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**EFFICIENT PREDICTIONS OF EXCITED STATE FOR
NANOMATERIALS USING ACES 3 AND 4**

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University Of Florida

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Final Report

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LIST OF EQUATIONS

| | | |
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| $\omega = PHP + PHQQ\omega - HQ - 1QHP$ | Equation 1 | 7 |
| $\omega = PHP + kPHQkQk\omega - HQk - 1QkHP$ | Equation 2..... | 7 |
| $\omega = S + D0HS + D0 + kS + D0HD'kD'kHS + D0D'k\omega - HD'k$ | Equation 3 | 7 |

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BACKGROUND:

Air Force requirements for development of optical nanomaterials, and thus development of a capability for excited state predictions, are pervasive and demanding. For example, in the Air Force research groups of Larry Burggraf, Ruth Pachter, and others, a common theme is the need for accurate descriptions of excited states for large molecules, molecular clusters, and extended systems. Properties involving electronic excited states include photo-electron spectra, band structure, excitons, and non-linear optics. In addition to optical properties, information about the assumed structure and stability of the material is equally essential. Structure comes from automatic geometry optimizations of bond lengths and angles to see what forms are preferred. The stability is deduced from the energetics of the various isomers of the materials, obtained from computed heats of reactions that provide the enthalpy and free energy for the species. Finally, a knowledge of the associated activation barriers provides essential info on whether the proposed material is stable or will likely undergo internal conversion or decompose.

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| To address these requirements, this project focuses on accurate and efficient predictions of materials properties by first-principle methods in the software package ACES by using large parallel computers, growing to the exascale. |
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The proposers' purpose was first to create in the software package ACES 4 a new implementation of the Super Instruction Architecture (SIAL) with a modular design architected for adaptability and testability, which avoids scalability traps, and offers dynamically managed distributed data structures with support for block sparsity and exploiting symmetry. The effort under the current agreement has achieved automated and optimized SIAL array handling and file structure, advanced memory allocation and optimal load balance, it created infrastructure for supporting GPUs and other device types, and it advanced smart server and analysis tools, and created a testing suite for SIAL features. This new capability was applied to accurately describe SinCn molecules having potential as quantum bits for future advanced quantum computing among other applications.

SCIENTIFIC ADVANCES:

Progress with Natural Transition Orbitals

The following summarizes some of our work with natural transition orbitals. The important findings are that the NTO's emphasize one single excitation from an occupied orbital, I , to an unoccupied orbital, A , in the description of an excited state. The equations they satisfy are shown in Figure 1.

NTO Rotation matrix (\mathbf{U} , \mathbf{V}) and amplitudes (λ)

$$(\boldsymbol{\gamma}\boldsymbol{\gamma}^\dagger)u_i = \lambda_i u_i, \quad (i = 1, \dots, N_o)$$

$$(\boldsymbol{\gamma}^\dagger\boldsymbol{\gamma})v_i = \lambda'_i v_i, \quad (i = 1, \dots, N_v)$$

$$\lambda_i \equiv \lambda'_i \geq 0, \quad (i = 1, \dots, N_o)$$

All HF orbitals ($\boldsymbol{\psi}$) are rotated into NTOs ($\boldsymbol{\phi}$)

$$(\boldsymbol{\phi}_1, \boldsymbol{\phi}_2, \dots, \boldsymbol{\phi}_{N_o}) = (\boldsymbol{\psi}_1, \boldsymbol{\psi}_2, \dots, \boldsymbol{\psi}_{N_o})\mathbf{U}$$

$$(\boldsymbol{\phi}'_1, \boldsymbol{\phi}'_2, \dots, \boldsymbol{\phi}'_{N_v}) = (\boldsymbol{\psi}'_1, \boldsymbol{\psi}'_2, \dots, \boldsymbol{\psi}'_{N_v})\mathbf{V}$$

Figure 1. Procedure for the generating NTOs from the transition moment, $\boldsymbol{\gamma}$. Different transition moment gives different qualities of NTOs (See Figure 2).

Note the dependence on the eigenvalues, $\lambda_1, \lambda_2, \dots$. One large λ indicates a dominant NTO. An NTO example is shown in the first frame of figure 2 where NTO's are obtained from EOM-CCSD using the equations in Figure 1 This shows the dominance of a few of the single excitation coefficients, R1.

Our intent is to build on this property of NTO's to invent a way to do high-level EOM-CCSD in computationally simpler ways. To do so, we require an easily generated source of NTO's. Results from several different, simpler sources are compared to those from EOM-CCSD in Figure 2.

