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
- ...

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

Schrödinger cat state

\[ |\Psi\rangle = \frac{1}{\sqrt{2}} (a(t)|\psi_A\rangle + d(t)|\psi_D\rangle) \]
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

\[ v(r, t) \overset{1-1}{\longleftrightarrow} \rho(r, t) \]

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

Time-dependent density-functional theory

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- Time-dependent Kohn-Sham system

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

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

of an auxiliary non-interacting Kohn-Sham system

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

with a local multiplicative potential

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

- Hamiltonian

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

- 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 \( \rho_0(r) \)
Linear Response Theory

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

\[ \rho(r, t) = \rho_0(r) + \delta\rho(rt) \]
Linear Response Theory

- Hamiltonian

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

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\[ \rho(r, t) = \rho_0(r) + \delta\rho(rt) \]

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

\[
\begin{align*}
\rho[v](r, t) &= \rho[v_0 + v_1](r, t) \\
&= \rho[v_0](r, t) \\
&\quad + \int \frac{\delta \rho[v](rt)}{\delta v(r't')} \bigg|_{v_0} v_1(r't') d^3r' dt' \\
&\quad + \int \int \frac{\delta^2 \rho[v](rt)}{\delta v(r't') \delta v(r''t'')} \bigg|_{v_0} v_1(r't')v_1(r''t'') d^3r' dt' d^3r'' dt'' \\
&\quad + \ldots
\end{align*}
\]
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 $\rho[v](r, t)$ around external potential $v_0$:

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

- Density-density response function of interacting system

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

- Response of non-interacting Kohn-Sham system:

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

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

$$
\chi_S(rt, r't') := \frac{\delta \rho_S[v_S](rt)}{\delta v_S(r't')} \bigg|_{v_{S,0}}
$$
Derivation of response equation

- Definition of time-dependent xc potential

\[ v_{xc}(rt) = v_{KS}(rt) - v_{ext}(rt) - v_H(rt) \]

- Take functional derivative

\[ \frac{\delta v_{xc}(rt)}{\delta \rho(r't')} = \frac{\delta v_{KS}(rt)}{\delta \rho(r't')} - \frac{\delta v_{ext}(rt)}{\delta \rho(r't')} - \frac{\delta (t - t')}{|r - r'|} \]

\[ f_{xc}(rt, r't') := \chi_S^{-1}(rt, r't') - \chi^{-1}(rt, r't') - W_c(rt, r't') \]
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\[ f_{xc}(rt, r't') := \chi^{-1}_{S}(rt, r't') - \chi^{-1}(rt, r't') - W_{c}(rt, r't') \]

- Act with response functions from left and right

\[ \chi_{S} W_{c} + f_{xc} = \chi^{-1}_{S} - \chi^{-1} \]

\[ \chi_{S}(W_{c} + f_{xc})\chi = \chi - \chi_{S} \]

- 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

\[ \rho_1(rt) = \int d^3 r' dt' \chi_S (rt, r't') \left[ v_1(r't') \right. \]
\[ + \left. \int d^3 r'' dt'' (W_c(r't', r''t'') + f_{xc}(r't', r''t'')) \rho_1(r''t'') \right] \]

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

\[ f_{xc}(r't', r''t'') = \frac{\delta v_{xc}[\rho](r't')}{\delta \rho(r''t'')} \bigg|_{\rho_0} \]
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:
  \[ \chi(r, t; r', t') = \Theta(t - t')\langle 0|[\hat{\rho}(r, t)_H, \hat{\rho}(r', t')_H]|0\rangle \]
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- Neutral excitation energies are poles of the linear response function!
  \[ \chi(\mathbf{r}, \mathbf{r}'; \omega) = \lim_{\eta \to 0^+} \sum_m \left( \frac{\langle 0|\hat{\rho}(\mathbf{r})_H|m\rangle\langle m|\hat{\rho}(\mathbf{r}')_H|0\rangle}{\omega - (E_m - E_0) + i\eta} - \frac{\langle 0|\hat{\rho}(\mathbf{r}')_H|m\rangle\langle m|\hat{\rho}(\mathbf{r})_H|0\rangle}{\omega + (E_m - E_0) + i\eta} \right) \]

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- Exact linear density response to perturbation \( v_1(\omega) \)
  \[ \rho_1(\omega) = \hat{\chi}(\omega)v_1(\omega) \]
Lehmann representation of linear response function

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

\[ \rho_1(\omega) = \hat{\chi}(\omega)v_1(\omega) \]

