First-Principle DFT Ground-State and TDDFT Excited-States Calculations: Theory and Computation

Eric Polizzi

Department of Electrical and Computer Engineering, University of Massachusetts, Amherst, USA
e-mail: polizzi@ecs.umass.edu

The Density Functional Theory (DFT) associated with the Kohn-Sham equations, has been widely used in computational material science and quantum chemistry over the past few decades. DFT provides (in principle) an exact method for calculating the ground state density and energy of a system of interacting electrons in terms of a set of single electron equations and exchange-correlation (XC) functionals. Furthermore, its time-dependent counterpart, TDDFT, has been proposed as a fundamental approach to investigate the dynamics of many-body systems and can effectively be used to obtain the excited states (i.e. electronic spectroscopy). In practice, the ability to capture the many-body effects within the DFT and TDDFT single electron pictures depend on the numerical approximations used for the exchange and correlation terms. Remarkably, however, the simplest adiabatic approximation such as ALDA is already capable to provide accurate excited-states simulation results (such as absorption spectra) for a large number of complex molecular systems, which can be directly compared with experimental data. TDDFT keeps then gaining in popularity as being among one of the most accurate and numerically affordable many-body techniques.

Although, first-principle calculations using DFT and TDDFT have provided a practical (i.e. numerically tractable) path for performing ground state and excited states calculations, they have also introduced new numerical challenges on their own. These past few years, however, the list of capabilities of the new FEAST eigenvalue algorithm [1] and solver (*www.feast-solver.org*) has considerably broadened the perspectives for enabling reliable and high-performance large-scale first-principle calculations of complex molecular systems and nanostructures. Not only the algorithm features some remarkable convergence and robustness properties [2], it can exploit a key strength of modern computer architectures, namely, multiple levels of parallelism.

Consequently, the software package has been very well received by the developers of electronic structure packages, and it is also currently featured as INTEL-MKL's main HPC eigenvalue solver.

From atoms to molecules and nanostructures, FEAST has become the backbone of our in-house NESSIE finite element simulator to perform state-of-the-art O(N) large-scale first-principle DFT and real-time TDDFT calculations. NESSIE's capabilities include first-principle all-electron (beyond pseudopotential) ground state and excited states calculations with applications ranging from electronic spectroscopy of complex molecules to THz electronics in Carbon-based materials. In order to address such realistic quantum simulations applied to large-scale atomistic systems, we operate FEAST beyond the current "black-box" solver by considering a fundamental redesign of the electronic structure numerical modeling. More specifically, FEAST has become a new flexible framework for addressing in particular: (i) the all-electron (full-potential) electronic structure problem; (ii) the self-consistent (SCF) problem for ground-sate DFT calculations; and (iii) the real-time propagation approach for excited-states TDDFT simulations. These recent results are briefly summarized in the following.

Electronic Structure Hamiltonian- an all-electron FEAST framework. The muffin-tin (domain-decomposition) approach, which has been used as early as the 1930's by the solid-state physics community, appears naturally suited to address specifically a multi-center atoms system. It can bring flexibility in the discretization step, reduce the computational efforts within the interstitial region alone, and should also guarantee maximum linear parallel scalability performances. While introducing the APW method [3], Slater outlined the main difficulty of the muffin-tin approach which leads to the formation of a non-linear eigenvalue problem in the interstitial region (since the boundary condi-

tions at the interface with the atom-centered regions are energy dependent). The mainstream approaches to all-electron (i.e. full potential) electronic structure calculations in solid-state physics rely then almost entirely on approximations such as direct linearization techniques (e.g. LAPW, LMTO, etc.). Alternatively, linear eigenvalue problems can also be obtained from pseudopotential approximation techniques using smooth but non-local potentials in atom-centered regions that eliminate the core states. In a recent work [4], we have proposed a reformulation of the real-space muffin-tin approach for solving the all-electron problem exactly with linear parallel scalability. The approach relies entirely on the capabilities of the FEAST algorithm framework, and it can be effectively used to bypass the traditional approximations.

DFT ground state calculations- a Non-linear FEAST for the SCF problem Using DFT, the resulting electronic structure problem becomes fully non-linear since the Hamiltonian operator depends on the occupied eigenfunctions. This resulting non-linear eigenvector problem is commonly addressed using a self-consistent field method (SCF) wherein a series of linear eigenvalue problems needs to be solved iteratively until convergence. Successfully reaching convergence by performing SCF iterations is of paramount importance to first-principle quantum chemistry and solid-state physics simulations software. In [5], we have proposed a new fundamental non-linear FEAST approach (named NLFEAST) for addressing the SCF problem that outperforms the traditional mixing-scheme/Newton techniques by providing a higher converge rate, convergence to the correct solution regardless of the choice of the initial guess, and a significant reduction of the eigenvalue solve time in simulations.

