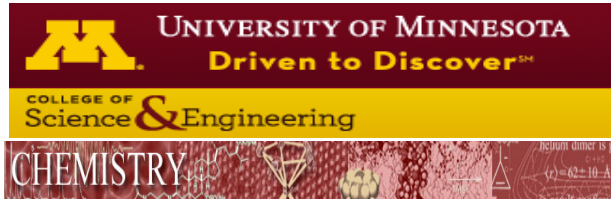


Charge Transfer and Charge Transport in Photoactivated Systems

Developing Electron-Correlated Methods for Excited State Structure and Dynamics in the NWChem Software Suite

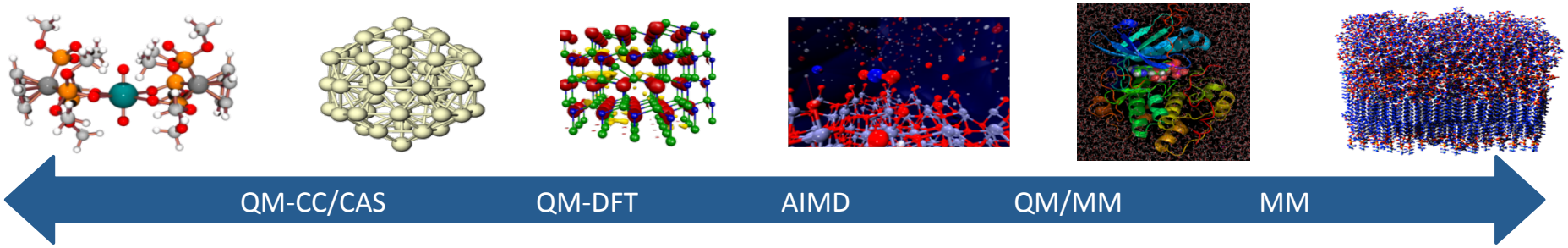
Christopher J. Cramer, Director, SciDAC-3 Application Project

How Do We Best Model Excited Electronic States?

How do we determine their energies, and their (non-adiabatic) couplings with one another, and with surrounding media, to understand their dynamical evolution and the role these phenomena play in charge transport?

Charge Transfer and Charge Transport in Photoactivated Systems

Developing Electron-Correlated Methods for Excited State Structure and Dynamics in the NWChem Software Suite



Investigators will develop methods, algorithms, and improved software tools for the reliable modeling of charge transfer and charge transport in photoactivated systems on leadership class computational platforms. Such processes are fundamental in solar energy devices, for example.

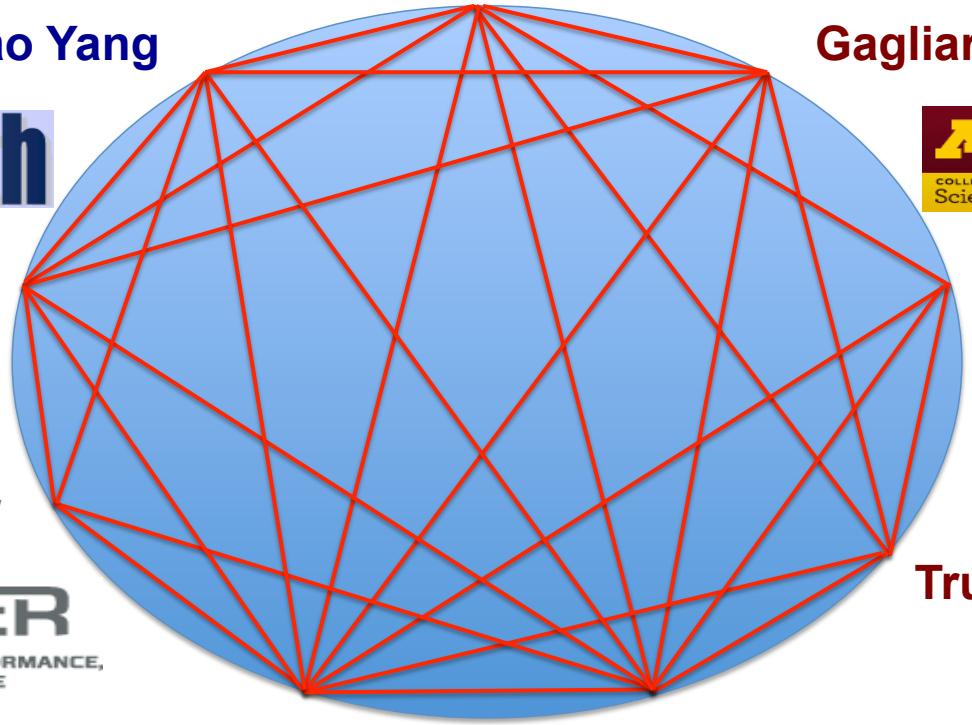
NWChem
High-Performance Computational Chemistry Software

