PROPAGATORS FOR QUANTUM SYSTEMS

Martti Puska, Lasse Tunturivuori, and Risto Nieminen
Laboratory of Physics, Helsinki University of Technology, POBox 1100, FIN-02015 HUT, Finland
Antti-Pekka Jauho
MIC-DTU, Building 345east, DK2800 Kongens Lyngby, Denmark

The time-dependent density functional theory (TDDFT) of electron- structure calculations is an exact formulation of the time-dependent quantum mechanics in which the basic variable is the electron density ($n(\mathrm{r},t)$) instead of the many-body wave function [1]. All the complexity of the many-body interactions between the electrons is buried in the so-called exchange-correlation potential v_{xc} for which reasonably well working approximations exist. The strength of the TDDFT is that in contrast to the usual time-independent DFT also excited states of the electron system can be treated. In practice, one ends up with solving a set one-body equations, the so-called Kohn-Sham (KS) equations.

If the time-dependent external perturbation on the electron system is strong, for example, it is a femtosecond laser pulse, the true time evolution of the system has to be calculated by solving the time-dependent KS Schrödinger equation

$$i\partial_t \phi_i = \hat{H}\phi_i, \tag{1}$$

where the Hamiltonian

$$\hat{H} = -\frac{\nabla^2}{2} + v_{ext}(\mathrm{r},t) + \int d\mathrm{r}' \frac{n(\mathrm{r}',t)}{|\mathrm{r}-\mathrm{r}'|} + v_{xc}[n(\mathrm{r},t)] \tag{2}$$

is time-dependent. The electron density depends on the occupied states as

$$n(\mathrm{r},t) = \sum_i^{occ} |\phi_i(\mathrm{r},t)|^2 \tag{3}$$

making the problem non-linear. Within this formalism also the time-dependence of the ionic configuration can be described.

In this group work we are interested mainly in the mathematical methods to solve the time propagation of the wave function according to Eq. (1). Several schemes have been proposed and tested [2]. The task can be separated to two parts: (*i*) the propagation of the wave function when the Hamiltonian is time-independent and (*ii*) the approximation of the time-evolution operator $\hat{U}(t,0)$ when the Hamiltonian depends on time. The first task requires the evaluation $\exp(-i\delta t\hat{H})\phi(0)$. The exponential $\exp(-i\delta t\hat{H})$ of the matrix corresponding to the Hamiltonian can not be calculated directly because the typical size of the matrix is of the order of 10^5 or more. Therefore iterative methods yielding directly $\exp(-i\delta t\hat{H})\phi(0)$ are used. The methods include the polynomial expansions (e.g. the Chebyshev propagator [3]), projection in Krylov subspaces (Lanczos propagator), and the spit-operator techniques (the usual second order scheme and the the fourth order Suzuki-Trotter propagator [4]). The latter task (*ii*) is encountered always in the TDDFT calculations. The approximations include the midpoint rule and the so-called Magnus expansions.

Many of the mathematical methods mentioned above are implemented in the TDDFT code OCTOPUS [5]. We can eventually run some test cases and demonstrations during the workshop. However, the use of the above time propagation methods is not restricted to TDFT. They can be used even in the context of the propagation of many-body wave functions.

Bibliography

[1] M.A.L. Marques and E.K.U. Gross. Annu. Rev. Phys. Chem. **55**, 427 (2004).

[2] A. Castro, M.A.L. Marques, and A. Rubio, J. Chem. Phys. **121**, 3425 (2004).

[3] R. Chen and H. Guo, HPCERC technical report 1998-004.

[4] O. Sugino and Y. Miyamoto, Phys. Rev. B **59**, 2579 (1999); **66**, 89901(E) (2002).

[5] http://www.tddft.org/programs/octopus/download/1.4/octopus.ps

SOLVING OF GREEN'S FUNCTIONS TO THE QUANTUM TRANSPORT

One way to model transport properties of the nanostructures is to use the Green's function method combined with the density-functional theory. The method allows so-called open boundary conditions between the nanostructure and the lead, making the finite-size effects small. The problem of the Green's function method is that it is computationally demanding.

In order to calculate the self-consistent electron density we need to solve single-particle Green's retarded function from the equation

$$\left(\omega + \frac{1}{2}\nabla^2 - V_{\text{eff}}(\mathbf{r}, n(\mathbf{r}))\right) G^r(\mathbf{r}, \mathbf{r}'; \omega) = \delta(\mathbf{r} - \mathbf{r}'). \tag{1}$$

In the equilibrium the Fermi levels in the right and left leads are equal ($f_L(\omega) = f_r(\omega)$) and the Green's lesser function is calculated from

$$G^<(\mathbf{r}, \mathbf{r}'; \omega) = 2 f_{L/R}(\omega)\, G^r(\mathbf{r}, \mathbf{r}'; \omega). \tag{2}$$

The electron density is calculated by integrating over the electron energy, ω

$$n(\mathbf{r}) = \frac{-1}{2\pi} \int_{-\infty}^{\infty} \text{Im}(G^<(\mathbf{r}, \mathbf{r}; \omega))\, d\omega. \tag{3}$$

This integration path is moved to the complex plane in order to avoid sharp peaks in the density of states. Because V_{eff} depends on $n(\mathbf{r})$ the solution has to be calculated iteratively.

In Eq. (2) we are only interested in the Green's function terms with $\mathbf{r} = \mathbf{r}'$, $G^r(\mathbf{r}, \mathbf{r})$. Is there a way of calculate only this part of G^r? Or some kind of approximation? In the discrete form G^r is

$$G^r(\mathbf{r}, \mathbf{r}'; \omega) \approx \sum_{i,j=1}^{N} g_{ij}(\omega)\, \phi_i(\mathbf{r})\, \phi_j(\mathbf{r}'), \tag{4}$$

Where we see that the interesting elements of the coefficient matrix g_{ij} are those whose basis functions $\phi_i(\mathbf{r})$ and $\phi_j(\mathbf{r}')$ are overlapping.

Finally we write Eq. (1) in the variational form so that the open boundary conditions are visible. I.e.,

$$\begin{aligned} &\int_\Omega \Big\{ -\nabla v(\mathbf{r}) \cdot \frac{1}{2}\, \nabla G^r(\mathbf{r}, \mathbf{r}'; \omega) + v(\mathbf{r}) \big[\omega - V_{eff}(\mathbf{r})\big] G^r(\mathbf{r}, \mathbf{r}'; \omega) \Big\}\, d\mathbf{r} \\ &\quad - \langle \hat{\Sigma}_L G^r, v\rangle - \langle \hat{\Sigma}_R G^r, v\rangle = v(\mathbf{r}'), \end{aligned} \tag{5}$$

$$\begin{aligned} &\langle \hat{\Sigma}_{L/R} G^r, v\rangle = \\ &\int_{\partial\Omega_{L/R}} \int_{\partial\Omega_{L/R}} \frac{1}{4} G^r(\mathbf{r}'_{L/R}, \mathbf{r}'; \omega) \frac{\partial^2 g_e(\mathbf{r}_{L'/R'}, \mathbf{r}_{L/R}; \omega)}{\partial \mathbf{n}_{L/R} \partial \mathbf{n}_{L'/R'}}\, v(\mathbf{r}_{L/R})\, d\mathbf{r}_{L'/R'}\, d\mathbf{r}_{L/R}. \end{aligned} \tag{6}$$

where $v(\mathbf{r})$ is a sufficiently smooth function. g_e is the Green's function in the extarnal region (leads) and it have zero boundary condition in the boundary $\partial\Omega_{L/R}$.