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Exact Time-Dependent Kohn-Sham Potential for Interacting Few-Body Systems

Rudolph J. Magyar - rjmagya@sandia.gov
Shock Physics Group, Org. 1443, Sandia National Laboratories, Albuquerque, New Mexico, USA

Time-dependent density functional theory enables practical simulations of the dynamic many-electron systems, but one of the biggest obstacles to reliable application is the quality of the approximate potential. It is often difficult to determine whether ever-more sophisticated approximations properly include new physics, as there exist few benchmark exact potentials. Towards this ends, we have developed and tested a scheme to extract the exact (non-adiabatic) time-dependent Kohn-Sham potential for few body systems. We will present some examples on 1D model systems. The approach is general and can be used to back engineer high-level quantum mechanical simulations to gain insight into TDDFT on a broad scale.

Time-Dependent Density Functional Theory (TDDFT)

- Highly successful and popular computational theory used to model mutually-interacting electron dynamics
- Opacities
- Chemical reactions
- Defect formation
- Radiation transport

Exact Potentials in TDDFT

Difficult to extract even when exact solutions are known. The following do not work well:

1. Van Leeuwen-type - target density to achieved density ratios
2. TD-Linear response search to determine better TD-KS potentials
3. Inverted Crank-Nicholson

Bohmian-Inspired Scheme

- Combine adiabatic solutions with fluid-mechanics-like potentials
- Known and exact for single electrons and spin-singlets
- Used in approximate form-already in TDDFT

$$v_S(x,t) = v_s^{adia}[n](x)\Big|_{n=n(x,t)} + v_s^{dyn}[n,V,\dot{V}](x,t)$$

$$V(x,t) = \nabla S(x,t) = J(x,t)/n(x,t) \qquad \frac{\partial}{\partial t}n(x,t) + \nabla \bullet J(x,t) = 0$$

$$\frac{\partial}{\partial t}S(x,t) + \frac{1}{2}\left(\nabla S(x,t)\right)^2 = -v_s^{dyn}(x,t)$$

One-Dimensional DFT

- Screened Coulomb interaction
- S is relatively easy to obtain numerically
- Exact solutions are computational tractable

$$S(x,t) = \int_{-\infty}^{x} dx' \frac{1}{n(x',t)}\left[\int_{-\infty}^{x'} dx'' \frac{\partial}{\partial t} n(x'',t) + J_0(t)\right]$$

One-Dimensional Hooke's Atom

- Model of a quantum well of harmonic confinement ω
- Exact solutions
- Screened Coulomb interaction with parameters λ and ε
- Spin-singlet state studied extensively
- Spin-triplet state, non-trivial with Aufbau effects in kinetic energy

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{2}\frac{d^2}{d^2x_i} + \frac{\lambda}{\sqrt{(x_1-x_2)^2+\varepsilon^2}} + \frac{\omega^2}{2}\sum_{i=1}^{2}x_i^2$$

The Exact Numeric Solution

- Gaussian orbital basis set – harmonic oscillator solutions
- Typical basis size required 22 Gaussians
- Ground and excited states found through diagonalization of exact many-body Hamiltonian within basis
- Time-evolution possible by acting on ground-state with a linear operator

Time-Dependent Perturbation 1: Linear External Field

- Model of photo-electric interaction with coupling constant κ
- Admits exact solutions – Harmonic Potential Theorem

$$\hat{H}_{TD-pert.} = \begin{cases} 0 & t \le 0 \\ \kappa\sum_{i=1}^{2} x_i & t > 0 \end{cases}$$

