Introduction to linear-response, and time-dependent density-functional theory

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Motivation

Where is electron dynamics important?

- Electron-hole pair creation and exciton propagation 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
- ...

Motivation - Decoherence in Quantum Mechanics

Today's Google frontpage: 126. birthday of Erwin Schrödinger

Schrödinger cat state

$$|\Psi\rangle = \frac{1}{\sqrt{2}}\left(a(t)|\psi_A\rangle + d(t)|\psi_D\rangle\right)$$

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-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.

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

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- 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

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

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 $\rho_0(\mathbf{r})$

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- For times $t > t_0$, switch on perturbation $v_1(\mathbf{r}, t)$: $\rightarrow$ leads to time-dependent density

$$\rho(\mathbf{r}, t) = \rho_0(\mathbf{r}) + \delta\rho(\mathbf{r}t)$$

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$$\rho(\mathbf{r}, t) = \rho_0(\mathbf{r}) + \delta\rho(\mathbf{r}t)$$

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

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

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:

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

- Density-density response function of interacting system

$$\chi(\mathbf{r}t,\mathbf{r}'t') := \frac{\delta\rho[v](\mathbf{r}t)}{\delta v(\mathbf{r}'t')}\Big|_{v_0}$$
$$\equiv \Theta(t-t')\langle 0|[\hat\rho(\mathbf{r},t)_H,\hat\rho(\mathbf{r}',t')_H]|0\rangle$$

- Response of non-interacting Kohn-Sham system:

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

- 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

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

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

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- 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

$$\begin{aligned}\rho_1 &= \chi v_1 \\ &= \chi_S v_1 + \chi_S (W_c + f_{xc})\rho_1\end{aligned}$$

- In integral notation

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

- 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 density-density response function:

$$\chi(\mathbf{r}, t;, \mathbf{r}', t') = \Theta(t - t')\langle 0|[\hat{\rho}(\mathbf{r}, t)_H, \hat{\rho}(\mathbf{r}', t')_H]|0\rangle$$

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- Neutral excitation energies are poles of the linear response function!

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

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

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

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- Relation to two-body Green's function

$$i^2G^{(2)}(\mathbf{r},t;,\mathbf{r}',t',\mathbf{r},t;,\mathbf{r}',t') = \chi(\mathbf{r},t;,\mathbf{r}',t') + \rho(\mathbf{r})\rho(\mathbf{r}')$$

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- Relation to two-body Green's function

$$i^2 G^{(2)}(\mathbf{r}, t; , \mathbf{r}', t', \mathbf{r}, t; , \mathbf{r}', t') = \chi(\mathbf{r}, t; , \mathbf{r}', t') + \rho(\mathbf{r})\rho(\mathbf{r}')$$

- Current-current response function:

$$\Pi_{\alpha,\beta}(\mathbf{r}, t; , \mathbf{r}', t') = \Theta(t - t')\langle 0|[\hat{j}_\alpha(\mathbf{r}, t)_H, \hat{j}_\beta(\mathbf{r}, t')_H]|0\rangle$$

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

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

- 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

$$\begin{aligned} f_{xc}^{\text{ALDA}}(\mathbf{r}t,\mathbf{r}'t') = \frac{\delta v_{xc}^{\text{ALDA}}[\rho](rt)}{\delta\rho(\mathbf{r}'t')} &= \delta(t-t')\delta(\mathbf{r}-\mathbf{r}')\frac{\partial v_{xc}^{\text{ALDA}}}{\partial\rho(\mathbf{r})}\Big|_{\rho_0(\mathbf{r})} \\ &= \delta(t-t')\delta(\mathbf{r}-\mathbf{r}')\frac{\partial^2 e_{xc}^{hom}}{\partial n^2}\Big|_{\rho_0(\mathbf{r})} \end{aligned}$$

Failures of the adiabatic approximation in linear response

- H_2 dissociation is incorrect

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

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, $f_{xc}^{\text{exact}} \stackrel{q\to 0}{\longrightarrow} 1/q^2$ divergent

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

Relation of TDHF eigenvalue problem to RPA, CIS and drCCD energies

- RPA equation

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \boldsymbol{\omega}$$

- RPA correlation energy

$$E_c^{\mathrm{RPA}} = \frac{1}{2} Tr(\boldsymbol{\omega} - \mathbf{A})$$

- CIS correlation energy from Tamm-Dancoff approximation TDA: $\mathbf{B} = \mathbf{0}$

$$E_c^{\mathrm{CIS}} = \frac{1}{2} Tr(\tilde{\boldsymbol{\omega}} - \mathbf{A})$$