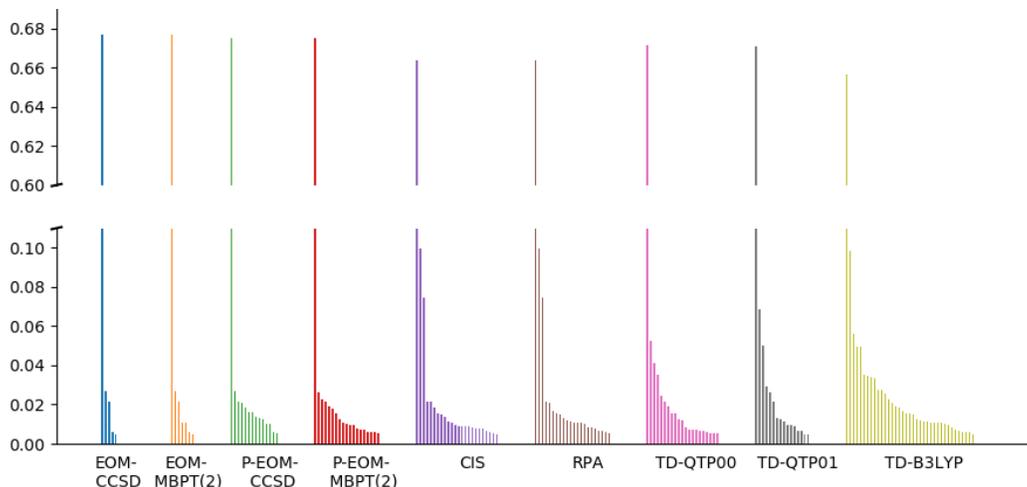


Figure 2. Importance of R1 coefficients with NTOs generated by different methods.

The first option is a second-order approximation to EOM-CCSD, EOM-MBPT2 that avoids a CCSD ground state calculation in favor of a much faster MBPT2. But this still requires most of the complexity of the excited state calculation to define the NTO's. However, if we have an alternative, in-expensive generation of NTO's, we can investigate the combination of MBPT2 for the ground state with the reduced space single excitations. So far, the best simpler NTO's seem to come from our new HASI development for TDDFT, QTP(01).

As the figure for acetone shows, using QTP(01) to generate the NTO's, provides R1 single excitation coefficients, where only a few coefficients are larger than 0.02. In particular, they are far better than those generated by B3LYP which tends to be the *de facto* standard in DFT/TDDFT.

In addition, by using NTO's to define a particular $I \rightarrow A$, tells us that the subset of double excitations required to fully describe this state can be reduced to those doubles that have I and A in common like Φ_{IJ}^{AB} , Φ_{IJ}^{BC} , Φ_{JK}^{AB} which are identified below as sectors 1, 2, 3. That is, the I, A excited state can be written as $\Psi^{EOM-CCSD} \rightarrow \Phi_I^A + \sum_{I,J,A,B} R_{IJ}^{AB} \Phi_{IJ}^{AB}$, where the different sectors in terms of spatial-orbitals are, R_{IJ}^{AB} , R_{IJ}^{BC} , and R_{JK}^{AB} .

Each of these double excitations have significant coupling with the $I \rightarrow A$, single excitation, Φ_I^A . But instead of the $\sim 10^6$ double excitations ($\sim O^2V^2$), that occur in a modest calculation ($10^2 100^2$) the effective number of double excitations is far less, saving orders of magnitude. Yet the result is effectively the same as obtained from the whole EOM-CCSD calculation (Figure 3), where the other choices involving less stringent sets of double excitations fall short of being able to describe the excited states accurately.

Much larger calculations are anticipated and a ~ 100 electron system would require about $\sim 50^2 250^2 \sim 10^{10}$ double excitations. For the three I, A sectors, the total would be $\sim OV + OV^2 + O^2V \sim 10^6$, or four orders of magnitude smaller.

However, it is not just the dimension of the doubles space that matters in an EOM-CCSD calculation, but the fact that when calculating the \bar{H} matrix one has to evaluate the $\sim O^2V^2$ terms that come from a product of \bar{H} with all the double excitation terms, which gives an $\sim O^2V^4$ scaling. Clearly, such a step can add much more to the calculation, much of which can be saved by the reduction in the R2 vector.

