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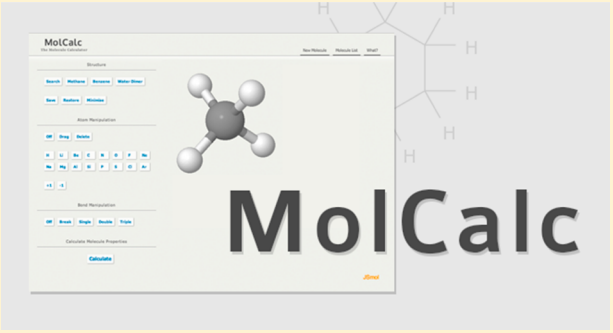
The Molecule Calculator: A Web Application for Fast Quantum Mechanics-Based Estimation of Molecular Properties

Jan H. Jensen* and Jimmy C. Kromann

Department of Chemistry, University of Copenhagen, Universitetsparken 5, 2100 Copenhagen, Denmark

Supporting Information

ABSTRACT: A new Web application called The Molecule Calculator (MolCalc) is described. The entry page is a molecular editor (JSmol) for interactive molecule building. The resulting structure can then be used to estimate molecular properties such as heats of formation and other thermodynamic properties, vibrational frequencies and vibrational modes, and molecular orbitals and orbital energies. These properties are computed using the GAMESS program at either the RHF/STO-3G (orbitals and orbital energies) or PM3 level of theory (all other properties) in a matter of seconds or minutes depending on the size of the molecule. The results, though approximate, can help students develop a chemical intuition about how molecular structure affects molecular properties, without performing the underlying calculations by hand, a nearly impossible task for all but the simplest chemical systems.



KEYWORDS: *First-Year Undergraduate/General, Second-Year Undergraduate, Organic Chemistry, Computer-Based Learning, Inquiry-Based/Discovery Learning, Thermodynamics, MO Theory, Spectroscopy*

The Molecule Calculator[1] (MolCalc) is a Web application that allows students to build small molecules and estimate properties such as molecular structure, thermodynamic properties, vibrational frequencies, vibrational modes, molecular orbitals, and orbital energies in a matter of seconds or minutes, depending on the size of the molecule. A video demonstrating these features can be found on the Web site.[2]

MolCalc was designed to be used for teaching and for assignments in which the students build their own molecules and estimate the molecular properties, as opposed to reading from tables in textbooks. MolCalc was designed to run fast, and therefore, the estimated molecular properties will not match experimental values exactly and, in some cases, will be quite different. The idea was to have students develop a chemical intuition about how molecular structure affects molecular properties, without performing the underlying calculations by hand (which would be nearly impossible for all but the simplest chemical systems). Similar to a pocket calculator or a symbolic math program (such as Mathematica or MAPLE), MolCalc allows an instructor to assign higher-level chemical problems that are not practically possible to solve otherwise. For example, an instructor might ask students to compute the effect of a substituent on a particular vibration and then rationalize the effect using molecular orbitals. Or an instructor might ask more open-ended questions such as build a molecule with an unusually long C−C single bond.[3]

HOW MOLCALC WORKS

MolCalc is split into two steps: building the molecule and calculating molecule properties. The editor is centered around the JSmol[4] plugin, which is a new JavaScript version of the popular Jmol[5] visualization program that, unlike Jmol, works on a broad range of devices without the use of Java, such as the iPhone and iPad. Different starting structures are provided, as well as the possibility to search for other structures using common names or SMILES.[6] The Chemical Identifier Resolver is used for searching and naming of structures.[7] The editor interface is based on a point-and-click approach with a clear intuitive workflow, as seen in Figure 1. JSmol is used for all molecule modifications as well as structure minimization using the MMFF force field.[8]

In the Molecule Calculator page, the structure is reoptimized at the PM3 level of theory[9] for a maximum of 50 steps, using the GAMESS program.[10] After the minimization, the student is presented with the PM3 minimized structure and the different calculation types. The PM3 structure can then be used to compute the heat of formation and other thermodynamic properties, vibrational frequencies and normal modes at the PM3 level of theory, or the molecular orbitals and orbital energies using the RHF/STO-3G level of theory. PM3 reproduces experimental heats of formation with an average error of 7.8 kcal/mol.[11] Thus, heats of formation of elements in their standard state can be significantly difference from zero. Vibrational frequencies computed with PM3 have errors of ca. 160 cm^{-1}.[12] These calculations are also performed with the GAMESS program. OpenBabel[13] is used to manage input and coordinate files.

