cdot n(x)\big)\, dx = 0$$
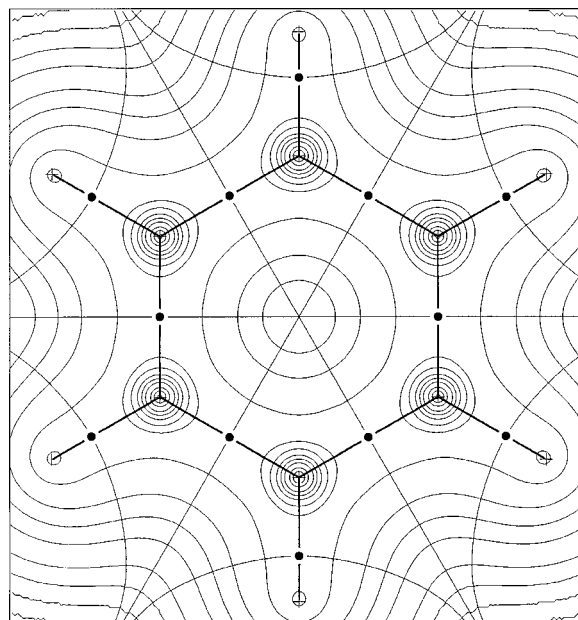
where the sum runs over all interatomic surfaces S_A of Ω_A. With values from Tables III and IV we get:

$$g(C1) = 0.0000466 \qquad \text{and}$$

$$g(H7) = -0.0001614.$$

Also, the total number of electrons in the molecule should be 42:

$$6 \cdot \int_{\Omega_C} \rho(x)\, dx + 6 \cdot \int_{\Omega_H} \rho(x)\, dx = 41.991882.$$

8. Produce various plots in 2D-View: Contour map (Fig. 3), gradient path map (Fig. 4), relief map (Fig. 5), and relief map of Lagrangian function $L(x)$ (Fig. 6).

9. Save work as an aim-file by clicking Save As... in the file menu.

DIBORANE

Similar calculations have been carried out for the diborane molecule. However, because of the structure of the molecule, some difficulties arise:

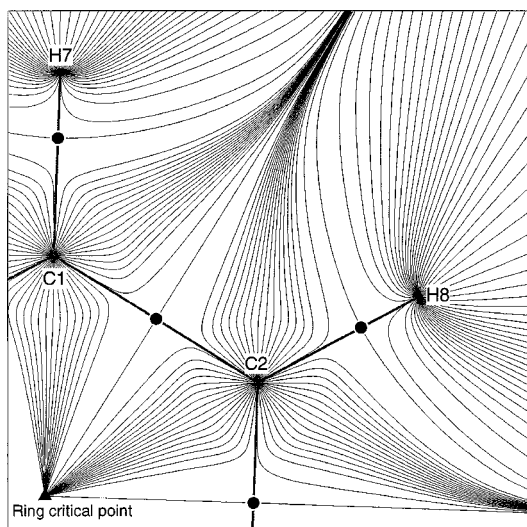1. With the default settings, the program cannot determine correct ring paths, because these are
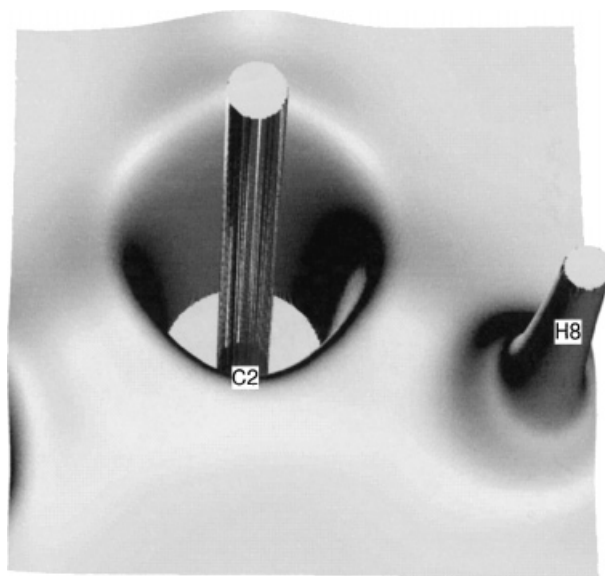
FIGURE 4.