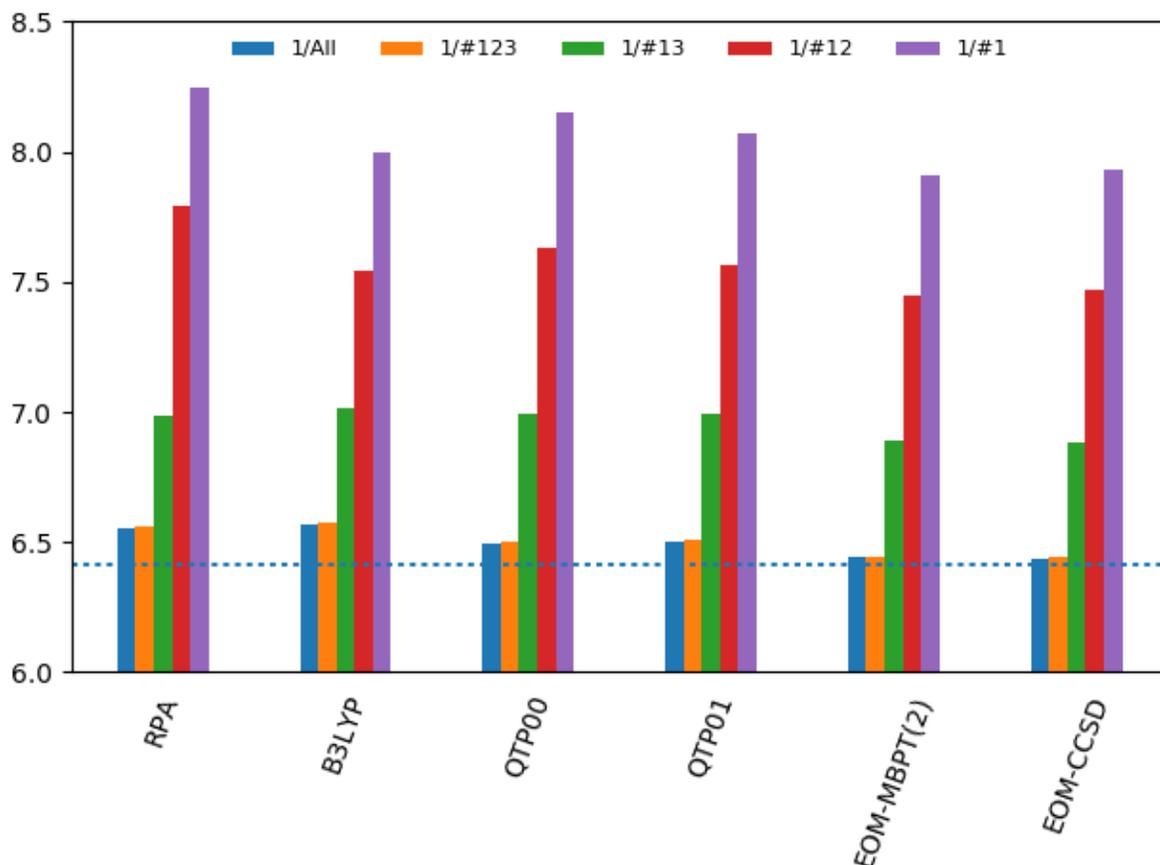


Figure 3. Comparison of an excitation energy in acetone with simpler approximations used to generate the NTO's. The blue dotted line indicates the normal EOM-CCSD excitation energy.

The ultimate model of this type still requires some attention to the required single and double excitations. In addition to the dominant Φ_I^A , the next most likely contributors will be other singles like Φ_J^B where the $J \rightarrow B$ excitation is also fairly highly weighted in the NTO transformation. The latter depends upon a second large λ_2 eigenvalue as shown in the NTO equations in Figure 1. When an NTO transformation results in an eigenvalue of 0.6 for one transition ($I \rightarrow A$) and 0.3 for another ($J \rightarrow B$), there is not a dominant NTO description. Instead, one needs to anticipate that two states are significantly mixing with each other, and the correct result for the two states will be sensitive to the mixing. This occurs in our studies of π - π^* excitations in nitrogen heterocycles. To allow full mixing between them, the two large eigenvalue NTO's from NTO transformation 1 can both be retained in R1 and R2 can be reduced

to the three sectors tied to I,A plus the three sectors tied to J,B. There will typically be some overlap that can be removed. In this way, Figure 4 shows that accurate answers occur only at the cost of two sets of R2 sectors, and two NTO single excitations. Using all the singles, which one can always do since it does not affect the scaling of the calculation, is still insufficient as the purple bars in Fig. 4 shows.