- Relation to two-body Green’s function

\[ i^2 G^{(2)}(\mathbf{r}, t; \mathbf{r}', t', \mathbf{r}, t; \mathbf{r}', t') = \chi(\mathbf{r}, t; \mathbf{r}', t') + \rho(\mathbf{r})\rho(\mathbf{r}') \]
Lehmann representation of linear response function

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- Relation to two-body Green’s function
  \[ i^2 G^{(2)}(r, t; r', t', r, t; r', t') = \chi(r, t; r', t') + \rho(r)\rho(r') \]

- Current-current response function:
  \[ \Pi_{\alpha, \beta}(r, t; r', t') = \Theta(t - t')\langle 0|\hat{j}_\alpha(r, t)_H\hat{j}_\beta(r, t')_H|0\rangle \]
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 \(\Omega_j\)

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

- 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 \( \omega_j \) 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**

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

- **Exchange-correlation kernel**

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

  \[ = \delta(t - t')\delta(r - r') \frac{\partial^2 e_{xc}^{\text{hom}}}{\partial n^2} \bigg|_{\rho_0(r)} \]
Failures of the adiabatic approximation in linear response

- $\text{H}_2$ dissociation is incorrect

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


- Sometimes problematic close to conical intersections

- Response of long chains strongly overestimated


- In periodic solids $f_{xc}(q, \omega, \rho) = c(\rho)$, whereas for insulators, $f_{xc}^{\text{exact}} \xrightarrow{q \to 0} 1/q^2$ 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**

\[
\begin{pmatrix}
A & B \\
-B & -A
\end{pmatrix}
\begin{pmatrix}
X \\
Y
\end{pmatrix}
= \begin{pmatrix}
X \\
Y
\end{pmatrix} \omega
\]

- **RPA correlation energy**

\[
E_{\text{c}}^{\text{RPA}} = \frac{1}{2} Tr(\omega - A)
\]

- **CIS correlation energy from Tamm-Dancoff approximation TDA: \( B = 0 \)**

\[
E_{\text{c}}^{\text{CIS}} = \frac{1}{2} Tr(\tilde{\omega} - A)
\]
Relation of TDHF eigenvalue problem to RPA, CIS and drCCD energies

- RPA equation

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-B & -A \\
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Y \\
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\]

- RPA correlation energy

\[
E^{\text{RPA}}_c = \frac{1}{2} Tr(\omega - A)
\]

- CIS correlation energy from Tamm-Dancoff approximation TDA: \( B = 0 \)

\[
E^{\text{CIS}}_c = \frac{1}{2} Tr(\tilde{\omega} - A)
\]

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

\[
B + AT + TA + TBT = 0, \quad t_{ij}^{ab} = T_{ia,jb}
\]

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

\[
E^{\text{drCCD}}_c = \frac{1}{2} Tr(BT)
\]
Relation of TDHF eigenvalue problem to RPA, CIS and drCCD energies

- RPA equation

\[
\begin{pmatrix}
A & B \\
-B & -A
\end{pmatrix}
\begin{pmatrix}
X \\
Y
\end{pmatrix}
= \begin{pmatrix}
X \\
Y
\end{pmatrix} \omega
\]

- Multiplication of RPA equation with \(X^{-1}\) from right yields

\[A + BT = X\omega X^{-1}, \quad \text{where } T := YX^{-1}\]

- Taking trace yields correlation energies

\[2E_{\text{drCCD}}^c = Tr(BT) = Tr(X\omega X^{-1} - A) = Tr(\omega - A) = 2E_{\text{RPA}}^c\]
Relation of TDHF eigenvalue problem to RPA, CIS and drCCD energies

- **RPA equation**

\[
\begin{pmatrix}
A & B \\
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\end{pmatrix}
\begin{pmatrix}
X \\
Y
\end{pmatrix}
= 
\begin{pmatrix}
X \\
Y
\end{pmatrix}
\omega
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\[
A + BT = X\omega X^{-1}, \quad \text{where } T := YX^{-1}
\]

- Taking trace yields correlation energies

\[
2E_{c}^{\text{drCCD}} = Tr(BT) = Tr(X\omega X^{-1} - A) = Tr(\omega - A) = 2E_{c}^{\text{RPA}}
\]

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

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

- Expanding yields drCCD Ricatti equation

\[
B + AT + TA + TBT = 0
\]

\[\rightarrow T := YX^{-1} \text{ satisfies drCCD amplitude equation}\]