Real-time TDDFT excited states calculations - a FEAST-based spectral approach Real-time TDDFT simulations are relatively recent approaches introduced by Yabana and Bertsch in [6], and becoming since then one important focus of the TDDFT research activities with, in particular, the development of the software packages Octopus, NWChem, and GPAW. The optical linear response can then be obtained using the standard formalism of dipole time-response from short-polarized impulses which has been largely documented in

the literature. In essence, once the induced dipole is computed in time-domain as a response of a short delta impulse in any given directions of the molecular system, the imaginary part of its Fourier transform provides the dipole strength function; and the absorption spectrum is then obtained along with the expected "true many-body" excited energy levels. Most importantly, the applicability of real-time TDDFT is not limited to linear responses of systems; it is a general and flexible framework that can address any forms of non-linear responses including ion dynamics. We propose to discuss a new accurate and scalable FEAST-based real-time propagation scheme for computing the excited states and absorption spectra of large complex systems with applications to electronic spectroscopy of molecules (see Figure 1) and plasmonic excitations in Carbon-based materials such as CNT and Nanoribbons (see Figure 2). This approach can be seen as an attractive robust and high-performance alternative to traditional split-operator technique for the evolution operator, or other PDE-based approaches such as Crank-Nicolson [7], [8].

Here, we propose to review the broader impacts of these new FEAST-based computational strategies. In particular, our TDDFT simulation results on plasmonic excitations in Carbon-based materials (CNT, Nanoribbons) will be thoroughly discussed.

REFERENCES

[1] E. Polizzi *Density-matrix-based algorithm for solving eigenvalue problems*, Phys. Rev. B, 79, p115112, (2009).

[2] P. Tang, E. Polizzi, *FEAST as a Subspace Iteration Eigen-Solver Accelerated by Approximate Spectral Projection*, SIAM Journal on Matrix Analysis and Applications, , 35(2), pp354-390, (2014).

[3] J. C. Slater, *Wave Functions in a Periodic Potential,* Phys. Rev., 51, pp846-851, (1937).

[4] A. Levin, D. Zhang, E. Polizzi *FEAST Fundamental Framework for Electronic Structure Calculations: ,* Comput. Phys. Comm., **183**, I11, pp2370-2375 (2012).

[5] B. Gavin, E. Polizzi, *Non-linear Eigensolver-Based Alternative to Traditional SCF Methods*, J. Chem. Phys. **138**, 194101 (2013).

[6] K. Yabana, G. F. Bertsch, *Application of the time-dependent local density approximation to optical activity,* Phys. Rev. A60 1271 (1999).

[7] Z. Chen, E. Polizzi *Spectral-based propagation schemes for time-dependent quantum systems with application to carbon nanotubes*, Phys. Rev. B, Vol. 82, 205410 (2010).