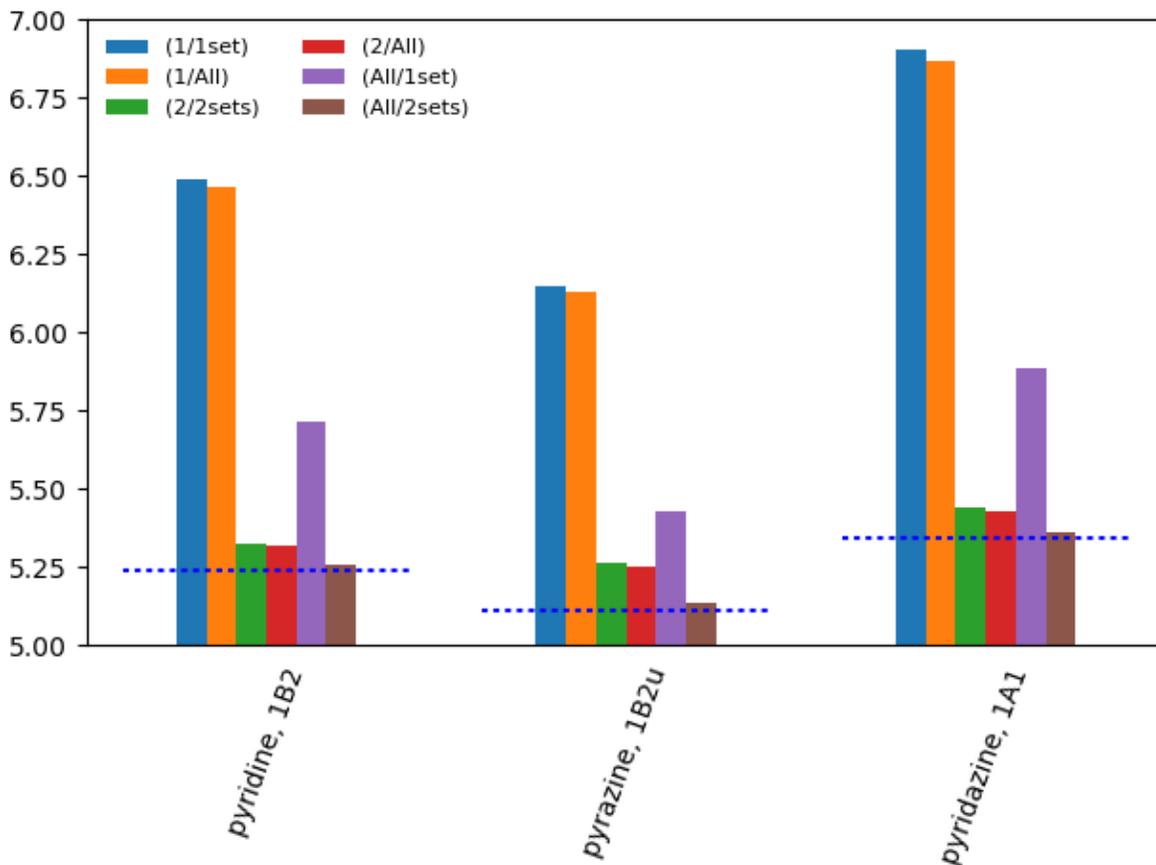


Figure 4. Three π - π^* excitations (in eV) in nitrogen heterocycles.

This feature is further shown in another way in Fig. 5.

Fig. 6 simply compares all R1 to the 2 NTO R1 choice when the three sectors of R2 are included for our full data set. Most of the states can be adequately described with a single NTO and the three sector R2 approximation, but not those in Fig. 4.

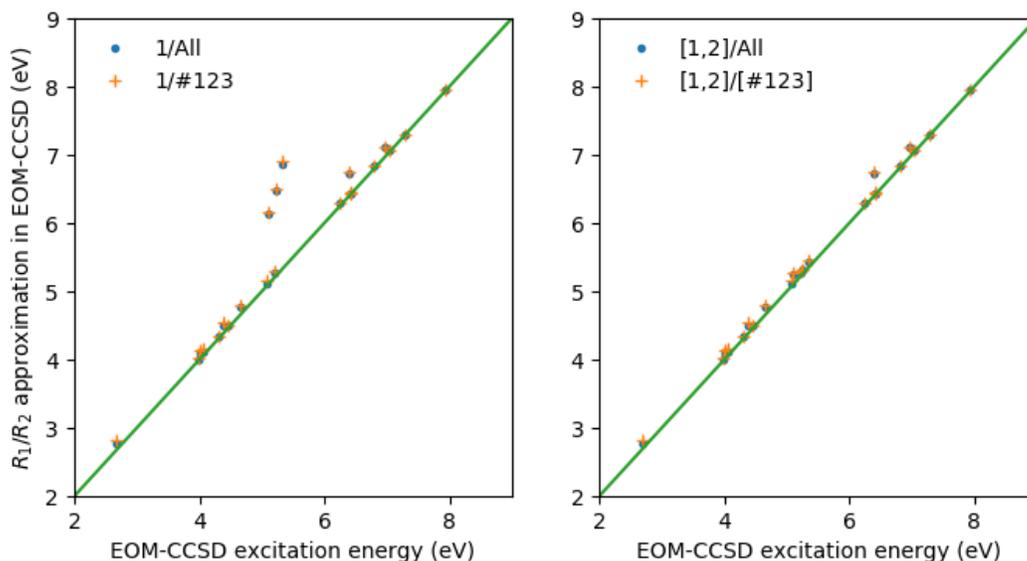


Figure 5. Approximated EOM-CCSD excitations in our test set (in eV).

