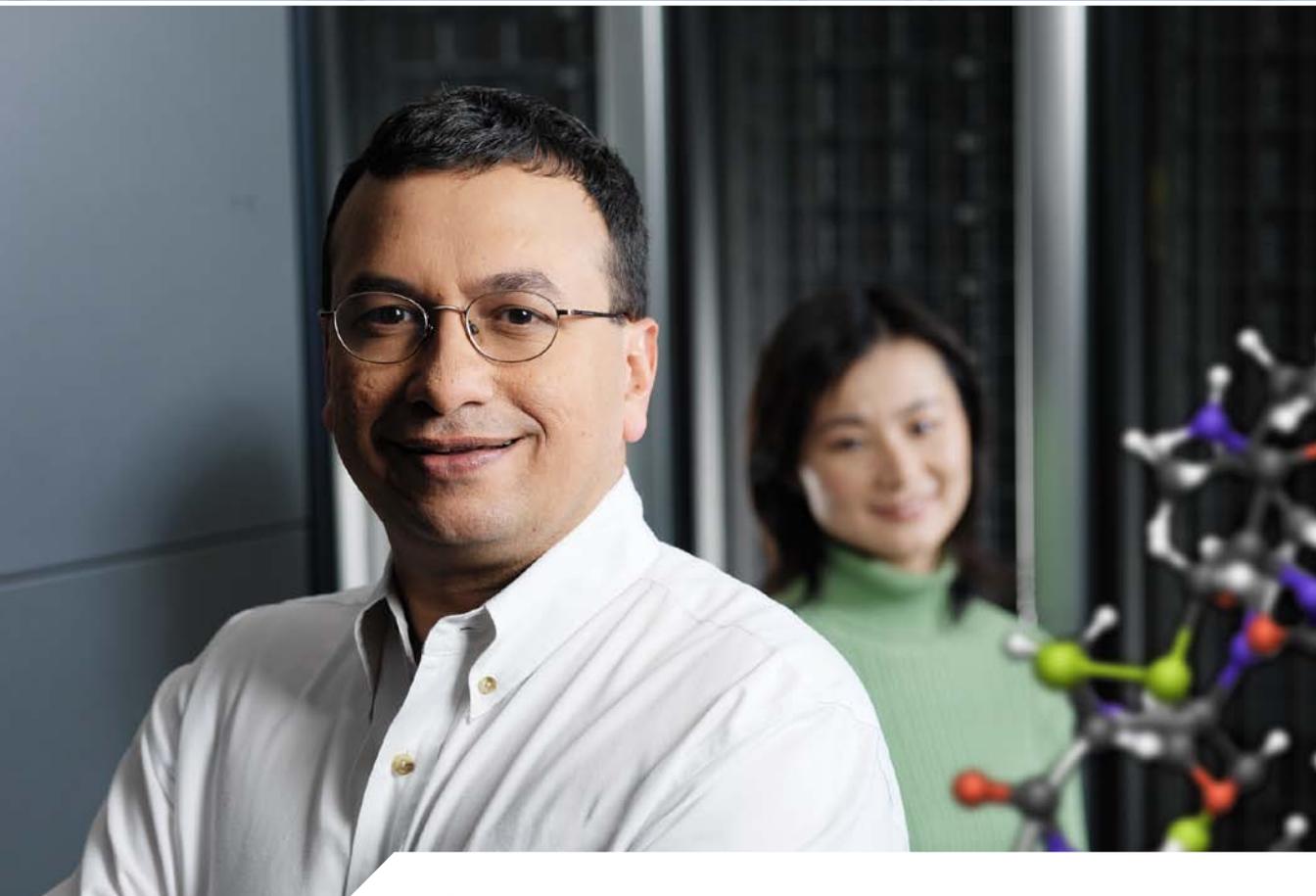


NWCHEM

HIGH-PERFORMANCE COMPUTATIONAL
CHEMISTRY SOFTWARE

NWChem

Delivering High-Performance
Computational Chemistry to Science



EMSL 

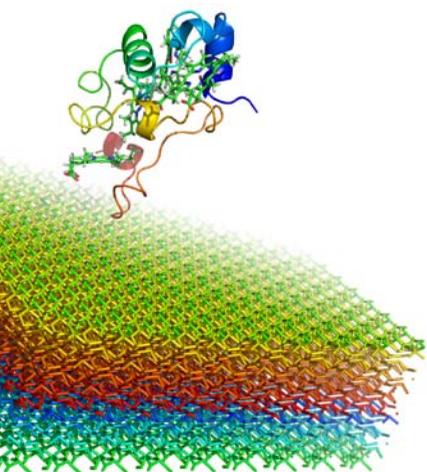
SCIENTIFIC INNOVATION THROUGH INTEGRATION