Pacific Northwest National Laboratory

University of Minnesota Driven to Discover℠
College of Science & Engineering

Berkeley Lab
Lawrence Berkeley National Laboratory

Team Composition



Cramer

Chao Yang

FASTMath

Esmond Ng

Gagliardi

University of Minnesota
Driven to Discover℠
College of Science & Engineering

Siepmann

Lenny Oliker

SUPER
Institute for Sustained Performance, Energy, and Resilience

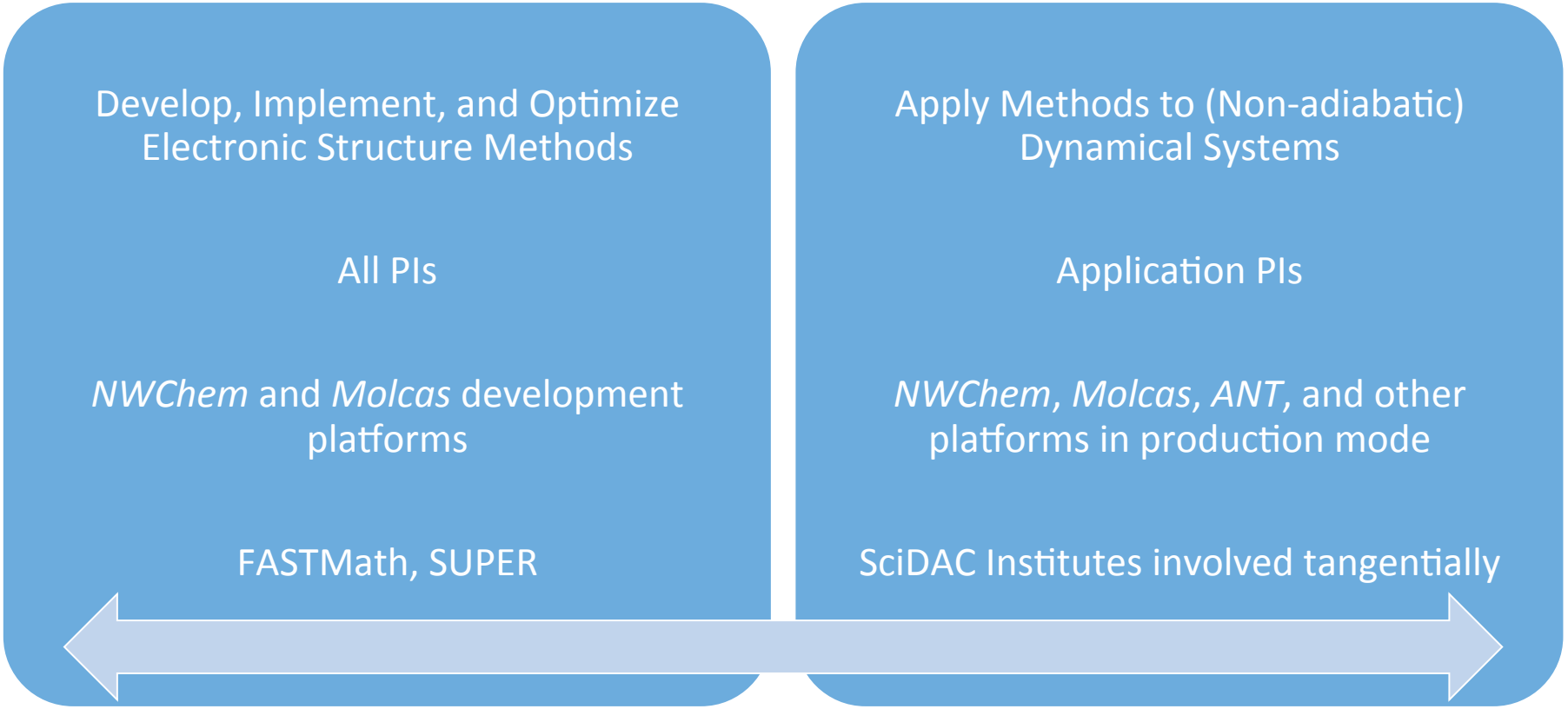
Truhlar

Bert DeJong

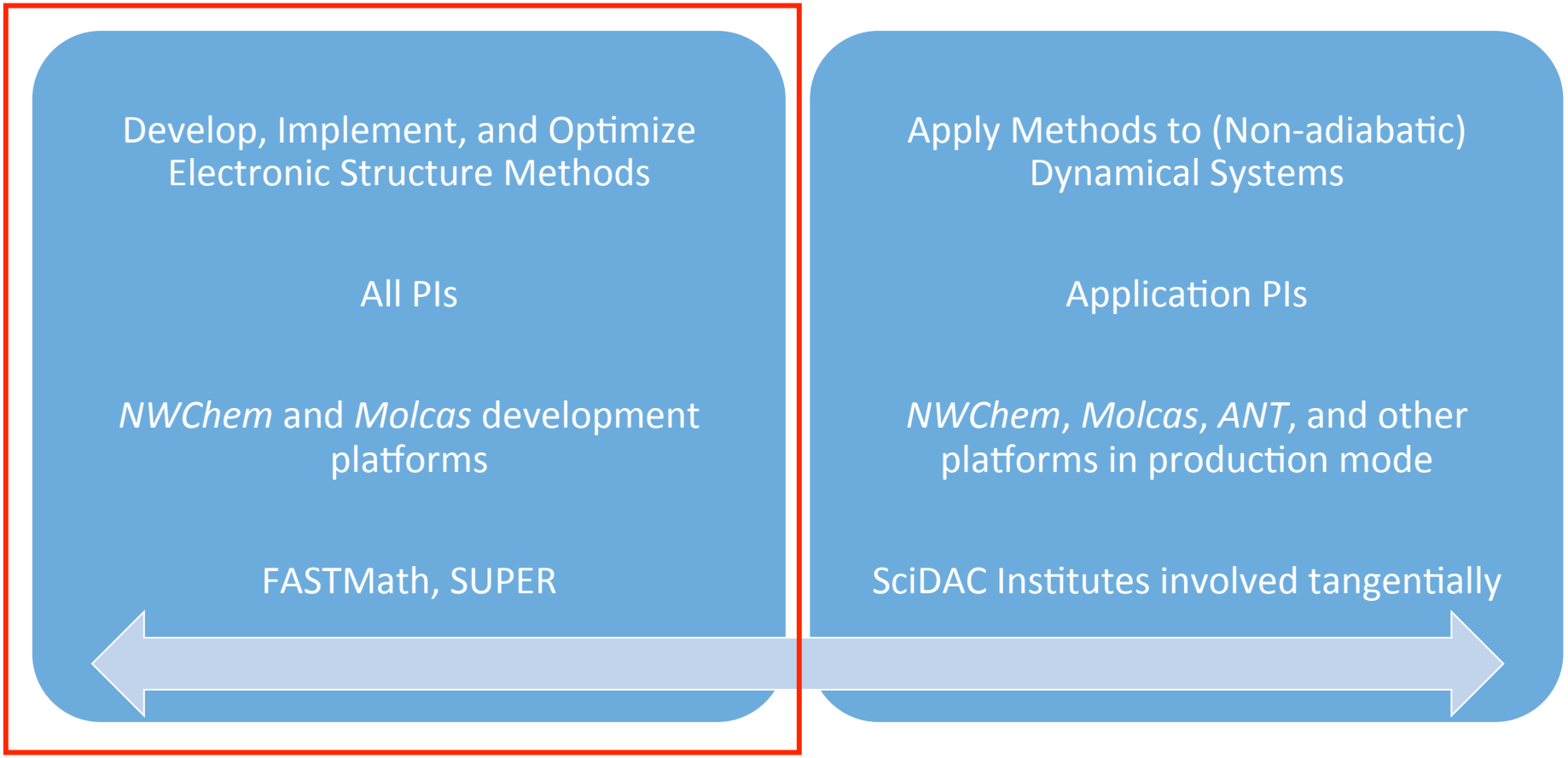
Niri Govind

NWChem
High-Performance Computational Chemistry Software

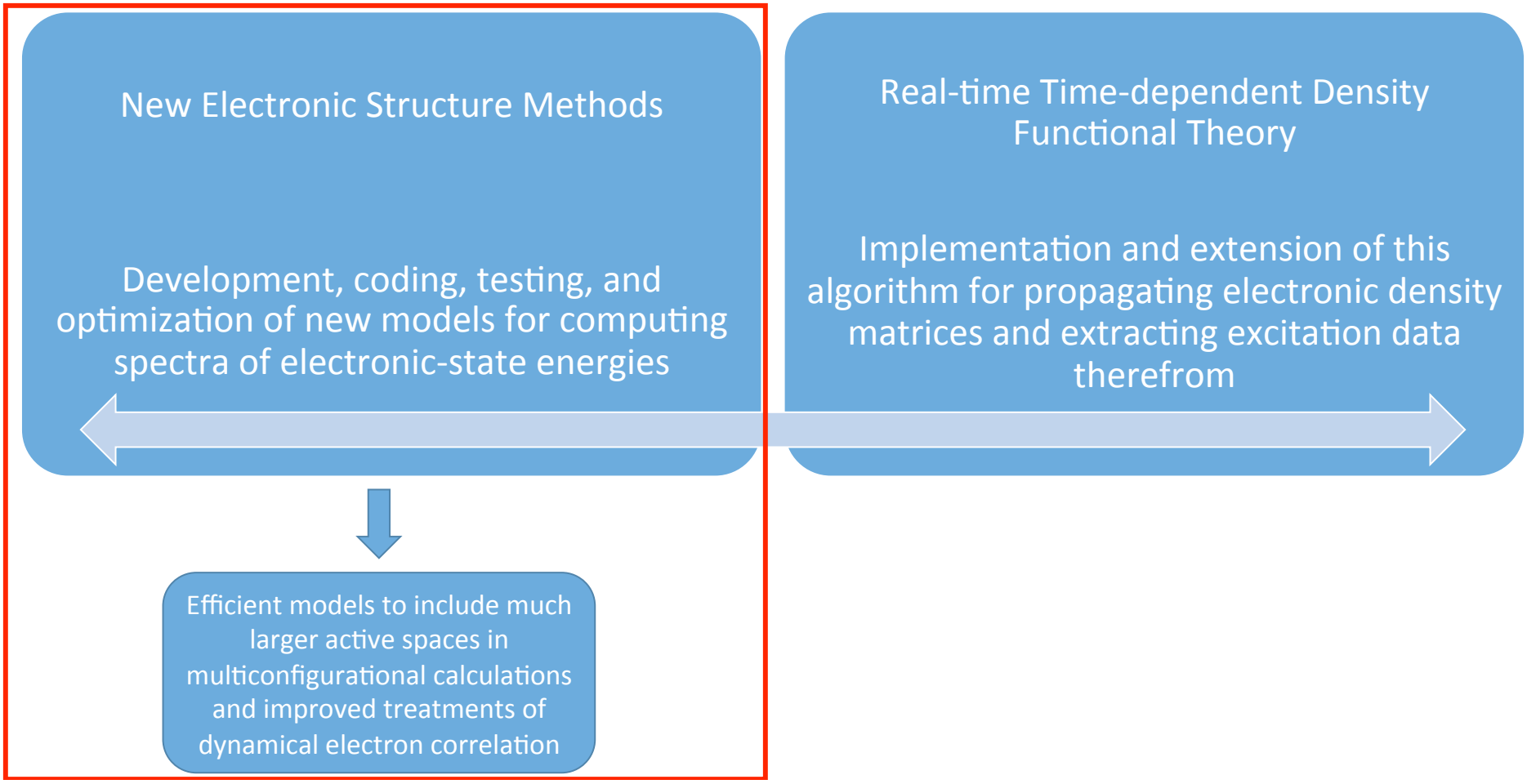
Research Strategy



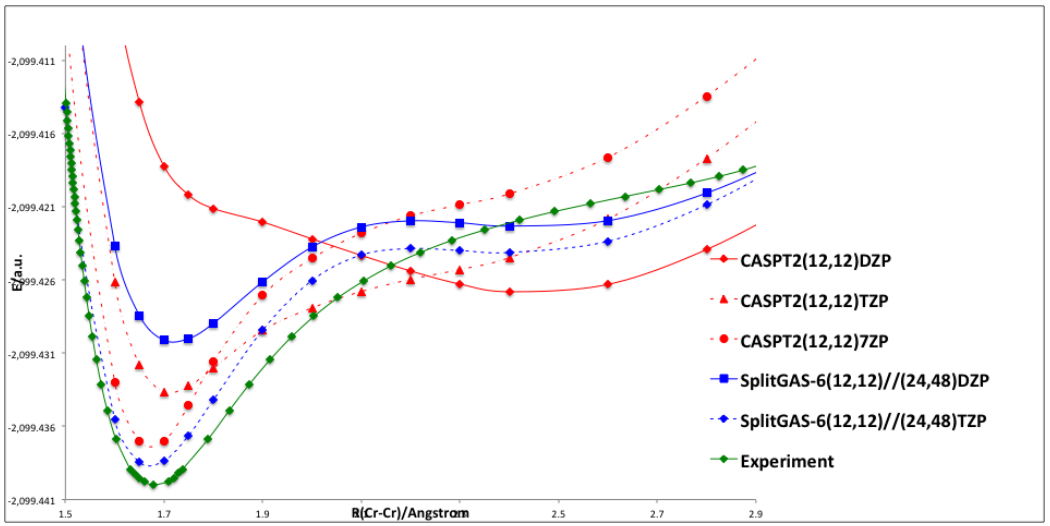
Research Strategy



Develop, Implement, and Optimize Electronic Structure Methods



The SplitGAS method for strongly correlated molecular systems



Potential energy curves for Cr_2 computed at various levels of multiconfigurational theory compared to experiment.

Li Manni, G.; Ma, D.; Aquilante, F.; Olsen, J.; Gagliardi, L. "SplitGAS Method for Strong Correlation and the Challenging Case of Cr_2" *Journal of Chemical Theory and Computation* **2013**, *9*, 3375-3384, (doi:10.1021/ct400046n).

Work was performed at the University of Minnesota

Scientific Achievement

SplitGAS-PT2 enables multiconfigurational treatment of a bimetallic system requiring an active space too large for more conventional methods

Significance and Impact

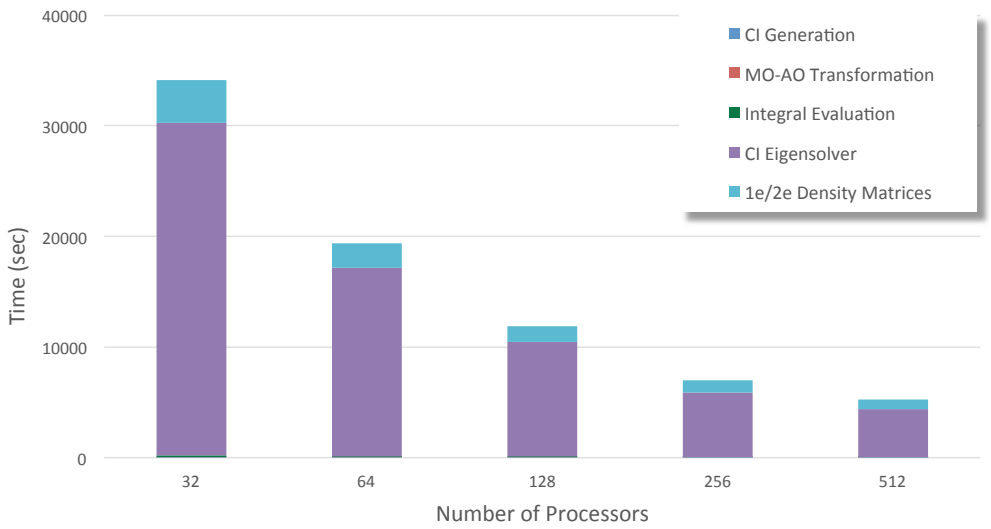
This method opens the door to modeling ground and excited states in systems characterized by significant multiconfigurational character, including especially transition-metal containing systems

Research Details

– The configuration interaction expansion, generated from a generalized active space, GAS, wave function is split in two parts, a principal part containing the most relevant configurations and an extended part containing less relevant, but not negligible, configurations

– The partition is based on an orbital criterion

Pushing Configuration Interaction to the Limit: Massively Parallel MCSCF



Total CPU time (in sec) and the individual contributions of one MCSCF iteration for the chromium trimer with an active space of 20 electrons in 20 orbitals and with different number of processors.

Vogiatzis, K. D.; Ma, D.; Olsen, J.; Gagliardi, L.; de Jong, W. "Pushing Configuration-Interaction to the Limit: Towards Massively Parallel MCSCF Calculations" *Journal of Chemical Theory and Computation*, submitted for publication.

Scientific Achievement

Largest and most complex multi-configuration excited-state simulations ever performed

Significance and Impact

We have developed and implemented an advanced, fast, and scalable GASSCF capability in *NWChem*

Research Details

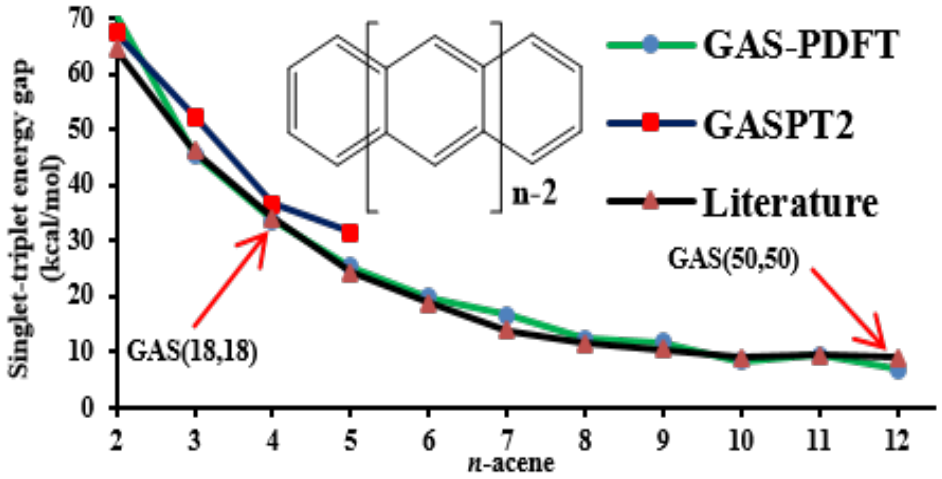
– First parallel GASSCF capability based on the serial LUCIA code has been integrated within *NWChem*'s parallel framework (in partnership with Jeppe Olsen, Aarhus University, Denmark)

– Initial correctness testing shows perfect agreement with reference implementations

– Next step is to demonstrate scaling to 100,000+ processors

Work was performed at the University of Minnesota and LBNL

Generalized-Active-Space Pair-Density Functional Theory



Singlet-triplet gaps in polyacenes [from naphthalene (*n* =2) to dodecacene (*n* =12)] calculated by GAS-PDFT, are compared with GASPT2 results and best available literature values.

Ghosh, S.; Cramer, C. J.; Truhlar, D. G.; Gagliardi, L. "Generalized-active-space pair-density functional theory: an efficient method to study large, strongly correlated, conjugated systems" *Chemical Science* **2017**, *8*, 2741-2750, (doi:10.1039/c6sc05036k).

Scientific Achievement

A new electronic structure method has been developed ideal for large, strongly correlated, (e.g., lengthily conjugated) systems

Significance and Impact

By implementing a new protocol combining density functional theory and multiconfiguration wave function theory, it is now possible to characterize the electronic structure of open-shell organic systems, including oligoacenes, that are important in magnetism and photovoltaic materials

Research Details

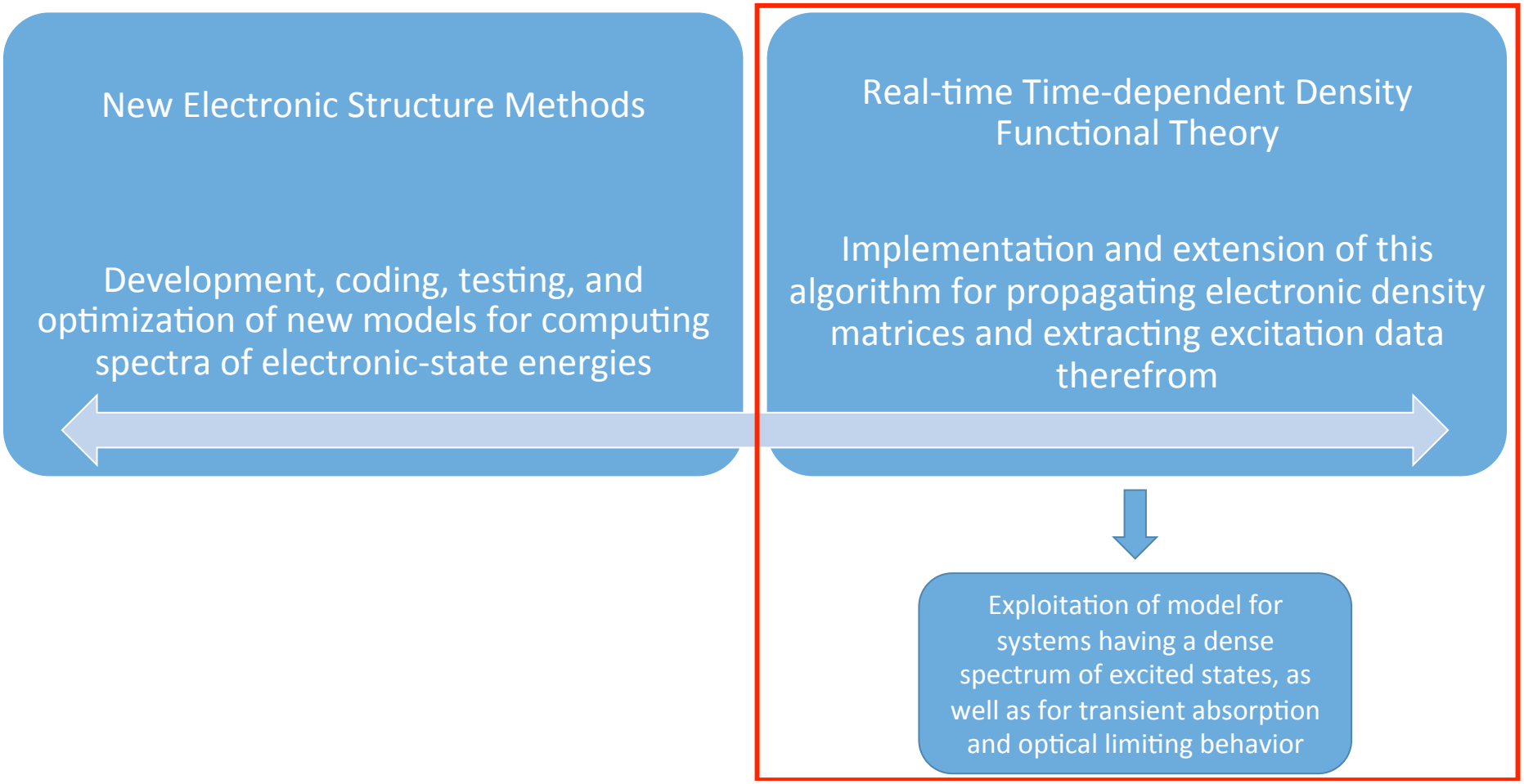
- Generalized-active-space pair-density functional theory (GAS-PDFT) is used to study singlet-triplet gaps in polyacenes
- unprecedently large active spaces of 50 electrons in 50 orbitals
- Dynamical correlation is recovered by using a pair-density functional

