New Features, New Chemistry

Gaussian 09 offers new features and performance enhancements which will enable you to model molecular systems of increasing size, with more accuracy, and/or under a broader range of real world conditions. We will introduce you to a few of these capabilities in detail here and outline the remainder.

Model Reactions of Very Large Systems with ONIOM

The ONIOM facility includes electronic embedding for MO:MM calculations whereby the electrostatic properties of the MM region are into account during computations on the QM region, and a fast, reliable optimization algorithm that takes the coupling between atoms in the model system and those only in the MM layer into account and uses microiterations for the MM layer between traditional optimization steps on the real system. Gaussian 09 provides many additional enhancements to the ONIOM facility, including the following:
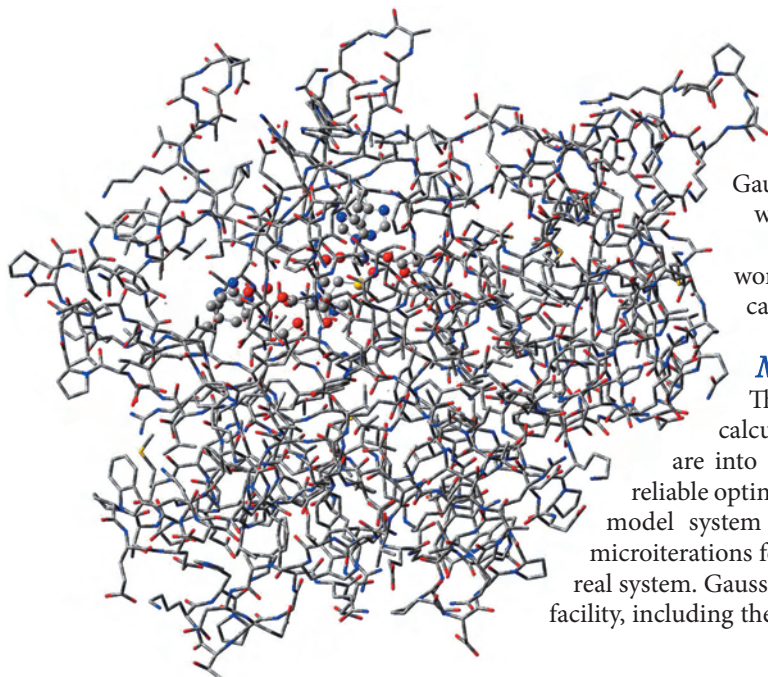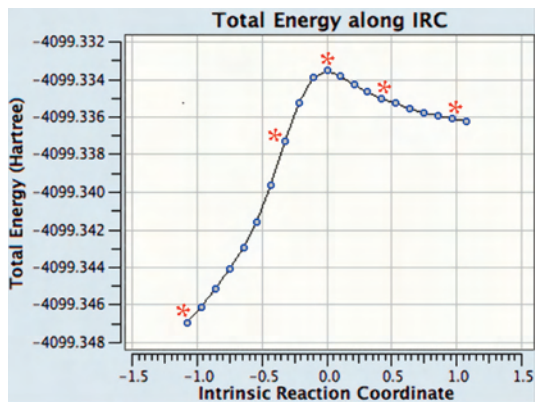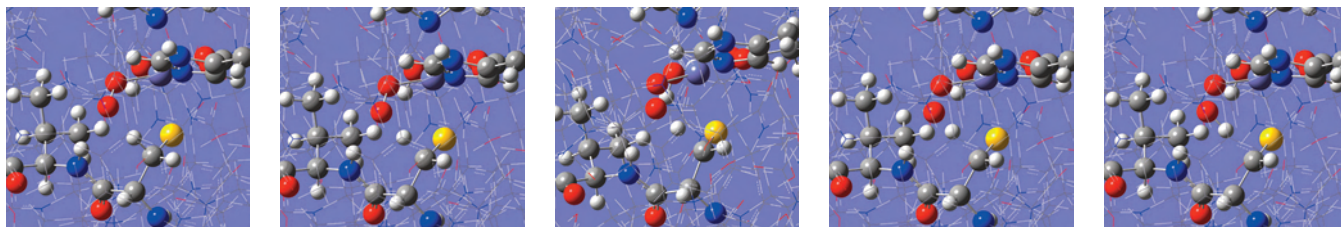
*Nonheme iron enzyme isopenicillin N synthase (IPNS) consists of 5368 atoms (hydrogens omitted above). It is representative of an important class of catalysts for fundamental biochemical processes. Modeling this molecule sheds light on how the protein matrix and the metal center separately contribute to the catalytic activity of the enzyme system. Reference: M. Lundberg, T. Kawatsu, T. Vreven, M. J. Frisch and K. Morokuma, JCTC **5** (2009) 222.*

◆ Transition state optimizations.
◆ Much faster IRC calculations.
◆ Frequency calculations including electronic embedding.
◆ Calculations in solution.
◆ General performance enhancements.
◆ Fully customizable MM force fields.
◆ New implementations of AM1, PM3, PM3MM, PM6 and PDDG semi-empirical methods with true analytic gradients and frequencies (parameters also fully customizable).