www.nwchem-sw.org

www.emsl.pnl.gov

NWChem software

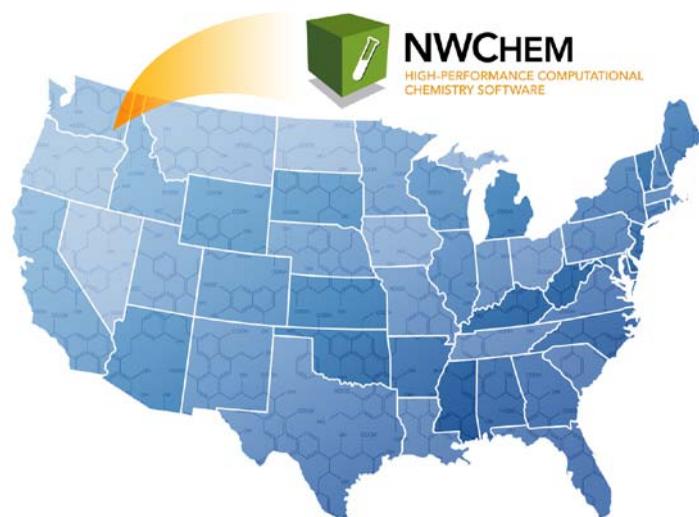
- » Biomolecules, nanostructures, and solid state
- » From quantum to classical, and all combinations
- » Gaussian functions or plane-waves
- » Scaling from one to thousands of processors
- » Properties and relativity
- » Open source



NWChem Introduction

NWChem is cutting-edge software that offers an extensive array of highly scalable, parallel computational chemistry methods needed to address a wide range of large, challenging scientific questions. As one of the U.S. Department of Energy's premier computational chemistry tools, NWChem is continuously developed at EMSL.

NWChem aims to provide its users with computational chemistry tools that are scalable both in their ability to treat large scientific computational chemistry problems efficiently and in their use of available parallel computing resources from high-performance parallel supercomputers to conventional workstation clusters. The software is available under the open-source Educational Community License version 2.0. Download your copy at www.nwchem-sw.org.



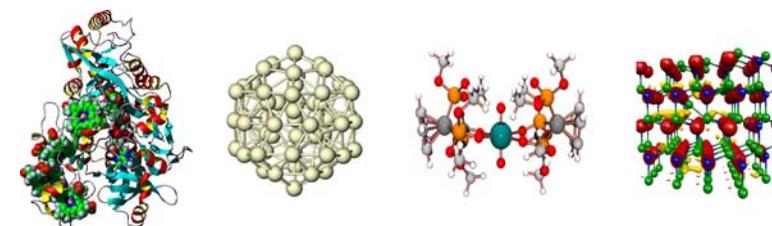
NWChem is part of the Molecular Sciences Software Suite (MS³). In addition to NWChem, MS³ includes the Global Array Toolkit, which provides an efficient and portable shared-memory programming interface for distributed-memory computers, and the Extensible Computational Chemistry Environment (Ecce), which provides a graphical user interface, scientific visualization tools, and an underlying data management framework.

Science and NWChem

NWChem enables researchers to run highly scalable, parallel computations on large, challenging scientific problems. Initially, the problems of interest were focused on environmental issues, but NWChem has recently been applied to the examination of metal clusters, biological systems, nanostructures, and materials.

NWChem offers an extensive array of computational chemistry methods needed to address scientific questions that are relevant to reactive chemical processes occurring in our everyday environment—photosynthesis, protein functions, and combustion, to name a few. They include a multitude of highly correlated methods, density functional theory (DFT) with many exchange-correlation functionals, plane-wave DFT with exact exchange and Car-Parrinello, molecular dynamics with AMBER and CHARMM force fields, and combinations of these.