FIGURE 6.

highly bent. Increasing the maximal number of bisection iterations in differential equation options to 60, and minimal distance to critical points to 0.1 produces accurate results.

2. The distribution of gradient paths in the surface between B1 and H5 (a hydrogen bonded to both borans) is very uneven. The program cannot satisfy the default in-
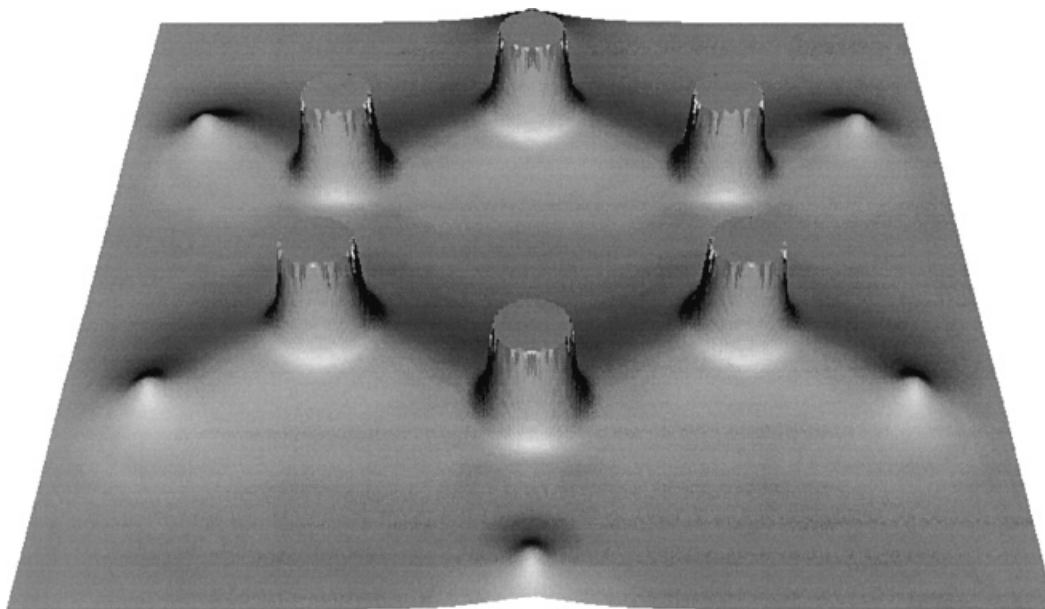

FIGURE 5.

TABLE V.

Integrated Properties of Atoms in Diborane (Total Calculated Energy: −52.832614782625, Virial $R = -V/T = 2.00039683$).