The green line indicates the energy from the normal EOM-CCSD. Three dots largely deviate from the line (left panel) are the excitations studied in Figure 4. This large error is corrected with two sets of NTO excitations (right panel).

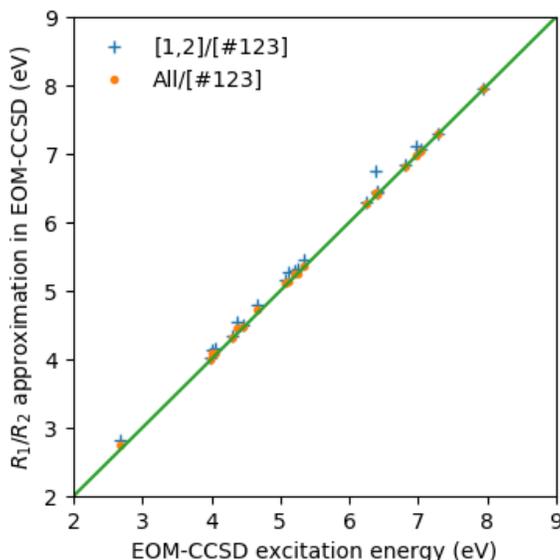


Figure 6. Approximated EOM-CCSD excitations in our test set (in eV).

The green line indicates the energy from the normal EOM-CCSD. The use of All R1 components in our test set (orange dots) shows excellent agreement to the reference EOM-CCSD energies (green line). Improving on the two NTO blue dots, as long as the two sets of sectors from NTO 1 and 2 are used.

The robust, low-scaling model that has evolved is all R1 and three sectors of R2 per major NTO contribution. Coupled to MBPT2 for the ground state, this reduces the overall scaling from $\sim M^6$ with the number of basis functions to $\sim M^5$.

Another major goal of our HASI work has been to generalize the EOM-MBPT2 method so that it not only offers a ground state second-order approximation, but also offers an accurate second-order type approximation for the excited state. EOM-MBPT2 works very well as currently construed, but a full ‘second-order’ method meaning one where only second-order effort is required for the excited state as well as the ground state would be a major step forward and one the field desperately needs, as those proposed to date (like CC2) do not work well. The reason they do not work well is that the role of R2 is compromised whenever any straight-forward partitioning of the double excitation \bar{H} matrix is made, as in CC2 or in our P-EOM-CCSD. The latter is great for Rydberg states but not valence ones. CC2 is also bad for Rydberg states. We now know from our studies of the three R2 sectors required per NTO to get accurate results, that there are critical $\langle R2|\bar{H}|R2\rangle$ effects that cannot be dismissed by separating them into a diagonal part and a correction.

The idea of partitioning is an old one. Any matrix problem can be separated into an effective eigenvalue form like

$$\omega = \langle P|\bar{H}|P\rangle + \langle P|\bar{H}|Q\rangle\langle Q|\omega - \bar{H}|Q\rangle^{-1}\langle Q|\bar{H}|P\rangle \quad \text{Equation 1}$$

In the standard form, P would be chosen to be all single excitations (S), with Q all doubles (D). The difficulty with inverting $\langle Q|\omega - \bar{H}|Q\rangle^{-1}$, a matrix of enormous dimension as discussed, usually means that the whole matrix is approximated by just its diagonal elements, $\langle Q|\omega - \bar{H}|Q\rangle^{-1} \sim \langle Q_k|\omega - \bar{H}|Q_k\rangle^{-1}$ which makes inversion trivial, to give

$$\omega = \langle P|\bar{H}|P\rangle + \sum_k \langle P|\bar{H}|Q_k\rangle\langle Q_k|\omega - \bar{H}|Q_k\rangle^{-1}\langle Q_k|\bar{H}|P\rangle \quad \text{Equation 2}$$

The excitation energy matrix is an effective Hamiltonian in the dimension of P.

But this misses the critical effects of terms that mix sectors 1, 2, and 3 like $\langle \Phi_{IJ}^{AB}|\bar{H}|\Phi_{JK}^{AB}\rangle$ and $\langle \Phi_{IJ}^{AB}|\bar{H}|\Phi_{IJ}^{BC}\rangle$, and such terms cannot be dismissed., as we have seen numerically. For that matter, do not forget that the matrix $\langle \Phi_{IJ}^{AB}|$ means all possible B,J, terms for a given I,A, (ie is column matrix of many terms) while $|\Phi_{IJ}^{AB}\rangle$ is a row matrix, so $\langle \Phi_{IJ}^{AB}|\bar{H}|\Phi_{JK}^{AB}\rangle$ provides a square matrix that also has off-diagonal elements as part of its contribution, that would also be neglected in a diagonal approximation.

