Introduction to real-space, linear-response, and time-dependent methods

Heiko Appel

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

Outline

Linear Response in DFT

- Response functions
- Casida equation
- Sternheimer equation

Real-space representation and real-time propagation

- Real-space representation for wavefunctions and Hamiltonians
- Time-propagation schemes
- Optimal control of electronic motion

Time-evolution of open quantum systems

- Stochastic Schrödinger equations, master equations
- Stochastic current DFT
- Stochastic quantum molecular dynamics

Motivation

Where is electron dynamics important?

► Electron-hole pair creation in solar cells

► Photosynthesis and energy transfer in light-harvesting antenna complexes

► Quantum computing (e.g. electronic transitions in ultracold atoms)

► Molecular electronics, quantum transport

Time-dependent density-functional theory

- One-to-one correspondence of time-dependent densities and potentials

$$v(\mathbf{r}, t) \quad \overset{1-1}{\longleftrightarrow} \quad \rho(\mathbf{r}, t)$$

> For fixed inital states, the time-dependent density determines uniquely the time-dependent external potential and hence all physical observables.

- Time-dependent Kohn-Sham system
  The time-dependent density of an interacting many-electron system can be calculated as density

$$\rho(\mathbf{r}, t) = \sum_{j=1}^{N} |\varphi_j(\mathbf{r}, r)|^2$$

of an auxiliary non-interacting Kohn-Sham system

$$i\hbar \partial_t \varphi_j(\mathbf{r}, t) = \left(-\frac{\hbar^2 \nabla^2}{2m} + v_S[\rho](\mathbf{r}, t) \right) \varphi_j(\mathbf{r}, t)$$

with a local multiplicative potential

$$v_S[\rho(\mathbf{r}', t')](\mathbf{r}, t) = v(\mathbf{r}, t) + \int \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d^3 r' + v_{xc}[\rho(\mathbf{r}', t')](\mathbf{r}, t)$$

E. Runge, and E.K.U. Gross, Phys. Rev. Lett. **52**, 997 (1984).

Linear Response Theory

- Hamiltonian

$$\hat{H}(t) = \hat{H}_0 + \Theta(t - t_0)v_1(\mathbf{r}, t)$$

- Initial condition: for times $t < t_0$ the system is in the ground-state of the unperturbed Hamiltonian $\hat{H}_0$ with potential v_0 and density $\rho_0(\mathbf{r})$

- For times $t > t_0$, switch on perturbation $v_1(\mathbf{r}, t)$. Leads to time-dependent density $\rho(\mathbf{r}, t) = \rho_0(\mathbf{r}) + \delta\rho(\mathbf{r}t)$

- Functional Taylor expansion of $\rho[v](\mathbf{r}, t)$ around v_0:

$$\begin{aligned}
\rho[v](\mathbf{r}, t) &= \rho[v_0 + v_1](\mathbf{r}, t) \\
&= \rho[v_0](\mathbf{r}, t) \\
&+ \int \frac{\delta\rho[v](\mathbf{r}t)}{\delta v(\mathbf{r}'t')}\Big|_{v_0} v_1(\mathbf{r}'t')d^3r'dt' \\
&+ \int\int \frac{\delta^2\rho[v](\mathbf{r}t)}{\delta v(\mathbf{r}'t')\delta v(\mathbf{r}''t'')}\Big|_{v_0} v_1(\mathbf{r}'t')v_1(\mathbf{r}''t'')d^3r'dt'd^3r''dt'' \\
&+ \dots
\end{aligned}$$

Computing Linear Response

Different ways to compute first order response in DFT

- ▶ Response functions, Casida equation

- ▶ (frequency-dependent) perturbation theory, Sternheimer equation

- ▶ real-time propagation with weak external perturbation

Response functions

- Functional Taylor expansion of $\rho[v](\mathbf{r}, t)$ around external potential v_0:

$$\rho[v_0 + v_1](\mathbf{r}, t) = \rho[v_0](\mathbf{r}) + \int \frac{\delta\rho[v](\mathbf{r}t)}{\delta v(\mathbf{r}'t')}\Big|_{v_0} v_1(\mathbf{r}'t')d^3r'dt' + \ldots$$

- Density-density response function of interacting system

$$\chi(\mathbf{r}t, \mathbf{r}'t') := \frac{\delta\rho[v](\mathbf{r}t)}{\delta v(\mathbf{r}'t')}\Big|_{v_0}$$

- Response of non-interacting Kohn-Sham system:

$$\rho[v_{S,0} + v_{S,1}](\mathbf{r}, t) = \rho[v_{S,0}](\mathbf{r}) + \int \frac{\delta\rho[v_S](\mathbf{r}t)}{\delta v_S(\mathbf{r}'t')}\Big|_{v_0} v_S(\mathbf{r}'t')d^3r'dt' + \ldots$$

- Density-density response function of time-dependent Kohn-Sham system

$$\chi_S(\mathbf{r}t, \mathbf{r}'t') := \frac{\delta\rho_S[v_S](\mathbf{r}t)}{\delta v_S(\mathbf{r}'t')}\Big|_{v_{S,0}}$$

Derivation of response equation

- Definition of time-dependent xc potential

$$v_{xc}(\mathbf{r}t) = v_{KS}(\mathbf{r}t) - v_{ext}(\mathbf{r}t) - v_H(\mathbf{r}t)$$

- Take functional derivative

$$\frac{\delta v_{xc}(\mathbf{r}t)}{\delta \rho(\mathbf{r}'t')} = \frac{\delta v_{KS}(\mathbf{r}t)}{\delta \rho(\mathbf{r}'t')} - \frac{\delta v_{ext}(\mathbf{r}t)}{\delta \rho(\mathbf{r}'t')} - \frac{\delta(t-t')}{|\mathbf{r}-\mathbf{r}'|}$$

$$f_{xc}(\mathbf{r}t,\mathbf{r}'t') = \chi_S^{-1}(\mathbf{r}t,\mathbf{r}'t') - \chi^{-1}(\mathbf{r}t,\mathbf{r}'t') - W_c(\mathbf{r}t,\mathbf{r}'t')$$

- Act with reponse functions from left and right

$$\chi_S \cdot \quad | \quad W_c + f_{xc} = \chi_S^{-1} - \chi^{-1} \quad | \quad \cdot \chi$$

$$\chi_S(W_c + f_{xc})\chi = \chi - \chi_S$$

- Dyson-type equation for response functions

$$\chi = \chi_S + \chi_S(W_c + f_{xc})\chi$$

First order density response

- Exact density response to first order

$$\rho_1 = \chi v_1$$
$$= \chi_S v_1 + \chi_S (W_c + f_{xc})\rho_1$$

- In integral notation

$$\rho_1(\mathbf{r}t) = \int d^3r' dt' \chi_S(\mathbf{r}t, \mathbf{r}'t') \Big[v_1(\mathbf{r}'t')$$
$$+ \int d^3r'' dt'' (W_c(\mathbf{r}'t', \mathbf{r}''t'') + f_{xc}(\mathbf{r}'t', \mathbf{r}''t''))\rho_1(\mathbf{r}''t'') \Big]$$

- For practical application: iterative solution with approximate kernel f_{xc}

$$f_{xc}(\mathbf{r}'t', \mathbf{r}''t'') = \frac{\delta v_{xc}[\rho](\mathbf{r}'t')}{\delta\rho(\mathbf{r}''t'')}\Big|_{\rho_0}$$

Lehmann representation of linear response function

▶ Exact many-body eigenstates

$$\hat{H}(t = t_0)|m\rangle = E_m|m\rangle$$

▶ Lehmann representation of linear response function:

$$\chi(\mathbf{r}, \mathbf{r}'; \omega) = \lim_{\eta \to 0^+} \sum_m \left(\frac{\langle 0|\hat{\rho}(\mathbf{r})|m\rangle\langle m|\hat{\rho}(\mathbf{r})|0\rangle}{\omega - (E_m - E_0) + i\eta} - \frac{\langle 0|\hat{\rho}(\mathbf{r}')|m\rangle\langle m|\hat{\rho}(\mathbf{r}')|0\rangle}{\omega + (E_m - E_0) + i\eta} \right)$$

Neutral excitation energies are poles of the linear response function!