To ensure a fast turnaround, MolCalc allows calculations on (closed shell) molecules with only doubly occupied molecular orbitals and with less than 11 non-hydrogen atoms. Only elements

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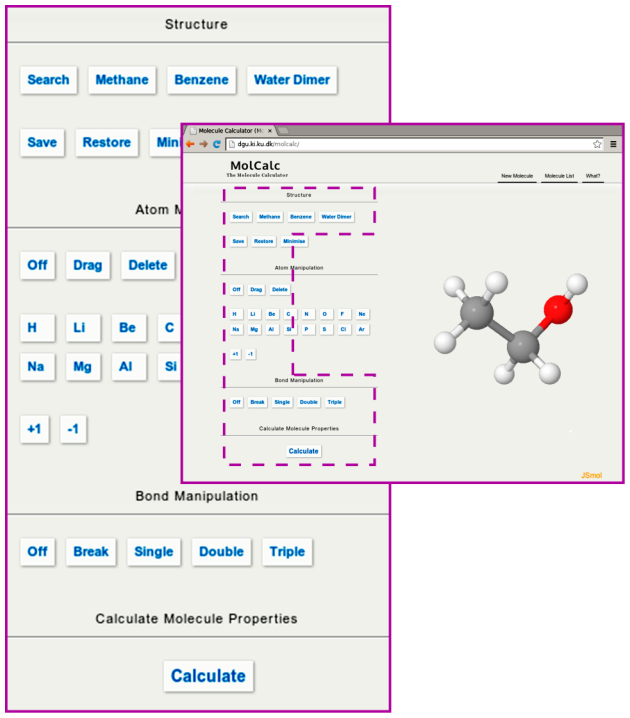

Figure 1. The Molecule Calculator (MolCalc) editor page (inset) and control buttons (enlarged, in back). The dashed lines in the inset correspond to the area displayed by the enlargement.

up to Ar are allowed. PM3 is chosen for its speed and the fact that it provides heats of formation. RHF/STO-3G is chosen for the orbital calculations because it provides the virtual orbitals, particularly the lowest unoccupied molecular orbital (LUMO) expected from the linear combination of atomic orbitals (LCAO) model. This is not always the case for larger basis sets.

USE IN TEACHING

One of the reviewers of this manuscript used MolCalc in teaching as part of the review and reports the following:

> *I found the software to be clear, intuitive, and user-friendly, ... I also found the software to be a powerful teaching tool providing students with opportunities to: (1) visualize three-dimensional molecular shapes, (2) create their own molecules following simple rules of valence, and (3) explore structure-property relationships in molecules in more interesting and profound interactive ways.*
> *In order to test students reactions, I had students in Physical Chemistry II carry out some lab/simulation exercises in two separate weeks within an introductory unit on molecular quantum mechanics/computational chemistry (see instructional resources in Supporting Information). The students took well to the assignments; they were able to navigate the software with relative ease; and they were impressed with the power and utility of molecular orbital theory as implemented in these programs to answer questions regarding molecular properties. The students realized the limitations of the software imposed by the low level of theory needed to speed the calculations, and yet they were able to learn how compositional and structural parameters affect molecular properties in a relative way and to understand some basic chemical principles on a deeper level.*

AVAILABILITY

MolCalc is avaliable on the Web[1] and the source code is distributed through Github under the GPL license.[14] The Github page also accepts bug reports and feature requests. The core of MolCalc is written in PHP5, jQuery, HTML5, and Python2.7, but is modular and can be installed on most Web servers, which makes it quite easy to add new capabilities to MolCalc. A copy of the GAMESS code must be obtained separately.[15]

ASSOCIATED CONTENT

Supporting Information

Two exercises for the students. This material is available via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: jhjensen@chem.ku.dk.

Notes

The authors declare no competing financial interest.

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