



Molden: a pre- and post-processing program for molecular and electronic structures*

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Summary

Molden is a software package for pre- and postprocessing of computational chemistry program data. Interfacing to the ab initio programs Gamess-US/UK and Gaussian and to the semi-empirical package MOPAC is provided. The emphasis is on computation and visualization of electronic and molecular properties but, e.g., reaction pathways can be simulated as well. Some molecular properties of interest are processed directly from the output of the computational chemistry programs, others are calculated in MOLDEN before display. The package features different options to display MOlecular electronic DENsity, each focusing on a different structural aspect: molecular orbitals, electron density, molecular minus atomic density and the Laplacian of the electron density. To display difference density, either the spherically averaged atomic density or the oriented ground state atomic density can be used for a number of standard basis sets. The quantum mechanical electrostatic potential or a distributed multipole expansion derived electrostatic potential can be calculated and atomic charges can be fitted to these potentials calculated on Connolly surface(s). Reaction pathways and molecular vibrations can be visualized. Input structures can be generated with a Z-matrix editor. A variety of graphics languages is supported: XWindows, postscript, VRML and Povray format.

Introduction

Quantum chemistry programs like Gaussian [1] and Gamess-US/UK [2,3] and the semiempirical program Mopac [4], have become widely accepted as valuable tools in fields as diverse as drug design, synthesis planning and material science. The continuous speedup of computer hardware has made calculations on systems of interest tractable to the bench chemist. This bench chemist, however, is often discouraged from using these computational tools because of the use of unfamiliar concepts or complicated user interfaces. Some vendors of computational chemistry programs are simplifying the use of their product by the development of a customized graphical interface. For

example, GaussView [5], SYBYL from Tripos [6] or CERIU from MSI [7] provide interfaces to one or more computational chemistry packages. High quality computer graphics is playing an increasingly important role in computational chemistry. Visualization of computational results is often the most important road to interpretation.

The program Molden adds the power of computer graphics to the interpretation of the calculations. Other visualization programs feature sophisticated routines to display structural details, but Molden is quite unique in its coverage of features of the electronic structure. Molden has been designed as a general purpose tool to overcome the barriers which might hamper the use of computational chemistry techniques and programs. It facilitates the access to these programs via interactive preparation of program input.

Molden does not only visualize results produced by other programs, but it also can calculate several interesting quantities which those programs do not

*The program MOLDEN is available as a free WWW service at the CAOS/CAMM Center WWW server <http://www.caos.kun.nl/~schaft/molden/molden.html>. It can also be downloaded for local installation; for information see the above Website for details.

provide or require multiple invocations of those programs. From now on we will refer to the first form of visualization as ‘direct visualization’ and the second form as ‘indirect visualization’. Prerequisites for indirect visualization such as the atomic coordinates, the basis set, the molecular orbital coefficients and the number of electrons, are read from the program outputs.

Quantities calculated by Molden are:

- the electrostatic potential (ESP),
- ESP charges (a fit of point charges to reproduce the electrostatic potential),
- the Distributed Multipole Analysis (DMA),
- the orbitals, the molecular density or the difference density,
- the Laplacian of the electron density.

Other quantities visualized by Molden, directly available from the output of computational chemistry programs, include the intermediate and final results of a geometry optimisation or saddle point location, together with related information such as energies, forces and convergence data, the self consistent field convergence and normal modes.

Although mainly designed as a pre-/post-processing tool for the computational chemistry programs mentioned before and with a focus on the electronic structure [8], Molden also provides more general applications to the user. Current options include:

- visualization of protein structures as available from the Brookhaven Protein Data Bank [9],
- visualization of information on protein secondary structure elements such as alpha helices, beta-sheets or random coil. When such information is not available from the PDB entry, it is generated according to the method described in an early version of the *VADAR* program [10],
- visualization of crystal structures from the Cambridge Structural Database [11] as specified in the *FDAT* file format [12], including the generation of symmetry equivalent positions and a unit cell and the display of multiple unit cells.

Supported file formats also include the XMOL format [13] and the Chemx format [14].

User documentation and details of the graphics and visualization aspects of the program are available as a Web document:

URL:

<http://www.caos.kun.nl/~schaft/molden/molden.html>

The appreciation of the program by both computational and bench chemists, may be illustrated by more than 1300 installations worldwide.

Methods

Molden as a preprocessor; the Z-matrix editor

Preparation of input for computational chemistry programs often is a problem for even the ‘computer literate’ bench chemist. The structure of an input file can be quite complex due to the large number of supported options and the sometimes complicated rules for parameter specification. Either Cartesian coordinates or a Z-matrix can be used for the specification of the molecular geometry. In the Z-matrix approach, atom positions are defined with respect to previously defined atoms by means of internal coordinates such as bond distances, bond angles and dihedral angles. For small molecules a Z-matrix can often be constructed by ‘hand’, but for larger molecules this quickly becomes tedious and complex.

Molden’s Z-matrix editor presents the user complete control over the molecular geometry. Modifications in internal variables are immediately reflected in the displayed structure and modifications in the structure are immediately incorporated in the current Z-matrix. New structures can be built, adding one atom at a time or by using internally or externally stored fragments. Internal coordinates can be specified to be variable, constant or ‘linked’ to other internal coordinates. In the latter case two or more internal coordinates are described with one variable. This is particularly useful in the construction of Z-matrices that reflect the molecular symmetry. Geometries constructed with the Z-matrix editor can be saved as a Z-matrix or using Cartesian coordinates.

Molden as a post-processor

Molden processes numerical information produced by computational chemistry programs. This processing can result in direct visualization, if all necessary information is already available. If such is not the case, additional visualization information will be calculated in an intermediate computational step.