▶ Exact linear density response to perturbation $v_1(\omega)$

$$\rho_1(\omega) = \hat{\chi}(\omega)v_1(\omega)$$

Excitation energies

- Dyson-type equation for response functions in frequency space

$$[\hat{1} - \hat{\chi}_S(\omega)(\hat{W}_c + \hat{f}_{xc}(\omega))]\rho_1(\omega) = \chi_S v_1(\omega)$$

- $\rho_1(\omega)$ has poles for exact excitation energies Ω_j

$$\rho_1(\omega) \to \infty \quad \text{for} \quad \omega \to \Omega_j$$

- On the other hand, rhs $\chi_S v_1(\omega)$ stays finite for $\omega \to \Omega_j$ hence the eigenvalues of the integral operator

$$[\hat{1} - \hat{\chi}_S(\omega)(\hat{W}_c + \hat{f}_{xc}(\omega))]\xi(\omega) = \lambda(\omega)\xi(\omega)$$

vanish, $\lambda(\omega) \to 0$ for $\omega \to \Omega_j$.

- Determines rigorously the exact excitation energies

$$[\hat{1} - \hat{\chi}_S(\Omega_j)(\hat{W}_c + \hat{f}_{xc}(\Omega_j))]\xi(\Omega_j) = 0$$

Casida equation

- (Non-linear) eigenvalue equation for excitation energies

$$\Omega \mathbf{F}_j = \omega_j^2 \mathbf{F}_j$$

with

$$\Omega_{ia\sigma,jb\tau} = \delta_{\sigma,\tau}\delta_{i,j}\delta_{a,b}(\epsilon_a - \epsilon_i)^2 + 2\sqrt{(\epsilon_a - \epsilon_i)}K_{ia\sigma,jb\tau}\sqrt{(\epsilon_b - \epsilon_j)}$$

and

$$K_{ia\sigma,jb\tau}(\omega) = \int d^3r \int d^3r' \phi_{i\sigma}(\mathbf{r})\phi_{j\sigma}(\mathbf{r})\Big[\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}(\mathbf{r}, \mathbf{r}', \omega)\Big]\phi_{k\tau}(\mathbf{r})\phi_{l\tau}(\mathbf{r})$$

- Eigenvalues ω_j are exact vertical excitation energies
- Eigenvectors can be used to compute oscillator strength
- Drawback: need occupied and unoccupied orbitals

Adiabatic approximation

- Adiabatic approximation: evaluate static Kohn-Sham potential at time-dependent density

$$v_{xc}^{\text{adiab}}[\rho](rt) := v_{xc}^{\text{static DFT}}[\rho(t)](rt)$$

- Example: adiabatic LDA

$$v_{xc}^{\text{ALDA}}[\rho](rt) := v_{xc}^{\text{LDA}}(\rho(t)) = -\alpha\rho(\mathbf{r}, t)^{1/3} + \ldots$$

- Exchange-correlation kernel

$$f_{xc}^{\text{ALDA}}(\mathbf{r}t, \mathbf{r}'t') = \frac{\delta v_{xc}^{\text{ALDA}}[\rho](rt)}{\delta\rho(\mathbf{r}'t')} = \delta(t - t')\delta(\mathbf{r} - \mathbf{r}')\frac{\partial v_{xc}^{\text{ALDA}}}{\partial\rho(\mathbf{r})}\Big|_{\rho_0(\mathbf{r})}$$

$$= \delta(t - t')\delta(\mathbf{r} - \mathbf{r}')\frac{\partial^2 e_{xc}^{hom}}{\partial n^2}\Big|_{\rho_0(\mathbf{r})}$$

Failures of the adiabatic approximation in linear response

- H_2 dissociation is incorrect

$$E(^1\Sigma_u^+) - E(^1\Sigma_g^+) \overset{R \to \infty}{\longrightarrow} 0 \qquad \text{(in ALDA)}$$

  Gritsenko, van Gisbergen, Grling, Baerends, JCP 113, 8478 (2000).

- sometimes problematic close to conical intersections

- response of long chains strongly overestimated
  Champagne et al., JCP 109, 10489 (1998) and 110, 11664 (1999).

- in periodic solids $f_{xc}(q, \omega, \rho) = c(\rho)$, whereas for insulators, $f_{xc}^{exact} \overset{q \to 0}{\longrightarrow} 1/q^2$ divergent

- charge transfer excitations not properly described
  Dreuw et al., JCP 119, 2943 (2003).

Sternheimer equation

On Nuclear Quadrupole Moments

R. STERNHEIMER
Los Alamos Scientific Laboratory, Los Alamos, New Mexico, and Brookhaven National Laboratory, Upton, New York*
(Received June 18, 1951)

units. If E_0 denotes the unperturbed $1s$ energy, the Schroedinger equation becomes

$$(H_0 + H_1)(u_0 + u_1) = E_0(u_0 + u_1), \qquad (3)$$

since the first-order perturbation of the energy is zero for s states. Upon subtracting $H_0 u_0 = E_0 u_0$, and to the first order in Q, we obtain

$$(H_0 - E_0)u_1 = -H_1 u_0. \qquad (4)$$

Sternheimer equation

- Perturbed Hamiltonian and states (zero frequency)

$$(\hat{H}_0 + \lambda H_1 + \ldots)(\psi_0 + \lambda \psi_1 + \ldots) = (E_0 + \lambda E_1 + \ldots)(\psi_0 + \lambda \psi_1 + \ldots)$$

- Expand and keep terms to first order in λ

$$\hat{H}_0 \psi_0 + \lambda H_1 \psi_0 + \lambda H_0 \psi_1 = E_0 \psi_0 + \lambda E_0 \psi_1 + \lambda E_1 \psi_0 + \mathcal{O}(\lambda^2)$$

- Use $\hat{H}_0 \psi_0 = E_0 \psi_0$

$$(\hat{H}_0 - E_0)\psi_1 = -(\hat{H}_1 - E_1)\psi_0, \qquad \text{Sternheimer equation}$$

Sternheimer equation in TDDFT

- (Weak) monochromatic perturbation

$$v_1(\mathbf{r}, t) = \lambda r_i \cos(\omega t)$$

- Expand time-dependent Kohn-Sham wavefunctions in powers of λ

$$\psi_m(\mathbf{r}, t) = \exp(-i(\epsilon_m^{(0)} + \lambda \epsilon_m^{(1)})t) \times$$
$$\left\{ \psi_m^{(0)}(\mathbf{r}) + \frac{1}{2}\lambda[\exp(i\omega t)\psi_m^{(1)}(\mathbf{r}, \omega) + \exp(-i\omega t)\psi_m^{(1)}(\mathbf{r}, -\omega)] \right\}$$

- Insert in time-dependent Kohn-Sham equation and keep terms up to first order in λ

Sternheimer equation in DFT

▶ Frequency-dependent response (self-consistent solution!)

$$\left[\hat{H}^{(0)} - \epsilon_j \pm \omega + i\eta\right]\psi^{(1)}(\mathbf{r}, \pm\omega) = \hat{H}^{(1)}(\pm\omega)\psi^{(0)}(\mathbf{r}),$$

with first-oder frequency-dependent perturbation

$$\hat{H}^{(1)}(\omega) = v(\mathbf{r}) + \int \frac{\rho_1(\mathbf{r}, \omega)}{|\mathbf{r} - \mathbf{r}'|} d^3r' + \int f_{xc}(\mathbf{r}, \mathbf{r}', \omega)\rho_1(\mathbf{r}', \omega) d^3r'$$

and first-order density response

$$\rho_1(\mathbf{r}', \pm\omega) = \sum_m^{\text{occ.}} \left\{ [\psi^{(0)}(\mathbf{r})]^*\psi^{(1)}(\mathbf{r}, \omega) + [\psi^{(1)}(\mathbf{r}, -\omega)]^*\psi^{(0)}(\mathbf{r}) \right\}$$

▶ Main advantages
  ▶ Only occupied states need to be considered
  ▶ Scales as N^2, where N is the number of atoms
  ▶ (Non-)Linear system of equations. Can be solved with standard solvers
▶ Disadvantage
  ▶ Converges slowly close to a resonance

Different types of perturbations

The response equations can be used for different types of perturbations

- ▶ Electric perturbations

$$v(\mathbf{r}) = \mathbf{r}_i$$

  Response contains information about polarizabilities, absorption, fluoresence, etc.
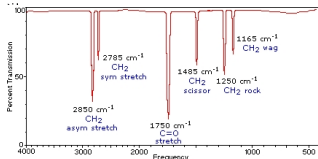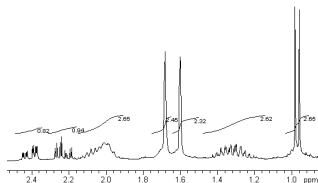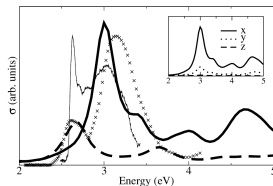
- ▶ Magnetic perturbations

$$v(\mathbf{r}) = \mathbf{L}_i$$

  Response contains e.g. NMR signals, etc.