U.S. DEPARTMENT OF ENERGY | Office of Science

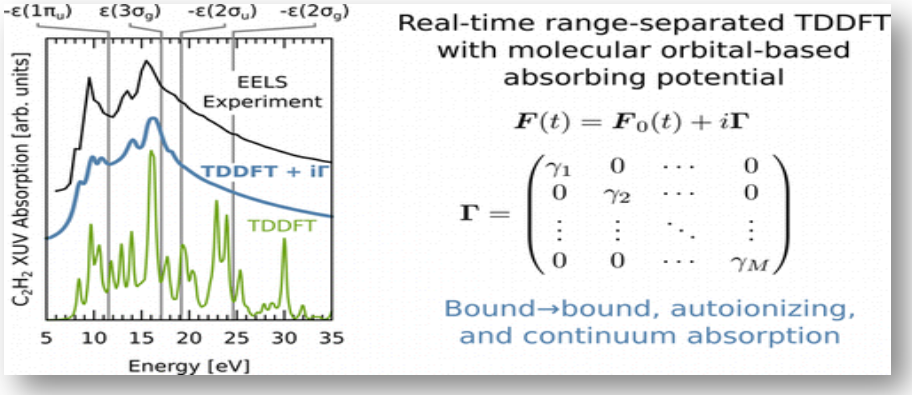
Work was performed at the University of Minnesota

UNIVERSITY OF MINNESOTA Driven to Discover℠ COLLEGE OF Science & Engineering

Develop, Implement, and Optimize Electronic Structure Methods



Near and Above Ionization Electronic Excitations with Non-Hermitian RT TD DFT



RT TD DFT computed extreme UV absorption spectrum of gas-phase acetylene with (blue) and without (green) an imaginary potential (iΓ), along with DFT Koopmans' IPs (gray). EELS data are shown in black.

Scientific achievement

Development of a RT TD DFT formulation for capturing below and above-ionization excitations, mimic modeling to continuum

Significance and Impact

First-principles ionization dynamics, removes spurious high-energy finite basis artifacts, correct bound-to-bound transitions, metastable resonance states, consistent absorption shapes, prescription for accurate EAs and IPs

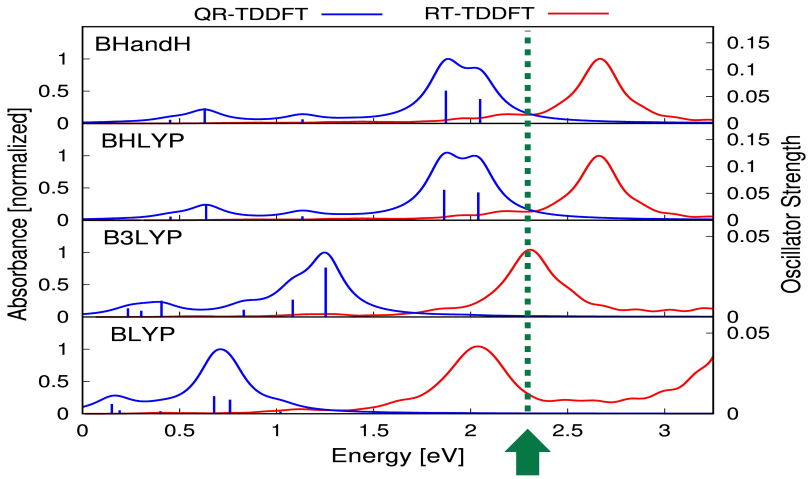
Research Details

- RT TD DFT based on non-Hermitian density matrix propagation , atom-centered basis, tuned range-separated DFT, imaginary molecular orbital-based absorbing potential
- Computed extreme ultraviolet absorption for acetylene, water, Freon 12 agree well with EELS data over a broad range 0-50 eV

Lopata, K.; Govind, N. "Near and Above Ionization Electronic Excitations with Non-Hermitian Real-Time Time-Dependent Density Functional Theory" *Journal of Chemical Theory and Computation* **2013**, *9*, 4939-4946, (doi:10.1021/ct400569s).

Work was performed at Pacific Northwest National Laboratory

Real-Time TD DFT vs. Quadratic-Response TD DFT for Excited State Absorption



Excited state absorption of coronene from RT TD DFT of LR TD DFT density (red) and discrete excitations of QR TD DFT (blue sticks) with simulated spectra (blue curve) using Lorentzian broadening

Bowman, D. N.; Asher, J. C.; Fischer, S. A.; Cramer, C. J.; Govind, N. "Excited-State Absorption in Tetrapyridyl Porphyrins: Comparing Real-Time and Quadratic-Response Time-Dependent Density Functional Theory" *Physical Chemistry Chemical Physics*, submitted for publication.

Work was performed at University of Minnesota and Pacific Northwest National Laboratory

Scientific achievement

A RT TD DFT formulation for computing transient absorption spectra by propagating excited-state density matrices following a delta-excitation has been found to be useful

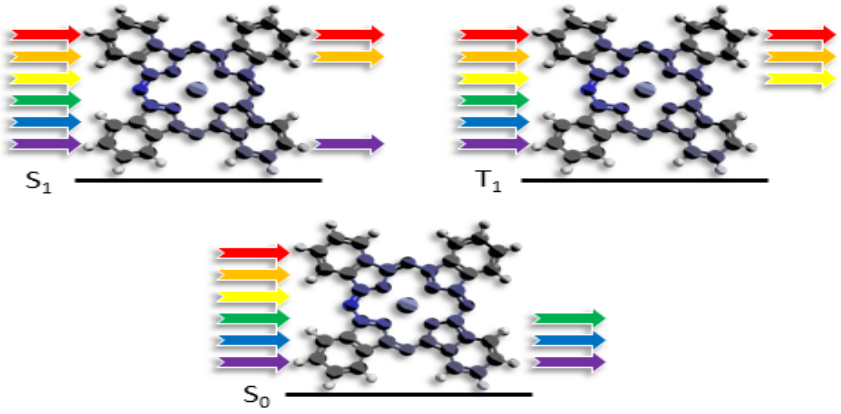
Significance and Impact

Modeling excitations *from* already excited states is not trivial as they are two-photon processes relative to the ground state, but such processes are important in many physical processes, e.g., optical limiting behavior of chromophores

Research Details

- Sensitivity of the model to basis set, reference states/densities, functionals, and exact exchange have been explored
- New model is considerably less sensitive to choice of functional than alternative quadratic-response TD DFT and is much more efficient for systems having a high density of states
- New research opportunity (for RT TD DFT in general) involves developing techniques to assign the nature of the transitions associated with individual absorption maxima/envelopes

Optical Limiting in Zinc Phthalocyanine



Schematic showing approximate transparency by wavelength of different electronic states of zinc phthalocyanine.

Fischer, S. A.; Cramer, C. J.; Govind, N. "Excited State Absorption from Real-Time Time-Dependent Density Functional Theory" *Journal of Chemical Theory and Computation* **2015**, *11*, 4294-4303, (doi:10.1021/acs.jctc.5b00473).

Fischer, S. A.; Cramer, C. J.; Govind, N. "Excited-State Absorption from Real-Time Time-Dependent Density Functional Theory: Optical Limiting in Zinc Phthalocyanine" *Journal of Physical Chemistry Letters* **2016**, *7*, 1387-1391, (doi: 10.1021/acs.jpclett.6b00282).

Scientific achievement

Development of a new excited-state absorption approach by combining linear-response (LR) and real-time (RT) TD DFT

Significance and Impact

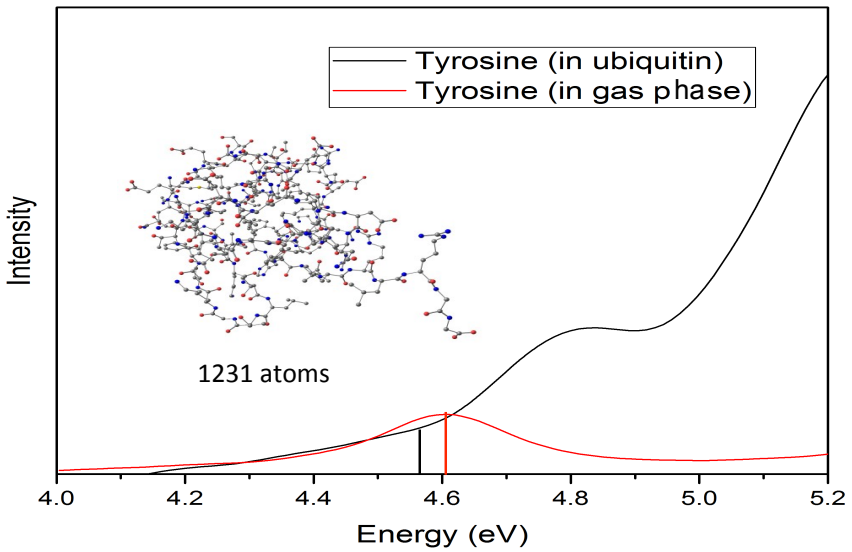
Ability to shed light on the excited-state response, transient absorption and the phenomenon of optical limiting of molecular complexes from first principles

Research Details

- Obtain relaxed excited-state density of the excited-state of interest using LR TD DFT gradients. Density represented as one-particle reduced density matrix
- Use RT TD DFT to propagate the excited-state density
- Validation of the approach on H_2, H_2^+, and oligofluorenes and comparison with QR TD DFT and experiment

Work was performed at University of Minnesota and Pacific Northwest National Laboratory

Real-time Propagation of Model Hamiltonian Density Matrices for Large Systems



Experimentally observed red shift of 0.06 eV in tyrosine spectra at 4.49 eV when embedded in ubiquitin protein environment is qualitatively (~0.04 eV) reproduced with the RT-INDO method.

Ongoing work at University of Minnesota and Pacific Northwest National Laboratory

Scientific achievement

Real-time dynamics using the Chebyshev propagator with different semiempirical Hamiltonians has been implemented in *NWChem*

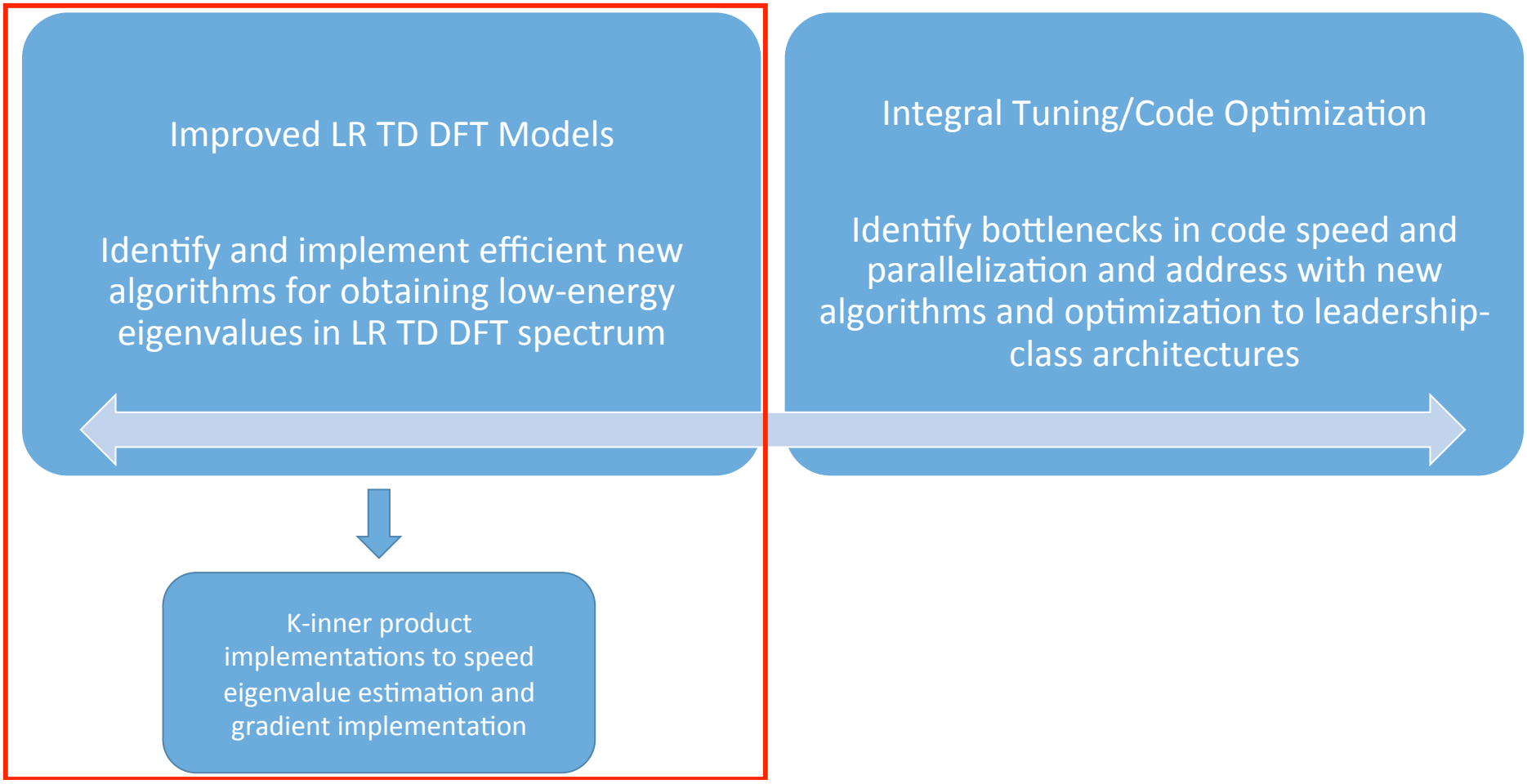
Significance and Impact

The INDO/S method can be used to model the UV-Vis spectra of medium to very large chemical systems