Visualization of reaction paths and normal modes

Examples of direct visualization include the use of Molden for the animation of reaction paths and normal modes of vibration of molecules.

During a reaction the molecular geometry generally will change. These geometrical or conformational changes are correlated with changes in the total energy. Molden can visualize reaction paths from Internal Reaction Coordinate (IRC) calculations, optimization and/or saddle runs. Molden complements such an animation with a plot of the energy versus geometry point.

Information on conformational flexibility resulting from thermal motion is present in the output of computational chemistry programs in the form of normal modes and their frequencies. Molden displays normal modes as a series of geometries. The starting geometry is gradually distorted by scaling the atomic displacement vectors that make up a normal mode. Molden allows the animation to be saved in the form of a VRML scene or a series of GIF files. The latter can be converted with external programs to commonly used animation file formats, such as GIF89a [15] also known as gifanim.

Figure 2 shows the racemization of hexahelicene as an example of direct visualization.

Some of Molden's options for the display of electronic structural information require information not directly available from the computational chemistry program output. In particular the handling of the electron density and charge distribution are far from trivial and require closer attention. Generally one or more additional computational steps are required to generate the required information.

Visualization of electron densities

Difference density

Plots of the difference or deformation density are often used [16–18] to visualize the effects of chemical bonding. In these plots of molecular density minus spherical atomic density, the accumulation and depletion of electron density during bond formation is shown. A classic example is the formation of banana shaped bonds in cyclopropane, as shown in Figure 3.

For some molecules it has been shown [18, 19] that the standard deformation density is small or even negative for certain covalent bonds, indicating that the use of spherically symmetric atomic ground state densities is not always the best atomic reference. Although atomic ground states are spherically symmetric, some degenerate atomic ground states are actually linear combinations of nonspherical oriented components. This degeneration can be lifted even at large interatomic distances, where the very weak long-range

influence of other atoms has an orienting effect on the free atom with a degenerate ground state. In such cases it is better to use the oriented nonspherical components of the spherically symmetric ground states [18–22]. Molden incorporates two algorithms for the construction of the difference density maps. The first uses spherically symmetric atomic densities and the second uses oriented non spherically symmetric atomic densities. The first algorithm is described below: The total molecular electron density σ is defined as the sum over the densities of the occupied Molecular Orbitals (MO's) [23]:

$$\sigma = \sum_i \text{occ}_i M O_i^2 = \sum_i \sum_r \sum_s \text{occ}_i c_{ir} c_{is} A O_r A O_s = \sum_r \sum_s P_{rs} A O_r A O_s, \quad (1)$$

where each $M O_i$ is a linear combination of Atomic Orbitals ($A O_r$) with coefficients c_{ir} . Each $M O_i$ is occupied with occ_i electrons. P_{rs} are the elements of the 1-electron density matrix:

$$P_{rs} = \sum_i \text{occ}_i c_{ir} c_{is}. \quad (2)$$

For the H_2 molecule, where the simplest wavefunction consists of a doubly occupied MO, consisting of an $1s$ orbital on atoms **a** and **b** this leads to:

$$M O = \{c_1 1s_a + c_2 1s_b\} \quad (3)$$

and the electron density is given by:

$$\sigma = 2 \left\{ c_1^2 1s_a^2 + 2c_1 c_2 1s_a 1s_b + c_2^2 1s_b^2 \right\} \quad (4)$$

or in matrix form:

$$(1s_a \ 1s_b) \begin{pmatrix} 2c_1^2 & 2c_1 c_2 \\ 2c_2 c_1 & 2c_2^2 \end{pmatrix} \begin{pmatrix} 1s_a \\ 1s_b \end{pmatrix} \quad (5)$$

where the matrix in the center is the 1-electron density matrix P . P can be thought of as composed of a set of atomic matrices, i.e. matrices referring to the same AO products as those available to the free atoms,

$$\begin{pmatrix} 2c_1^2 & 0 \\ 0 & 2c_2^2 \end{pmatrix} \quad (6)$$

and the overlap density matrix, with matrix elements referring to products of AO's centered on different atoms.

