

VAMP

VAMP is a semi-empirical molecular orbital package for molecular organic and inorganic systems. VAMP is an ideal intermediate module between force-field and first principles methods and is capable of rapidly calculating many physical and chemical molecular properties. VAMP is optimized to be numerically stable and fast, enabling most calculations to be run interactively on a PC.

OVERVIEW

VAMP provides fast and reliable predictions of structural and electronic properties of molecules. VAMP is an ideal choice when making trade-offs between the speed of force-field methods and the accuracy of first-principles methods. VAMP is optimized to be numerically stable and fast, enabling users to perform high throughput calculations using even a PC.

Semiempirical molecular orbital (MO) theory was developed as an everyday tool for answering questions related to standard problems in the laboratory. VAMP provides an efficient way of obtaining these results, including a simple graphical interface to make these powerful methods easily accessible. The tasks that can be performed by VAMP include geometry optimization, transition state search and optimization, and the evaluation of many chemical and physical properties.

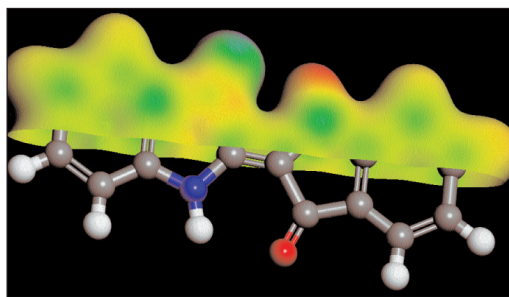
The breadth of VAMP encompasses organic, inorganic, and organometallic molecules, polymers, oligomers, and peptides. Because of its speed, VAMP can be used to perform scans over wide areas of a potential energy surface or reaction pathway; or it can be used to perform high-throughput calculations on hundreds or even thousands of molecules. Such results can be used in conjunction with Quantitative Structure-Activity Relationships (QSAR) to create a formidable

predictive tool for areas such as drug design.

VAMP contains other truly unique features that make it a powerful tool for any researcher in the chemical, pharmaceutical, or materials industry who needs to predict properties of new compounds.

For example, VAMP contains three methods designed explicitly to handle transition elements, an area very challenging for semiempirical methods MNDO/d¹, AM1*² and PM6³. The AM1* method predicts accurate geometries and energies for metals such as Ti, Zr, and Mo. The method, in addition, increases the accuracy of results for non-transition elements such as Al, Si, and P. The new PM6 method provides parameters for 70 elements include transition metals.

VAMP is the only program that calculates both ESR hydrogen hyperfine coupling constants and



The dye indigo showing a section of isosurface with the electrostatic potential mapped onto the electron density. Molecular electrostatic potential and total electronic density calculated using VAMP. Image generated using Materials Studio's volumetric analysis tools.

^{13}C chemical shifts. Current accuracy (standard deviations from experiment) is about 0.5 Gauss for ESR coupling constants and 6-8 ppm for ^{13}C chemical shifts⁴.

Solvent effects must be considered when determining the properties of molecules in almost all real situations, yet these are often ignored by calculations. Solvent effects are simulated in integrals via a multipole approximation, rather than an exact calculation.

VAMP uses two different models for solvation: numerical Self-Consistent Reaction Field (SCRF)⁵ calculations, and CONductor-like Screening MOdel (COSMO)⁵. Such models are essential for understanding the properties of molecules in solution and are easily included in VAMP calculations.

VAMP computes optical excitation spectra (UV/vis) using the ZINDO Hamiltonians which were parameterized for this very purpose. ZINDO provides a number of different model Hamiltonians^{7,8} that can be selected according to the desired property, accuracy, and available elements. The parameterization includes a wide number of transition metals, allowing the prediction of UV spectra for organometallic compounds as well as for organic molecules.

Electrostatic potential maps are often essential for understanding the activity of a molecule. VAMP includes routines for a rapid and accurate evaluation of the potential. The Natural Atomic Orbital-Point Charge (NAO-PC)⁹ model is used for molecular electrostatic properties. The type of analysis obtained using NAO-PC provides a more exact picture of the molecular electronics than the normal population analysis—a picture that rivals the accuracy of ab initio methods hundreds of times slower.

Finally, VAMP provides a number of molecular properties such as ionization potential, multipole moments, accurate molecular polarizabilities, atomic polarizabilities, and optical spectra.

THE MATERIALS STUDIO ADVANTAGE

VAMP is operated from within the Materials Studio[®] software environment that provides a user-friendly interface, complying with Windows[®] standards. Materials Visualizer offers a wide range of model building and visualization tools that allow you to rapidly construct models of the system of interest, select the VAMP module with two mouse clicks, and run a semi-empirical calculation.

VAMP can, of course, be used to compute molecular properties as described above; or it can be used in conjunction with other modules in the Materials Studio suite of programs. VAMP predictions provide good starting points for refinement with more accurate calculations such as density functional theory (DFT). Alternatively, VAMP can compute optical & IR spectra, ^{13}C NMR shifts, or optical polarizability on molecular structures predicted by other modules of Materials Studio.