- ▶ Atomic displacements

$$v(\mathbf{r}) = \frac{\partial v(\mathbf{r})}{\partial \mathbf{R}_i}$$

  Response contains e.g. phonons, etc.

Outline

Real-space grids

- Simulation volumes: sphere, cylinder, parallelepiped
- Minimal mesh: spheres around atoms, filled with uniform mesh of grid points
- Typically zero boundary condition, absorbing boundary, optical potential
- Finite-difference representation ("stencils") for the Laplacian/kinetic energy
- Pseudopotentials
- Domain-parallelization
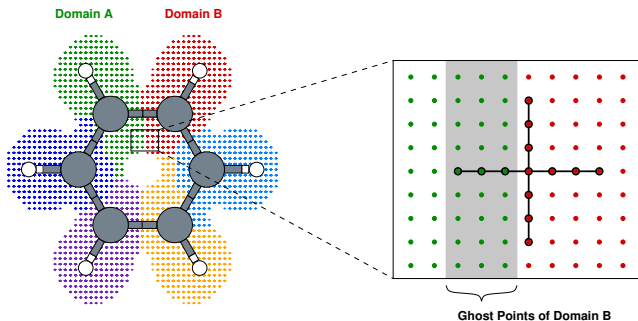
Real-space grids

- Example: five-point finite difference Laplacian in 2D

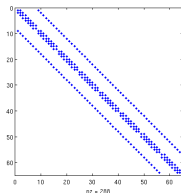$$-\frac{1}{2m}\frac{\partial^2 \psi}{\partial x^2} \approx \frac{1}{2m}\frac{1}{h^2}\Big[-\psi(i-1,j) + 2\psi(i,j) - \psi(i+1,j)\Big]$$

$$-\frac{1}{2m}\frac{\partial^2 \psi}{\partial y^2} \approx \frac{1}{2m}\frac{1}{h^2}\Big[-\psi(i,j-1) + 2\psi(i,j) - \psi(i,j+1)\Big]$$

- Stencil notation for kinetic energy

$$\frac{1}{2m}\frac{1}{h^2}\begin{pmatrix} & -1 & \\ -1 & 4 & -1 \\ & -1 & \end{pmatrix}\psi(i,j)$$

- Leads to sparse matrices

Real-space grids

- Size of Hamiltonian matrix can easily reach $10^7 \times 10^7$

- Basic operation $\hat{H}\psi \longrightarrow$ sparse matrix vector operations

- Sparse solvers
  - Conjugate gradients
  - Krylov subspace/Lanczos methods
  - Davidson or Jacobi-Davidson algorithm
  - Multigrid methods

Real-time evolution for the time-dependent Kohn-Sham system

► Time-dependent Kohn-Sham equations

$$i\hbar\partial_t\varphi_j(\mathbf{r},t) = \left(-\frac{\hbar^2\nabla^2}{2m} + v_S[\rho](\mathbf{r},t)\right)\varphi_j(\mathbf{r},t)$$

$$v_S[\rho(\mathbf{r}',t')](\mathbf{r},t) = v(\mathbf{r},t) + \int\frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d^3r' + v_{xc}[\rho(\mathbf{r}',t')](\mathbf{r},t)$$

$$\rho(\mathbf{r},t) = \sum_{j=1}^{N}|\varphi_j(\mathbf{r},r)|^2$$

► Initial value problem

$$\varphi_j(\mathbf{r},t) = \varphi_j^{(0)}(\mathbf{r})$$

► Time-evolution operator $\hat{U}(t,t_0)$

$$\varphi_j(\mathbf{r},t) = \hat{U}(t,t_0)\varphi_j(\mathbf{r},t_0)$$

Properties of $\hat{U}(t, t_0)$

- $\hat{U}(t, t_0)$ is a non-linear operator
- The propagator is unitary $\hat{U}^\dagger = \hat{U}^{-1}$
- In the absence of magnetic fields the propagator is time-reversal symmetric

$$\hat{U}^{-1}(t, t_0) = \hat{U}(t_0, t)$$

- Equation of motion for the propagator

$$i\hbar\partial_t\hat{U}(t, t_0) = \hat{H}(t)\hat{U}(t, t_0), \qquad \hat{U}(t_0, t_0) = \hat{1}$$

- Representation in integral form

$$\hat{U}(t, t_0) = \hat{1} - i\int_{t_0}^{t} d\tau \hat{H}(\tau)\hat{U}(\tau, t_0)$$

- Iterated solution of integral equation - time-ordered exponential

$$\hat{U}(t, t_0) = \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \ldots \int_{t_0}^{t} dt_n \hat{T}[\hat{H}(t_1)\hat{H}(t_2)\ldots\hat{H}(t_n)]$$

$$= \hat{T}\exp(-i\int_{t_0}^{t} d\tau \hat{H}(\tau))$$

Real-time evolution - Short-time propagation

- Group property of exact propagator

$$\hat{U}(t_1, t_2) = \hat{U}(t_1, t_3)\hat{U}(t_3, t_2)$$

- Split propagation step in small short-time propagation intervals

$$\hat{U}(t, t_0) = \prod_{j=1}^{N-1} \hat{U}(t_j, t_j + \Delta t_j)$$

- Why is this a good idea?
    - If we want to resolve frequencies up to $\omega_{\max}$, the time-step should be no larger than $\approx 1/\omega_{\max}$
    - The time-dependence of the Hamiltonian is small over a short-time interval
    - The norm of the time-ordered exponential is proportional to Δt.

Real-time evolution - Magnus expansion

► Time-ordered evolution operator

$$\hat{U}(t, t_0) = \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \ldots \int_{t_0}^{t} dt_n \hat{T}[\hat{H}(t_1)\hat{H}(t_2)\ldots\hat{H}(t_n)]$$

$$= \hat{T} \exp(-i \int_{t_0}^{t} d\tau \hat{H}(\tau))$$

► Magnus expansion

$$\hat{U}(t + \Delta t, t) = \exp\left(\hat{\Omega}_1 + \hat{\Omega}_2 + \hat{\Omega}_3 + \cdots\right)$$

► Magnus operators

$$\hat{\Omega}_1 = -i \int_t^{t+\Delta t} \hat{H}(\tau)d\tau$$

$$\hat{\Omega}_2 = \int_t^{t+\Delta t} \int_t^{\tau_1} [\hat{H}(\tau_1), \hat{H}(\tau_2)]d\tau_2 d\tau_1$$

$$\vdots$$

Real-time evolution - Magnus expansion

- Second-order Magnus propagator - Exponential midpoint rule

$$\hat{U}^{(2)}(t + \Delta t, t) = \exp\left(\hat{\Omega}_1\right) + O(\Delta t^3)$$
$$\hat{\Omega}_1 = -i\hat{H}(t + \Delta t/2) + O(\Delta t^3).$$