$$\begin{pmatrix} 0 & 2c_1 c_2 \\ 2c_2 c_1 & 0 \end{pmatrix} \quad (7)$$

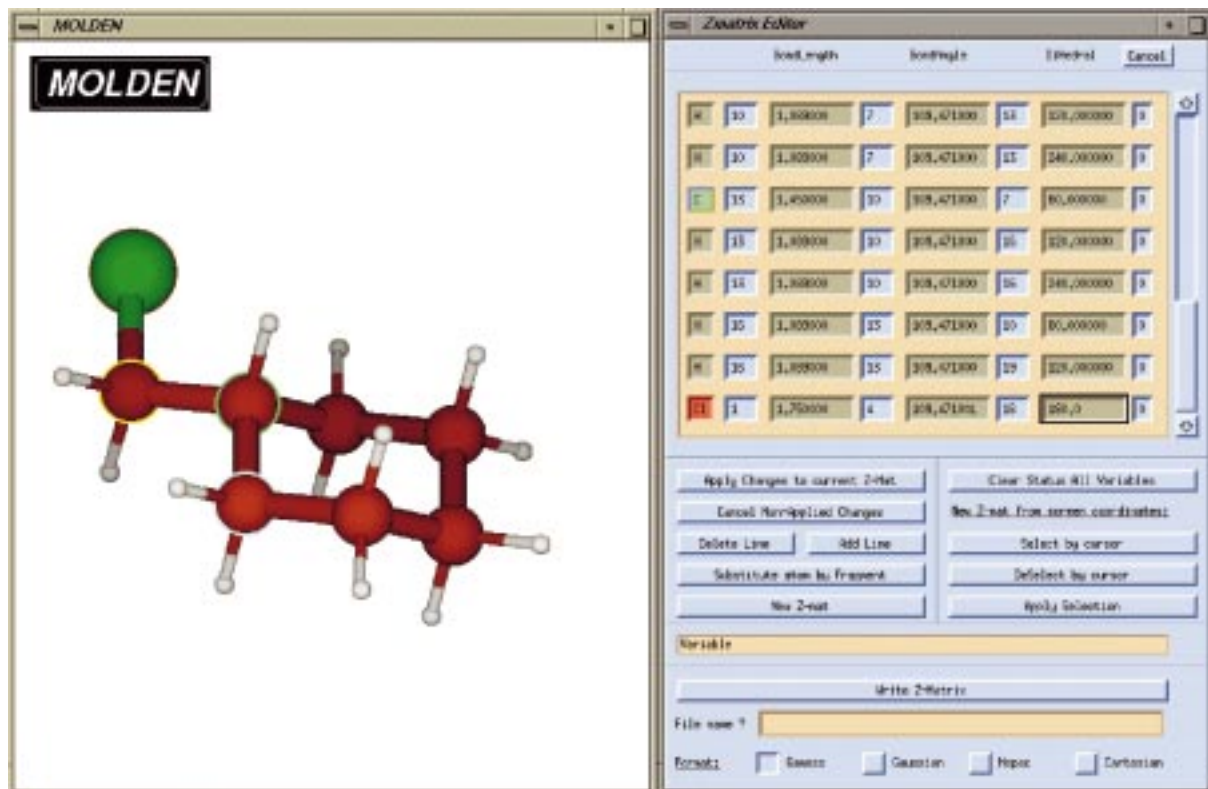


Figure 1. Molden's Z-matrix Editor option. The left screen window displays the 'editable' molecule; the right screen window the corresponding Z-matrix and the edit-control buttons.

We now define the difference or deformation density as the molecular density minus the spherical atomic density. In the case of the H_2 molecule this becomes:

$$\begin{pmatrix} 2c_1^2 - 1 & 2c_1c_2 \\ 2c_2c_1 & 2c_2^2 - 1 \end{pmatrix} \quad (8)$$

If an atomic groundstate is not spherical symmetric, a difference density plot will show a misleading decrease in electron density along some bonds. For example, in the case of H_2O_2 (Figure 4), accumulation of charge density is absent along the O-O axis (the x -axis in the molecular frame). In this example oxygen has a $3P$ ground state. One of the not spherical symmetric components is $p_x^2 p_y^1 p_z^1$. Here the electron density has a maximum along the x -axis. Subtracting a spherically symmetric atom $p_x^{4/3} p_y^{4/3} p_z^{4/3}$ can in such a case result in subtracting too much density in the y and z directions and too little in the x direction. In general, if an atom in a molecule has retained much of its ground state character, it will have a preferred orientation. The effect is most pronounced for the atoms O, F, S and Cl,

whereas for example C usually has retained most of its spherically symmetric character.

The algorithm in Molden that uses oriented non spherically symmetric atomic densities, modifies the atomic density D_{atom} of O, F, S and Cl atoms such that the sum of $(D_{\text{mol}}(i, j) - D_{\text{atom}}(i, j))^2$ becomes minimal, with D_{mol} being the atomic part of the molecular density matrix and i and j running over the p_x, p_y, p_z atomic orbitals. Application of this approach to the H_2O_2 molecule results in the plot shown in Figure 5 with the expected increase in electron density along the O-O axis.

The electron density difference function to be minimized becomes in matrix form:

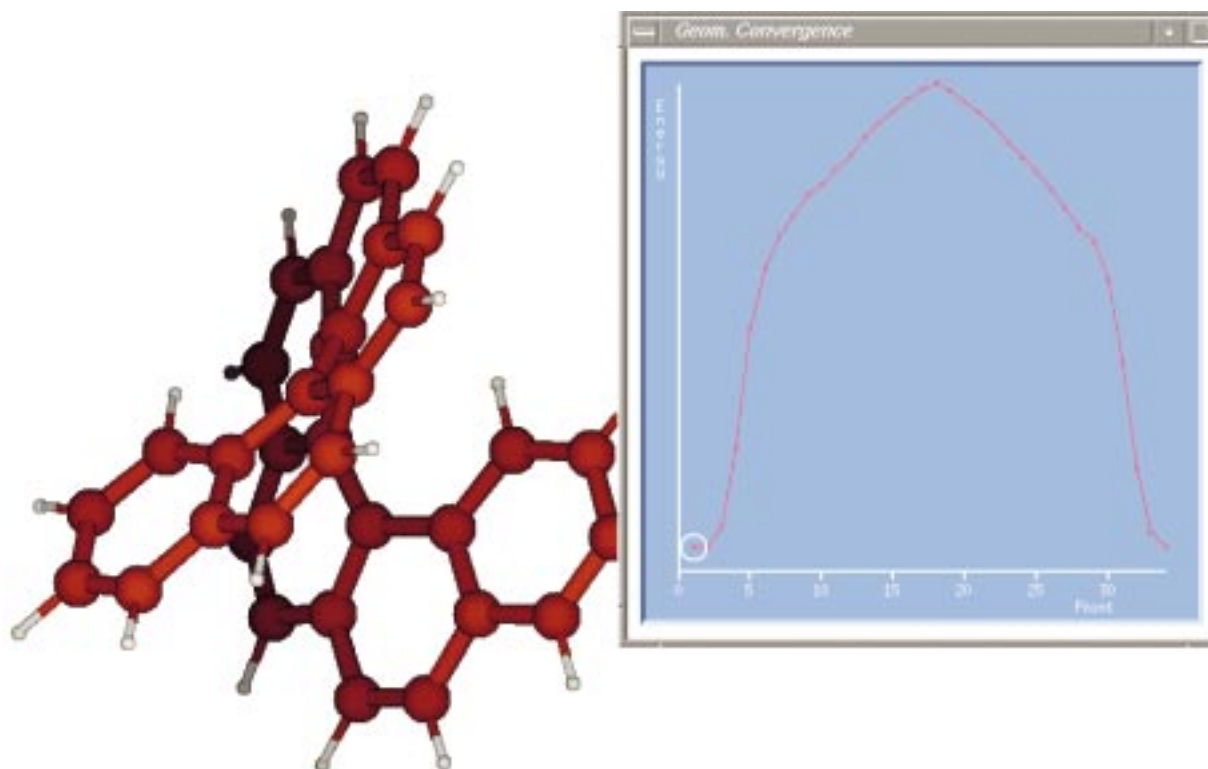


Figure 2. Racemization of hexahelicene. The left hand window of the screen shows the animation. In the right hand window an energy plot is displayed simultaneously. By selecting a position on the energy plot, the corresponding molecular geometry will be displayed.

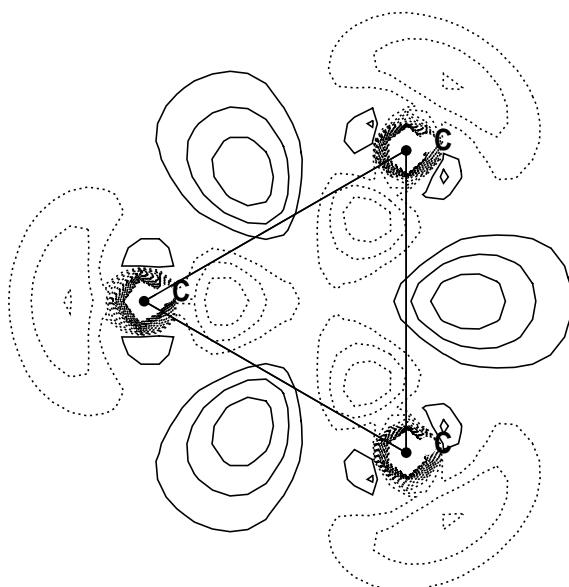


Figure 3. Cyclopropane sto3g basisset Molecular density minus Atomic density. The 'standard' approach displays the correct density distribution with 'banana bonds'; an increase of electron density positioned outside the C-C bond axes (solid contours) and a depletion of electron density in the inner ring around the carbon atoms (dashed contours).

$$\begin{aligned}
 & \begin{pmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{pmatrix}^{\text{Mol}} \\
 & - \begin{pmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{pmatrix}^{\text{Atom}} \\
 & \times \begin{pmatrix} R_{xx} & R_{xy} & R_{xz} \\ R_{yx} & R_{yy} & R_{yz} \\ R_{zx} & R_{zy} & R_{zz} \end{pmatrix}
 \end{aligned} \quad (9)$$

where matrix R is a rotation matrix defined by three Euler angles. The sum of the squares of this difference matrix $\sum_{i=x,y,z} \sum_{j=x,y,z} D_{ij}^2$ is the quantity that is actually minimized.

The atomic density matrices are stored internally for a number of frequently used basis-sets and elements.