NWChem runs large chemistry problems efficiently and is used by thousands of researchers worldwide to investigate questions about chemical processes by applying theoretical techniques to predict the structure, properties, and reactivity of chemical and biological species ranging in size from tens to millions of atoms.



With NWChem, researchers can tackle molecular systems including biomolecules, nanostructures, actinide complexes, and materials.

Partner with NWChem

NWChem was designed in a modular fashion to make it easier to develop new modules, to extend current modules, and interface between modules and with other programs. Programs that have an interface with NWChem include VENUS, NBO, POLYRATE, and Python.

Platform Availability

NWChem is designed to provide the best time-to-solution on desktops, clusters of conventional workstations, and high-performance parallel supercomputers. It is uniquely tailored to be scalable to thousands of processors, both in its ability to treat large problems efficiently and in its use of available parallel computing sources to obtain results faster. NWChem runs on a wide variety of architectures, interconnects, and operating systems.

Comprehensive Suite of Scalable Capabilities

NWChem provides many methods for computing the properties of molecular and periodic systems using standard quantum mechanical descriptions of the electronic wavefunction or density. Its classical molecular dynamics capabilities provide for the simulation of macromolecules and solutions, including the computation of free energies using a variety of force fields. These approaches may be combined to perform mixed quantum-mechanics and molecular-mechanics simulations.

The specific methods for determining molecular electronic structure, molecular dynamics, and pseudopotential plane-wave electronic structure and related attributes are listed in the following sections.

Molecular Electronic Structure

The molecular electronic structure methods in NWChem are all based on Gaussian basis sets.

- » Hartree-Fock (RHF, UHF, high-spin ROHF)
- » DFT with a broad range of state-of-the-art exchange-correlation functionals, including LDA; GGA; meta-GGAs; a variety of hybrid-DFT forms such as B3LYP, PBE0, Becke Half and Half, X3LYP and others; range-separated forms; dispersion corrected functionals; and double-hybrid forms
- » Time-dependent DFT (TDDFT) for excited states of molecules, clusters, nanosystems
- » Second-order perturbation theory (MP2) with RHF and UHF references
- » Complete active space self-consistent field theory (CASSCF)

Energies and analytic first derivatives with respect to atomic coordinates are available for all the above methods except TDDFT, where derivatives are computed numerically. Analytic second derivatives with respect to atomic coordinates are available for RHF and UHF and closed-shell DFT with most exchange-correlation functionals.

The following methods are available to compute energies only.

- » Iterative CCSD, CCSDT, and CCSDT_Q methods and their EOM-CC counterparts for RHF, ROHF, and UHF references
- » Active-space CCSD_t and EOM-CCSD_t approaches
- » Completely renormalized CR-CCSD(T) and CR-EOM-CCSD(T) correction to EOM-CCSD excitation energies
- » Locally renormalized CCSD(T) and CCSD(T_Q) approaches
- » Non-iterative approaches based on similarity transformed Hamiltonian: the CCSD(2)_T and CCSD(2) formalisms
- » MP2 with RHF reference and resolution of the identity integral approximation MP2 (RI-MP2) with RHF and UHF references
- » Selected CI with second-order perturbation correction

For all methods, the following may be performed.

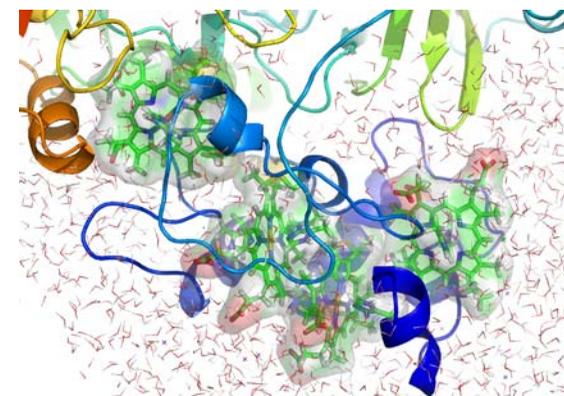
- » Single point energy calculations
- » Geometry optimization with constraints (minimization and transition state)
- » Molecular dynamics on the fully *ab initio* potential energy surface
- » Automatic computation of numerical first and second derivatives
- » Normal mode vibrational analysis in Cartesian coordinates
- » ONIOM hybrid calculations
- » Conductor-Like Screening Model (COSMO) calculations
- » Electrostatic potential from fit of atomic partial charges
- » Spin-free one-electron Douglas-Kroll calculations
- » Electron transfer (ET)
- » Vibrational SCF and DFT