- Fourth-order Magnus propagator

$$\hat{U}^{(4)}(t + \Delta t, t) = \exp\left(\hat{\Omega}_1 + \Omega_2\right) + O(\Delta t^5)$$
$$\hat{\Omega}_1 = -i(\hat{H}(\tau_1) + \hat{H}(\tau_2))\frac{\Delta t}{2} + O(\Delta t^5).$$
$$\hat{\Omega}_2 = -i[\hat{H}(\tau_1), \hat{H}(\tau_2)]\frac{\sqrt{3}\Delta t^2}{12} + O(\Delta t^5).$$
$$\tau_{1,2} = t + (\frac{1}{2} \pm \frac{\sqrt{3}}{6})\Delta t$$

Real-time evolution - Crank-Nicholson/Cayley propagator

- Padé approximation of exponential, e.g. lowest order (Crank-Nicholson)

$$\exp(-i\hat{H}\Delta t) \approx \frac{1 - i\hat{H}\Delta t/2}{1 + i\hat{H}\Delta t/2}$$

- Need only action of operator on a state vector

$$|\Psi(t + \Delta t)\rangle = \frac{1 - i\hat{H}\Delta t/2}{1 + i\hat{H}\Delta t/2}|\Psi(t)\rangle$$

- (Non-)Linear system of equations at each time-step

$$(1 + i\hat{H}\Delta t/2)|\Psi(t + \Delta t)\rangle = (1 - i\hat{H}\Delta t/2)|\Psi(t)\rangle$$

Real-time evolution - Operator splitting methods

- Typically, the Hamiltonian has the form $\hat{H} = \hat{T} + \hat{V}$

- $\hat{T}$ is diagonal in momentum space, $\hat{V}$ in position space

- Baker-Campbell-Hausdorff relation

$$e^{\hat{A}} e^{\hat{B}} = \exp(\hat{A} + \hat{B} + \frac{1}{2}[\hat{A}, \hat{B}] + \ldots)$$

- Split-Operator

$$\exp(-i\Delta t(\hat{T} + \hat{V})) \approx \exp(-i\Delta t\hat{T}/2) \exp(-i\Delta t\hat{V}) \exp(-i\Delta t\hat{T}/2)$$

Use FFT to switch between momentum space and real-space.

- Higher-order splittings possible, but require more FFTs

Real-time evolution - Enforced time reversal symmetry

- Enforced time-reversal symmetry

$$\exp(+i\frac{\Delta t}{2}\hat{H}(t+\Delta t))|\Psi(t+\Delta t)\rangle = \exp(-i\frac{\Delta t}{2}\hat{H}(t))|\Psi(t)\rangle$$

- Propagator with time-reversal symmetry

$$\hat{U}^{\mathrm{ETRS}}(t+\Delta t,t) = \exp(-i\frac{\Delta t}{2}\hat{H}(t+\Delta t))\exp(-i\frac{\Delta t}{2}\hat{H}(t))$$

Real-time evolution - Matrix exponential

$$\hat{U}^{\mathrm{CN}}(t + \Delta t, t) = \frac{1 - i\hat{H}\Delta t/2}{1 + i\hat{H}\Delta t/2}$$

$$\hat{U}^{\mathrm{EM}}(t + \Delta t, t) = \exp\left(-i\Delta t\hat{H}(t + \Delta t/2)\right)$$

$$\hat{U}^{\mathrm{SO}}(t + \Delta t, t) = \exp(-i\Delta t\hat{T}/2)\exp(-i\Delta t\hat{V})\exp(-i\Delta t\hat{T}/2)$$

$$\hat{U}^{\mathrm{ETRS}}(t + \Delta t, t) = \exp(-i\frac{\Delta t}{2}\hat{H}(t + \Delta t))\exp(-i\frac{\Delta t}{2}\hat{H}(t))$$

$$\cdots$$

Real-time evolution - Matrix exponential

$$\hat{U}^{\text{CN}}(t + \Delta t, t) = \frac{1 - i\hat{H}\Delta t/2}{1 + i\hat{H}\Delta t/2}$$

$$\hat{U}^{\text{EM}}(t + \Delta t, t) = \exp\left(-i\Delta t\hat{H}(t + \Delta t/2)\right)$$

$$\hat{U}^{\text{SO}}(t + \Delta t, t) = \exp(-i\Delta t\hat{T}/2)\exp(-i\Delta t\hat{V})\exp(-i\Delta t\hat{T}/2)$$

$$\hat{U}^{\text{ETRS}}(t + \Delta t, t) = \exp(-i\frac{\Delta t}{2}\hat{H}(t + \Delta t))\exp(-i\frac{\Delta t}{2}\hat{H}(t))$$

$$\cdots$$

Real-time evolution - Matrix exponential

C. Moler and C. Van Loan, Nineteen Dubious Ways to Compute the Exponential of A Matrix, SIAM Review 20, 801 (1978)

C. Moler and C. Van Loan, Nineteen Dubious Ways to Compute the Exponential of A Matrix,
Twenty-Five Years Later, SIAM Review 45, 3 (2003)

Task: Compute exponential of operator/matrix

- ▶ Taylor series
- ▶ Chebyshev polynomials
- ▶ Padé approximations
- ▶ Scaling and squaring
- ▶ Ordinary differential equation methods
- ▶ Matrix decomposition methods
- ▶ Splitting methods

Task: Compute $e^{\hat{A}}v$ for given v

- ▶ Taylor series
- ▶ Chebyshev rational approximation
- ▶ Lanczos-Krylov subspace projection

Real-time evolution - Conclusion

So, which method should I use?

- No clear winner
- Depends on spectral properties of Hamiltonian ...
- ... and the basis set or discretization
- Symplectic and/or time-reversal property required?

Default propagator in octopus:

Enforced time-reversal symmetric (ETRS) propagator with 4th order Taylor expansion of exponential

Do not rely on a single propagator.
Always check time-evolution by comparing different schemes!

Real-time evolution - Movie time

Proton scattering of fast proton with ethene

Octopus code

- ▶ Octopus: real-space, real-time TDDFT code, available under GPL

    http://tddft.org/programs/octopus/wiki/index.php/Main_Page

    (Parsec: real-space, real-time code using similar concepts)

- ▶ libxc: Exchange-Correlation library, available under LGPL
  (used by many codes: Abinit, APE, AtomPAW, Atomistix ToolKit, BigDFT, DP,
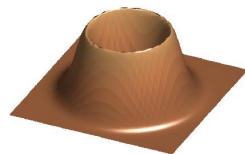 ERKALE, GPAW, Elk, exciting, octopus, Yambo)

    http://tddft.org/programs/octopus/wiki/index.php/Libxc

Optimal control theory

Control of ring current in a quantum ring
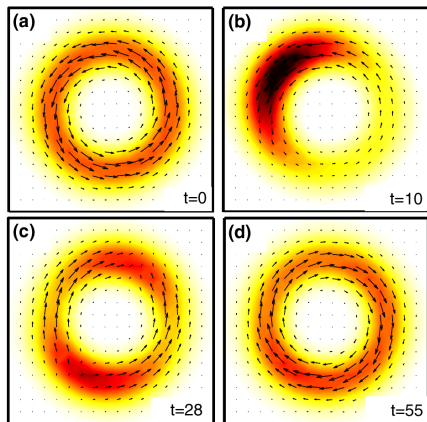
external potential

density profile

Optimal Control of Quantum Rings by Terahertz Laser Pulses, E. Räsänen, et. al, Phys. Rev. Lett. 98, 157404 (2007).