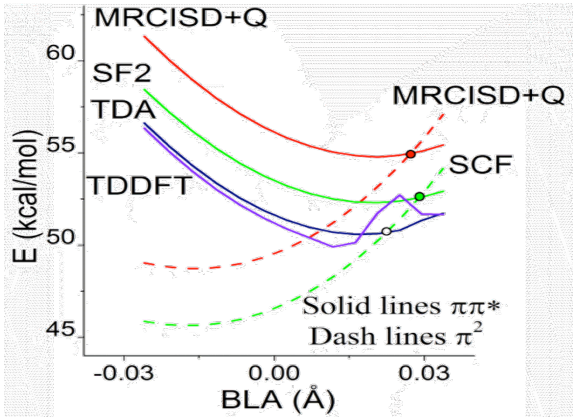
Research Details

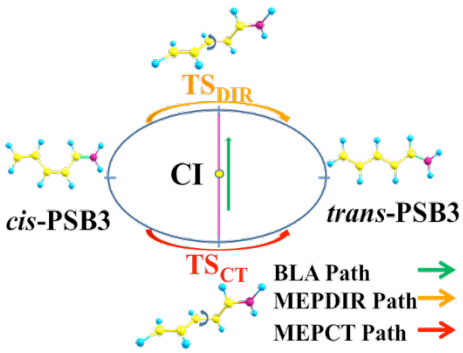
- INDO/S gives good agreement with RT TD DFT for small molecules and agrees well with experiment for a range of systems
- The model is so fast that snapshots from molecular dynamics trajectories (or Monte Carlo sampling) that include explicit solvation can be used to model solvatochromic effects as well as dynamical broadening of computed spectra
- A topic for further study is the coupling of the electronic propagation to nuclear propagation so as to permit true non-adiabatic dynamics

Develop, Implement, and Optimize Electronic Structure Methods



Combined SCF and Spin-Flip Tamm-Dancoff Density Functional Approach





The energy profile along the BLA path calculated by SF2, and TDDFT and TDA methods with M05-2X compared to MRCISD+Q results.

Xu, X.; Gozem, S.; Olivucci, M.; Truhlar, D. G. "Combined Self-Consistent-Field and Spin-Flip Tamm–Dancoff Density Functional Approach to Potential Energy Surfaces for Photochemistry" *Journal of Physical Chemistry Letters* **2013**, *4*, 253-258, (doi:10.1021/jz301935x).

Work was performed at the University of Minnesota

Scientific Achievement

New approach (SF2) for calculating potential energy surfaces for photochemical reactions by combining self-consistent-field calculations for single-reference ground and excited states with symmetry corrected spin-flip Tamm-Dancoff approximation calculations for multi-reference electronic states

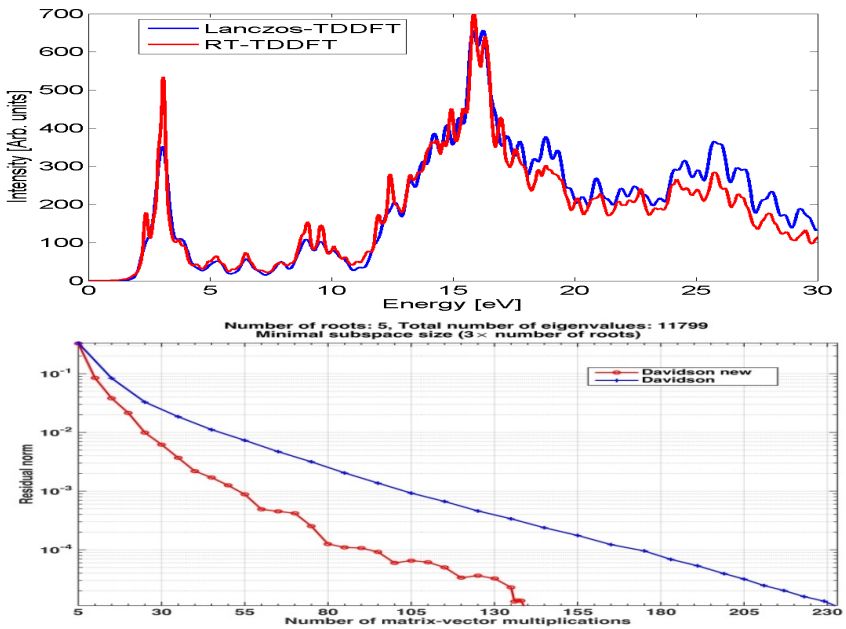
Significance and Impact

The method, SF2 yields potential energy profiles comparable to much more expensive MRCISD+Q for cis-trans isomerization reaction of retinal model PSB3 along key paths in the vicinity of a conical intersection

Research Details

- Uses high-X functionals M05-2X (or M06-2X, M08-HX, and M08-SO)
- useful when 2 electronic states have quite different correlation energies such that both dynamic and static correlation effects have to be considered

Fast algorithm for absorption spectrum calculation in linear response TD DFT



(top) K-inner product Lanczos algorithm vs a real-time TDDFT simulation. (bottom) New K-inner product based Davidson algorithm 2 times faster than existing Davidson algorithm for 10 smallest positive eigenvalues.

Brabec, J.; Lin, L.; Shao, M. Y.; Govind, N.; Yang, C.; Saad, Y.; Ng, E. G. "Efficient Algorithms for Estimating the Absorption Spectrum within Linear Response TD DFT" *Journal of Chemical Theory and Computation* **2015**, *11*, 5197-5208, (doi:10.1021/acs.jctc.5b00887).

Scientific Achievement

We developed fast algorithms for estimating absorption spectrum in the linear response TD DFT framework that are at least 2x faster than existing algorithms

Significance and Impact

The new algorithms have been implemented in *NWChem* and will benefit many *NWChem* users

Research Details

– Developed a K-inner product Lanczos algorithm for estimating the absorption spectrum without explicitly computing any eigenvalues of the linear response Hamiltonian in TD DFT

– Developed a fast K-inner product based Davidson and locally optimal preconditioned conjugate gradient (LOBPCG) algorithms for computing a few small positive eigenvalues of the linear response Hamiltonian

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Work was performed at LBNL and PNNL

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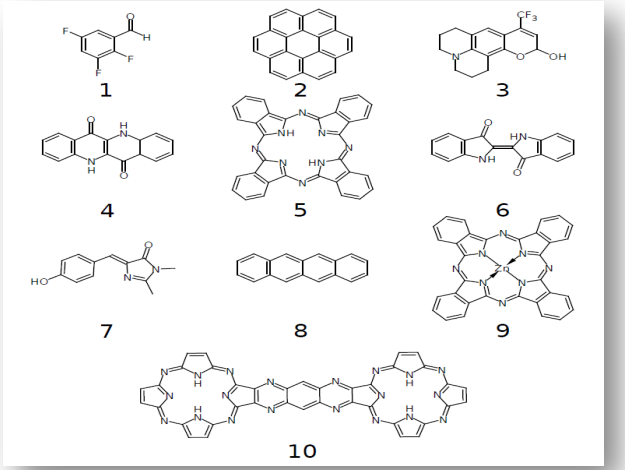
Implementation of Analytic Linear Response (LR) TD DFT Gradients in *NWChem*



Structures of organic dye molecules used for the calculation of absorption and emission maxima and Stokes shifts.

Silverstein, D. W.; Govind, N.; van Dam, H. J. J.; Jensen, L. "Simulating One-Photon Absorption and Resonance Raman Scattering Spectra Using Analytical Excited State Energy Gradients within Time-Dependent Density Functional Theory" *Journal of Chemical Theory and Computation* **2013**, *9*, 5490-5503, (doi:10.1021/ct4007772).

Work was performed at PNNL and Penn State University

Scientific achievement

Development of a parallel implementation of analytical linear-response (LR) TD DFT gradients in *NWChem*

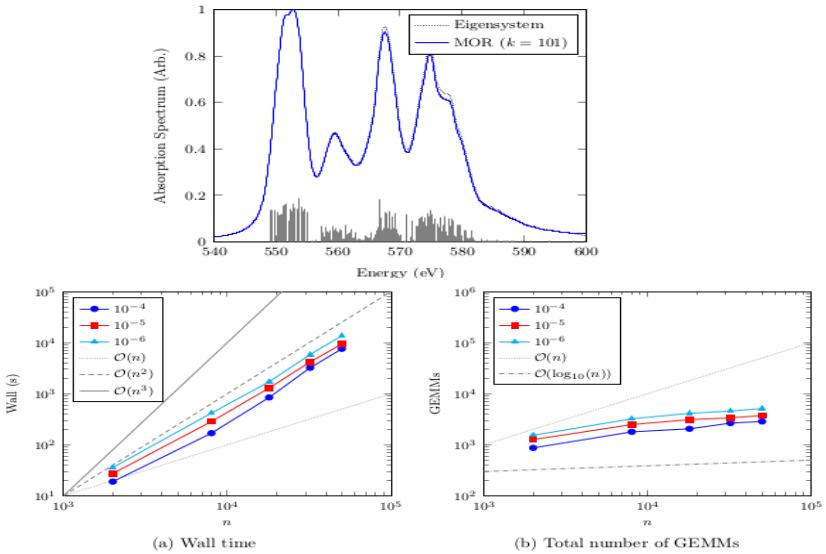
Significance and Impact

Excited state optimizations, dynamics, solvatochromatic studies (VEM), vibronic effects, and excited state properties can now be computed

Research Details

- Parallel implementation of LR TD DFT excited-state gradients in *NWChem* based on the Lagrangian approach of Furche & Ahlrichs
- Validation of the approach with calculations of the Stokes shifts for a range of organic dye molecules using a diverse set of exchange-correlation functionals (traditional, global hybrids and range-separated hybrids) and vibronic effects in one-photon absorption (OPA) and resonance Raman scattering (RRS)

Model Order Reduction Algorithm for Absorption Spectrum



(a) Wall time (b) Total number of GEMMs

(top) The absorption spectrum produced by a 101-order model matches well with that from a full diagonailzation. (bottom) The computation scaling with respect to matrix size.

Scientific achievement

We developed a novel model order reduction (MOR) algorithm for approximating absorption spectrum associated with core excitation of large nanosystems in the linear response TD DFT framework

Significance and Impact

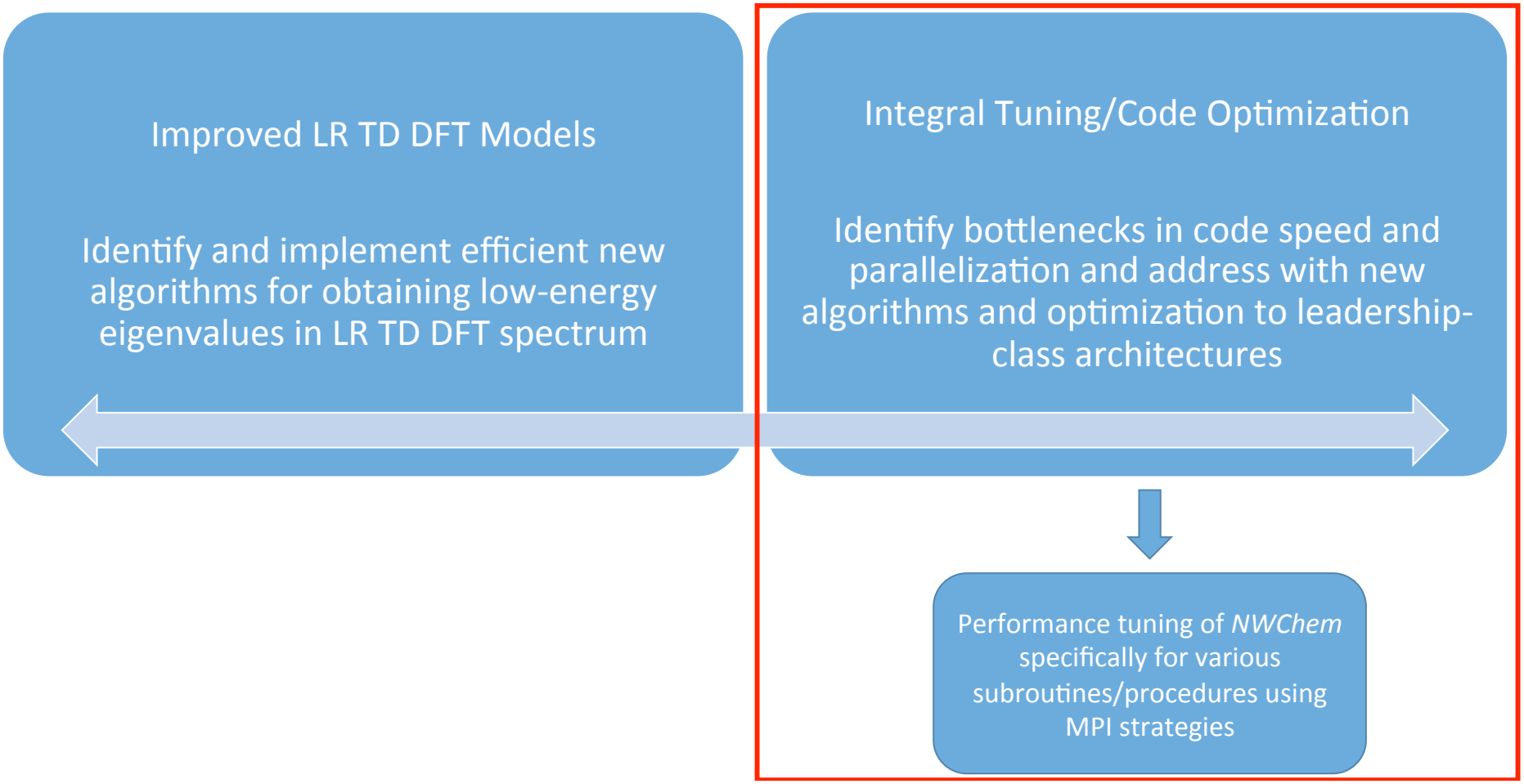
The new algorithm, which has been implemented in the Chronus Quantum software, provides a powerful computational tool for analyzing high energy excited states in BES SciDAC and EFRC projects