Property	Results for Atom B1	Results for Atom H3	Results for Atom H7
N	2.9278818803e+000	1.6838933109e+000	1.7038301374e+000
L	2.3158810578e−004	8.9828148536e−005	2.5455891963e−005
G	2.3750825903e+001	8.6347456503e−001	9.2780636365e−001
K	2.3751057491e+001	8.6356439318e−001	9.2783181954e−001
V	−4.7501883394e+001	−1.7270389582e+000	−1.8556381832e+000
E	−2.3760482623e+001	−8.6390708143e−001	−9.2820001104e−001
I	4.8369114547e−001	6.1520224463e−001	5.9573643714e−001
R_{-1}	1.0398673618e+001	1.7084237794e+000	1.7438946534e+000
R_1	1.7513728182e+000	2.2805288740e+000	2.2005758313e+000
R_2	1.8687159211e+000	3.8486116219e+000	3.3914955843e+000
R_4	5.8324779443e+000	1.8642590252e+001	1.2273504710e+001
GR_{-1}	−1.9203811134e+001	−2.6546852562e+000	−2.2536324882e+000
GR_0	−6.7229485181e+000	−3.6323676181e+000	−2.7935394446e+000
GR_1	−4.1228579830e+000	−6.3214127095e+000	−4.3385580066e+000
GR_2	−4.8644234632e+000	−1.3335419643e+001	−8.0833146915e+000
M_x	6.1620751365e−002	−1.6476958740e−001	−1.3002932021e−005
M_y	6.1381114382e−006	−3.2274079204e−001	−4.2556984940e−006
M_z	−4.7441074179e−006	−4.6927788898e−006	−4.4244732441e−001
V_{ne}^0	−5.1993368089e+001	−1.7084237794e+000	−1.7438946534e+000
VC_{ne}^0	−5.2003682307e+001	−1.7087626891e+000	−1.7442405996e+000
V_{ne}	−6.2407196219e+001	−9.3529298333e+000	−1.1321241737e+001
VC_{ne}	−6.2419576286e+001	−9.3547852267e+000	−1.1323487596e+001
V_{ee}	1.9328069364e+001	4.2446827201e+000	5.1967049588e+000
VC_{ee}	1.9331903582e+001	4.2455247617e+000	5.1977358585e+000
V_{rep}	1.4899490322e+001	7.6263004003e+000	9.4662408062e+000
V_{tot}	−4.7520085964e+001	−1.7284848264e+000	−1.8572467895e+000
Q_{xx}	9.3587297497e−002	9.7362995500e−002	4.8869539931e−001
Q_{xy}	3.2014158666e−005	3.6233530777e−001	−1.7980376780e−004
Q_{xz}	−2.1933317412e−005	1.1369439812e−005	−1.5385552973e−005
Q_{yy}	1.4665331410e−001	3.9323131045e−001	−1.4822974116e−001
Q_{yz}	−9.8624812239e−005	−4.8288526452e−006	2.1484320813e−005
Q_{zz}	−2.4024061160e−001	−4.9059430595e−001	−3.4046565815e−001
F_{Ax}	−1.3379192369e−001	−1.7278364288e−001	−9.4276240870e−006
F_{Ay}	−2.1787346245e−004	−3.0175930628e−001	−1.0564320247e−005
F_{Az}	1.0102027929e−003	−1.6050374112e−005	−3.4513495926e−001
F_{Bx}	1.5685202260e+000	1.4567554141e+000	−1.0235664602e−005
F_{By}	3.4471363223e−006	1.9271921175e+000	4.9078022456e−006
F_{Bz}	−3.2593080746e−008	−2.3093719873e−005	2.3437419389e+000
VOL_1	1.9769486072e+001	8.2954371177e+001	5.9325909444e+001
VOL_2	1.8366020652e+001	6.3861218827e+001	4.8931048694e+001
$NVOL_1$	2.9258317567e+000	1.6465346820e+000	1.6854130256e+000
$NVOL_2$	2.9238034222e+000	1.6192981632e+000	1.6705121628e+000
V_{BAS}	−4.6863546154e+001	−1.1850678196e+000	−1.0077801617e+000
V_{SURF}	−6.3833724041e−001	−5.4197113865e−001	−8.4785802151e−001
EF_x	7.4539344428e−002	−1.7570988470e−001	2.5327984850e−005
EF_y	1.0585631229e−004	−2.9569830622e−001	−8.4662530720e−006
EF_z	−1.0350520882e−003	2.1388574763e−005	−3.0656573473e−001

TABLE VI.
Integrated Properties of Interatomic Surfaces in Diborane.

Property	Results for Surface between A = B1 and B = H3	Results for Surface between A = B1 and B = H5
N	0.938160	0.706251
L	−0.204176	−0.271561
G	0.653846	0.553541
K	0.449670	0.281980
GRN	0.000000	0.000000
$VR_{-1,A}$	0.469683	0.328220
$VR_{-1,B}$	0.762191	0.607242
$VR_{0,A}$	0.572611	0.459372
$VR_{0,B}$	1.419255	1.139803
$VR_{1,A}$	0.713886	0.730035
$VR_{1,B}$	2.800173	2.194189
$VR_{2,A}$	0.860460	1.383931
$VR_{2,B}$	5.904543	4.362299
VR_{-1}	1.231875	0.935462
VR_0	1.991866	1.599175
VR_1	3.514060	2.924225
VR_2	6.765003	5.746230
V_A	−0.227334	−0.091851
V_B	−0.541805	−0.415265
V	−0.769139	−0.507116
SGN_x	−0.175785	0.139183
SGN_y	−0.295848	0.000011
SGN_z	0.000000	−0.148508
SGN	1.774847	0.987515
AREA	39.965239	28.488448