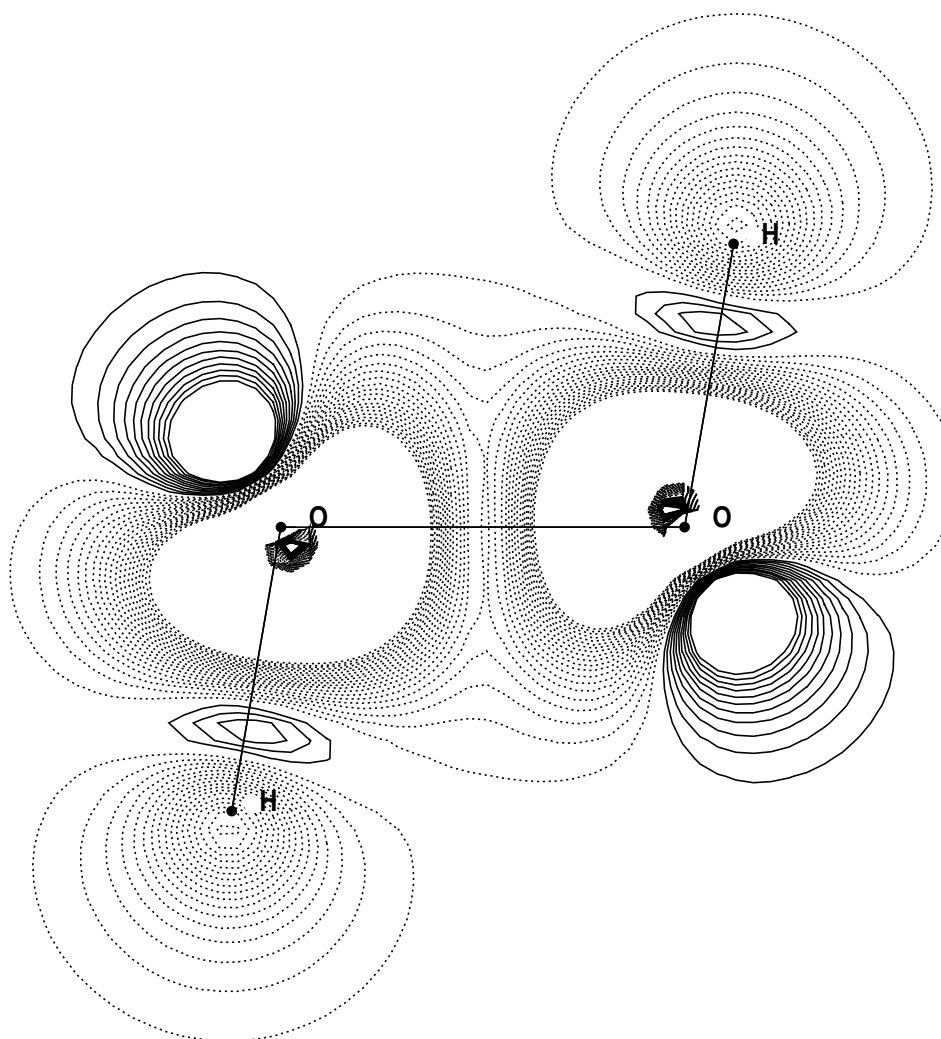


Figure 4. H_2O_2 *sto3g* molecular density minus spherical atomic density (standard approach). Misleading density plot as a result of neglecting the directional character of atomic density. Accumulation of charge density (solid contours) is absent along the O-O axis.

Molecular orbitals

The second Molden option related to orbital display is the visualization of orbitals such as frontier molecular orbitals as used in Frontier Molecular Orbital (FMO) theory calculations [24].

Figure 6 shows the HOMO in the Diels-Alder cycloaddition transition state of butadiene with ethylene, which FMO theory predicts to be a HOMO-LUMO reactant combination.

The Laplacian of the electron density

A third Molden option for the display of orbital related electron density information is the Laplacian of the electron density. Bader showed [25–28] how this quantity can provide interesting information about

the chemical bond. Most computational chemistry programs have no provision to calculate it.

In Molden the Laplacian is calculated according to the following equations. By definition, the Laplacian of the electron density is the trace of the second derivative matrix of the density.

$$\nabla^2\sigma = \frac{\delta^2\sigma}{\delta x^2} + \frac{\delta^2\sigma}{\delta y^2} + \frac{\delta^2\sigma}{\delta z^2} = \sum_r \sum_s P_{rs} \left(\frac{\delta^2}{\delta x^2} + \frac{\delta^2}{\delta y^2} + \frac{\delta^2}{\delta z^2} \right) A O_r A O_s \quad (10)$$

The Atomic Orbitals (AO's) are constructed as a linear combination of Cartesian gaussian type orbitals (*gto*'s) [29] ϕ_{lmn} with fixed coefficients and exponents α :

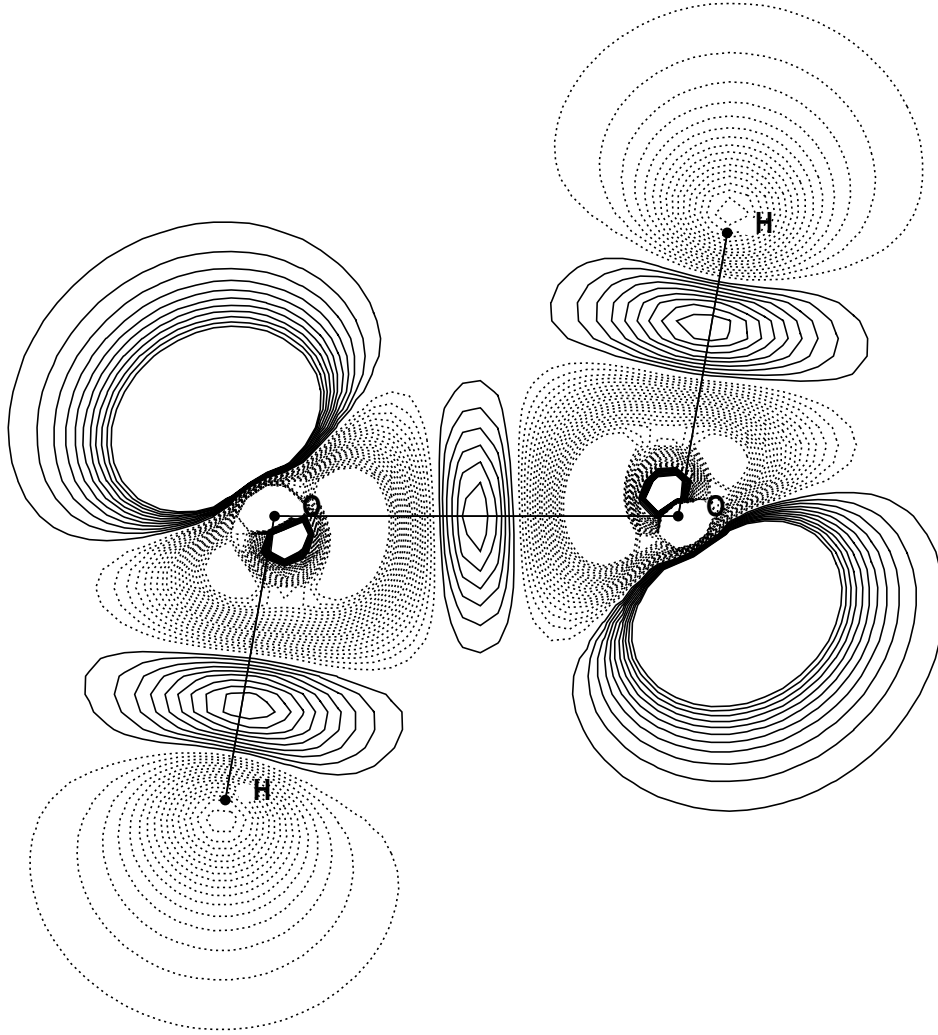


Figure 5. H_2O_2 *sto3g* molecular density minus Oriented Oxygens, with proper treatment of directional character of atomic density, resulting in the accumulation of density (solid contours) along the O-O axis.