Research Details

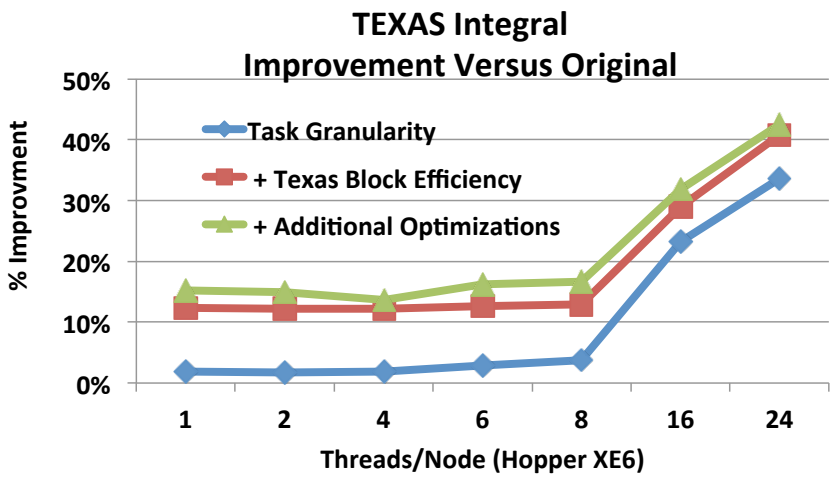
- Uses rational interpolation to construct a rational Krylov subspace from which a reduced order model is built to estimate the absorption spectrum within a specific energy window.
- Exploits the structure of the problem to improve computational efficiency

Beeumen, R. v.; Williams-Young, D. B.; Kasper, J. M.; Yang, C.; Ng, E. G.; Li, X. "A Model Order Reduction Algorithm for Estimtating the Absorption Spectrum" *Journal of Chemical Theory and Computation*, submitted for publication.

Develop, Implement, and Optimize Electronic Structure Methods



Performance Tuning for *NWChem* Texas Integrals



Results collected on Hopper@NERSC ($C_{20}H_{40}$)
Performance improvement is relative to runtime.

Scientific achievement

The performance of the TEXAS two-electron integral package in *NWChem* has been significantly improved

Significance and Impact

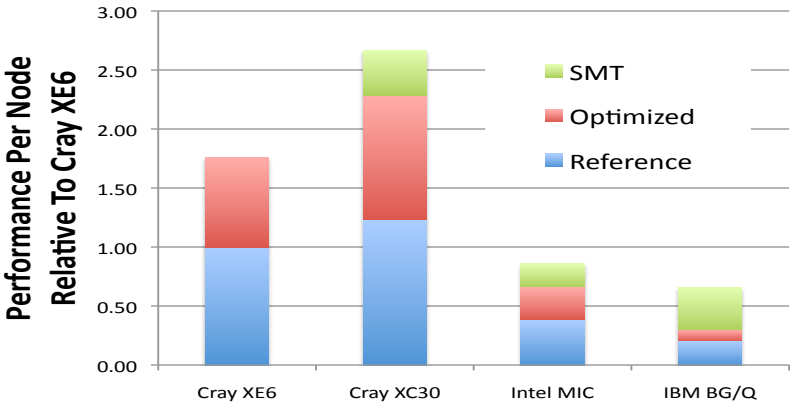
Faster time-to-solution enables larger and more accurate excited-state simulations with *NWChem*

Research Details

- Improved load balance in dynamic task assignment provides up to 34% speedup on 24 cores; addressing task granularity exploits the structure of the problem to improve computational efficiency
- Improving the efficiency of the blocking structure provides a 10% speedup for all configurations
- Other minor improvements include using better sorting algorithms, removing redundant computations, unrolling loops, etc., leading to additional speedups of up to 44%

de Jong, W. A.; Lin, L.; Shan, H.; Yang, C.; Oliker, L. "Towards Modeling Complex Mesoscale Molecular Environments" In *Proceedings of the International Conference on Computational and Mathematical Methods in Science and Engineering, CMMSE2014* **2014**.

Further Performance Tuning of TEXAS package for *NWChem*



The performance optimization results for TEXAS package on the Cray XE6,Cray XC30, Intel MIC, and IBM BG/Q. Results are normalized to Cray XE6. (Reference: Original Code, Optimized: Optimization Code, SMT: With Simultaneous Multithreading).

Scientific achievement

The performance of the TEXAS two-electron integral package in *NWChem* has been further improved with optimization of the tensor contraction engine

Significance and Impact

Faster time-to-solution enables larger and more accurate excited-state simulations with *NWChem*

Research Details

- Improved performance of TEXAS package up to 1.75X on four different leading platforms; the performance results show that our tuning strategy enable performance portability
- Implemented a memory-efficient MPI+OpenMP version for TEXAS package. This hybrid code performs comparably to the flat-MPI version while consuming substantially less memory
- Preliminary 30% improvement of TCE (CCSD(T)) module on Cray XE6

Shan, H.; Austin, B.; De Jong, W.; Oliker, L.; Wright, N. J.; Apra, E. "Performance Tuning of Fock Matrix and Two-Electron Integral Calculations for *NWChem* on Leading HPC Platforms" In *High Performance Computing Systems. Performance Modeling, Benchmarking and Simulation*; Jarvis, S. A., Wright, S. A., Hammond, S. D., Eds.; Springer International Publishing: **2014**, pp. 261-280.

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Work was performed at PNNL and LBNL

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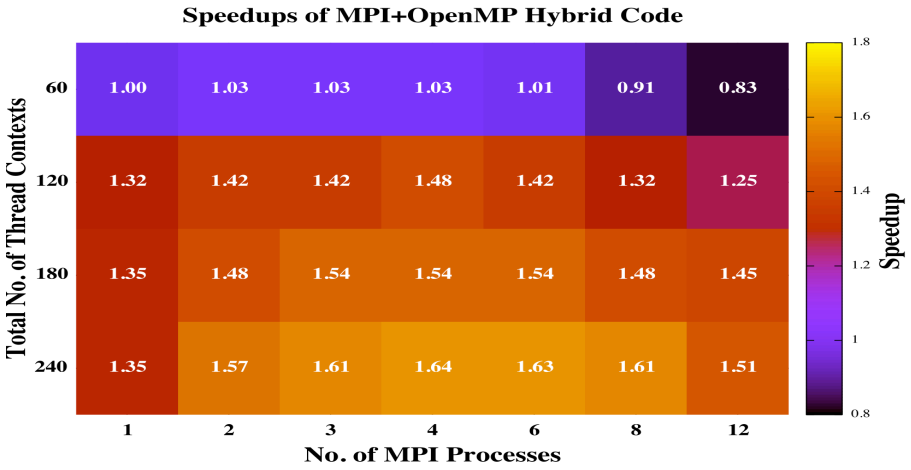
OpenMP Performance Tuning for *NWChem*



Performance improvement of hybrid MPI+OpenMP over flat MPI code for Fock matrix construction on Intel MIC architecture. The hybrid code exploits all 240 hardware thread contexts on card.

Shan, H.; Williams, S.; Jong, W. d.; Oliker, L. "Thread-level parallelization and optimization of *NWChem* for the Intel MIC architecture" In *Proceedings of the Sixth International Workshop on Programming Models and Applications for Multicores and Manycores*; ACM: 2712391, **2015**, pp. 58-67, (doi:10.1145/2712386.2712391).

Scientific achievement

NWChem performance has been optimized by implementing thread-level parallelism on the Intel Phi many-core architecture

Significance and Impact

Faster time-to-solution enables larger and more accurate excited-state simulations with _NWChem_

Research Details

- SUPER Institute collaboration implemented OpenMP parallelism for two *NWChem* modules
- Native mode optimization to prepare for next-generation NERSC8 Cori
- Threading is essential to exploit full capability of MIC architecture
- Performance of triples part of CCSD(T) improved 65x over original flat MPI implementation
- Flat MPI constrained to single process because of memory limitation
- Performance of Fock matrix construction improved 1.64x over original flat MPI
- Flat MPI constrained to 60 MPI processes

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Work was performed at PNNL and LBNL

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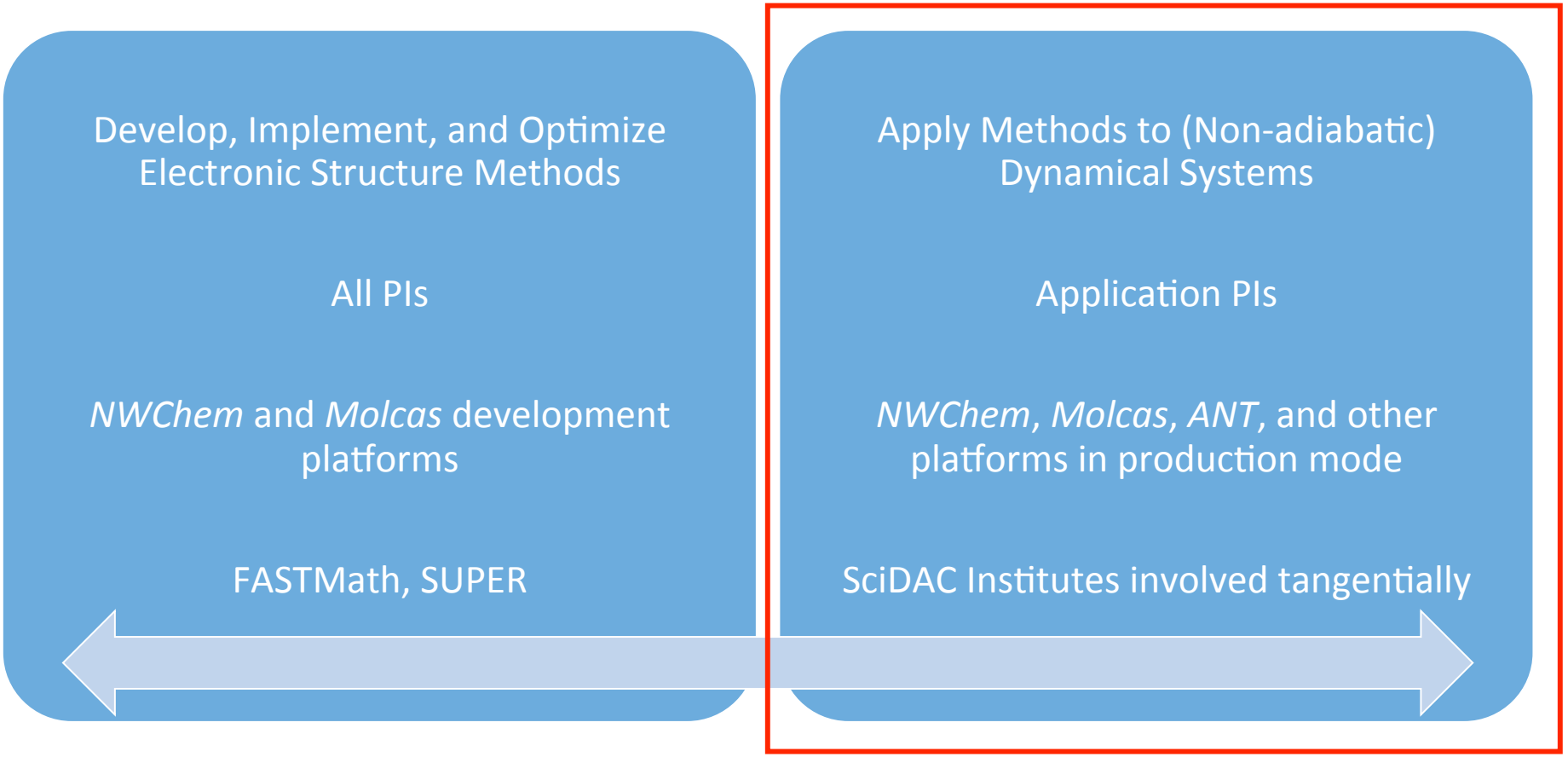
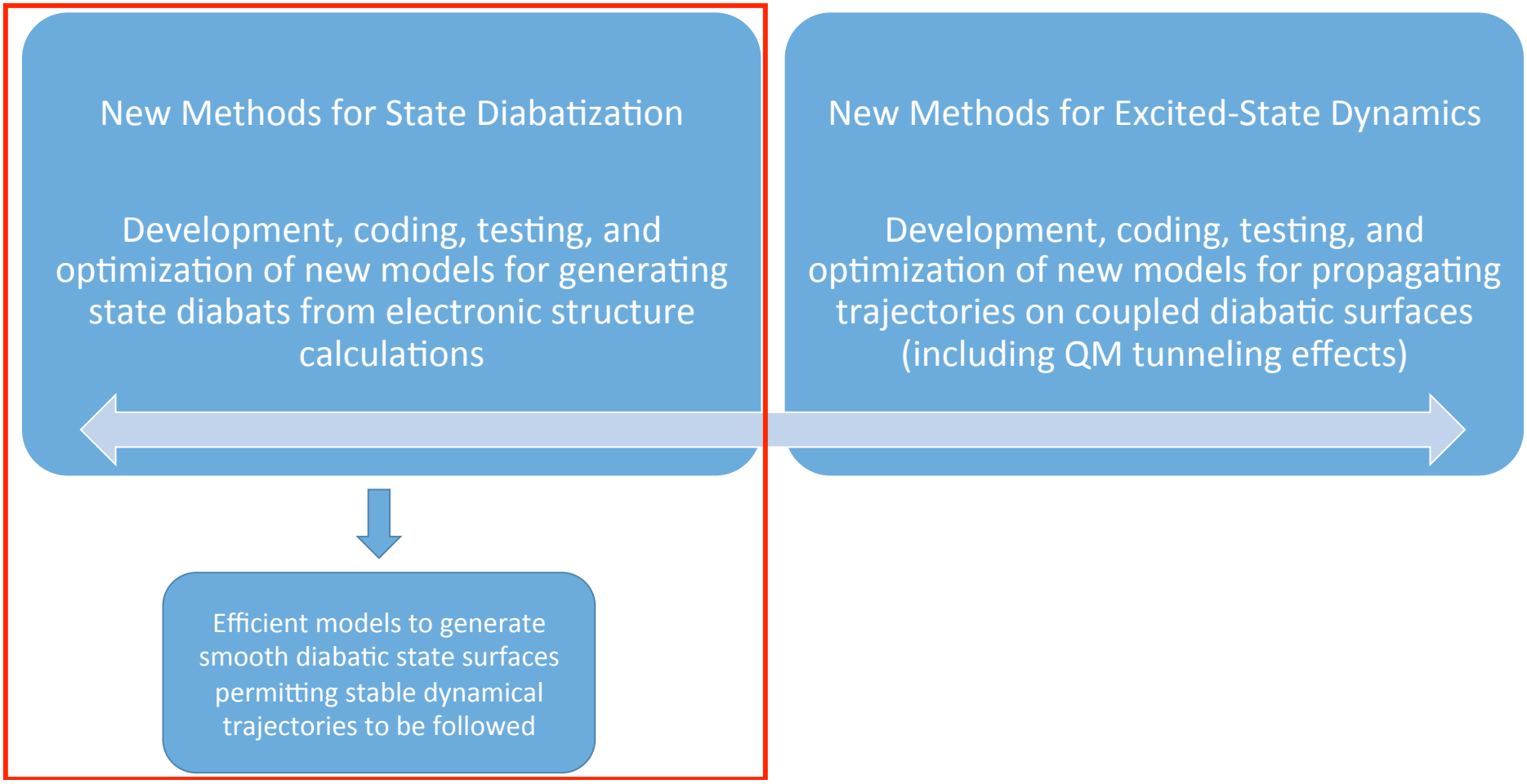
Research Strategy