Optimal control theory

Goal: find optimal laser pulse $\epsilon(t)$ that drives the system to a desired state Φ_f

- maxize overlap functional

$$J_1[\Psi] = |\langle\, \Psi(T)\, |\, \Phi_f\, \rangle|^2.$$

- constrain laser intensity

$$J_2[\epsilon] = -\alpha_0 \int_0^T \epsilon^2(t)\, dt.$$

- Lagrange multiplier density to ensure evolution with TDSE

$$J_3[\Psi,\chi,\epsilon] = -2\,\mathsf{Im} \int_0^T \left\langle \chi(t)\, \left|\, \left(\mathrm{i}\partial_t - \hat{H}(t)\right)\right|\, \Psi(t)\right\rangle\, dt,$$

Find maximum of $J_1[\Psi] + J_2[\epsilon] + J_3[\Psi,\chi,\epsilon]$

Optimal control theory

- First variation of the functional

$$\delta J = \delta_\Psi J + \delta_\chi J + \delta_\epsilon J = 0$$

- Control equations

$$\delta_\Psi J = 0 \quad : \quad \left(i\partial_t - \hat{H}(t)\right)|\chi(t)\rangle = 0, \qquad |\chi(T)\rangle = |\Phi_f\rangle\langle\Phi_f|\Psi(T)\rangle$$
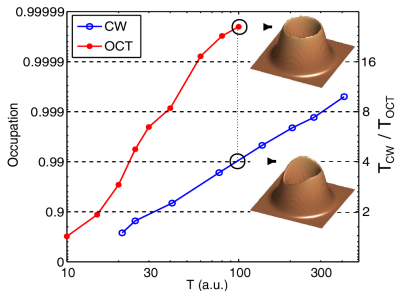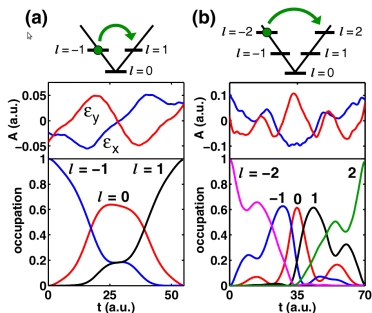
$$\delta_\chi J = 0 \quad : \quad \left(i\partial_t - \hat{H}(t)\right)|\Psi(t)\rangle = 0, \qquad |\Psi(0)\rangle = |\Phi_i\rangle,$$

$$\delta_\epsilon J = 0 \quad : \quad \alpha_0\,\epsilon(t) = -\mathsf{Im}\,\langle\chi(t)|\hat{\mu}|\Psi(t)\rangle.$$

Optimal control theory

Optimal laser pulse and level population

Optimal Control of Quantum Rings by Terahertz Laser Pulses, E. Räsänen, et. al, Phys. Rev. Lett. 98, 157404 (2007).

Outline

Linear Response in DFT

- ▶ Response functions

- ▶ Casida equation

- ▶ Sternheimer equation

Real-space representation and real-time propagation

- ▶ Real-space representation for wavefunctions and Hamiltonians

- ▶ Time-propagation schemes

- ▶ Optimal control of electronic motion

Time-evolution of open quantum systems

- ▶ Stochastic Schrödinger equations, master equations

- ▶ Stochastic current DFT

- ▶ Stochastic quantum molecular dynamics
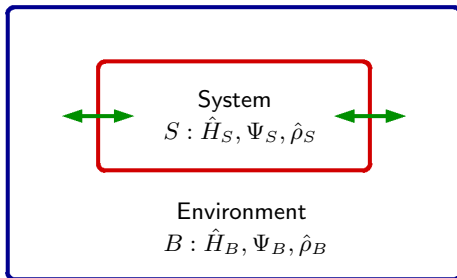
Why Open Quantum Systems?

General aspects:

- Cannot have perfectly isolated quantum systems

- Dissipation and Decoherence

- Every measurement implies contact with an environment
  One actually needs to bring a system into contact with an environment (i.e. measurement apparatus), in order to perform a measurement
  $\rightarrow$ environment as (continuos) measurement of the system.

Research fields:

- Quantum computing/Quantum information theory

- (time-resolved) transport and optics

- (driven) quantum phase transitions

- Quantum measurement

Open Quantum System

$$S + B : \hat{H}_S \otimes H_B, \Psi, \hat{\rho}$$

System
$S : \hat{H}_S, \Psi_S, \hat{\rho}_S$
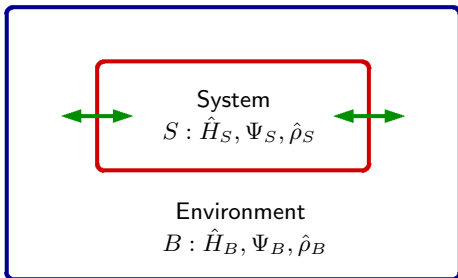
Environment
$B : \hat{H}_B, \Psi_B, \hat{\rho}_B$

Hamiltonian of combined system

$$\hat{H} = \hat{H}_S \otimes \hat{I}_B + \hat{I}_S \otimes \hat{H}_B + \hat{H}_{SB}$$

Open Quantum System

$$S + B : \hat{H}_S \otimes H_B, \Psi, \hat{\rho}$$
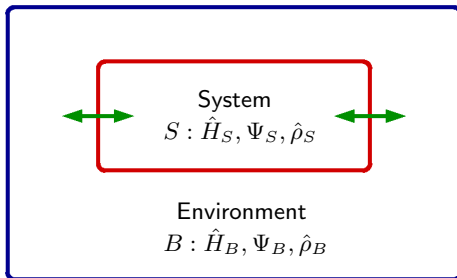

Hamiltonian of combined system

$$\hat{H} = \hat{H}_S \otimes \hat{I}_B + \hat{I}_S \otimes \hat{H}_B + \hat{H}_{SB}$$

Unitary time evolution

$$i\partial_t \Psi(t) = \hat{H}(t)\Psi(t) \qquad \frac{d}{dt}\hat{\rho}(t) = -i\left[\hat{H}(t), \hat{\rho}(t)\right]$$

Reduced system dynamics

$$S + B : \hat{H}_S \otimes H_B, \Psi, \hat{\rho}$$

System
$S : \hat{H}_S, \Psi_S, \hat{\rho}_S$

Environment
$B : \hat{H}_B, \Psi_B, \hat{\rho}_B$

Tracing over bath degrees of freedom

$$\hat{\rho}_S = \mathsf{Tr}_B \hat{\rho}$$

$$\frac{d}{dt} \hat{\rho}_S(t) = -i \mathsf{Tr}_B \left[\hat{H}(t), \hat{\rho}(t) \right]$$

Feshbach Projection-Operator Method

$$\hat{H} = \hat{H}_S + \hat{H}_B + \alpha\hat{H}_{SB}, \qquad H_B\chi_n(x_B) = \varepsilon_n\chi_n(x_B)$$

Feshbach Projection-Operator Method

$$\hat{H} = \hat{H}_S + \hat{H}_B + \alpha\hat{H}_{SB}, \qquad H_B\chi_n(x_B) = \varepsilon_n\chi_n(x_B)$$

Expand total wavefunction in arbitrary complete and orthonormal basis of the bath

$$\Psi(x_S, x_B; t) = \sum_n \phi_n(x_S; t)\chi_n(x_B)$$

Feshbach Projection-Operator Method

$$\hat{H} = \hat{H}_S + \hat{H}_B + \alpha\hat{H}_{SB}, \qquad H_B\chi_n(x_B) = \varepsilon_n\chi_n(x_B)$$

Expand total wavefunction in arbitrary complete and orthonormal basis of the bath

$$\Psi(x_S, x_B; t) = \sum_n \phi_n(x_S; t)\chi_n(x_B)$$

Projection Operators

$$\hat{P}_n := \hat{I}_S \otimes |\chi_n\rangle\langle\chi_n| \qquad \hat{Q}_n := \hat{I}_S \otimes \sum_{j \neq n} |\chi_j\rangle\langle\chi_j|$$

Feshbach Projection-Operator Method

$$\hat{H} = \hat{H}_S + \hat{H}_B + \alpha\hat{H}_{SB}, \qquad H_B\chi_n(x_B) = \varepsilon_n\chi_n(x_B)$$

Expand total wavefunction in arbitrary complete and orthonormal basis of the bath

$$\Psi(x_S, x_B; t) = \sum_n \phi_n(x_S; t)\chi_n(x_B)$$

Projection Operators

$$\hat{P}_n := \hat{I}_S \otimes |\chi_n\rangle\langle\chi_n| \qquad \hat{Q}_n := \hat{I}_S \otimes \sum_{j \neq n} |\chi_j\rangle\langle\chi_j|$$