tegration accuracy of 10^{-5} when integrating over this surface. Relaxing the absolute accuracy to 10^{-4} produces satisfactory results.
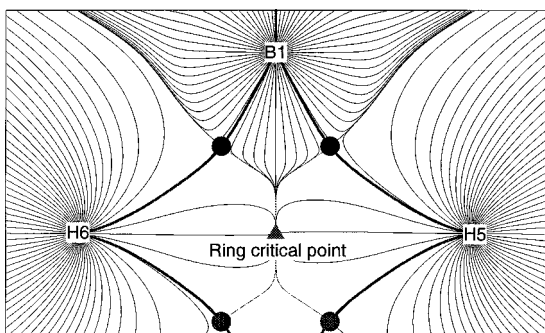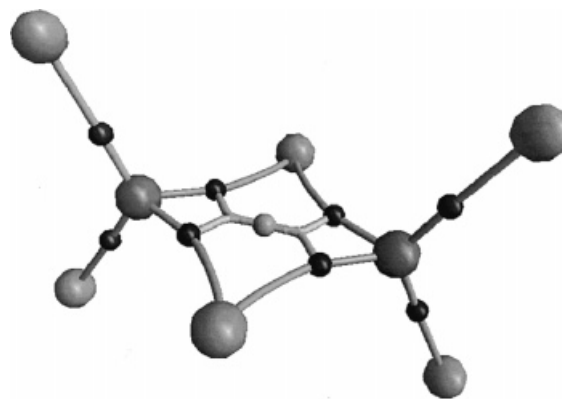
FIGURE 8.

FIGURE 7.

Integration results are presented in Table V for volume integration and Table VI for surface integration. Check of integration accuracy:

$$g(B1) = -0.003269, \qquad g(H3) = 0.000056, \qquad \text{and}$$
$$g(H5) = 0.038345.$$

Number of electrons:

$$2 \cdot \int_{\Omega_{B1}} \rho(x)\,dx + 4 \cdot \int_{\Omega_{H3}} \rho(x)\,dx$$
$$+ 2 \cdot \int_{\Omega_{H5}} \rho(x)\,dx = 15.998996.$$

Pictures and plots: Screen shot of 3D-View (Fig. 7), gradient path map in ring plane (Fig. 8), gradient path map of interatomic surface between B1 and H5 (Fig. 9).

TRYPTOPHAN

Another less simple example is the tryptophan molecule (wave function basis set: 6-311g**). Critical points and bond paths can be calculated without difficulty. Again, there are problems calculating ring paths. Because of a very uneven distribution of gradient paths in the ring plane near the hydrogen bridge, the program is not able to compute the connection between the ring critical point and the bond critical point between H12 and O25.

TABLE VII.

Integrated Properties of Atoms in Tryptophan (Total Calculated Energy: −682.358536381611, Virial $R = -V/T = 2.00054192$).