At the SCF and DFT level of theory, various (response) properties are available, including NMR shielding tensors and indirect spin-spin coupling.

Quantum Mechanics/Molecular Mechanics (QM/MM)

The QM/MM module in NWChem provides a comprehensive set of capabilities to study ground- and excited-state properties of large molecular systems. The QM/MM module can be used with practically any quantum mechanical method available in NWChem. The following tasks are supported.

- » Single point energy and property calculations
- » Excited-state calculations
- » Optimizations and transition-state search
- » Dynamics
- » Free energy calculations



QM/MM studies of electronic and structural properties of iron heme groups in c-type cytochrome (IFc3)

Pseudopotential Plane-Wave Electronic Structure

The NWChem Plane-Wave (NWPW) module uses pseudopotentials and plane-wave basis sets to perform DFT calculations. This method's efficiency and accuracy make it a desirable first-principles method of simulation in the study of complex molecular, liquid, and solid-state systems. Applications for this first-principles method include the calculation of free energies, search for global minima, explicit simulation of solvated molecules, and simulations of complex vibrational modes that cannot be described within the harmonic approximation.

The NWPW module is a collection of the following three modules.

- » PSPW (PSeudopotential Plane-Wave) – A gamma point code for calculating molecules, liquids, crystals, and surfaces
- » Band – A band structure code for calculating crystals and surfaces with small band gaps (e.g., semi-conductors and metals)
- » PAW (Projector Augmented Wave) – A gamma point projector augmented plane-wave code for calculating molecules, crystals, and surfaces

The following capabilities are available.

- » Constant energy and constant temperature Car-Parrinello molecular dynamics (extended Lagrangian dynamics)
- » LDA, PBE96, and PBE0 exchange-correlation potentials (restricted and unrestricted)
- » SIC, pert-OEP, Hartree-Fock, and hybrid functionals (restricted and unrestricted)
- » Hamann, Troullier-Martins, Hartwigsen-Goedecker-Hutter norm-conserving pseudopotentials with semicore corrections
- » Geometry/unit cell optimization, frequency, transition-states
- » Fractional occupation of molecular orbitals for metals
- » AIMD/MM capability in PSPW
- » Constraints needed for potential of mean force (PMF) calculation
- » Wavefunction, density, electrostatic, Wannier plotting
- » Band structure and density of states generation

Molecular Dynamics

The NWChem Molecular Dynamics (MD) module can perform classical simulations using the AMBER and CHARMM force fields, quantum dynamical simulations using any of the quantum mechanical methods capable of returning gradients, and mixed quantum mechanics molecular dynamics simulation and molecular mechanics energy minimization.

Classical molecular simulation functionality includes the following methods.

- » Single configuration energy evaluation
- » Energy minimization

- » Molecular dynamics simulation
- » Free energy simulation (MCTI and MSTP with single or dual topologies, double-wide sampling, and separation-shifted scaling)

The classical force field includes the following elements.

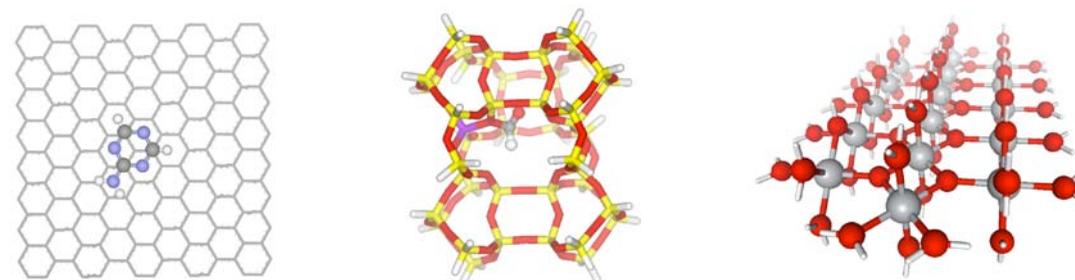
- » Effective pair potentials
- » First-order polarization
- » Self-consistent polarization
- » Smooth particle mesh Ewald
- » Twin-range energy and force evaluation
- » Periodic boundary conditions
- » SHAKE constraints
- » Constant temperature and/or pressure ensembles
- » Dynamic proton hopping using the Q-HOP methodology
- » Advanced system setup capabilities for biomolecular membranes