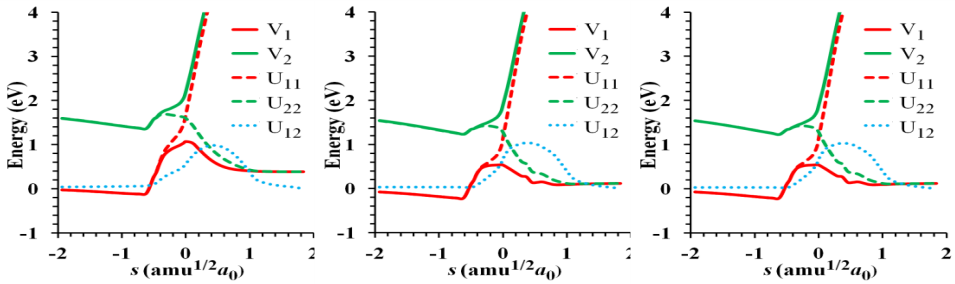


Apply Methods to (Non-adiabatic) Dynamical Systems



Fourfold-way Diabatization with CASSCF Diabatic Orbitals

Chemical reaction: Li+ HF→ LiF+ H



CASSCF DMOs
CASSCF energies

MC-QDPT DMOs
MC-QDPT energies

CASSCF DMOs
MC-QDPT energies

V_1, V_2 } Adiabatic energies

U_{11}, U_{22} } Diabatic energies

U_{12} Diabatic coupling

Diabats and adiabats associated with alternative orbital and energy choices followed by diabatization.

Yang, K. R.; Xu, X. F.; Truhlar, D. G. "Direct diabatization of electronic states by the fourfold-way: Including dynamical correlation by multi-configuration quasidegenerate perturbation theory with complete active space self-consistent-field diabatic molecular orbitals" *Chemical Physics Letters* **2013**, *573*, 84-89, (doi:10.1016/j.cplett.2013.04.036).

Scientific achievement

Improved model for smooth diabatic potential energy surfaces and couplings for photochemical simulations

Significance and Impact

Avoids discontinuities associated with derivative couplings when running dynamics with adiabatic surfaces

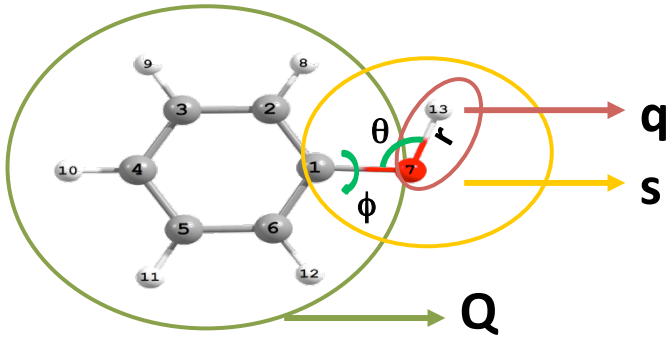
Research Details

- Improved algorithm for diabatic states by including dynamical correlation with multi-configuration quasidegenerate perturbation theory (MC-QDPT)while using diabatic MOs from complete-active-space SCF (CASSCF) calculations
- Method available in multiple codes
  - HONDOPLUS
  - GAMESS
  - *NWChem*

Work was performed at the University of Minnesota

Diabatic Potential Energy Surfaces for the Photodissociation of Phenol

Anchor Points Reactive Potential (APRP):



- **Reactive coordinate: q**
- **Secondary coordinate: s**
- **Tertiary coordinate: Q**

} Fit with general functional forms

→ MM-like potentials

Work was performed at the University of Minnesota

Scientific achievement

New method (the Anchor Points Reactive Potential) has been developed to fit high dimensional potential energy surfaces

Significance and Impact

Full-dimensional PESs for reactive systems with many degrees of freedom opens new doors for simulations

Research Details

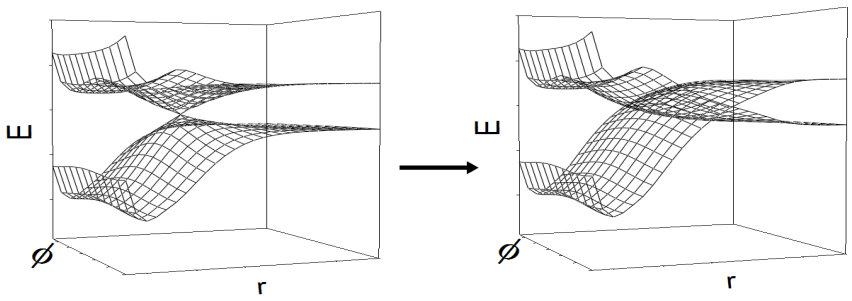
– 33-dimensional diabatic PESs and couplings have been constructed for phenol

– Dynamics study of photodissociation of phenol with ANT program

Xu, X. F.; Yang, K. R.; Truhlar, D. G. "Diabatic Molecular Orbitals, Potential Energies, and Potential Energy Surface Couplings by the 4-fold Way for Photodissociation of Phenol" *Journal of Chemical Theory and Computation* **2013**, *9*, 3612-3625, (doi:10.1021/ct400447f).

Xu, X. F.; Zheng, J. J.; Yang, K. R.; Truhlar, D. G. "Photodissociation Dynamics of Phenol: Multistate Trajectory Simulations including Tunneling" *Journal of the American Chemical Society* **2014**, *136*, 16378-16386, (doi:10.1021/ja509016a).

Diabatization with the Dipole, Quadrupole, and Electrostatic Potential



On the left is a diagram of two potential energy surfaces near a conical intersection in the adiabatic representation. On the right, are the transformed surfaces in the diabatic representation; these surfaces are easier to use for dynamics calculations.

Hoyer, C. E.; Xu, X. F.; Ma, D. X.; Gagliardi, L.; Truhlar, D. G. "Diabatization based on the dipole and quadrupole: The DQ method" *Journal of Chemical Physics* **2014**, *141*, 114104 (doi:10.1063/1.4894472).

Hoyer, C. E.; Parker, K.; Gagliardi, L.; Truhlar, D. G. "The DQ and DQ Phi electronic structure diabatization methods: Validation for general applications" *Journal of Chemical Physics* **2016**, *144*, 194101 (doi:10.1063/1.4948728).

Scientific achievement

Development and application of a new method for calculating adiabatic to diabatic transformations to study photodynamics

Significance and Impact

Will lower the cost and improve the accuracy of photodynamic simulations with application to energy and biosystems

Research Details

- Adiabatic potential energy surfaces are difficult to fit when they are closely coupled, which is common in photodynamics
- In the diabatic representation, the surfaces vary smoothly in these regions
- The DQΦ diabatization method transforms adiabats to diabats using three physical properties: the dipole moment (D), quadrupole moment (Q), and electrostatic potential (Φ).
- We are applying this method to the photodissociation of methylamine and the photoisomerization of retinal to further test and improve the method

U.S. DEPARTMENT OF ENERGY | Office of Science

Work was performed at the University of Minnesota

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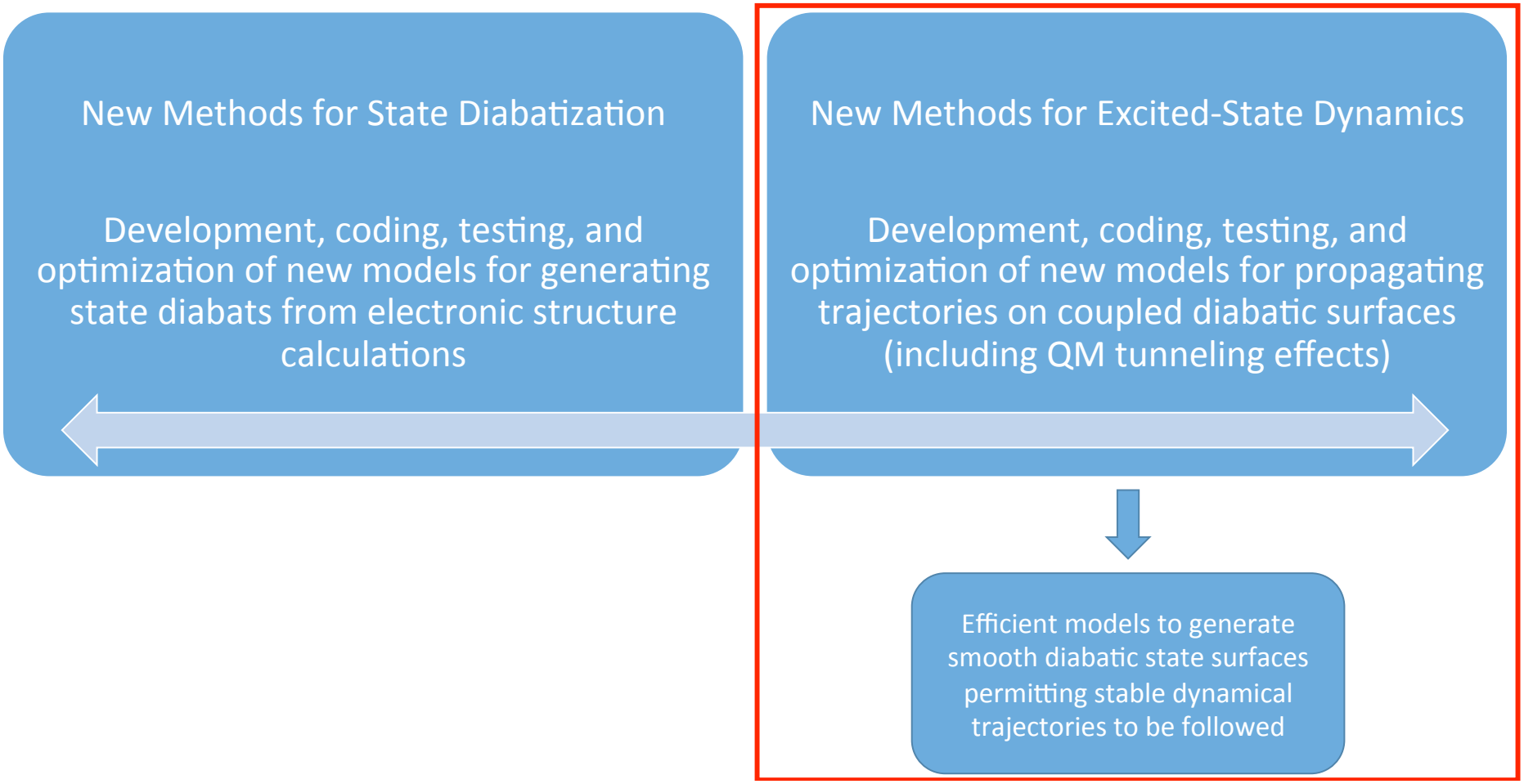
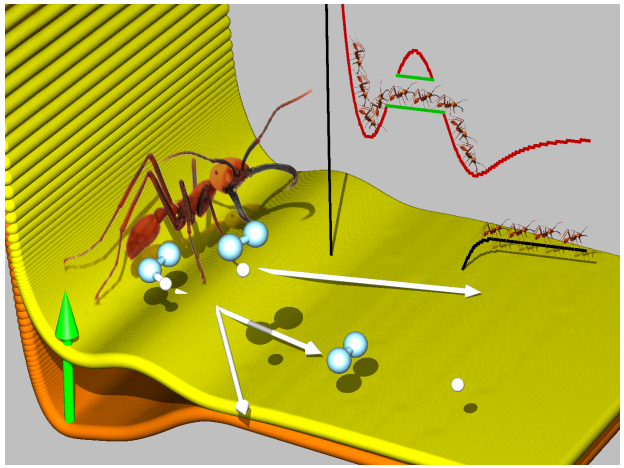
Apply Methods to (Non-adiabatic) Dynamical Systems



ANT (Adiabatic and Nonadiabatic Trajectories) Program



Illustrative graphic emphasizing the quantum-mechanical effects that must be accounted for in order to accurately model molecular dynamics trajectories on coupled electronic state-energy surfaces.

