A bridge between force-field and full *ab initio* methods

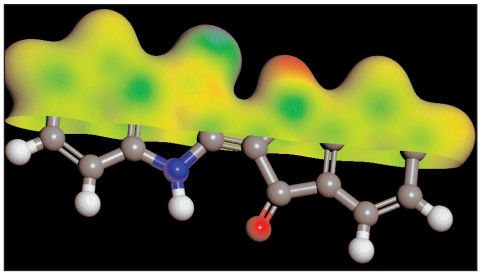
Semi-empirical program for fast geometry and transition state optimizations, and rapid access to a range of molecular properties

Reliable prediction of thermodynamics, ^{13}C chemical shifts, solvent effects, electrostatics, and optical spectra

MS Modeling Datasheet

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.



▲ *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.*

VAMP allows fast and reliable calculations to be performed on large systems utilisingthe MINDO/3[1], MNDO[2], AM1[3], and PM3[4] semi-empirical methods.

The tasks that can be performed by VAMP range from geometry optimization, transition state search and optimization to the evaluation of many chemical and physical properties. It allows researchers to calculate and obtain good starting geometries and states before density functional theory (DFT) refinement. Properties and spectra of previously optimized structures (using DFT) can be obtained using VAMP, and also VAMP can be used to perform quick potential energy scans and reaction path calculations. VAMP can optimize monomers and oligomers, calculate input charges for molecular dynamics simulations for UV/VIS spectra calculations, to calculate potential energy surfaces for force-field parameterization, and for IR spectra calculations where force-fields are not applicable.

VAMP includes routines implementing the Natural Atomic Orbital-Point Charge (NAO-PC)[5] model for molecular electrostatic properties. It gives accurate dipole, quadrupole, and higher moments, and high quality Molecular Electrostatic Potentials (MEPs), many times faster than comparable methods. NAO-PC is available for the standard semi-empirical Hamiltonian methods - MNDO, AM1, and PM3. The simple type of distributed multipole analysis obtained using NAO-PC provides a more exact picture of the molecular electronics than the normal population analysis. Molecular quadrupoles calclated with MNDO, AM1, or PM3 agree at least as well with experiment as those calculated using ab initio theory at the MP2/6-31G* level[6]. VAMP can successfully optimize geometries for which other semi-empirical programs cannot find the minimum. The program also contains two different transition state optimizers: eigenvector following and Powell's method.

VAMP contains two new semi-empirical methods - MNDO/d[7] and AM1*[8]. The latter is designed to handle transition elements. VAMP is an excellent tool for prescreening and fast geometry optimization calculations in many research areas such as homogeneous catalysis.

Solvent effects are simulated using numerical Self-Consistent Reaction Field (SCRF)[9] calculations for ground and excited states; and COnductor-like Screening MOdel (COSMO)[10] for ground states. The SCRF calculations use Tomasi's numerical method, with a cavity bounded by the solvent-excluded surface. The SCRF calculations also use NAO-PC electrostatic properties.

VAMP is the only program that calculates both ESR hydrogen hyperfine coupling constants and ^{13}C chemical shifts[11] using artificial neural nets. Current accuracy (standard deviations from experiment) is

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about 0.5 Gauss for ESR coupling constants and 6-8 ppm for ^{13}C chemical shifts.

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

The Materials Studio Advantage

VAMP is an MS Modeling product and is operated from within the Materials Studio® software environment. Materials Studio 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.

A flexible client-server architecture means that calculations can be run on Windows 2000 or XP, Linux (running on Intel 32 bit compatible systems), and IRIX servers located elsewhere on your network. Results are returned to your PC, where they may be displayed and analyzed. You can easily produce high quality graphics of molecular structures, molecular orbitals, electrostatic potentials, or charge densities. Find more information in the 'System Details' section of this document.

How Does VAMP Work?

VAMP uses semi-empirical techniques in which many of the more complex integrals are removed or replaced using approximations. Empirical parameters and functions are used to compensate for the errors introduced by removing integrals. These empirical parameters are fitted to reproduce experimental data. More suitable methods for the evaluation of energetic data are MINDO/3, MNDO, AM1, and PM3.

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) routine[12] 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: Jon Baker's EF optimizer and Powell's transition state optimizer.

Features and Capabilities

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

1. Calculation Tasks

- Open- and closed-shell Hartee-Fock methods: Restricted (RHF), Unrestricted (UHF) and spin-Annihilated Unrestricted Hartee-Fock, (A-UHF)
- Geometry optimization
- Transition state and 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 PECI.

2. Hamiltonians

- 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* : New Hamiltonian developed for Materials Studio with standard AM1 parameters for : H, C, N, O, F and parameter sets with d-orbitals for P, S, Cl, Mo and first row d-elements

3. Job Control Options

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

4. 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 (*)
- ^{13}C chemical shifts
- Optical spectra (*)
- Heat of formation, entropy, and heat capacity.

5. 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.

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