Access to New Science in NWChem

With the NWChem 6.0 release, many new capabilities are now available to the user community. These new capabilities within the highly scalable framework of NWChem provide computational chemists with a unique tool to perform cutting-edge science, as described in the following sections.

Ground-State Calculations with DFT

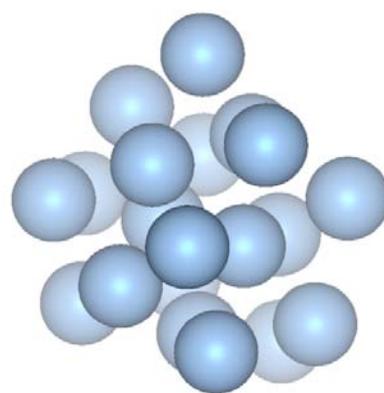
The local basis implementation of DFT in NWChem uses atom-centered Gaussian type orbitals (GTO) and can be applied to study molecules, finite clusters, and nanosystems. An exhaustive suite of exchange-correlation functionals is available, including traditional DFT, hybrid functionals, meta-type functionals, range-separated forms, double-hybrid functionals, and dispersion corrections. Relativistic effects, including spin-orbit coupling, can also be included in DFT calculations. Recent representative studies include surface absorption with dispersion corrected DFT, excited-state properties of oxide materials, and polarizabilities of water clusters.



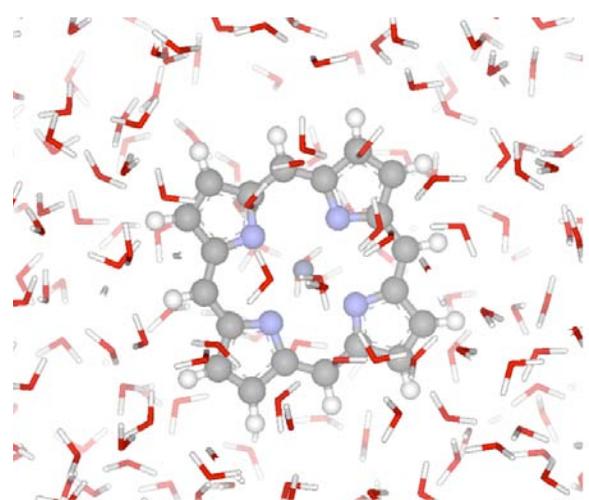
Left: Adsorption of aminotriazines on graphene using dispersion corrected DFT. Center: Formyl cation bound to a Brønsted acid site in a zeolite cavity. Right: Ground- and excited-state properties of TiO₂ rutile.

Excited-State Calculations with TDDFT

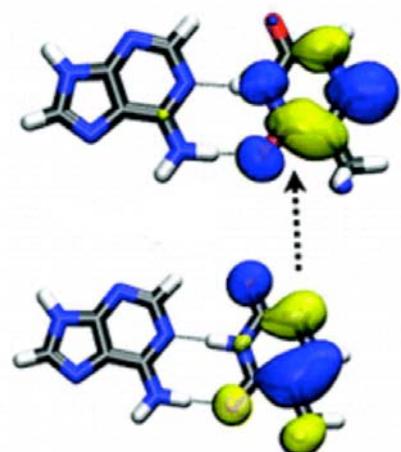
TDDFT has become an attractive and efficient tool for reliable excited-state calculations involving single excitations in a wide range of systems spanning molecules to materials. However, a major drawback lies in the quality of the exchange-correlation functionals. It is well known that various commonly used functionals are reasonably accurate for valence excited states but fall short in the prediction of charge-transfer (CT) and Rydberg states. The recently developed range-separated functionals have been shown to be very encouraging for CT transitions and outperform their non-range-separated counterparts. Results with these functionals are also comparable with very high levels of theory like EOMCC. Several range-separated exchange-correlation functionals have been recently implemented and extensively validated in NWChem.