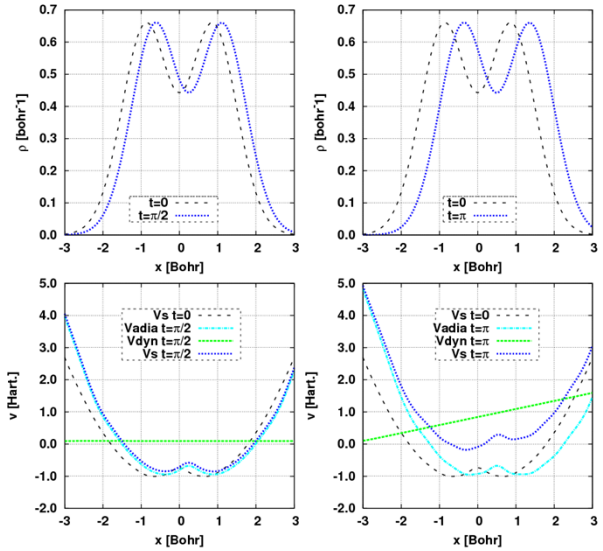
$$n(x,t) = n_0(x - X(t)) \quad X(t) = \frac{\kappa}{\omega^2}(1-\cos(\omega t))$$

$$S(x,t) = \frac{\kappa}{\omega}x\sin(\omega t)$$

$$v_S^{adia}(x,t) = \frac{\omega^2}{2}(x-X(t))^2 + v_{HXC}^0(x-X(t))$$

$$v_S^{dyn}(x,t) = \omega^2 x X(t) - \kappa x$$

$$v_s(x,t) = \frac{\omega^2}{2}x^2 + v_{HXC}^0(x-X(t)) - \kappa x$$



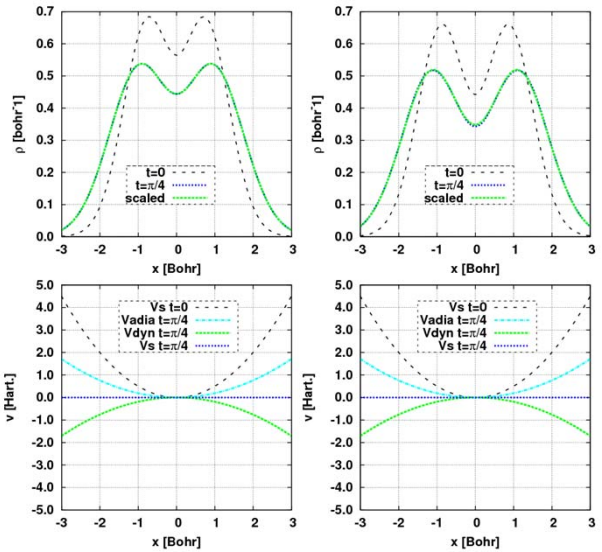
Time-Dependent Perturbation 2: Coulomb Explosion

- Model of an irradiation event
- Admits exact, scaling solution when λ=0
- Caveat about TDDFT as perturbation is not power expandable in time

$$\hat{H}_{TD-pert.} = \begin{cases} 0 & t \le 0 \\ -\frac{\omega^2}{2}\sum_{i=1}^{2} x_i^2 & t > 0 \end{cases}$$

$$n(x,t) = \frac{1}{\sqrt{1+\omega^2t^2}}\, n_0\left(\frac{x}{\sqrt{1+\omega^2t^2}}\right)$$

$$S(x,t) = \frac{\omega^2 x^2 t}{2(1+\omega^2t^2)}$$



Conclusions

- For two non-trivial 1D systems, the exact TD Kohn-Sham potential can be decomposed into adiabatic and dynamic contributions with ground-state theory providing the former and fluid-dynamic-like equations providing the latter.
- A Harmonic density expands, to a good approximation, according to a scaling formula even when interactions are present.
- If this decomposition hold more generally for non-harmonic external potentials and in 3D, a new universal constraint on the TD-KS wave-functions must hold, the spatially-varying phase on the KS orbitals must be the same for all occupied orbitals.
- This decomposition, if universally true, provides a route to new functionals by combining state-of-the-art ground-state functionals with approximations from fluid dynamics in a liner fashion.

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