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

$$ (H_0 + H_1)(u_0 + u_1) = E_0(u_0 + u_1), $$

(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

$$ (H_0 - E_0)u_1 = -H_1 u_0. $$

(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 \( \lambda \)

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

- Use \( \hat{H}_0 \psi_0 = E_0 \psi_0 \)

\[ (\hat{H}_0 - E_0)\psi_1 = -(\hat{H}_1 - E_1)\psi_0, \quad \text{Sternheimer equation} \]
Sternheimer equation in TDDFT

- (Weak) monochromatic perturbation

\[ v_1(r, t) = \lambda r_i \cos(\omega t) \]

- Expand time-dependent Kohn-Sham wavefunctions in powers of \( \lambda \)

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

- Insert in time-dependent Kohn-Sham equation and keep terms up to first order in \( \lambda \)
Sternheimer equation in DFT

- Frequency-dependent response \((\text{self-consistent solution!})\)

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

with first-order frequency-dependent perturbation

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

and first-order density response

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

- 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, fluorescence, etc.

- **Magnetic perturbations**
  
  \[ v(\mathbf{r}) = L_i \]

  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.
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Real-space representation and real-time propagation
- Real-space representation for wavefunctions and Hamiltonians
- Time-propagation schemes
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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

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

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

- Stencil notation for kinetic energy

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

- Leads to sparse matrices
Real-space grids

- Size of Hamiltonian matrix can easily reach $10^7 \times 10^7$
- Basic operation $\hat{H}\psi \rightarrow$ 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

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

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

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

▶ Initial value problem

\[ \varphi_j (r, t) = \varphi_j ^{(0)} (r) \]
Real-time evolution for the time-dependent Kohn-Sham system

- **Time-dependent Kohn-Sham equations**

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

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

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

- **Initial value problem**

\[
\varphi_j(r, t) = \varphi_j^{(0)}(r)
\]

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

\[
\varphi_j(r, t) = \hat{U}(t, t_0) \varphi_j(r, t_0)
\]
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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- Equation of motion for the propagator
  \[
  i\hbar \partial_t \hat{U}(t, t_0) = \hat{H}(t)\hat{U}(t, t_0), \quad \hat{U}(t_0, t_0) = \hat{1}
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- Representation in integral form
  \[ \hat{U}(t, t_0) = \hat{1} - i \int_{t_0}^{t} d\tau \hat{H}(\tau)\hat{U}(\tau, t_0) \]
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  \]

- Representation in integral form
  \[
  \hat{U}(t, t_0) = 1 - i \int_{t_0}^{t} d\tau \hat{H}(\tau)\hat{U}(\tau, t_0)
  \]

- Iterated solution of integral equation - time-ordered exponential
  \[
  \hat{U}(t, t_0) = \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \cdots \int_{t_0}^{t} dt_n \hat{T}[\hat{H}(t_1)\hat{H}(t_2)\cdots\hat{H}(t_n)]
  \]
  \[
  = \hat{T} \exp(-i \int_{t_0}^{t} d\tau \hat{H}(\tau))
  \]
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 \( \omega_{\text{max}} \), the time-step should be no larger than \( \approx 1/\omega_{\text{max}} \)
  - The time-dependence of the Hamiltonian is small over a short-time interval
  - The norm of the time-ordered exponential is proportional to \( \Delta t \).
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

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

- Fourth-order Magnus propagator

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

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

\[ \hat{U}^{\text{ETRS}}(t + \Delta t, t) = \exp(-i \frac{\Delta t}{2} \hat{H}(t + \Delta t)) \exp(-i \frac{\Delta t}{2} \hat{H}(t)) \]
Real-time evolution - Matrix exponential

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

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

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

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

\[ \ldots \]
Real-time evolution - Matrix exponential

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

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\[ \ldots \]
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)


**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)

Optimal control theory

Control of ring current in a quantum ring

Optimal control theory

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

- maximize overlap functional
  \[
  J_1[\Psi] = \left| \langle \Psi(T) | \Phi_f \rangle \right|^2.
  \]

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

- Lagrange multiplier density to ensure evolution with TDSE
  \[
  J_3[\Psi, \chi, \epsilon] = -2 \operatorname{Im} \int_0^T \langle \chi(t) \left| \left( i\partial_t - \hat{H}(t) \right) \right| \Psi(t) \rangle \, dt,
  \]

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

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

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

\[ \delta_{\epsilon} J = 0 : \quad \alpha_0 \epsilon(t) = -\text{Im} \langle \chi(t) | \hat{\mu} | \Psi(t) \rangle. \]
Optimal control theory

Optimal laser pulse and level population