Optical properties of silver clusters

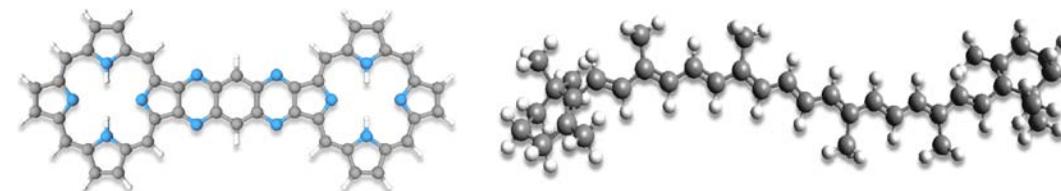


Left: Charge transfer excitations in zinc porphyrin in aqueous solution. Right: Lowest excitations in the AT base pair.

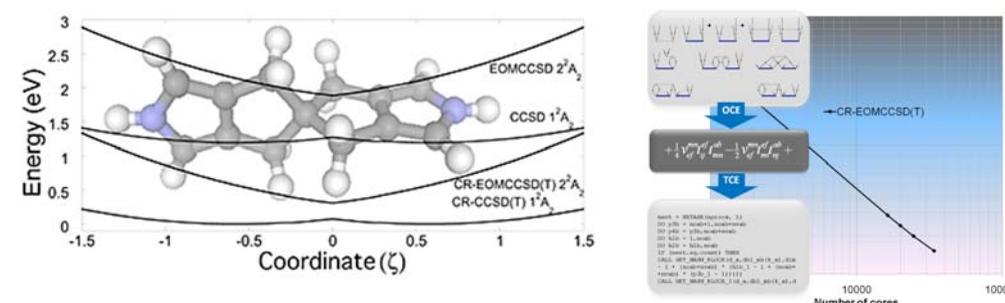


High Accuracy Is Scalable to Large Problem Sizes

A comprehensive understanding of excited-state processes is crucial in many areas of chemistry, and NWChem has the methodologies capable of providing reliable characterization of excitation energies and excited-state potential energies. Several recent implementations based on the Equation-of-Motion Coupled Cluster (EOMCC) formalism offer a unique chance to address these problems. The largest up-to-date EOMCC calculations demonstrated that by taking advantage of ever-growing computer power, the calculations with the EOMCC methodologies are possible for systems composed of 200-300 correlated electrons.



Left: EOMCC excitation energies for the oligoporphyrin dimer are in very good agreement with experiment (J. Chem. Phys. 2010, 32:154103.). Right: Formalisms can be also applied to systems of biological relevance (β -carotene).

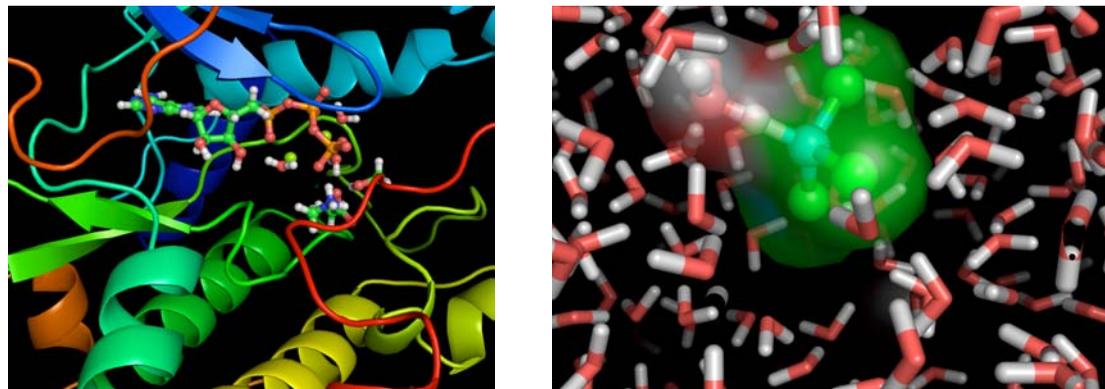


Left: Highly correlated EOMCC methods can handle electron transfer processes in challenging open-shell systems (J. Phys. Chem. A. 2010, 114:8764.). Right: CR-EOMCCSD(T) implementation was shown to scale across 34,008 cores.

