Spectral Propagation Schemes for TDDFT Calculations with Applications to Molecules and CNTs

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Problem

In nanoelectronic applications, efficient time-dependent simulations have become increasingly important for characterizing the electron dynamics under time dependent external perturbations such as electromagnetic fields, pulsed lasers, and particle scattering.

Reliable modeling approaches in time domain, however, are often limited in term of trade-off between robustness and performances, and a direct numerical treatment is difficult.

Contributions

In this work, we aim to go beyond these limitations by introducing high performance numerical schemes to compute the solution of the time-ordered evolution operator. The numerical treatment of these evolution operators often gives rise to the matrix exponential, commonly treated using approximations such as split-operator techniques. In contrast, the efficiency of the time-domain propagation techniques described here, is enhanced by reliance on the capabilities of the FEAST [1] algorithm for solving the eigenvalue problem. FEAST has the ability to re-use the basis of a precomputed subspace as suitable initial guess for solving the series of eigenvalue problems, which makes convergence fast.

In addition, in order to reduce even further the number of large-scale eigenvalue problem, two highly optimized propagation schemes (Gauss and BTPS) [2] have been proposed and implemented.

RT-TDDFT Theory

For a system which is composed of N electrons, the electron dynamics can be described by a set of one body equations, each one is of the form:

$$i\hbar\frac{\partial}{\partial t}\psi_j(\mathbf{r},t) = \left[\frac{-\hbar^2}{2m}\nabla^2 + v_{KS}[n](\mathbf{r},t)\right]\psi_j(\mathbf{r},t)$$

Under Adiabatic Local density approximation (ALDA), the exchange correlation term is local in both space and time. Using a single electron picture, and in the time dependent density functional theory (TDDFT) framework, the solutions of the self-consistent stationary Kohn-Sham Schrodinger type equation are taken as initial wave functions.

After we obtain self-consistent ground states, N ground state Kohn-Sham orbitals will be propagated over time. Here we perform all electron calculation and update potential (solving Poisson equation) in each time step.

The solution of Equation can be written as:

$$\Psi(t) = \mathcal{T}\exp\left\{\frac{-i}{\hbar}\int_0^t d\tau\hat{H}(\tau)\right\}\Psi_0$$

often, small time step is chosen so H can be viewed as constant in that time interval.

Spectral Propagation Schemes

By using FEAST, the eigenvalue problem is reformulated into solving a set of well-defined independent linear systems along a complex energy contour. The Hamiltonian at each time step can be directly decomposed as: $\mathbf{D} = \mathbf{P}^T\mathbf{H}\mathbf{P}$

The direct propagation for small time step reads:

$$\Psi(t) = \mathcal{T}\left\{\prod_i\left[\mathbf{P}_i\exp\left(\frac{-i}{\hbar}\Delta_t\mathbf{D}_i\right)\mathbf{P}_i^T\mathbf{S}\right]\right\}\Psi_0$$

$$\hat{U}(t,0) = \mathcal{T}\exp\left\{-\mathrm{i}\int_0^t d\tau\hat{H}(\tau)\right\} = \hat{U}(t,t_{N-1})\cdots\hat{U}(t_2,t_1)\cdot\hat{U}(t_1,0)$$

Gauss quadrature Integration error

Approximation to evolution operator

$$\mathcal{T}\exp\left\{-\mathrm{i}\xi\sum_i^P\omega_i\hat{H}(t_i)\right\} \xrightarrow{\text{Rectangular rule}} \exp\left\{-\mathrm{i}\hat{H}(t_1)\Delta t\right\}$$

Anti-commutation error P is small

$$\mathcal{T}\left\{\prod_i^P\exp\left[-\mathrm{i}\xi\omega_i\hat{H}(t_i)\right]\right\}$$

Direct approach

Approximation to exponential of Hamiltonians

Polynomial expansion Splitting techniques, etc.