The most inclusive way to avoid this problem is to choose P=S+D₀ to be not only singles but NTO selected doubles as well, and limit Q to the remainder of the doubles, call them D'. Then a diagonal approximation for the inverse matrix can likely be used.

Now the partitioned formula assumes the form

$$\omega = \langle S + D_0|\bar{H}|S + D_0\rangle + \sum_k \frac{\langle S + D_0|\bar{H}|D'_k\rangle\langle D'_k|\bar{H}|S + D_0\rangle}{\langle D'_k|\omega - \bar{H}|D'_k\rangle} \quad \text{Equation 3}$$

The first term would be the all R1 and the three sector R2 approximation reported that tends to work well for dominant NTO states. When two NTO's are required, then all R1 is the same, but two sets of R2 sectors are required.

A further possible simplification that is being considered is to use elements of our frozen natural orbital (FNO) approach. This means take the NO's that arise from a second-order approximation to the *excitation energy*. We have shown in prior work that normal ground state FNO's enable a reduction of the virtual space by ~40%. Doing the same for excited states requires a realistic second-order excited state approximation which is one of our HASI objectives. Part of this is the use of MBPT2 for the ground state, but right now the EOM-MBPT2 excited states do not benefit from any further second-order approximation for the excited state. Using both techniques, the effective dimension of the double excitation space can be reduced to less than $\sim 10^3$ compared to the 10^5 or 10^6 that would otherwise be required.

Once all of the above are implemented into a special purpose code to exploit the fact that only a few of the single excitations are critical, and the contributing double excitations can be drastically reduced to a subset of all possibilities; the dimensionality of the problem is comparatively modest making *ab initio* EOM-CC applicable to quite large systems. When this new, low-scaling theory is coupled to ACES 4, which offers massively parallel implementation, a new treatment of large molecule excited states would be readily available. Furthermore, as this report will make clear in the next section, ACES 4 is written to be able to handle such enormous matrices while exploiting their sparsity at the hardware level. Thus, the combination is much more powerful than the sum of the parts, making highly accurate studies of excited states applicable to quantum dots and other nanomaterials. This work is terminating because of funding.

Progress with new density functional methods

The publications should be consulted for details of our many other developments under this project. A new DFT functional termed QTP(01) was introduced primarily to accurately describe Rydberg excited states and charge-transfer excitations, both long-term failures of TDDFT. QTP(01) is far better than the prior DFT alternatives. Uniquely, the QTP DFT functionals are non-empirical or minimally empiricized, compared to virtually all other functionals in use. This has been made possible by invoking an ionization potential eigenvalue theorem we proved, based upon adiabatic TDDFT. This also means 'we are getting the right answers for the right reasons.'

The figure shows the correct treatment of charge-transfer states with *ab initio* methods, our STEOM-CC and EOM-CC, versus standard DFT like B3LYP and Cam-B3LYP, for the charge transfer excitation energy of $C_2F_4 \rightarrow C_2H_4$ as a function of the distance between the donor and acceptor, $1/R_{DA}$. Note how well Cam-QTP(01) and (00) do.