Total Energy along IRC

IRC Energy Plot. The ONIOM facility in Gaussian 09 was used to optimize the transition structure for the reaction under investigation, taking advantage of its fully coupled macro/micro iterative optimization scheme, which explicitly includes the quadratic coupling of the QM region within the MM region. The optimized transition structure verified with a frequency calculation and then used as the starting point for and IRC calculation to compute the reaction path, resulting in the plot at the left.
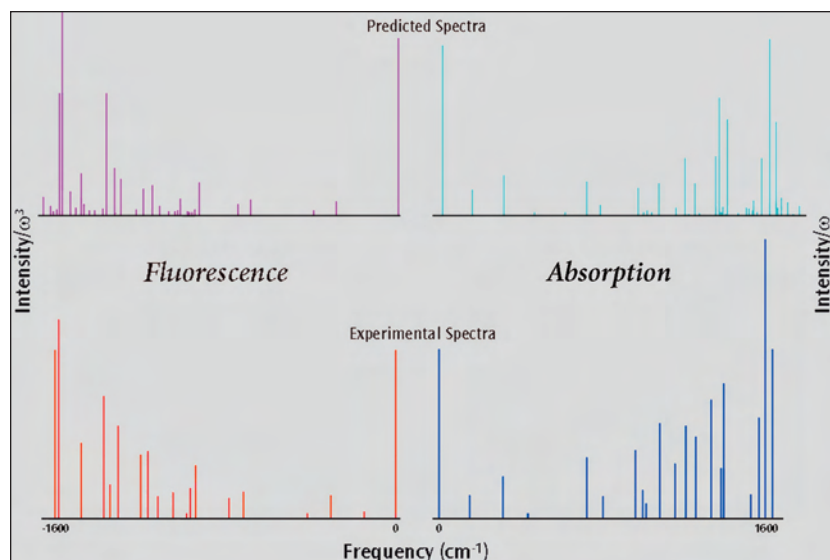
Structures from the computed IRC. The corresponding points on the energy plot have been marked with asterisks (moving from left to right). The center structure is the transition state. In the course of the reaction path, we see a proton transfer occur near the yellow sulfur atom. GaussView 5 produced these images as frames in the IRC animation.

Expanding the limits of computational chemistry SM

Study Excited States in the Gas Phase and in Solution

Gaussian 09 includes many new features intended for studying excited state systems, reactions and processes:

◆ Analytic time-dependent DFT (TD-DFT) gradients.
◆ The EOM-CCSD method.
◆ State-specific solvation excitations and de-excitations.
◆ Franck-Condon and Herzberg-Teller analysis (and FCHT).
◆ Full support for CIS and TD-DFT calculations in solution (equilibrium and non-equilibrium).

Comparing predicted and experimental spectra of the Q_x band of porphyrin. These graphs compare the high definition quasiline absorption and emission bands, plotting the computed and experimental intensities divided by ω (absorption) or ω^3 (emission). The calculations used the DFT ground state and excited state TD-DFT methods with the PBE1PBE functional (aka PBE0) for optimizations and frequencies, and employed the Franck-Condon Herzberg-Teller method for computing the amplitudes for electronic transitions from the ground and excited state frequency analyses.

All of these capabilities are included in Gaussian 09.

The frequency axis in the computed spectra is shrunk by a factor of 0.95 for a better comparison to experiment (see the paper for additional computational details). **Reference**: F. Santoro, A. Lami, R. Improta and V. Barone, *J. Chem. Phys.* **128** (2008) 224311.

Many More New Features
Among Gaussian 09's many other new features are the following:

◆ *Significantly enhanced solvation features:* In addition to the excited state features mentioned above, the SCRF facility also includes a new implementation incorporating a continuous surface charge formalism that ensures continuity, smoothness and robustness of the reaction field, and which also has continuous derivatives with respect to atomic positions and external perturbing fields. This results in faster, more reliable optimizations (taking no more steps than the gas phase) and accurate frequency calculations in solution.

◆ Analytic gradients for the Brueckner Doubles (BD) method.

◆ Additional spectra prediction: analytic DFT first hyperpolarizabilities and numeric second hyperpolarizabilities, analytic static and dynamic Raman intensities, analytic dynamic ROA intensities, improved anharmonic frequency calculations.

◆ Population analysis of individual orbitals.

◆ Fragment-based initial guess and population analysis.

◆ *Ease of use features:* reliable restarts of many more calculation types, fragment definitions within molecule specifications, freezing atoms by type, fragment, ONIOM layer and/or residue, selecting/sorting normal modes of interest during a frequency calculation, saving/reading post-SCF amplitudes, saving/reading normal modes.

◆ Many new DFT functionals, including ones incorporating long range corrections, empirical dispersion, and double hybrids.

◆ Substantial performance improvements throughout the program, including optimizations for large molecules, frequency calculations on large molecules (as much as 16x in parallel), IRC calculations (~3x faster), and optical rotations (~2x faster).