[8] J. Jerome, E. Polizzi, *Discretization of Time Dependent Quantum Systems: The Evolution Operators* Applicable Analysis, pp1-24 (2014).
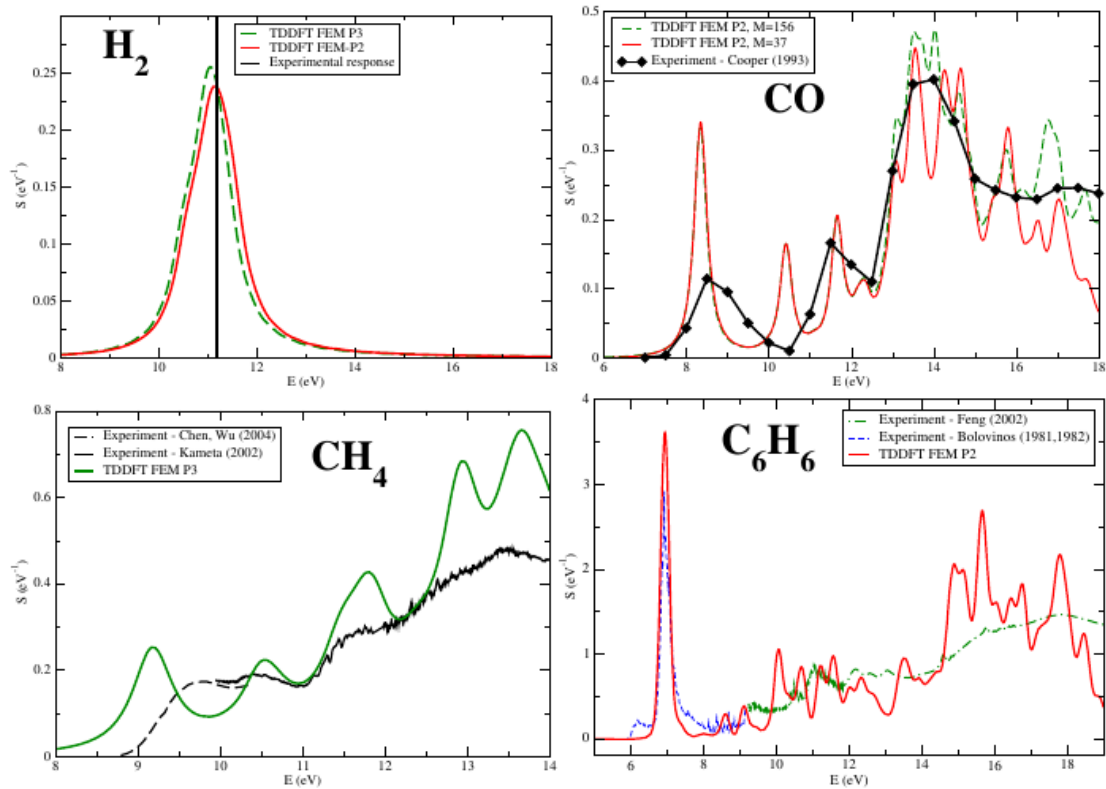
Fig. 1. *Some TDDFT/ALDA simulation results on small molecules using the FEAST-based spectral approach within the all-electron (P2,P3) FEM NESSIE framework. One notes that the simulated optical responses compare remarkably well with the experimental data (the y-axis also shows the dipole oscillator strength in eV for both the simulated and the experimental curves).*
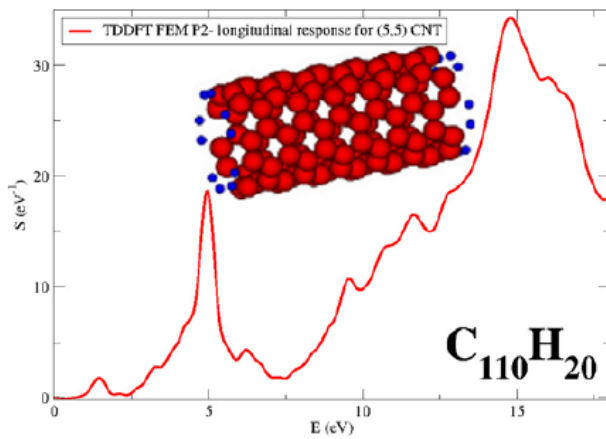
SIMULATION DATA:

- Real-space discretization: FEM-P2 $N = 400K$, $nnz = 5,700K$ (nnz: # of non-zero elements).
- Real-time discretization: $\Delta_t = 20as$, T = 10fs i.e. 500 time steps
- Initialization: Ground state DFT calculation
- 340 states to propagate - Spectral decomposition: ~ 1000 modes
- FEAST-MPI solver: 2 intervals (~ 500 modes by interval and 750 subspace size), Gauss-8 by interval, direct sparse solver per Gauss node (i.e. 16 linear systems solved in parallel by time-step)
- HPC Gordon Xsede with 16 nodes (256 cores): 40h simulation time

Fig. 2. *Absorption spectrum of a short (5,5) CNT (H-terminated) excited along the tube's longitudinal direction, which contains 110 Carbon and 20 Hydrogen atoms i.e. 680 electrons (340 states w/o spin). One notes that the CNT appears already long enough to reproduce some experimental characteristics of long SW-CNT [Phys. Rev. Lett. 94, 087402 (2005)], i.e. π plasmonic excitation at 5.1eV follows by a $\pi + \sigma$ plasmon at higher energy (17.6eV in the experiments). The simulation data provide information about scalability performances of the spectral-based approach. The propagation is using all three levels of parallelism of the FEAST solver. Here, the total simulation time depends mainly on the time taken for the direct shared-memory solver (PARDISO) to solve our large sparse inner linear system with multiple right-hand sides on a given node. This time could drop significantly if more parallel power were available at this level, and/or using iterative techniques. For much larger systems where more search intervals would be needed, linear parallel scalability can be achieved by adding an additional appropriate number of compute nodes.*