$$\phi_{lmn} = N_{lmn} x^l y^m z^n \exp -\alpha(x^2 + y^2 + z^2) \quad (11)$$

N_{lmn} is the normalisation constant:

$$N_{lmn} = \left[\frac{(8\alpha)^{l+m+n} l! m! n!}{(2l)!(2m)!(2n)!} \right]^{\frac{1}{2}} \left(\frac{2\alpha}{\pi} \right)^{\frac{3}{4}} \quad (12)$$

The calculation of the Laplacian now breaks down into derivatives over products of *gto*'s:

$$\frac{\delta^2 \phi_i \phi_j}{\delta x^2} = \frac{\delta^2 \phi_i}{\delta x^2} \phi_j + 2 \frac{\delta \phi_i}{\delta x} \frac{\delta \phi_j}{\delta x} + \phi_i \frac{\delta^2 \phi_j}{\delta x^2} \quad (13)$$

The explicit formulas for the first and second derivatives over primitive gaussians are given by:

$$\frac{\delta \phi_{lmn}}{\delta x} = \left(-2\alpha x + \frac{l}{x} \right) \phi_{lmn} \quad (14)$$

$$\frac{\delta^2 \phi_{lmn}}{\delta x^2} = \left(\left(-2\alpha - \frac{l}{x^2} \right) + \left(-2\alpha x + \frac{l}{x} \right)^2 \right) \phi_{lmn} \quad (15)$$

Derivatives over y and z follow by analogy. The last two equations do *not* hold for $x = 0$ and in Molden this has been solved programmatically by letting x , y or z be the smallest possible number within machine precision for these cases.

The recovery of the shell structure by the Laplacian in carbon monoxide is shown in Figure 7.

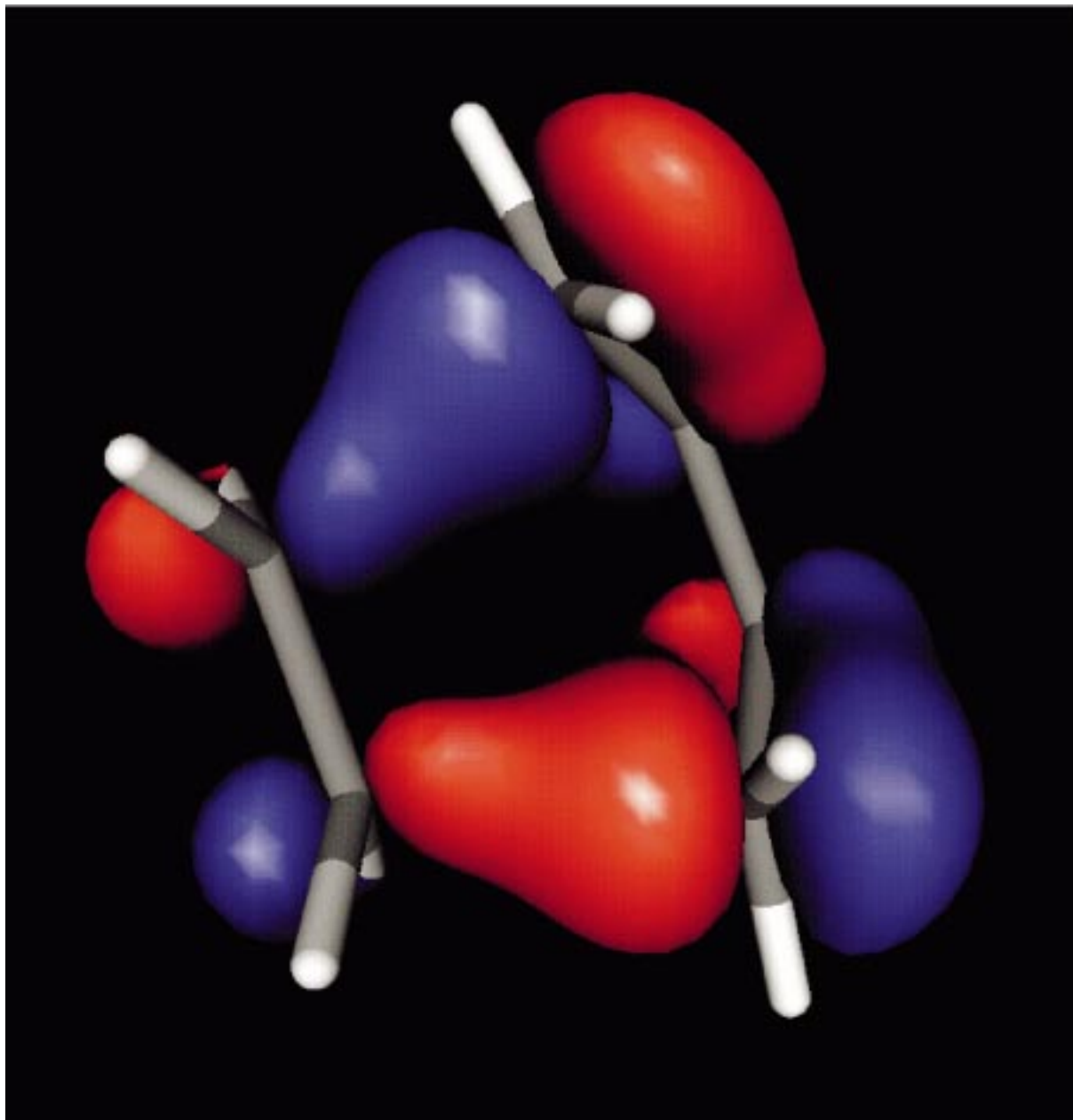


Figure 6. Highest Occupied Molecular Orbital of a Diels-Alder cycloaddition transition-state of butadiene with ethylene. Shown are the contour surfaces of orbital amplitude 0.25 (blue) and -0.25 (red).