NWChem offers several variants of the EOMCC formalism—from rudimentary EOMCC models with singles and doubles (EOMCCSD) to more sophisticated methods accounting for the effect of triple excitations, such as the non-iterative CR-EOMCCSD(T) method and the iterative EOMCCSDT approach and its active-space variant. These accurate formalisms can be used not only for calculations of vertical excitation energies, but also to characterize excited-state potential energy surfaces. Various EOMCC approaches can be fully integrated with the multiscale approaches, enabling simulations of excited-state processes in realistic settings. The correlated methodologies are utilized in this case as high-accuracy drivers for the quantum part of QM/MM and Embedded Clusters formalisms. This functionality provides a unique opportunity for the study of excited states in molecular systems in solution and localized excited states in materials. Another advantage of TCE-generated CC codes is the ability to use various types of reference functions for closed- and open-shell systems, including RHF, ROHF, UHF, and DFT references. Recently developed solvers for the EOMCC theory enable users to deal with excited states of highly diversified configurational structure.

Extensive QM/MM Capabilities Are Seamlessly Integrated

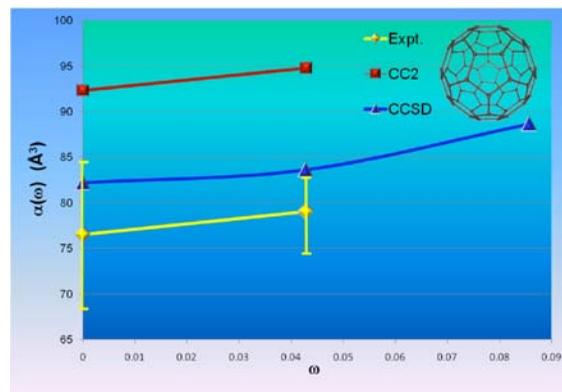
The new QM/MM module provides a seamless integration between molecular mechanics and most quantum-mechanical theories in NWChem. It boasts an extensive array of capabilities geared toward the comprehensive description of ground-state, excited-state, and dynamical properties of large molecular systems for chemistry and biology. For example, QM/MM was used to model the catalytic properties in proteins.



Left: Applying QM/MM: Modeling catalytic properties of protein kinases. Right: simulating reactions in aqueous solutions.

High Accuracy Is Achievable for Molecular Properties and Excited States

With the recently developed linear-response coupled-cluster module, high-precision calculations for static and dynamic molecular properties are possible. Several levels of theory have been implemented, including models based on singles and doubles (LR-CCSD) as well as more sophisticated theories based on the singles, doubles, and triples (LR-CCSDT). The recent studies of static and dynamic polarizabilities for polyacenes and C_{60} molecules clearly demonstrate the great potential of the LR-CC theory in retaining the essential part of the correlation effects (*J. Chem. Phys.* 2007. 127:144105. and *J. Chem. Phys.* 2008. 129: 226101.). The LR-CCSD approach also enables highly-accurate estimates of the static hyperpolarizabilities for systems where low-rank methods fail (*J. Chem. Phys.* 2009. 130:194108.).