Apply to TDSE

$$i\partial_t \hat{P}_n\Psi(t) = \hat{P}_n\hat{H}\hat{P}_n\Psi(t) + \hat{P}_n\hat{H}\hat{Q}_n\Psi(t)$$

$$i\partial_t \hat{Q}_n\Psi(t) = \hat{Q}_n\hat{H}\hat{Q}_n\Psi(t) + \hat{Q}_n\hat{H}\hat{P}_n\Psi(t)$$

P. Gaspard, M. Nagaoka, JCP, **111**, 5675 (1999).

Feshbach Projection-Operator Method

Effective equation for $\hat{P}\Psi$ (still fully coherent)

$$
i\partial_t \hat{P}\Psi(t) = (\hat{P}\hat{H}\hat{P})\hat{P}\Psi(t) + \overbrace{\hat{P}\hat{H}\hat{Q}e^{-i\hat{Q}\hat{H}\hat{Q}t}\hat{Q}\Psi(0)}^{\text{Source Term}}
$$

$$
\underbrace{-i\int_0^t d\tau\, \hat{P}\hat{H}\hat{Q}e^{i\hat{Q}\hat{H}\hat{Q}(t-\tau)}\hat{Q}\hat{H}\hat{P}\hat{P}\Psi(\tau)}_{\text{Memory Term}}
$$

Feshbach Projection-Operator Method

Effective equation for $\hat{P}\Psi$ (still fully coherent)

$$
i\partial_t \hat{P}\Psi(t) = (\hat{P}\hat{H}\hat{P})\hat{P}\Psi(t) + \overbrace{\hat{P}\hat{H}\hat{Q}e^{-i\hat{Q}\hat{H}\hat{Q}t}\hat{Q}\Psi(0)}^{\text{Source Term}}
$$

$$
\underbrace{-i\int_0^t d\tau \hat{P}\hat{H}\hat{Q}e^{i\hat{Q}\hat{H}\hat{Q}(t-\tau)}\hat{Q}\hat{H}\hat{P}\hat{P}\Psi(\tau)}_{\text{Memory Term}}
$$

$\Longrightarrow$ Formal similarity to quantum transport formulation of Kurth and Stefanucci et. al.

Feshbach Projection-Operator Method

Effective equation for $\hat{P}\Psi$ (still fully coherent)

$$i\partial_t \hat{P}\Psi(t) = (\hat{P}\hat{H}\hat{P})\hat{P}\Psi(t) + \overbrace{\hat{P}\hat{H}\hat{Q}e^{-i\hat{Q}\hat{H}\hat{Q}t}\hat{Q}\Psi(0)}^{\text{Source Term}}$$

$$\underbrace{-i\int_0^t d\tau\, \hat{P}\hat{H}\hat{Q}e^{i\hat{Q}\hat{H}\hat{Q}(t-\tau)}\hat{Q}\hat{H}\hat{P}\hat{P}\Psi(\tau)}_{\text{Memory Term}}$$

$\implies$ Formal similarity to quantum transport formulation of Kurth and Stefanucci et. al.

Non-Markovian Stochastic Schrödinger equation

- perturbative expansion to second order in $\alpha\, H_{SB}$
- random phase approximation, dense bath spectrum, bath in statistical equilibrium

$$i\partial_t \psi(t) = \hat{H}_S \psi(t) + \alpha \sum_\alpha \eta_\alpha(t)\hat{V}_\alpha \psi(t)$$

$$-i\alpha^2 \int_0^t d\tau \sum_{\alpha\beta} \underbrace{C_{\alpha\beta}(t-\tau)}_{\text{Bath correlation functions}} \hat{V}_\alpha^\dagger e^{-i\hat{H}_S(t-\tau)}\hat{V}_\beta \psi(\tau) + \mathcal{O}(\alpha^3)$$

P. Gaspard, M. Nagaoka, JCP, **111**, 5675 (1999).

Markovian Stochastic Schrödinger equation

δ-correlated bath

$$C_{\alpha\beta}(t - \tau) = D_{\alpha\beta}\delta(t - \tau)$$

Stochastic Schrödinger equation in Born-Markov approximation

$$i\partial_t \psi(t) = \hat{H}_S \psi(t) + \alpha \sum_\alpha \eta_\alpha(t)\hat{V}_\alpha \psi(t)$$
$$- i\alpha^2 \sum_{\alpha\beta} D_{\alpha\beta} \hat{V}_\alpha^\dagger \hat{V}_\beta \psi(t) + \mathcal{O}(\alpha^3)$$

Statistical average:

$$\rho_S(t) = \frac{\overline{|\psi(t)\rangle\langle\psi(t)|}}{\langle\psi(t)\,|\,\psi(t)\rangle}$$

- Valid for time-dependent Hamiltonians
- Gives always physical states
- Sound starting point to formulate stochastic TDDFT

Connection to Lindblad equation

Stochastic Schrödinger equation in Born-Markov approximation

$$i\partial_t \psi(t) = \hat{H}_S \psi(t) + \alpha \sum_\alpha \eta_\alpha(t) \hat{V}_\alpha \psi(t)$$
$$- i\alpha^2 \sum_{\alpha\beta} D_{\alpha\beta} \hat{V}_\alpha^\dagger \hat{V}_\beta \psi(t) + \mathcal{O}(\alpha^3)$$

$\implies$ Lindblad equation can be derived from the Stochastic Schrödinger equation

Lindblad equation

$$\frac{d}{dt}\hat{\rho}_S(t) = -i\left[\hat{H}_S, \hat{\rho}_S(t)\right] + \sum_k \gamma_k \left(\hat{V}_k \hat{\rho}_S(t)\hat{V}_k^\dagger - \frac{1}{2}\hat{V}_k^\dagger \hat{V}_k \rho_S(t) - \frac{1}{2}\hat{\rho}_S(t)\hat{V}_k^\dagger \hat{V}_k\right)$$

On the generator of quantum mechanical semigroups, G. Lindblad, Commun. Math. Phys., **48**, 119-130 (1976).

Note: We can consider the Stochastic Schrödinger equation also in non-Markovian form

Markovian Stochastic Schrödinger equation

δ-correlated bath

$$C_{\alpha\beta}(t - \tau) = D_{\alpha\beta}\delta(t - \tau)$$

Stochastic Schrödinger equation in Born-Markov approximation

$$i\partial_t\psi(t) = \hat{H}_S\psi(t) + \alpha \sum_\alpha \eta_\alpha(t)\hat{V}_\alpha\psi(t)$$
$$- i\alpha^2 \sum_{\alpha\beta} D_{\alpha\beta}\hat{V}_\alpha^\dagger\hat{V}_\beta\psi(t) + \mathcal{O}(\alpha^3)$$

Statistical average:

$$\rho_S(t) = \overline{\frac{|\,\psi(t)\,\rangle\langle\,\psi(t)\,|}{\langle\,\psi(t)\,|\,\psi(t)\,\rangle}}$$

- ▶ Valid for time-dependent Hamiltonians
- ▶ Gives always physical states
- ▶ Sound starting point to formulate stochastic TDDFT

TDDFT for Open Quantum Systems

- Approach in terms of density matrices

  K. Burke, R. Car, and R. Gebauer, Phys. Rev. Lett. **94**, 146803 (2005).

- Approach in terms of stochastic Schrödinger equations

  M. Di Ventra and R. D'Agosta, Phys. Rev. Lett. **98**, 226403 (2007).

- Comparison to classical stochastic systems:

$$\text{Fokker-Planck equation} \iff \text{Langevin equation}$$

Stochastic Time-Dependent Current-Density-Functional Theory

Can prove: For fixed bath operators $\hat{V}$ and fixed initial states Φ_0 and Ψ_0

$$\overline{\mathbf{j}(\mathbf{r}, t)} \quad \overset{1:1}{\longleftrightarrow} \quad \mathbf{A}(\mathbf{r}, t)$$

M. Di Ventra and R. D'Agosta, Phys. Rev. Lett. **98**, 226403 (2007).

Stochastic Time-Dependent Current-Density-Functional Theory

Can prove: For fixed bath operators $\hat{V}$ and fixed initial states Φ_0 and Ψ_0

$$\overline{\mathbf{j}(\mathbf{r}, t)} \quad \overset{1:1}{\longleftrightarrow} \quad \mathbf{A}(\mathbf{r}, t)$$