| Property	Results for Atom H12	Results for Atom N14	Results for Atom H15	Results for Atom O25
N	9.6524198408e−001	8.5051521102e+000	5.5834781751e−001	9.3033617925e+000
L	−3.3442096066e−004	−1.7482094135e−003	9.0547017536e−005	−2.2525970707e−004
G	6.1141740326e−001	5.5297745721e+001	4.4201928515e−001	7.5596480574e+001
K	6.1108298230e−001	5.5295997512e+001	4.4210983217e−001	7.5596255315e+001
V	−1.2225003856e+000	−1.1059374323e+002	−8.8412911731e−001	−1.5119273589e+002
E	−6.1141414039e−001	−5.5325963519e+001	−4.4234942033e−001	−7.5637222437e+001
I	6.7634351391e−002	4.2902229802e−001	3.9162812206e−002	4.4797887010e−001
R_{-1}	1.2613689643e+000	1.9418072622e+001	8.7845673077e−001	2.3195599377e+001
R_1	1.0435294613e+000	9.4412505568e+000	5.2747944592e−001	9.5481328403e+000
R_2	1.4751412657e+000	1.4923710772e+001	6.8886306186e−001	1.4263233105e+001
R_4	5.6217611070e+000	6.2924301263e+001	2.4976782060e+000	5.6332688156e+001
GR_{-1}	−1.7678197665e+000	−3.5917573169e+001	−1.1730273130e+000	−4.4764882602e+001
GR_0	−1.9768650437e+000	−1.9671442469e+001	−1.1788728115e+000	−2.4597789057e+001
GR_1	−2.8451612239e+000	−2.5680079331e+001	−1.5915660651e+000	−3.1149415442e+001
GR_2	−5.0437816481e+000	−4.8602909136e+001	−2.7386852466e+000	−5.5510943873e+001
M_x	7.5291310276e−002	3.9971869863e−002	−3.9190013718e−002	−8.9715493833e−004
M_y	7.5574658923e−002	−1.6647319098e−001	1.5879025299e−001	−2.0475332298e−001
M_z	−4.0547142861e−002	1.5015984315e−002	−1.1408297637e−002	2.2640593141e−001
V_{ne}^0	−1.2613689643e+000	−1.3592650835e+002	−8.7845673077e−001	−1.8556479502e+002
VC_{ne}^0	−1.2617106522e+000	−1.3596332902e+002	−8.7869469293e−001	−1.8561506203e+002
V_{ne}	−1.8765656397e+001	−2.8768597402e+002	−9.9403522198e+000	−3.2820993253e+002
VG_{ne}	−1.8770739762e+001	−2.8776390430e+002	−9.9430449280e+000	−3.2829884020e+002
V_{ee}	8.7480490102e+000	9.7994250382e+001	4.5264832826e+000	1.0251962038e+002
VC_{ee}	8.7504187395e+000	9.8020795711e+001	4.5277094462e+000	1.0254739157e+002
V_{rep}	1.7545529003e+001	1.7709055832e+002	9.0571191310e+000	1.7700422597e+002
V_{tot}	−1.2252107583e+000	−1.1067334598e+002	−8.8592579704e−001	−1.5129461423e+002
Q_{xx}	2.7011956681e−001	2.5975745188e−001	−3.2425268661e−002	−7.2478685212e−001
Q_{xy}	2.8884610650e−001	−4.9015655706e−001	−2.6143644359e−002	2.6557651505e−001
Q_{xz}	−1.0286837480e−001	−4.6424609103e−001	1.8476134825e−003	3.2129037902e−001
Q_{yy}	1.4280121392e−002	1.8156393524e+000	6.9320455247e−002	3.4704683714e−001
Q_{yz}	−1.0296182712e−001	−4.6886443139e−001	−9.8119010497e−003	3.3098154009e−001
Q_{zz}	−2.8439968820e−001	−2.0753968043e+000	−3.6895186586e−002	3.7774001498e−001
F_{Ax}	−1.5284311282e−001	1.7202065439e−001	1.3093819580e−002	−4.0547629231e−002
F_{Ay}	−1.1873655969e−001	−7.0310995952e−001	−5.1661645804e−002	−1.4477397823e+000
F_{Az}	4.8286162798e−002	1.1182135931e−001	4.3186102673e−003	1.5176518629e+000
F_{Bx}	1.1993236423e+000	−3.9670325298e+000	−3.7667869883e−001	8.8140612748e+000
F_{By}	1.9770732800e+000	1.7556344492e+001	1.5998988219e+000	1.8226432238e+001
F_{Bz}	−9.6808885500e−001	−3.1801737796e+000	−1.9031857373e−001	−7.6055170502e−001
VOL_1	4.5474971854e+001	1.0571214988e+002	2.7581636481e+001	1.1986309256e+002
VOL_2	3.6126972456e+001	9.0600175894e+001	2.0427856041e+001	1.0118691585e+002
$NVOL_1$	9.5026880815e−001	8.4828784174e+000	5.4561370511e−001	9.2740220904e+000
$NVOL_2$	9.3684586898e−001	8.4612042260e+000	5.3542110278e−001	9.2470831909e+000
V_{BAS}	−1.1141822683e+000	−1.0866928242e+002	−8.4820372664e−001	−1.4991981062e+002
V_{SURF}	−1.0831811726e−001	−1.9244608087e+000	−3.5925390669e−002	−1.2729252685e+000
EF_x	−4.9455387350e−002	1.3353976453e−001	1.1580957843e−002	−8.8568219128e−002
EF_y	−4.2283435049e−002	−5.2708976547e−001	−4.7916213426e−002	−4.7137753226e−001
EF_z	1.8726939634e−002	5.6504605985e−002	3.2732164758e−003	1.4251216015e−001
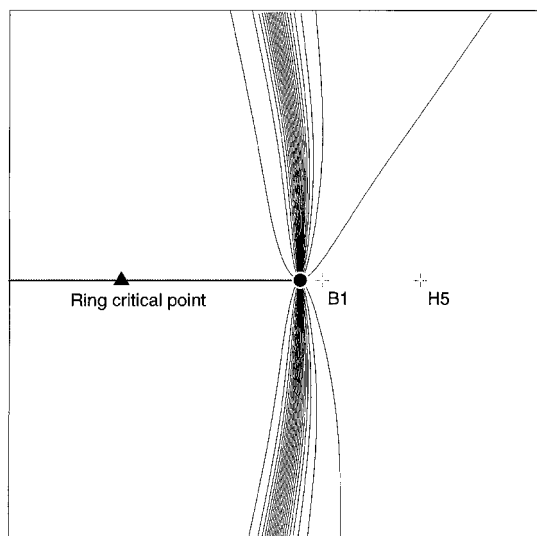
FIGURE 9.