Molecular charge distribution

Distributed multipole analysis

The calculation of the interaction energy of two molecules, as implemented in all force field based programs, is crucially dependent on a correct description of the electrostatic contribution. Most force field methods describe this term as a sum of Coulomb interac-

tions between partial atomic charges. This however does not take into account the fact that an atom in the field of other atoms is polarized and exerts an electric force which is not equal in all directions. By representing the molecular charge distribution by a set of point multipoles on a number of centers (often atomic centers), the electrostatic interaction can be modeled far more accurately [30, 31]. Such a model



Figure 7. CO sto3g, surface of constant Laplacian ($=-0.3$), showing the 1s and valence shells of carbon and oxygen.

automatically includes the effect of lone pair and π electron density on the intermolecular forces and is widely used to model complexes of polar [32] and aromatic molecules [33], for the prediction of protein side chain structures [34] and nucleic acid base pairs [35], and crystal structures [36]. Calculations in the references quoted were performed with the Orient [37] and DMAREL [38] packages, where the latter is specifically designed for crystal structure simulations.

The Distributed Multipole Analysis has been described by Stone [30, 31] in a general way, but explicit formulae for the required integrals have not been reported in the literature. Molden has incorporated the calculation of multipole moments according to the following formalism.

The Coulomb interaction of two charge distributions can be expressed as a multipole expansion in the form [31]:

$$U_{\text{elec}} = (4\pi\epsilon_0)^{-1} \sum_{l_1 l_2 m_1 m_2} [l_1 l_2] R^{-(l_1+l_2+1)} Q_{l_1 m_1} Q_{l_2 m_2} S_{l_1, l_2, l_1+l_2}^{m_1, m_2} \quad (16)$$

where $[l_1 l_2]$ denotes the numerical factor $[(2l_1 + 2l_2 + 1)! / (2l_1! (2l_2)!)]^{1/2}$, the Q_{lm} describe the charge distributions, and S is a function of the relative orientation of molecules. The Q_{lm} are complex for $m > 0$:

$$Q_{l,m} = (-)^m \frac{1}{\sqrt{2}} (Q_{lmc} + i Q_{lms}), \quad (17)$$

$$Q_{l,-m} = \frac{1}{\sqrt{2}} (Q_{lmc} - i Q_{lms})$$

A molecular charge distribution can be described as a set of multipole expansions at centers T , where T consists of atomic centers and centers due to interatomic overlap density. According to the gaussian product theorem [39], the product of two gaussian type orbitals ϕ^A and ϕ^B centered at atomic positions A and B and with exponents α and β , is itself a gaussian function, centered at point T given by:

$$\bar{T} = (\alpha \bar{A} + \beta \bar{B}) / (\alpha + \beta) \quad (18)$$

In modern Ab Initio programs the AO 's are grouped in shells, where the s, p and/or d orbitals in a shell are a fixed linear combination of the same primitive gaussians, and therefore all contribute to a given site T associated with a product of primitive gaussians. The Q_{lm} are calculated as the expectation value of the regular spherical harmonics [31]:

$$Q_{lmc}(T) = \sum_{rs} P_{rs} d_{ri} d_{sj} \langle \phi_i | R_{lmc} | \phi_j \rangle, \quad (19)$$

$$Q_{lms}(T) = \sum_{rs} P_{rs} d_{ri} d_{sj} \langle \phi_i | R_{lms} | \phi_j \rangle,$$

Here P_{rs} is an element of the density matrix, r and s run over all AO 's within shell I and II respectively and each AO is expressed as a linear combination of gaussian primitive functions ϕ_i : $AO_i = \sum_r d_{ri} \phi_i$.

A multipole expansion about the point T can be represented as a multipole expansion about any other point S by means of the formula [30]:

$$Q_{lm}(S) = \sum_{k=0}^l \sum_{q=-k}^k \left[\begin{pmatrix} l+m \\ k+q \end{pmatrix} \begin{pmatrix} l-m \\ k-q \end{pmatrix} \right]^{1/2} \times Q_{kq}(T) R_{l-k, m-q}(S-T) \quad (20)$$

Thus the proliferation of expansion centers can be reduced by shifting some or all of the overlap charge distribution to the atomic centers. Molden offers three schemes for shifting the overlap charge distribution:

- shift all overlap density to the atomic sites (default),
- shift all overlap density to the nearest atomic site or to a site halfway between the bonds,
- only shift overlap density between non bonded atoms.

Molden calculates the multipole moments up to the hexadecapole (rank=4), since explicit terms in Equation 16 are only available up to the hexadecapole moment [31].

We now turn to explicit formulae for the integrals of type $\langle \phi_i | R_{lmc} | \phi_j \rangle$. The regular spherical harmonics can be written as a linear combination of powers of Cartesian coordinates $R = \sum_r g_r x^{l_r} y^{m_r} z^{n_r}$ and

$$\langle \phi_i | R | \phi_j \rangle = \sum_r g_r \langle \phi_i | x^{l_r} y^{m_r} z^{n_r} | \phi_j \rangle \quad (21)$$