ANT 2016, J. Zheng, Z. H. Li, A. W. Jasper, D. A. Bonhommeau, R. Valero, R. Meana-Pañeda, S. L. Mielke, D. G. Truhlar.

Scientific achievement

A portable and versatile code has been developed and documented for propagating molecular dynamics trajectories including many quantum mechanical phenomena

Significance and Impact

Non-adiabatic molecular dynamics simulations including tunneling are now feasible

Research Details

– Treatment of electronically nonadiabatic processes
  - Coherent switches with decay of mixing (CSDM)
  - Improved surface hopping methods
  - Semiclassical Ehrenfest method

– Army Ants Tunneling methods
  - Treats unimolecular tunneling – electronically adiabatic or nonadiabatic
  - Tunneling paths defined by a valence internal coordinate or a combination of two stretch coordinates

– Direct dynamics
  - Interfaces to *Gaussian09*, *Molpro*, MOPAC-*mn*

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Work was performed at the University of Minnesota

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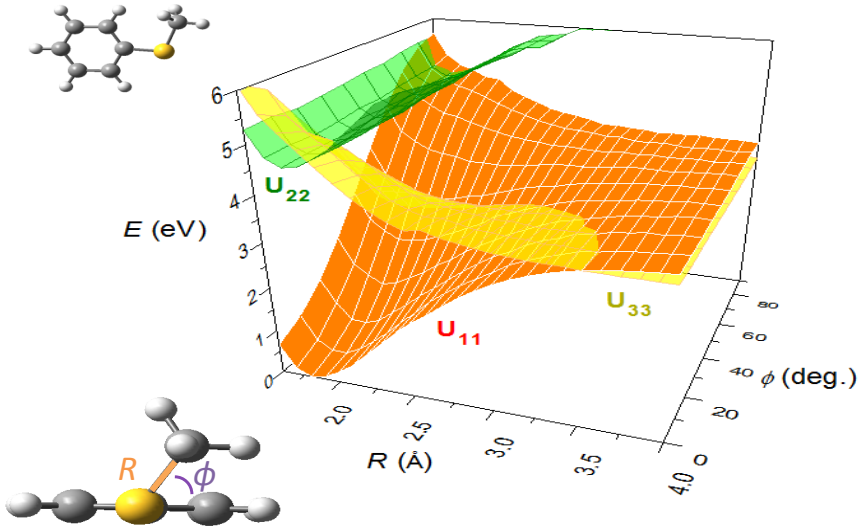
Extension of Non-Adiabatic Dynamics to High Dimensional Coupled Surfaces



Diabatic potential energy surfaces along the two reactive coordinates, *R* (S–CH_3 bond stretch) and ϕ (C-C-S-C torsion) with other coordinates fixed at their values for the ground-state equilibrium geometry.

Li, S. H. L.; Xu, X. F.; Hoyer, C. E.; Truhlar, D. G. "Nonintuitive Diabatic Potential Energy Surfaces for Thioanisole" *Journal of Physical Chemistry Letters* **2015**, *6*, 3352-3359, (doi: 10.1021/acs.jpclett.5b01609).

Scientific achievement

Developed a 3x3 coupled diabatic potential energy surface matrix in 42 dimensions for the $C_6H_5SCH_3 \rightarrow C_6H_5S\cdot + \cdot CH_3$ photodissociation reaction

Significance and Impact

Non-adiabatic molecular dynamics simulations are now feasible for studying the detailed mechanism of the photoreaction

Research Details

- Analytic diabatic potential and coupling functions were fitted to ab initio data with dynamic electron correlation. (XMC-QDPT)
- A multi-level scheme, called Anchor Points Reactive Potential, enabled the construction of potential functions and couplings for high-dimensional systems by treating reactive coordinates globally and other coordinates by system-specific, reaction-coordinate-specific MM.

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Work was performed at the University of Minnesota

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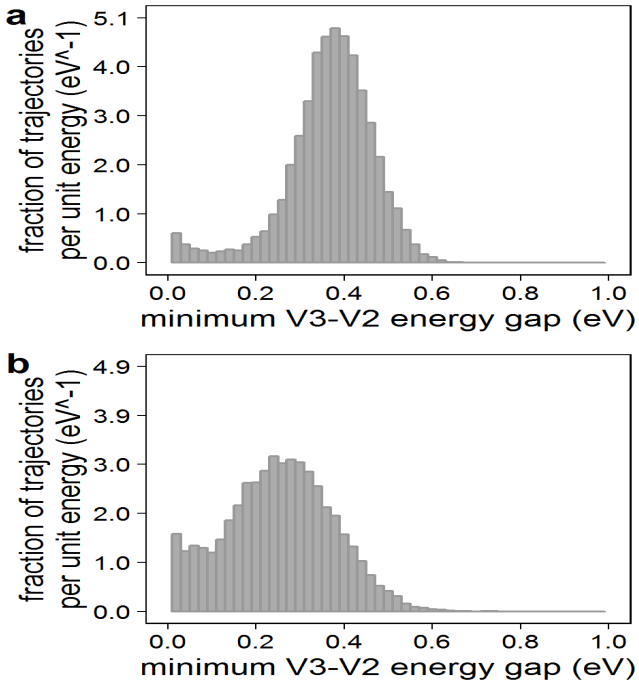
Thioanisole Photodissociation Dynamics on Full-Dimensional Potential Energy Surfaces



Distributions of the minimum gap between V_2 and V_3 during each trajectory, with the S–CH_3 stretching mode initially unexcited (a) or excited (b).

Scientific achievement

Vibrational influence on non-adiabatic dynamics included in simulations

Significance and Impact

The influence of conical intersections coupled with vibrational dynamics on trajectory evolutions on multiple state surfaces can now be modeled

Research Details

- Full 42-dimensional potential energy functions including dynamical electron correlation of the three lowest singlet states are constructed for this reaction.
- Tens of thousands of semi-classical trajectories are run in the dynamical simulations.
- It is observed, from the distribution of the minimum energy gap between the second (V_2) and the third (V_3) adiabatic states during each trajectory, that most of the trajectories do not directly pass an important V_2-V_3 conical intersection. However, if the S–CH_3 stretching mode gets excited as a trajectory starts, it comes closer to the conical intersection. Further investigation is in progress on how this behavior may affect its dynamics.

Li, S. H. L.; Truhlar, D. G. "Full-dimensional ground- and excited-state potential energy surfaces and state couplings for photodissociation of thioanisole" *Journal of Chemical Physics* **2017**, *146*, 064301 (doi:10.1063/1.4975121).

U.S. DEPARTMENT OF ENERGY | Office of Science

Work was performed at the University of Minnesota

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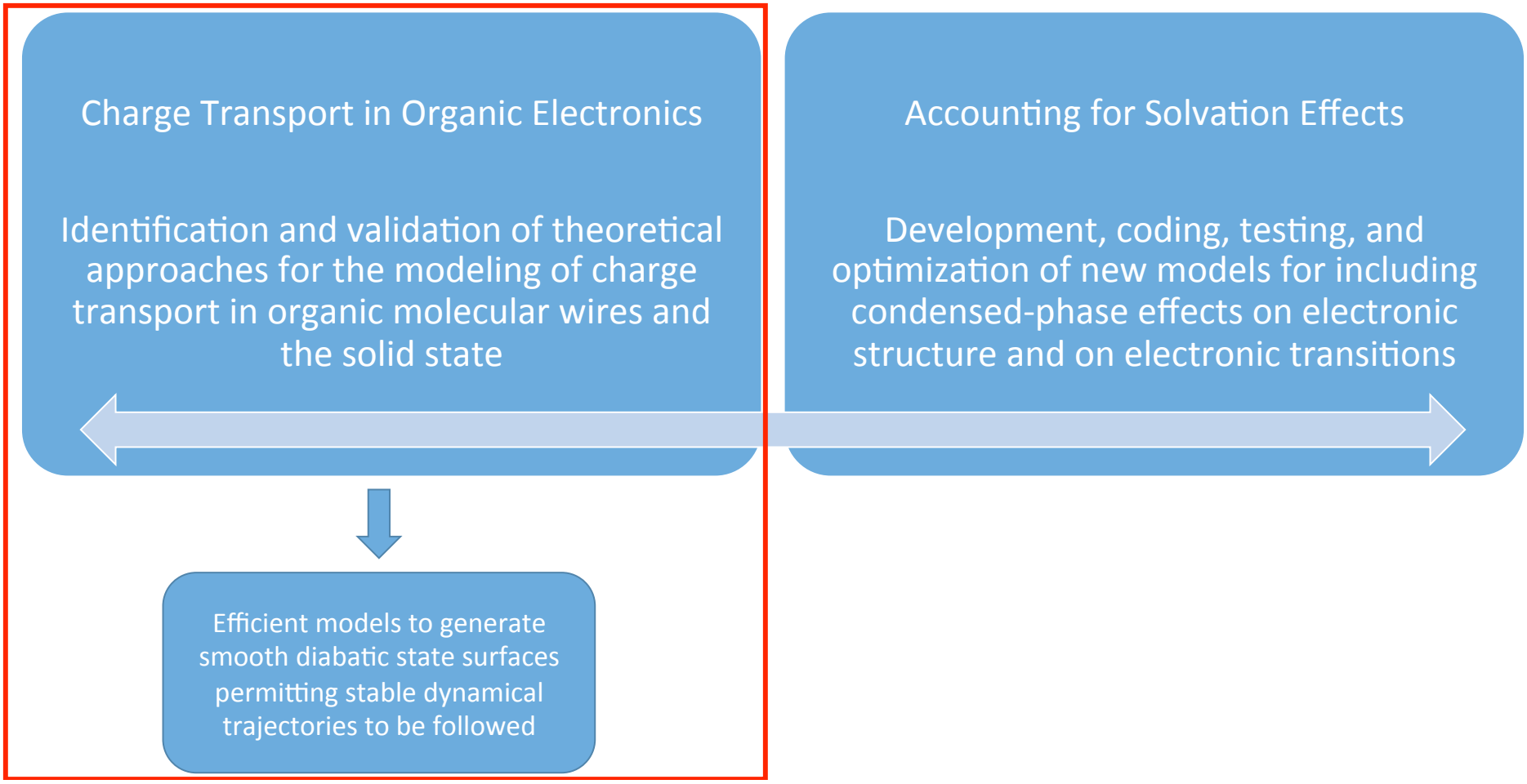
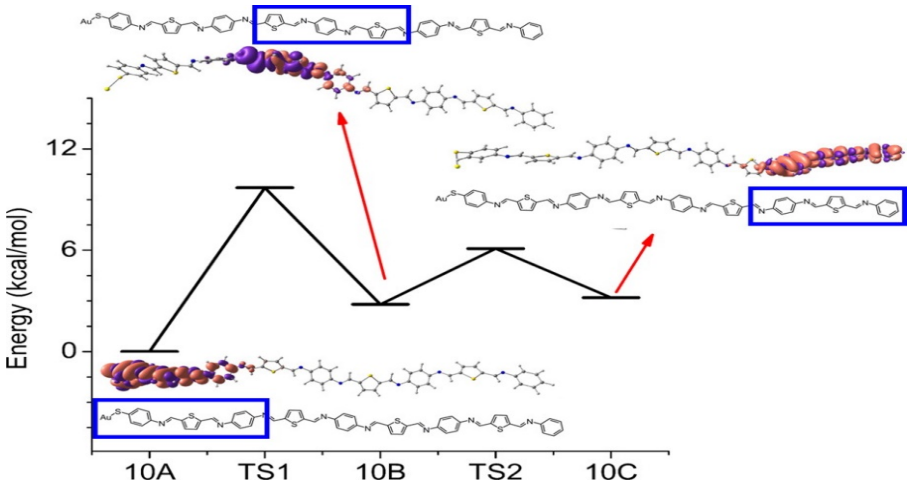
Apply Methods to (Non-adiabatic) Dynamical Systems



Charge Hopping Bottlenecks in Thiophene-Containing Molecular Wires



Potential energy surface illustrating the nature of charge hopping as a conformational phenomena in long thiophene-containing molecular wires.

Smith, C. E.; Odoh, S. O.; Ghosh, S.; Gagliardi, L.; Cramer, C. J.; Frisbie, C. D. "Length-Dependent Nanotransport and Charge Hopping Bottlenecks in Long Thiophene-Containing pi-Conjugated Molecular Wires" *Journal of the American Chemical Society* **2015**, *137*, 15732-15741, (doi:10.1021/jacs.5b07400).