M. Di Ventra and R. D'Agosta, Phys. Rev. Lett. **98**, 226403 (2007).

Mapping of fully interacting stochastic TDSE to stochastic TDKS equations

$$i\partial_t \psi_j(\mathbf{r}, t) = \left[\hat{H}^{\mathrm{KS}}(t) - \underbrace{\frac{1}{2} i \hat{V}^\dagger \hat{V}}_{\text{damping}} + \underbrace{l(t)\hat{V}}_{\text{fluctuations}} \right] \psi_j(\mathbf{r}, t)$$

Stochastic Time-Dependent Current-Density-Functional Theory

Can prove: For fixed bath operators $\hat{V}$ and fixed initial states Φ_0 and Ψ_0

$$\overline{\mathbf{j}(\mathbf{r}, t)} \quad \overset{1:1}{\longleftrightarrow} \quad \mathbf{A}(\mathbf{r}, t)$$

M. Di Ventra and R. D'Agosta, Phys. Rev. Lett. **98**, 226403 (2007).

Mapping of fully interacting stochastic TDSE to stochastic TDKS equations

$$i\partial_t \psi_j(\mathbf{r}, t) = \left[\hat{H}^{\mathrm{KS}}(t) - \underbrace{\frac{1}{2} i \hat{V}^\dagger \hat{V}}_{\text{damping}} + \underbrace{l(t)\hat{V}}_{\text{fluctuations}} \right] \psi_j(\mathbf{r}, t)$$

$l(t)$: stochastic process

$$\overline{l(t)} = 0, \qquad \overline{l(t)l(t')} = \delta(t - t')$$

Assumes

- Markovian approximation: no bath memory
- Weak coupling to the bath (second order in H_{SB})

Choice of bath operators: a simple model

Order-N scheme and bath operators which obey Fermi statistics

$$V_{kk'}^j(\mathbf{r}) = \delta_{kj}(1 - \delta_{kk'})\sqrt{\gamma(\mathbf{r})f_D(\epsilon_k)}\,|\,\psi_j(\mathbf{r})\,\rangle\langle\,\psi_{k'}(\mathbf{r})\,|$$

Yu. V. Pershin, Y. Dubi, and M. Di Ventra, Phys. Rev. B **78**, 054302 (2008).

Fermi-Dirac distribution

$$f_D(\varepsilon_k) = \left[1 + \exp\left(\frac{\varepsilon_k - \mu}{k_B T}\right)\right]^{-1}$$

Local relaxation rates

$$\gamma_{kk'}(\mathbf{r}) = |\,\psi_k(\mathbf{r})\,\rangle\gamma_0\langle\,\psi_{k'}(\mathbf{r})\,|$$

Quantum jump algorithm
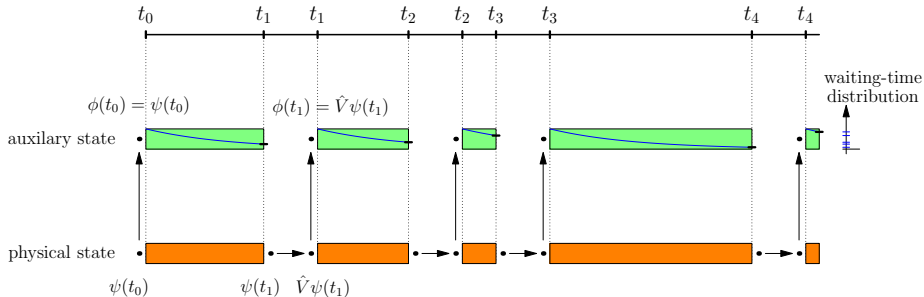
1) Draw uniform random number $\eta_j \in [0, 1]$
2) Propagate auxilary state under non-Hermitian Hamiltonian

$$i\partial_t \phi = \hat{H}_0 \phi - i\hat{V}^\dagger \hat{V} \phi$$

3) Propagate physical state under norm-conserving Hamiltonian

$$i\partial_t \psi = \hat{H}_0 \psi - i\hat{V}^\dagger \hat{V} \psi + i||\hat{V}\psi||^2 \psi$$

4) If norm of auxilary wave function drops below η_j, act with bath operator

$$||\phi(t_j)|| \leq \eta_j, \qquad \psi(t_j) = \hat{V}\psi(t_j), \ \phi(t_j) = \psi(t_j)$$

5) Go to step 1)

$$\Longrightarrow \text{Leads to piecewise deterministic evolution}$$

Application: Laser excitation of Neon dimer with clamped nuclei
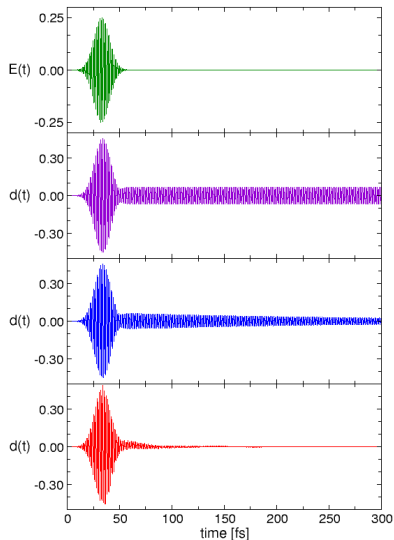
Laser pulse, 50 fs pulse duration
peak intensity 2.2×10^{15} W/cm^2

Application: Laser excitation of Neon dimer with clamped nuclei
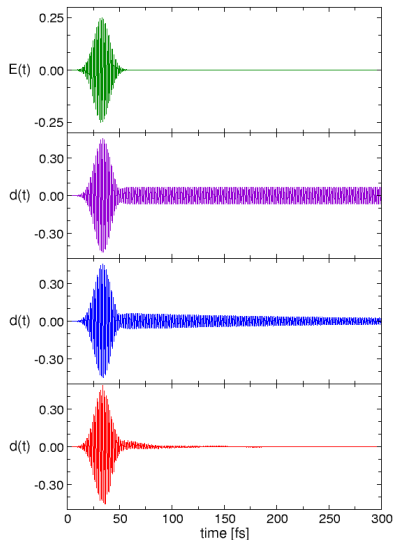
Laser pulse, 50 fs pulse duration
peak intensity 2.2×10^{15} W/cm^2

closed quantum system

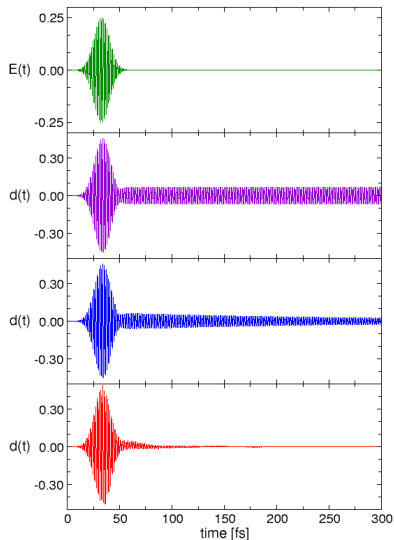# Application: Laser excitation of Neon dimer with clamped nuclei
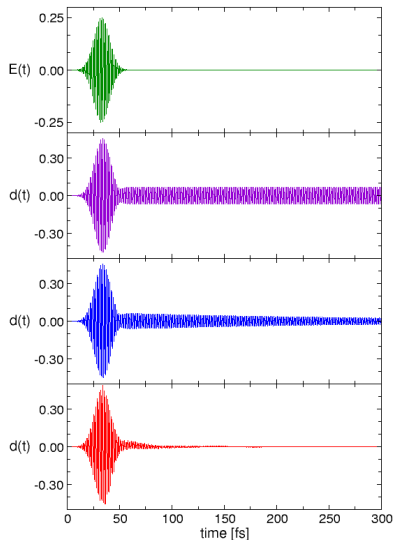
Laser pulse, 50 fs pulse duration
peak intensity 2.2×10^{15} W/cm^2

closed quantum system

open quantum system
relaxation rate $\tau = 150$ fs

Application: Laser excitation of Neon dimer with clamped nuclei

Laser pulse, 50 fs pulse duration
peak intensity 2.2×10^{15} W/cm^2

closed quantum system

open quantum system
relaxation rate $\tau = 150$ fs

open quantum system
relaxation rate $\tau = 15$ fs

Molecular Dynamics for Open Systems

Standard approaches like Car-Parinello MD, Born-Oppenheimer MD, Ehrenfest MD:

- Electronic degrees of freedom are treated with closed system approach

Molecular Dynamics for Open Systems

Standard approaches like Car-Parinello MD, Born-Oppenheimer MD, Ehrenfest MD:

- Electronic degrees of freedom are treated with closed system approach
- Damping is added only to nuclear EOM (Langevin terms, velocity dep. forces)

Molecular Dynamics for Open Systems

Standard approaches like Car-Parinello MD, Born-Oppenheimer MD, Ehrenfest MD:

- Electronic degrees of freedom are treated with closed system approach
- Damping is added only to nuclear EOM (Langevin terms, velocity dep. forces)

However:

Electrons are the first to experience energy transfer to a bath

Molecular Dynamics for Open Systems

Standard approaches like Car-Parinello MD, Born-Oppenheimer MD, Ehrenfest MD:

- Electronic degrees of freedom are treated with closed system approach
- Damping is added only to nuclear EOM (Langevin terms, velocity dep. forces)

However:

Electrons are the first to experience energy transfer to a bath

Nuclei feel bath directly but also through electron-ion interaction
$$\implies \text{different forces on nuclei}$$

Molecular Dynamics for Open Systems

Standard approaches like Car-Parinello MD, Born-Oppenheimer MD, Ehrenfest MD:

- Electronic degrees of freedom are treated with closed system approach
- Damping is added only to nuclear EOM (Langevin terms, velocity dep. forces)

<div align="center">

However:

Electrons are the first to experience energy transfer to a bath

Nuclei feel bath directly but also through electron-ion interaction
$\implies$ different forces on nuclei

Need open quantum theory for both electrons and nuclei

</div>

Stochastic Quantum Molecular Dynamics

Extension of stochastic TDCDFT to include nuclear degrees of freedom

$$i\partial_t \Psi = \hat{H}(t)\Psi - \frac{1}{2}i\hat{V}^\dagger \hat{V}\Psi + l(t)\hat{V}\Psi$$

$$\hat{H}(t) = \hat{T}_{\mathrm{e}}(\underline{\mathbf{r}}, t) + \hat{W}_{\mathrm{ee}}(\underline{\mathbf{r}}) + \hat{U}_{\mathrm{ext,e}}(\underline{\mathbf{r}}, t) + \\ \hat{T}_{\mathrm{n}}(\underline{\mathbf{R}}, t) + \hat{W}_{\mathrm{nn}}(\underline{\mathbf{R}}) + \hat{U}_{\mathrm{ext,n}}(\underline{\mathbf{R}}, t) + \\ \hat{W}_{\mathrm{en}}(\underline{\mathbf{r}}, \underline{\mathbf{R}})$$

Total current

$$\overline{\langle J(x,t)\rangle} = \overline{\langle j(r,t)\rangle} + \overline{\langle J(R,t)\rangle}, \qquad x = (r, R)$$

For given initial state $\Psi(x, t = 0)$ and bath operators $V_\alpha(x, t)$

$$\overline{\langle J(x,t)\rangle} \overset{1:1}{\longleftrightarrow} A(x, t)$$

Heiko Appel, Massimiliano Di Ventra, Phys. Rev. B **80**, 212303 (2009). Heiko Appel, Massimiliano Di Ventra, http://dx.doi.org/10.1016/j.chemphys.2011.05.001 (2011).

Stochastic Quantum Molecular Dynamics: practical scheme

Extension of stochastic TDCDFT to include nuclear degrees of freedom

$$i\partial_t \Psi(x,t) = \hat{H}(t)\Psi(x,t) - \frac{1}{2}i\hat{V}^\dagger\hat{V}\Psi(x,t) + l(t)\hat{V}\Psi(x,t)$$

In practice: resort as approximation to classical nuclei

Bath operators

$$V_{kk'}^j(r, R(t); t) = \delta_{kj}(1 - \delta_{kk'})\sqrt{\gamma(r, R(t); t)f_D(\epsilon_k)}\,|\psi_j(r, R(t); t)\rangle\langle\psi_{k'}(r, R(t); t)|$$
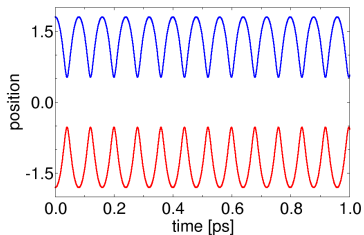
Ehrenfest forces as approximation for classical nuclei

$$M_\alpha\ddot{\mathbf{R}}_\alpha(t) = -\int \Psi^*\nabla_{\mathbf{R}_\alpha}\hat{H}_e\Psi d\underline{\mathbf{r}}$$

Note:

Wavefunctions are stochastic $\implies$ stochastic force on the nuclei

Heiko Appel, Massimiliano Di Ventra, Phys. Rev. B **80**, 212303 (2009).
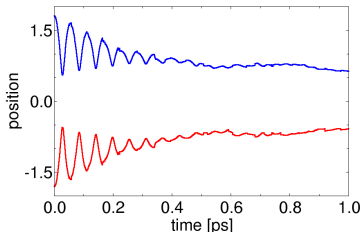
Vibronic excitation of Neon dimer, moving nuclei

closed quantum system
stretched initial condition

Vibronic excitation of Neon dimer, moving nuclei
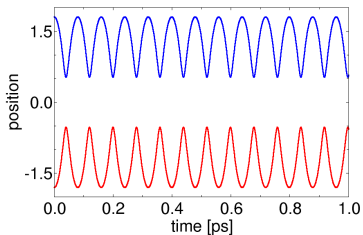
closed quantum system
stretched initial condition
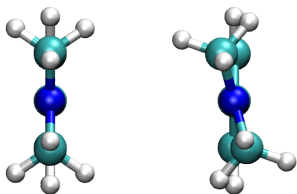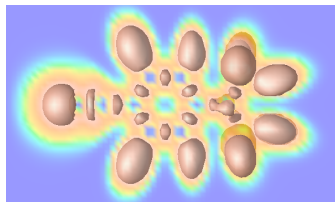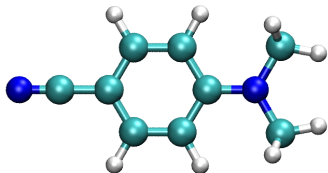
open quantum system
relaxation rate $\tau = 300$ fs

Maxwell-Boltzmann velocity distribution at
jumps

$$f(\vec{v}) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m\vec{v}^2}{2kT}\right)$$

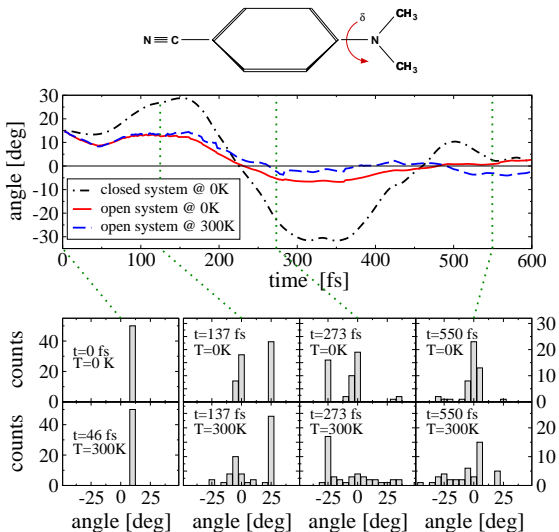Average over 15 stochastic realizations

Stochastic Quantum MD simulation for 4-(N,N-Dimethylamino)benzonitrile

Electron Localization Function

Rotated dimethyl group as
initial condition

Stochastic Quantum MD simulation for 4-(N,N-Dimethylamino)benzonitrile

Heiko Appel, Massimiliano Di Ventra, Phys. Rev. B **80**, 212303 (2009).

Thanks to the people over at tddft.org

and

Thank you for your attention!