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$$E_c^{\mathrm{CIS}} = \frac{1}{2} Tr(\tilde{\boldsymbol{\omega}} - \mathbf{A})$$

- Keeping only particle-hole ring contractions, yiels matrix Ricatti equation for CCD cluster amplitudes

$$\mathbf{B} + \mathbf{AT} + \mathbf{TA} + \mathbf{TBT} = \mathbf{0}, \qquad t_{ij}^{ab} = T_{ia,jb}$$

- Correlation energy in direct ring Coupled Cluster Doubles (drCCD)

$$E_c^{\mathrm{drCCD}} = \frac{1}{2} Tr(\mathbf{BT})$$

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- Multiplication of RPA equation with $\mathbf{X}^{-\mathbf{1}}$ from right yields

$$\mathbf{A} + \mathbf{BT} = \mathbf{X}\boldsymbol{\omega}\mathbf{X}^{-\mathbf{1}}, \qquad \text{where } \mathbf{T} := \mathbf{Y}\mathbf{X}^{-\mathbf{1}}$$

- Taking trace yields correlation energies

$$2E_c^{\mathrm{drCCD}} = Tr(\mathbf{BT}) = Tr(\mathbf{X}\boldsymbol{\omega}\mathbf{X}^{-\mathbf{1}} - \mathbf{A}) = Tr(\boldsymbol{\omega} - \mathbf{A}) = 2E_c^{\mathrm{RPA}}$$

Relation of TDHF eigenvalue problem to RPA, CIS and drCCD energies

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$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \boldsymbol{\omega}$$

- Multiplication of RPA equation with $\mathbf{X}^{-1}$ from right yields

$$\mathbf{A} + \mathbf{BT} = \mathbf{X}\boldsymbol{\omega}\mathbf{X}^{-1}, \qquad \text{where } \mathbf{T} := \mathbf{YX}^{-1}$$

- Taking trace yields correlation energies

$$2E_c^{\mathrm{drCCD}} = Tr(\mathbf{BT}) = Tr(\mathbf{X}\boldsymbol{\omega}\mathbf{X}^{-1} - \mathbf{A}) = Tr(\boldsymbol{\omega} - \mathbf{A}) = 2E_c^{\mathrm{RPA}}$$

- Multiplication of RPA equation with $(\mathbf{T}, -1)$ from left and $\mathbf{X}^{-1}$ from right

$$(\mathbf{T},\ -1) \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{1} \\ \mathbf{YX}^{-1} \end{pmatrix} = (\mathbf{T},\ -1) \begin{pmatrix} \mathbf{1} \\ \mathbf{YX}^{-1} \end{pmatrix} \mathbf{X}\boldsymbol{\omega}\mathbf{X}^{-1}$$

- Expanding yields drCCD Ricatti equation

$$\mathbf{B} + \mathbf{AT} + \mathbf{TA} + \mathbf{TBT} = \mathbf{0}$$

$\longrightarrow \mathbf{T} := \mathbf{YX}^{-1}$ satisfies drCCD amplitude equation

G. Scuseria, et. al. J. Chem. Phys. **129**, 231101 (2008).

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Sternheimer equation

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On Nuclear Quadrupole Moments

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(Received June 18, 1951)

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

$$(H_0+H_1)(u_0+u_1)=E_0(u_0+u_1), \tag{3}$$

since the first-order perturbation of the energy is zero for s states. Upon subtracting $H_0u_0=E_0u_0$, and to the first order in Q, we obtain

$$(H_0-E_0)u_1=-H_1u_0. \tag{4}$$

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

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

- 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

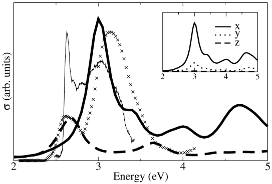
Different types of perturbations

The response equations can be used for different types of perturbations

- Electric perturbations

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

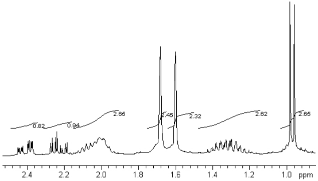
Response contains information about polarizabilities, absorption, fluoresence, etc.



- Magnetic perturbations

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

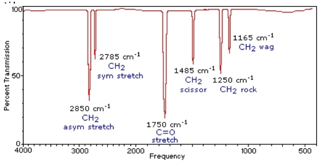
Response contains e.g. NMR signals, etc.