Scientific achievement

Semiclassical activation energies for charge transport via thermal conformational changes were found to correlate well with observed conductivities

Significance and Impact

Understanding how conformation influences conjugation and charge transport informs systematic modifications in structure that can be made to influence charge transport properties

Research Details

- The potential surface of the neutral π conjugated wires was exhaustively sampled through a 5ps ab initio molecular dynamics trajectory at the PBE-D3 level in order to identify all polaronic minima
- Transition-state structures between polaronic minima were found through systematic modifications in structure
- Polaron hopping can go beyond “nearest neighbor” hopping with appropriate coupled vibrations
- The M06-HF/TZP level of theory was useful for obtaining relevant polaronic states

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Work was performed at the University of Minnesota

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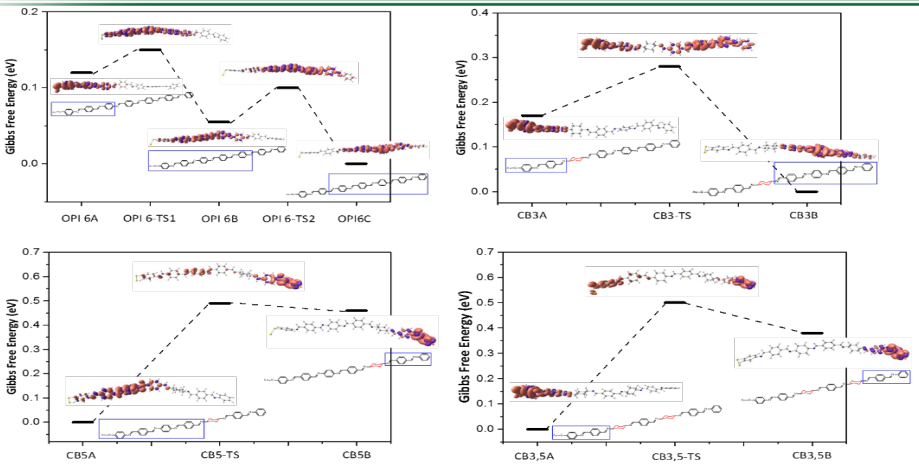
Thermally Assisted Polaron Tunneling in 4 nm Molecular Wires



Minima and transition-state energies for charge hopping in conjugated and conjugation-broken wires showing charge localization on the adiabatic surface.

Taherinia, D.; Smith, C. E.; Ghosh, S.; Odoh, S. O.; Balhorn, L.; Gagliardi, L.; Cramer, C. J.; Frisbie, C. D. "Charge Transport in 4 nm Molecular Wires with Interrupted Conjugation: Combined Experimental and Computational Evidence for Thermally Assisted Polaron Tunneling" *ACS Nano* **2016**, *10*, 4372-4383, (doi:10.1021/acsnano.5b08126).

Work was performed at the University of Minnesota

Scientific achievement

Vibronic motions contributing to charge transport were characterized and their influence on polaron migration as it is accelerated by nuclear tunneling were successfully assessed

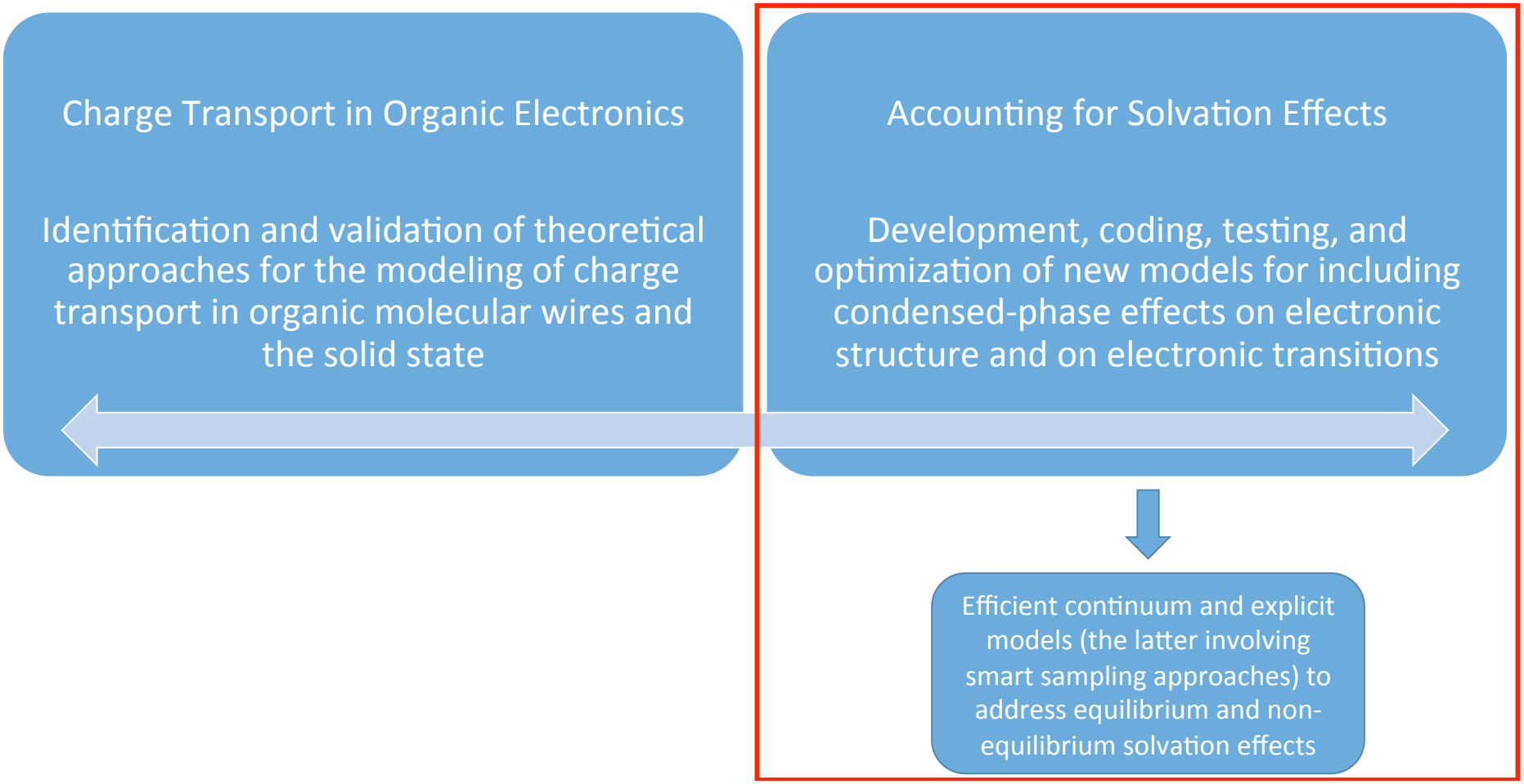
Significance and Impact

The coupling of charge transport with nuclear dynamics is critically important to maximizing the conductivity of molecular wires

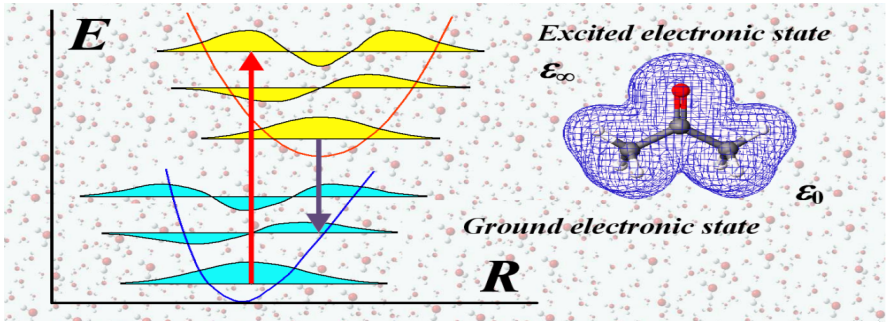
Research Details

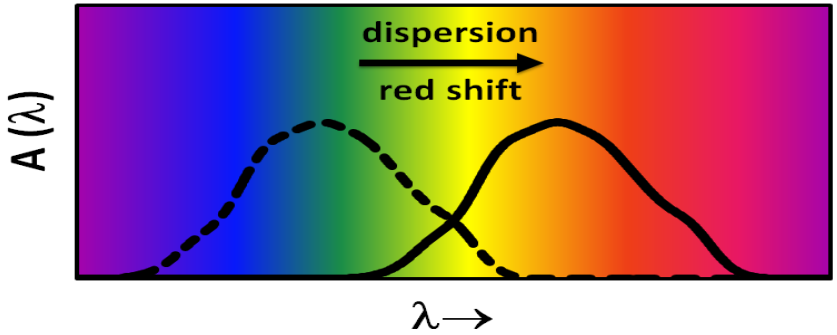
- Stationary points were characterized with the CAM-B3LYP functional, and sensitivity to functional choice was demonstrated, with hybrid functionals key to localization of the polaron in a manner consistent with experiment
- Prediction of polaronic lengths of ~5 conjugated rings is consistent with experimental transitions from ballistic to hopping charge-transfer kinetics at such lengths
- Hopping is accelerated by *nuclear* tunneling when higher frequency motions are associated with polaron migration (e.g., bond stretches compared to torsions)

Apply Methods to (Non-adiabatic) Dynamical Systems



Medium Effects on Excited-State Energy Surfaces





Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. "Uniform Treatment of Solute-Solvent Dispersion in the Ground and Excited Electronic States of the Solute Based on a Solvation Model with State-Specific Polarizability" *Journal of Chemical Theory and Computation* **2013**, *9*, 3649-3659, (doi:10.1021/ct400329u).

Scientific achievement

A new efficient treatment of the solute–solvent dispersion contribution to solvatochromic shifts based on state-specific polarizability has been developed

Significance and Impact

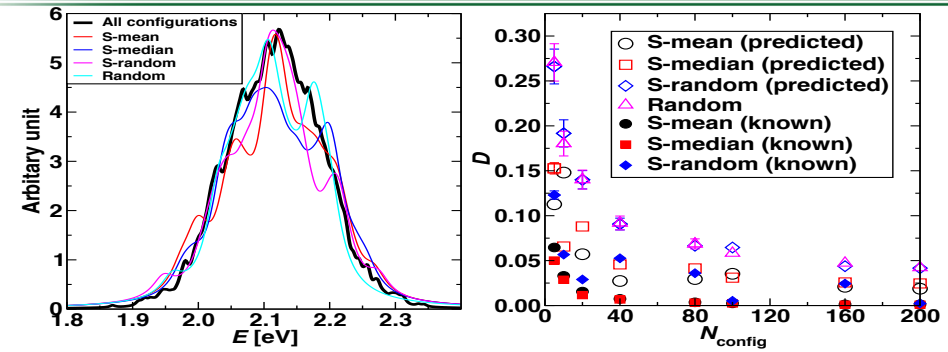
One can now compute vertical excitation and emission spectra in solution more realistically

Research Details

- The model uses only two descriptors, namely, the averaged molecular dipole polarizability of the solute and the refractive index of the solvent
- It efficiently predicts solvatochromic shifts for a number of systems where solute–solvent dispersion dominates the observed (generally red) shift
- We have incorporated this model into *NWChem* to combine a state-specific treatment of the solvent polarization with a state-specific treatment of dispersion

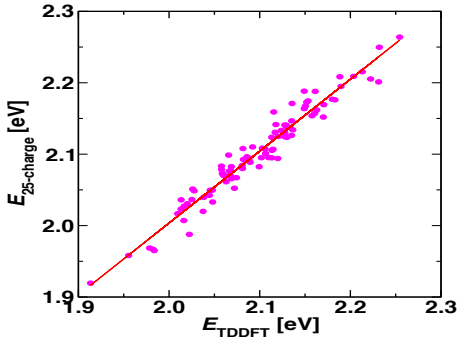
Work was performed at the University of Minnesota with subsequent implementation at PNNL

Optimized Selection of Sets of Representative Solvent Configurations



(Left) Excitation energy distributions for QB in acetonitrile obtained from 1600 uncorrelated configurations and from subsets of 40 configurations selected by different approaches. (Right) Similarity scores obtained for subsets of different sizes selected using either the predictor equation or the known means and medians; the smaller *D* values for the latter indicate that future work should focus on improving the predictor equation.

Correlation of excitation energies for QB in acetonitrile calculated using 25 explicit solvent molecules with static partial charges for the remainder versus those obtained from calculations with 500 explicit solvent molecules.



Scientific achievement

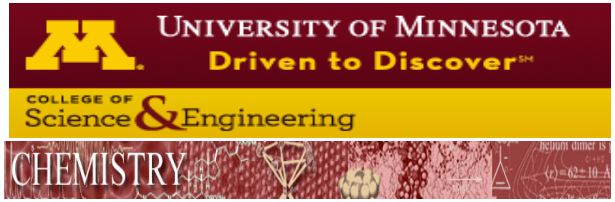
A predictor equation has been developed for the selection of representative solvent configurations and an approach to reduce the number of explicit solvent molecules has been validated

Significance and Impact

Reduced both number of configurations & number of solvent molecules needed for high-level electronic structure calculations

Research Details

- Investigated the adsorption spectra of 1-methyl-8-oxyquinolinium betaine (QB) chromophore in neat and mixed solvents
- Generated solvent configurations using force-field-based Monte Carlo simulations and calculated adsorption spectra using quantum-mechanical approaches
- Evaluated the performance of smart selection schemes for reducing the number of configurations through similarity metric *D* for two distributions (using Lorentzian to smear excitation energy of individual configurations)
- Reduced number of solvent molecules needed in QM calculation by replacing explicit solvent molecules with static partial charges



Charge Transfer and Charge Transport in Photoactivated Systems

Developing Electron-Correlated Methods for Excited State Structure and Dynamics in the NWChem Software Suite

Christopher J. Cramer, Director, SciDAC-3 Application Project