HOW DOES VAMP WORK?

VAMP uses semi-empirical techniques in which many of the more complex terms are ignored or replaced using approximations. Empirical parameters and functions are used to compensate for the errors introduced by these approximations. These empirical parameters are fitted to reproduce experimental data. Suitable methods for the evaluation of energetic data are MINDO/3¹⁰, MNDO¹¹, AM1¹², and PM3¹³. Accurate optical spectra can be obtained using the INDO⁷ and CNDO⁸ methods.

VAMP uses semi-empirical calculations to determine a molecular wavefunction which can then be used to derive molecular properties such as energy and dipole moments. The molecular wavefunction is constructed according to the LCAO method in which molecular orbitals are obtained as a linear combination of Slater-type atomic orbitals. Semi-empirical methods can use Slater functions by evaluating the two-electron integrals via a multipole approximation, rather than an exact calculation.

By default, VAMP performs a MNDO Hamiltonian calculation. However, you can use controls on the VAMP setup dialog to select AM1, PM3, MNDO/C or MINDO/3 Hamiltonians. The elements for which each of these methods is parameterized are given in the 'Features and Capabilities' section of this document.

Geometry may be optimized in VAMP by several different schemes. The default optimizer is Jon Baker's Eigenvector Following (EF) routine¹⁴ which was chosen for its reliability and excellent general performance. A typical geometry optimization starts either by calculating all or part of the Hessian matrix, or by estimating its diagonal values. VAMP also offers two different and very effective transition state optimizers: EF and Powell's transition state optimizer.

You can access VAMP through the MaterialsScript API. Scripting allows you to automate repetitive task and customize workflows.

FEATURES AND CAPABILITIES

Features marked with an asterisk (*) can not be accessed via the user interface, but are available by modifying the input file.

Calculation Tasks

- Open- and closed-shell Hartree-Fock methods: Restricted (RHF), Unrestricted (UHF) and spin-Annihilated Unrestricted Hartree-Fock, (A-UHF)
- Geometry optimization
- Transition state optimization
- Vibrational frequency calculation
- Solvent effects: Self-Consistent Reaction Field (SCRF) and COnductor-like Screening MOdel (COSMO) (available solvents are acetone, acetonitrile, benzene, carbon tetrachloride, chloroform, diethyl ether, dimethyl sulfoxide, ethanol, methanol, methylene chloride, n-hexane, n-hexadecane, nitrobenzene, pyridine, water)
- CI calculations : Full, CIS, CISD and PECl

Hamiltonians

- PM6 [H through Bi, with the exception of trans-Lanthanides]
- MNDO [H, He, Li, Be, B, C, N, O, F, Mg, Al, Si, P, S, Cl, K, Ca, Zn, Ge, Br, Sn, I, Hg, Pb]
- MNDO/C is an MNDO method designed to be used with a perturbational theory correction for electron correlation. It is only parameterized for C, H, N and O
- AM1 [H, B, C, N, O, F, Mg, Al, Si, P, S, Cl, Zn, Ge, Br, Sn, I, Hg]
- PM3 [H, Li, Be, B, C, N, O, F, Na, Mg, Al, Si, P, S, Cl, Ca, Zn, Ga, Ge, As, Se, Br, Cd, In, Sn, Sb, Te, I, Hg, Tl, Pb, Bi]
- MNDO/d : standard MNDO parameters for : H, He, Li, Be, B, C, N, O, F, and MNDO/d parameters for: Na, Mg, Al, Si, P, S, Cl, Zn, Br, Cd, I, Hg
- AM1* : Standard AM1 parameters for H, C, N, O, F, and parameter sets with d-orbitals for elements Al-Cl, Ti-Zn, Br, Zr Mo, I, and Au.
- CNDO/1 [H, Li, Be, B, C, N, O, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, I, Lu, La, Ce Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb]

- CNDO/2 [H, Li, Be, B, C, N, O, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag]
- INDO/1 [H, Li, Be, B, C, N, O, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, I]
- INDO/2 [H, Li, Be, B, C, N, O, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br]

Job Control Options

- VAMP jobs can be run as background processes on a server or as synchronous (interactive) jobs on your PC.

Properties

- Electron density
- Molecular orbitals (canonical), or localized orbitals
- Electrostatic potentials
- Atomic charges : NAO-PC, Coulson, and Mulliken
- Molecular and atomic multipoles
- Static first-order polarizabilities(*)
- ESR hyperfine coupling constants to hydrogen(*)
- ¹³C chemical shifts
- Optical spectra
- Heat of formation, entropy, and heat capacity.

Analysis of VAMP results

- Volumetric display of: total electronic density, spin density, electrostatic potential, molecular orbitals, and localized orbitals
- Thermodynamic properties (enthalpy, entropy, and heat capacity)
- Atomic charges and bond orders.

To learn more about Materials Studio, go to

accelrys.com/materials-studio

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