- Atomic displacements

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

Response contains e.g. phonons, etc.



Outline

Linear Response in DFT

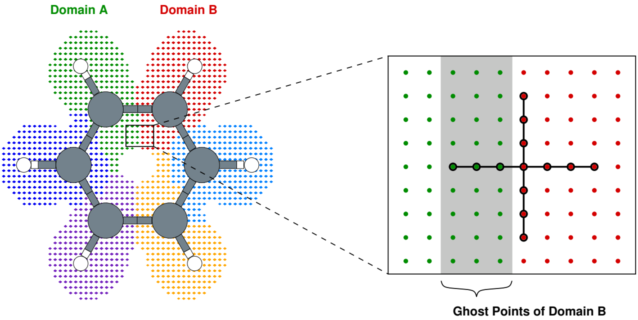
- Response functions
- Casida equation
- Sternheimer equation

Real-space representation and real-time propagation

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

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

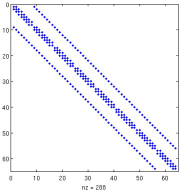
- Example: five-point finite difference Laplacian in 2D

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

- 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 10^7x10^7
- 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

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

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- Initial value problem

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- 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

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

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- 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

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

Real-time evolution - Magnus expansion

- Second-order Magnus propagator - Exponential midpoint rule

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

- 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

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

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

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

- Split-Operator

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

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

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

Real-time evolution - Matrix exponential

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

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

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

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

$$\ldots$$

Real-time evolution - Matrix exponential

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$$\dots$$

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 - Movie time

Proton scattering of fast proton with ethene

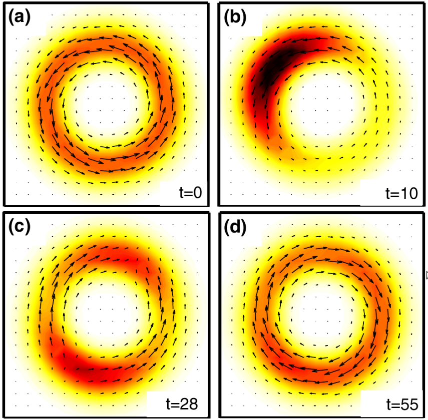
Octopus code

- 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)

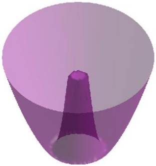
- libxc: Exchange-Correlation library, available under LGPL
  (used by many codes: Abinit, APE, AtomPAW, Atomistix ToolKit, BigDFT, DP, ERKALE, GPAW, Elk, exciting, octopus, Yambo)
  http://tddft.org/programs/octopus/wiki/index.php/Libxc

Optimal control theory

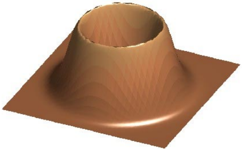
Control of ring current in a quantum ring



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

- maximize 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

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

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

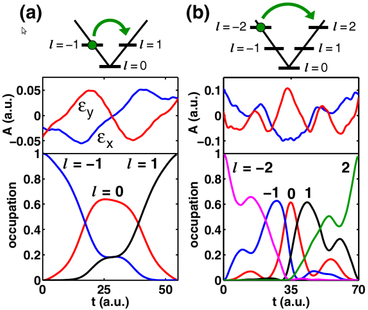
$$\delta_\Psi J = 0 \quad : \quad \left(i\partial_t - \hat{H}(t)\right) |\, \chi(t)\, \rangle = 0, \qquad |\, \chi(T)\, \rangle = |\, \Phi_f\, \rangle \langle\, \Phi_f \,|\, \Psi(T)\, \rangle$$

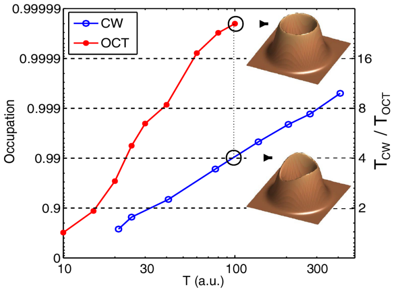
$$\delta_\chi J = 0 \quad : \quad \left(i\partial_t - \hat{H}(t)\right) |\, \Psi(t)\, \rangle = 0, \qquad |\, \Psi(0)\, \rangle = |\, \Phi_i\, \rangle\,,$$

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

Optimal control theory

Optimal laser pulse and level population





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