Direct spectral decomposition using FEAST

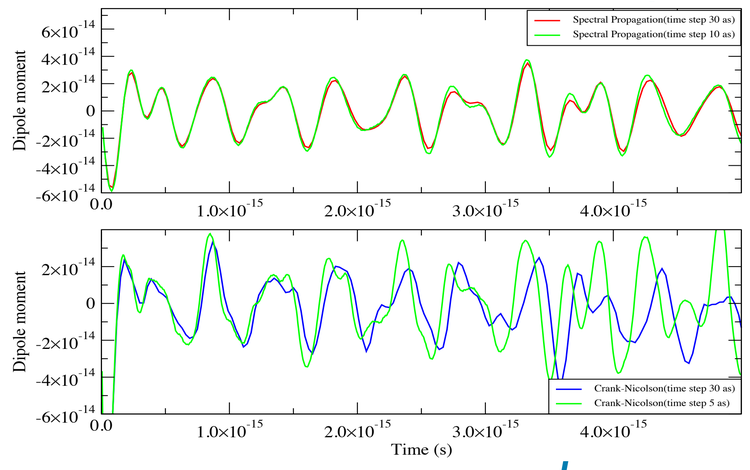
Two numerical errors are respectively involved in our spectral propagation schemes: 1. integration error from the numerical quadrature. 2. an error on the anti-commutation resulting from the decomposition of the exponential.

From our simulation, integration error is more important to keep the evolution accurate. There is a mathematical proof which can be found in [3].

Spectral schemes vs C-N

Crank-Nicolson (C-N) is the propagation scheme used by mainstream of the community. However, C-N requires propagation time step to be extremely small in order to get accurate and stable result (typically 2 attosecond).

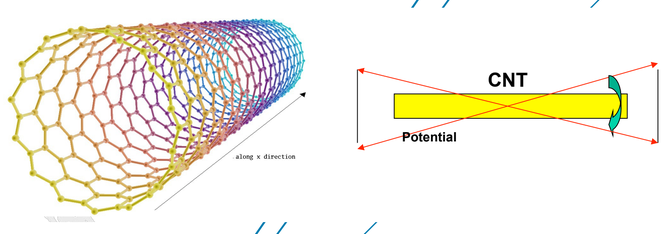
The figure below is the comparison of dipole moment for carbon monoxide (CO) obtained using both our spectral propagation scheme and C-N. The result shows spectral scheme is stable for large time step (30 as), while C-N fails quickly when we increase the time step.



Spectral propagation scheme can provide larger time steps, and more importantly all the linear system within FEAST can be solved in parallel (C-N is sequential). The efficiency and robustness of our spectral propagation scheme makes simulation of large system feasible.