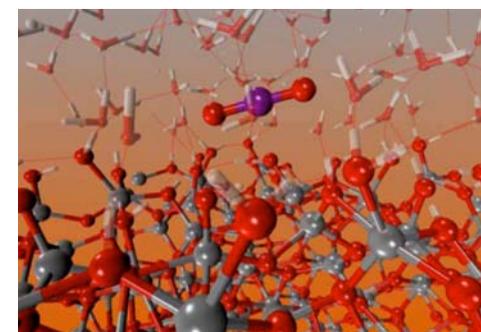


Excellent agreement between dipole polarizabilities of C_{60} calculated with NWChem using LR-CCSD and experimental values

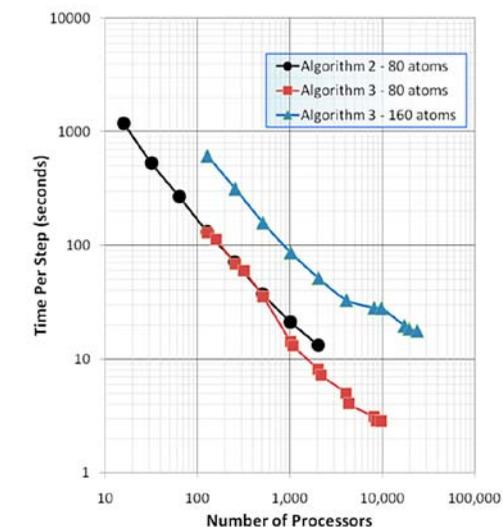
Highly Scalable Plane Wave For Solid-State With Exact Exchange

The NWChem highly scalable Plane-Wave module now enables users to use exact exchange and the Self-Interaction Correction (SIC) within its framework for complex molecular, liquid, and solid-state systems. In addition, great improvements in parallel performance allow users to study larger systems at longer time scales with faster time-to-solution. Scaling to 24,000 processors has been demonstrated for a 160-atom hematite cluster using density functional theory with exact exchange.

NWChem's Car-Parrinello simulation capability, incorporating relativistic effects, was used to model the behavior of uranium in complex solution environments (*J. Chem. Phys.* 2008. 128:124507.) and on iron-oxide surfaces as well as clay layers.



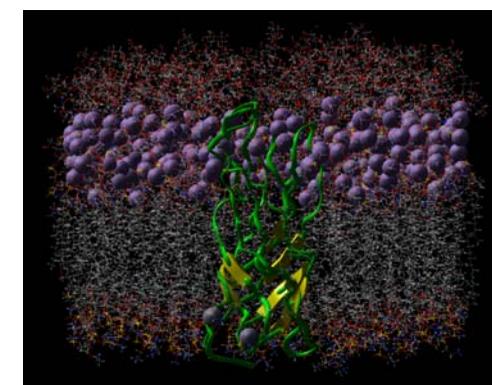
Unique relativistic Car-Parrinello simulations of uranyl in water interacting with complex mineral surfaces



NWChem's plane-wave module with exact exchange can scale to over 24,000 processors for relatively small solid-state systems.

Molecular Dynamics Can Tackle Large Complex Systems

The Molecular Dynamics (MD) module of NWChem is designed for the simulation of biomolecular systems with special features that facilitate the setup of complex systems, such as membrane proteins embedded in microbial membranes. These capabilities have been used to perform the first-ever computer simulations of outer membrane proteins in lipopolysaccharide membranes in a study of the OprF outer membrane protein of *Pseudomonas aeruginosa*.



MD simulations model the outer membrane of *Pseudomonas aeruginosa*.

EMSL High-Performance Software Development Group

The High-Performance Software Development Group at EMSL focuses on developing next-generation molecular modeling software for newly evolving computer technologies, especially massively parallel computers. It has the primary responsibility for developing and supporting the Molecular Sciences Software Suite (MS³) that offers comprehensive, integrated capabilities to enable scientists to understand complex chemical systems at the molecular level.

Source code, binaries, documentation, and more are available on the NWChem web site.

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Niri Govind Marat Valiev

Bert de Jong

Wide network of active developers and collaborators

List of collaborators can be found on the NWChem web site



MS³

MOLECULAR SCIENCE
SOFTWARE SUITE



ECCE

EXTENSIBLE COMPUTATIONAL
CHEMISTRY ENVIRONMENT



NWCHEM

HIGH-PERFORMANCE COMPUTATIONAL
CHEMISTRY SOFTWARE



GA TOOLS

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GA Toolkit www.emsl.pnl.gov/docs/global

Ecce ecce.emsl.pnl.gov

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EMSL, a national scientific user facility at Pacific Northwest National Laboratory, provides integrated experimental and computational resources for discovery and technological innovation in the environmental molecular sciences to support the needs of DOE and the nation.