FIGURE 10.

Integration works without problems. Table VII shows results of the volume integration for H12, N14, H15, and O25. Table VIII contains results of integration over the interatomic surfaces between C11 and H12, and between H12 and O25. Picture: Screen shot of 3D-View (Fig. 10).
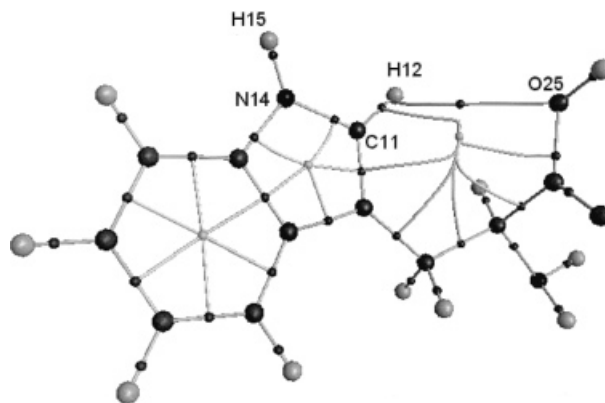
Check of accuracy whith Gauss' theorem: $g(H12) = 0.002065$.

TABLE VIII.

Integrated Properties of Interatomic Surfaces in Tryptophan.

Property	Results for Surface between A = C11 and B = H12	Results for Surface between A = H12 and B = O25
N	1.009142	0.041466
L	−0.098455	−0.043299
G	0.539633	0.033937
K	0.441178	−0.009362
GRN	−0.000000	−0.000000
$VR_{-1,A}$	0.656200	0.033392
$VR_{-1,B}$	0.723824	0.037881
$VR_{0,A}$	1.090584	0.087647
$VR_{0,B}$	0.833279	0.125613
$VR_{1,A}$	1.877027	0.236285
$VR_{1,B}$	1.094899	0.421105
$VR_{2,A}$	3.335375	0.659732
$VR_{2,B}$	1.670486	1.430675
VR_{-1}	1.380023	0.071273
VR_0	1.923863	0.213260
VR_1	2.971925	0.657390
VR_2	5.005861	2.090607
V_A	−0.046191	−0.012611
V_B	−0.097668	−0.019397
V	−0.143859	−0.032008
SGN_x	−0.054575	−0.005571
SGN_y	−0.042412	0.000151
SGN_z	0.016830	−0.002723
SGN	0.204636	−0.008679
$AREA$	36.893948	11.422466

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