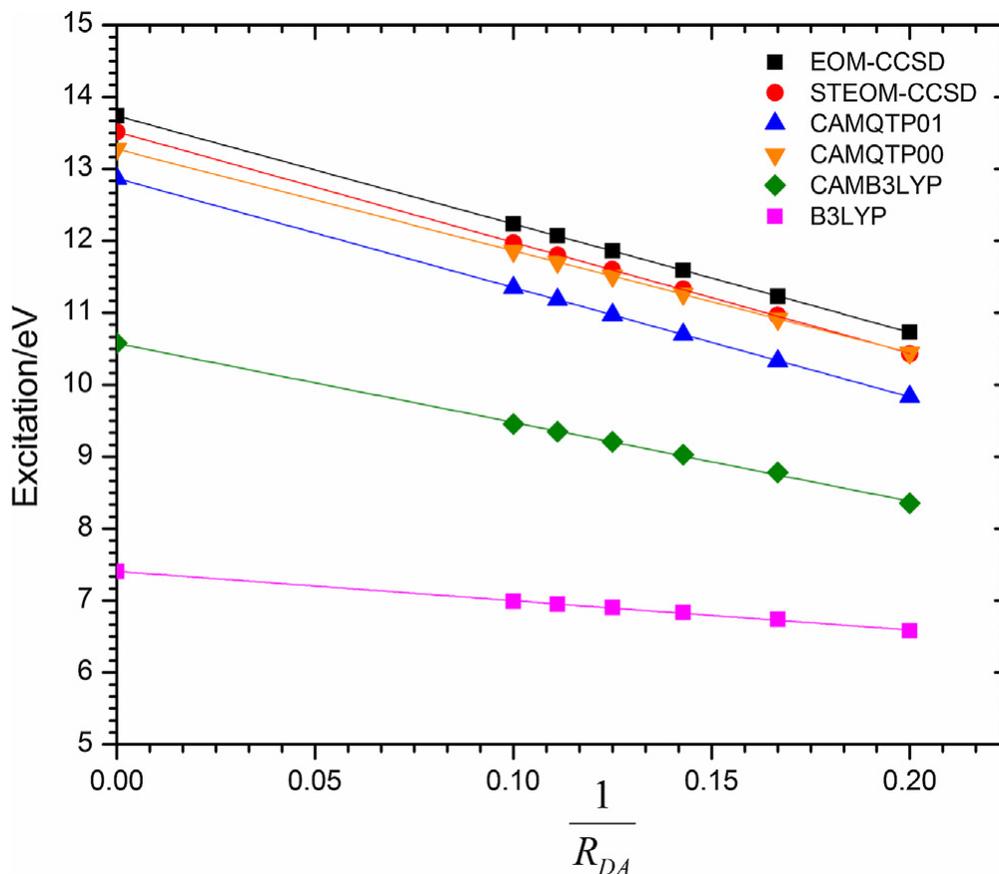


Figure 7. Charge-transfer from ethylene to tetrafluoro ethylene.

There are many other theory advances discussed in the publications and prior quarterly reports we will not address them here. But one should note, these are all major, state-of-the-art developments cut short by funding. See the history of that above in the document. At this point we will address the ACES 4 development.

Overview of ACES 4

Aces 4 is a new implementation of Super Instruction Architecture with a modular design which was architected for adaptability and testability, avoids scalability traps, and offers dynamically managed distributed data structures with support for block sparsity and exploiting symmetry. The system is comprised of a Domain Specific Programming Language called SIAL along with its compiler and runtime system.

Two versions are available, a parallel version based on MPI and a single process version (with no MPI dependency). The latter is useful during development work and also demonstrates the modularity of the system: In the future it would be possible to replace MPI with a different communication layer without significant changes to the rest of the system.

Aces4 runs on systems ranging from laptops to leadership class supercomputers and has been successfully run on the following systems: HiPerGator @ University of Florida, DOD Garnet Cray XE6, DOD Haise IBM iDataPlex, DOD Armstrong Cray XC30, DOD Shepard Cray XC30, DOD Excalibur Cray XC40, DOE Titan Cray XK7. DOD Thunder, OSX 10.9 and greater and Windows64 under cygwin.

Quantum Chemistry Methods Implemented

Implemented methods include Restricted and unrestricted Hartree-Fock and gradients,

- Restricted and unrestricted second-order Möller-Plesset (MP2, MBPT2) energy and gradients
- Restricted coupled-cluster singles and doubles (CCSD) including linearized variations (LCC) and gradients
- Restricted standard and lambda triples corrections to coupled-cluster singles and doubles (CCSD(T))
- Restricted configuration interaction singles (CIS) including the corrections from perturbative doubles (CIS(D)) or coupled-cluster perturbation theory (CIS-CCPT)
- Restricted equation-of-motion (EOM) coupled-cluster theory for second-order MBPT, coupled-cluster singles and doubles including linearized variations, and second-order coupled-cluster perturbation theory

One-electron response properties for all coupled-cluster based methods

- Restricted 2nd-order molecular-cluster perturbation theory (MCPT)
- Restricted fragment-effective-field coupled-cluster perturbation theory (FEF-CCPT) and configuration interaction singles corrected by FEF-CCPT

The latter two are newly developed methods that rely extensively on the ability of Aces4 to handle block sparsity.

Runtime System

The runtime system manages parallelism, data movement, and checkpointing. In particular, during the AFRL-HASI program, the following features and enhancements to Acse4 have been implemented.

- Disk-backed array handling has been optimized and integrated into an automatic check-pointing mechanism that allows easy restart on SIAL program boundaries. Disk-backed array handling and check-pointing are integrated by using common files that avoid duplicate writes. The check-pointing mechanism handles sparsity and its implementation exploits the underlying parallel file system (via MPI IO).
- A custom data-flow analysis has been added to the SIAL compiler to inform the disk-backing mechanism when making decisions about which blocks to write to disk.
- The program supports sparsity in such a way that no memory for data or metadata is allocated for unused blocks.
- The infrastructure for transferring data between GPU memory and a host and executing all SIAL operations on blocks on a GPU. This is currently done by annotating SIAL

programs with regions that should be done on a GPU. Once regions have been annotated, the runtime system then manages the data transfers optimally (in the sense of avoiding unnecessary data transfers) and transparently.

- A load balance optimization where the mapping from tasks to processors is aware of sparsity and symmetry.
- A testing suite based on google test exercises the complete set of SIAL. In addition, tests have been provided for each Quantum Chemistry method. The testing suite allows modifications and extensions to the system with confidence that correctness is preserved in the process.
- Extensive runtime error checking.
- Although not funded by HASI, we note that our collaborators have used Aces4 to implement a meteorology application. This demonstrates that the Super Instruction concept is applicable in more domains than quantum chemistry.