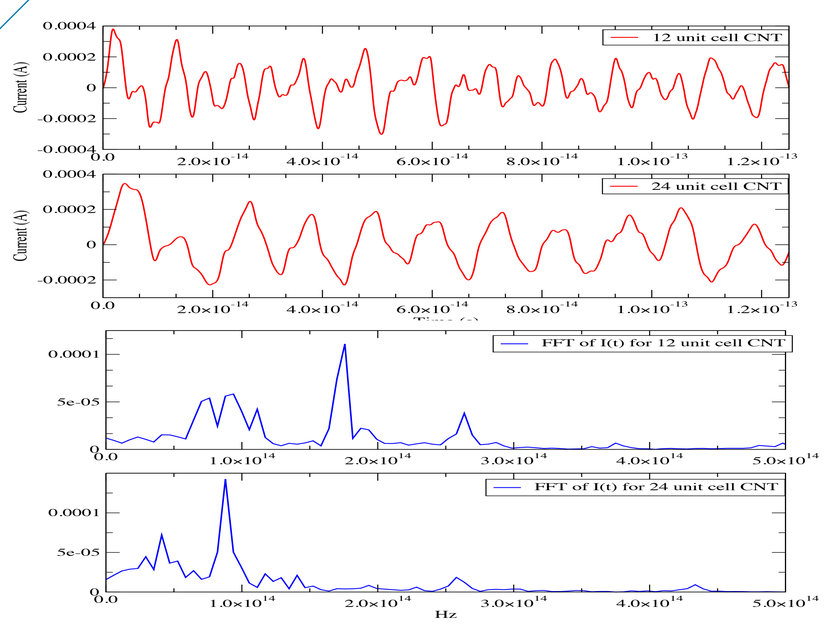
Electron THz response in CNT

We perform 3D simulations of an isolated CNT which is sandwiched between two electrodes producing a AC voltage at THz frequency. In this calculation, an empirical pseudopotential is used, a very short pulse (time domain) is injected into the CNT. We calculate the current density in the middle of the tube, then Fourier transform the current density in order to get the responses of the CNT.



The corresponding phase velocity of the resonance frequency is: v=1.14*10^8 cm/s. We can see that the phase velocity is constant, showing that the high-frequency electron response is dominated by single-particle excitations rather than collective plasmon.

Our simulations show that we have obtained a phase velocity which is consistent with the Fermi velocity 8* 10^7 cm/s which was also measured in a recent experiment.

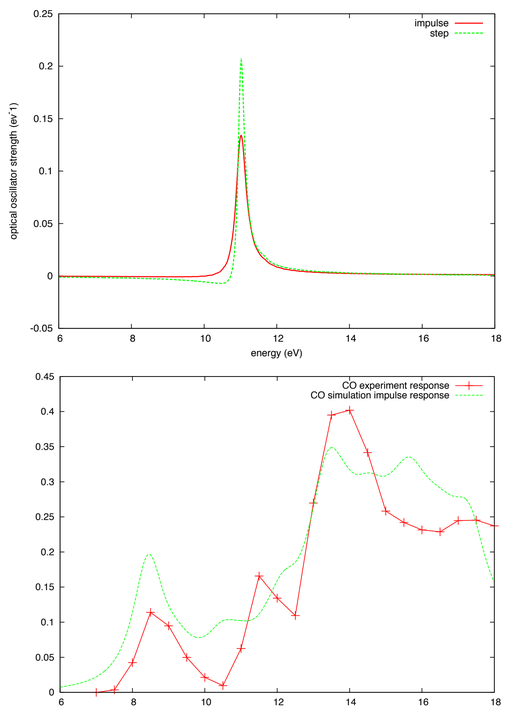


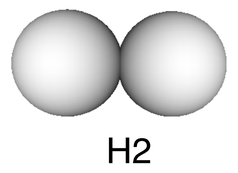
Molecule Optical response

Our model consider all-electron calculation, real-mesh techniques (3D cubic finite-element method), and real time propagation of the Kohn-Sham equations. In order to get optical responses for molecules, we apply a weak delta kick (impulsive potential) or step function potential to the system, let it evolve over time, then Fourier transform the dipole moment to get the optical oscillator strength.

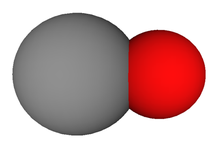
For H2, we apply both potentials, and reach the same optical response. Our result of the first excited energy is 11eV while the experiment results is 11.19 eV. For CO the first excited energy reads 8.5 eV, which experiment shows 8.47 eV.

Because we have all electron calculation and direct spectral decomposition. Our results shows very good agreement with the experiments. And in order to go to larger molecules and CNTs, we are actively working on parallelism of our schemes.





H2



CO

References

[1] E. Polizzi, "Density-matrix-based algorithm for solving eigenvalue problems," *Physical Review B,* vol. 79, no. 11, p. 115112, 2009.

[2] Z. Chen and E. Polizzi, *Phys. Rev. B,* vol. 82, no. 20, p. 205410, Nov 2010.

[3] J. Jerome and E. Polizzi. Discretization of time dependent quantum systems: The evolution operator, (Submitted, under review)