An expression for $\langle \phi_i | x^{l_r} y^{m_r} z^{n_r} | \phi_j \rangle$ can be derived in analogy for that of the overlap integral as described by Saunders [40]:

$$\langle \phi_{l_1 m_1 n_1}^A | x^{l_r} y^{m_r} z^{n_r} | \phi_{l_2 m_2 n_2}^B \rangle = \exp[-\alpha\beta(\overline{AB})^2/(\alpha+\beta)] I_x I_y I_z \quad (22)$$

in which:

$$\begin{aligned} I_x &= \sum_{i=0}^{l_1+l_2} f_i(l_1, l_2, \overline{TA}_x, \overline{TB}_x) \int_{-\infty}^{\infty} x^{i+l_r} e^{-(\alpha+\beta)x^2} dx \\ &= \sum_{i=0}^{l_1+l_2} f_i(l_1, l_2, \overline{TA}_x, \overline{TB}_x) \frac{(2(i+l_r)-1)!!}{(2(\alpha+\beta))^{i+l_r}} \\ &\quad \times \left(\frac{\pi}{(\alpha+\beta)} \right)^{1/2} \delta(i+l_r) \end{aligned}$$

with $\delta(k) = 0$ for odd k and $\delta(k) = 1$ for even k , \overline{TA}_x is the x component of the vector connecting atomic center A with the center of the gaussian product T , \overline{TB}_x is the x component of the vector connecting atomic center B with the center of the gaussian product T , $(\overline{AB})^2 = (\vec{A} - \vec{B}) \cdot (\vec{A} - \vec{B})$, $(2l-1)!! = 1 \times 3 \times 5 \cdots (2l-1)$ and

$$\begin{aligned} f_k(l_1, l_2, \overline{TA}_x, \overline{TB}_x) &= \sum_{i=0, l_1}^{i+j=k} \sum_{j=0, l_2} (\overline{TA})_x^{l_1-i} \\ &\quad \binom{l_1}{i} (\overline{TB})_x^{l_2-j} \binom{l_2}{j} \end{aligned} \quad (23)$$

Expressions for I_y and I_z can be obtained by replacing l with m and n respectively and replacing x by y and z respectively. Molden can thus calculate distributed multipole moments for ab initio wavefunctions as read from the outputs of the beforementioned

Computational Chemistry packages. These distributed multipole moments can be used to calculate an approximate electrostatic potential using the expression for the Coulomb interaction of two multipole expansions described above. The distributed multipole moments are also used to generate input for the DMAREL program.

The electrostatic potential and ESP derived charges

Since the majority of force field packages is not capable to deal with distributed multipoles, point atomic charges are frequently used to describe the electrostatic component of the energy in force field calculations. One way to obtain these charges is by fitting an atom-centered monopole approximation to the molecular electrostatic potential, MEP. The MEP can be used to predict the sites in a molecule which are most reactive towards protonation or more generally, towards an electrophilic attack.

As first defined by Bonaccorsi et al. [41], the MEP, $V(\mathbf{r})$ represents the value, at first order of perturbation, of the interaction energy between molecule M and a proton located in \mathbf{r} :

$$V(\mathbf{r}) = \sum \frac{Z_a}{|\mathbf{r} - \mathbf{r}_a|} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (24)$$

The first term corresponds to nuclear repulsion from the nuclei with charge Z_a and the second originates from electronic attraction between the proton and the electron density ρ . The latter is equivalent to the Nuclear Attraction Integrals (NAI) required for the construction of the 1-electron Fock matrix in Hartree-Fock calculations [40]. The algorithm currently implemented in Molden calculates the NAI's utilizing the Rys Polynomial Method [42, 43] and a scheme developed by Besler et al. [44] where the MEP is calculated on a number of Connolly surfaces, generated by scaling the van der Waals radii of the atoms. Fitting is accomplished by a least-squares procedure. It has been noted that charges computed by such a procedure may be conformationally dependent and procedures exist which allow for the fitting of charges to multiple conformations [45]. It has also been noted [46] that sometimes not all charges can be determined with the simple least-squares procedure. By application of a singular value decomposition to the least-squares matrix an estimate of the number of charges that can be assigned with statistical validity can be obtained. Both the fitting of charges to multiple conformations and the singular value decomposition approach have not yet been used in Molden.

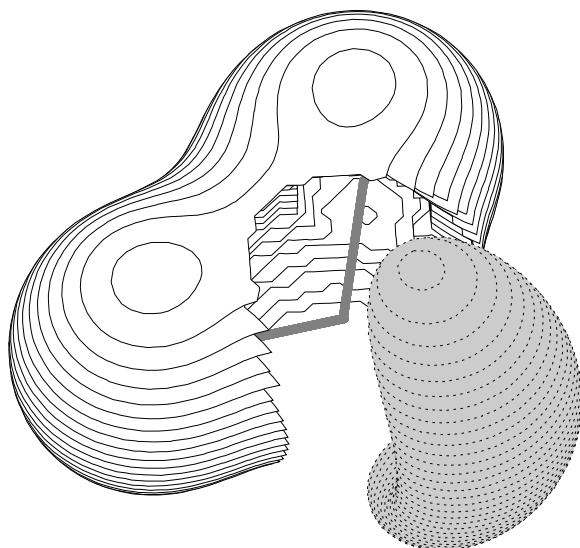


Figure 8. The Molecular Electrostatic Potential for the water molecule, MEP= ± 1.0 Hartree (grey area = -1.0).

Molden calculates the MEP for a variety of plots; the 2D contour plot, the 3D iso-contour plot as in Figure 8 and color-coded on a van der Waals surface.

Discussion

We have presented a description of the current state of development of Molden. The animation options and the treatment of difference density, the Laplacian of the electron density, the distributed multipoles and the electrostatic potential have been extended and where necessary theoretically underpinned. Ongoing development includes the incorporation of charges fitted to the DMA derived electrostatic potential. Preliminary calculations have shown that the computational costs of the procedure are orders of magnitude less than those of the traditional ESP charge calculations. The location of extrema on the electrostatic potential map, the interfacing to the DMAREL program and visualization of the spin density are other Molden developments. Some computational chemistry programs are being interfaced to Molden, e.g., the Quantum Theory [47], the MOLPRO package [48] and the ADF package [49] (Prof. A. Bencini, Inorganic Computational Chemistry, University of Florence). Molden has established a sizeable user base world wide.

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