In progress tasks

There are several in-progress tasks that remain unfinished due to lack of funding and resulting loss of personnel.

In order to take advantage of recent advances in tensor contraction technology, we were in the process of replacing the tensor package currently used in Aces4 with TBLIS, a tensor package developed at the University of Texas. This work remains incomplete.

Optimizations that enable more overlap between communication and computation by automatically prefetching data have been implemented. Preliminary results show a significant decrease in measured idle time waiting for block arrival. The implementation needs to be generalized and the effect on overall system performance evaluated at scale. The next step would be to extend prefetching to encompass data transfers to GPUs. Data transfer time can, in some cases, be larger than the savings by performing a calculation on a GPU. Extended prefetching that could hide the CPU-GPU latency could allow GPUs to be exploited in significantly more situations.

PUBLICATIONS AND PRESENTATIONS

Papers published

B.A. Sanders, J. Byrd, N. Jindal, V. F. Lotrich, D. Lyakh, A. Perera, and R.J. Bartlett, "Aces4: A Platform for Computational Chemistry Calculations with Extremely Large Block-Sparse Arrays, Proceedings of the International Parallel and Distributed Processing Symposium (IPDPS)," Orlando. May, 2017.

J. Byrd, Rodney Bartlett, and B.A. Sanders, "On Preparing the Super Instruction Architecture and Aces4 for Future Computer Systems." Published in "Exascale Scientific Applications: Programming Approaches for Scalability, Performance, and Portability" Editor, T. P. Straatsma, November 2017..

J.N. Byrd, J.J. Lutz, Y. Jin, D.S. Ranasinghe, J.A. Montgomery, Jr., A. Perera, X.F. Duan, L.W. Burggraf, B.A. Sanders, and R.J. Bartlett, "Predictive coupled-cluster isomer orderings for some Si_nC_m ($m, n \leq 12$) clusters: A pragmatic comparison between DFT and complete basis limit coupled-cluster benchmarks," J. Chem. Phys. 145, 024312 (2016).

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R. J. Bartlett.

August, 2017. National ACS Meeting, symposium in Honor of Peter Pulay, Computers in Chemistry, Washington, DC.

November 2016 – Computational Chemistry, Theoretical Chemistry Conference, Jackson, MS.

July 2016 - International Society for Theoretical Chemical Physics (ISTCP-IX), Grand Forks, ND

September 2016 – Department of Chemistry, The Johns Hopkins University, Baltimore, MD

June 2016 – Center for Theoretical and Computational Chemistry, University of Oslo, Norway

February 2016 – Workshop Honoring Peter Schwerdtfeger's 60th Birthday, Center for Theoretical Chemistry and Physics, New Zealand Institute for Advanced Study, Albany New Zealand

December 2015 – 2015 International Chemical Congress of Pacific Basin Societies (Pacifichem), Honolulu, HI

November 2015 – 67th Southeastern and 71st Southwestern Regional Meeting of the American Chemical Society, Memphis, TN

May 2015 – Frontiers in Electronic Structure Theory, a meeting in honor of Sourav Pal's, 60th Birthday , Director, CSIR- National Chemical Laboratory, Pune, in Goa, India
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May , 2017, “Aces4: A Platform for Computational Chemistry Calculations with Extremely Large Block-Sparse Arrays” MOLSII Workshop on Core Software Blocks in Quantum Chemistry: Tensors and Integrals. Asilomar, CA..

May 2017, “Aces4: A Platform for Computational Chemistry Calculations with Extremely Large Block-Sparse Arrays International Parallel and Distributed Processing Symposium.” Orlando.

August, 2017, “Emerging Systems and the Super Instruction Architecture”. American Chemical Society Meeting. Washington DC. .

Nov 2016, International Workshop on Software Engineering in Parallel Programming, Amsterdam, Netherlands. (keynote speaker)

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LIST OF SYMBOLS, ABBREVIATIONS AND ACRONYMS

| | |
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| AFRL | Air Force Research Laboratory |
| CIS | configuration interaction singles |
| CIS(D) | corrections from perturbative doubles |
| CCSD | corrections to coupled-cluster singles and doubles |
| CCSD(T) | corrections to coupled-cluster singles and doubles (triples) |
| EOM | equation-of-motion |
| FEF-CCPT | fragment-effective-field coupled-cluster perturbation theory |
| FNO | frozen natural orbital |
| MCPT | molecular-cluster perturbation theory |
| RXAP | Photonic Materials Branch, Functional Materials Division, Materials and Manufacturing Directorate |
| SIAL | Super Instruction Architecture |