Exact exchange
(spín current) density-functional methods
for magnetic properties, spin-orbit effects,
and excited states

*DFT with orbital-dependent functionals*

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Overview

• Why are we interested in new types of functionals in DFT? What is wrong with standard density-functional methods?

• Reconsidering the KS formalism

• Orbital-dependent functionals and their derivatives, the OEP approach
  – Examples of applications

• Spin-current density-functional theory
  – Formalism
  – Spin-orbit effects in semiconductors

• Time-dependent density-functional methods
  – Reconsidering the basic formalism
  – Shortcomings of present TDDFT methods
  – Exact-exchange TDDFT

• Concluding remarks
Shortcomings of standard Kohn-Sham methods

Shortcomings due to approximations of exchange-correlation functionals

- Static correlation not well described
  (Description of bond breaking problematic)
- Van-der-Waals interactions not included
- Limited applicability of time-dependent DFT methods
  - Excitations into states with Rydberg character not described
  - Charge-transfer excitations not described
  - Polarizabilities of chain-like conjugated molecules strongly overestimated
- Qualitatively wrong orbital and eigenvalue spectra
  due to unphysical Coulomb self-interactions
  - Calculation of response properties, e.g., excitation energies or NMR data, impaired
  - Anions often not accessible
  - Interpretation of chemical bonding and reactivity impaired
  - Orbitals or one-particle states do not represent those underlying the thinking of chemists and physicists?

Orbital-dependent functionals can help to solve these problems
Reconsidering of the Kohn-Sham formalism

Relation between ground state electron density $\rho_0$, real and KS wave functions $\Psi_0$ and $\Phi_0$, and real and KS Hamiltonian operators with potentials $\hat{v}_{\text{ext}}$ and $\hat{v}_s$

\[
\hat{T} + \hat{v}_s \leftrightarrow \Phi_0 \leftrightarrow \rho_0 \leftrightarrow \Psi_0 \leftrightarrow \hat{T} + \hat{V}_{ee} + \hat{v}_{\text{ext}}
\]

Relations between $\rho_0$, $\hat{v}_{\text{ext}}$, $\hat{v}_s$, $\Psi_0$, and $\Phi_0$ are circular
Each quantity determines any single one of the others

Thomas-Fermi method
\[
\hat{v}_{\text{ext}} \longrightarrow \rho_0 \longrightarrow E_0[\rho_0]
\]

Conventional view on conventional KS methods
\[
\hat{v}_{\text{ext}} \longrightarrow \hat{T} + \hat{v}_{\text{ext}} + \hat{u}[\rho_0] + \hat{v}_{xc}[\rho_0] \longrightarrow \phi_j \longrightarrow \rho_0 \longrightarrow E_0[\rho_0]
\]

Orbitals often considered as auxiliary quantities to generate density without physical meaning. However, KS approach works because of orbital-dependent functional $T_s[\{\phi_j\}]$ for noninteracting kinetic energy.
Kohn-Sham methods with orbital-dependent functionals

\[ \hat{v}_{\text{ext}} \rightarrow \hat{T} + \hat{v}_{\text{ext}} + \hat{u}[\rho_0] + \hat{v}_{xc}[\phi_j] \rightarrow \phi_j \rightarrow \rho_0 \rightarrow U[\rho_0], \int dr \ v_{\text{ext}}(r) \rho_0(r) \]

Examples for orbital-dependent functionals

**Exchange energy**

\[
E_x = - \sum_{a,b}^{\text{occ.}} \int dr dr' \ \frac{\phi_a(r') \phi_b(r') \phi_b(r) \phi_a(r)}{|r' - r|}
\]

**meta-GGA functionals**

\[
E_{xc} = \int dr \ \epsilon_{xc}([\rho, \nabla \rho, \nabla^2 \rho, \tau]; r) \rho(r) \text{ with } \tau(r) = \frac{1}{2} \sum_a^{\text{occ.}} [\nabla \phi_a(r)]^2
\]

Orbital-dependent functional \( F[\{\phi_j\}] \) are implicit density functionals \( F[\{\phi_j[\rho]\}] \)
Alternative view on the Kohn-Sham formalism

- KS system is meaningful model system associated with real electron system, electron density mediates this association
- KS potential $v_s$ defines physical situation as well as it does $v_{\text{ext}}$
- Depending on situation quantities like $E_0$ or $E_{xc}$ are considered as
  - functionals $E_0[v_s]$ or $E_{xc}[v_s]$ of $v_s$
  - as functionals $E_0[\rho_0]$ or $E_{xc}[\rho_0]$ of $\rho_0$

If obtained by KS approach free of Coulomb self-interactions then
- KS eigenvalues approximate ionization energies
- KS eigenvalue differences approximate excitation energies and band gaps
- KS orbitals, eigenvalues correspond to accepted chemical, physical pictures
Derivatives of orbital-dependent functionals, the OEP equation

Exchange-correlation potential

\[ v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\{\phi_j\}]}{\delta \rho(\mathbf{r})} \]

Integral equation for \( v_{xc} \) by taking derivative \( \frac{\delta E_{xc}}{\delta v_s(\mathbf{r})} \) in two ways

\[
\int d\mathbf{r}' \frac{\delta E_{xc}}{\delta \rho(\mathbf{r}')} \frac{\delta \rho(\mathbf{r}')}{\delta v_s(\mathbf{r})} = \int d\mathbf{r}' \sum_a^{\text{occ.}} \frac{\delta E_{xc}}{\delta \phi_a(\mathbf{r}')} \frac{\delta \phi_a(\mathbf{r}')}{\delta v_s(\mathbf{r})}
\]

\[
\int d\mathbf{r}' \ X_s(\mathbf{r}, \mathbf{r}') \ v_{xc}(\mathbf{r}') = t(\mathbf{r})
\]

KS response function

\[ X_s(\mathbf{r}, \mathbf{r}') = 4 \sum_a^{\text{occ.}} \sum_s^{\text{unocc.}} \frac{\phi_a(\mathbf{r}) \phi_s(\mathbf{r}) \phi_s(\mathbf{r}') \phi_a(\mathbf{r}')}{\epsilon_a - \epsilon_s} \]

Perturbation theory yields

\[ \frac{\delta \phi_a(\mathbf{r}')}{\delta v_s(\mathbf{r})} = \sum_{j \neq a} \phi_j(\mathbf{r}') \ \frac{\phi_j(\mathbf{r}) \phi_a(\mathbf{r})}{\epsilon_a - \epsilon_j} \]

Derivative of \( E_{xc}[\{\phi_j\}] \) yields

\[ \frac{\delta E_{xc}}{\delta \phi_a(\mathbf{r}')} \]

Numerically stable procedures for solids with plane-wave basis sets
Numerical instabilities for molecules with Gaussian basis sets
(Effective) Exact exchange methods

\[ \sum_{a} \sum_{s} \frac{\phi_{a}(r)\phi_{s}(r) \langle \phi_{s} | \hat{v}_{x} | \phi_{a} \rangle}{\varepsilon_{a} - \varepsilon_{s}} = \sum_{a} \sum_{s} \frac{\phi_{a}(r)\phi_{s}(r) \langle \phi_{s} | \hat{v}_{x}^{NL} | \phi_{a} \rangle}{\varepsilon_{a} - \varepsilon_{s}} \]

Instead of evaluating density-functional for \( v_{x}(\rho; r) \), e.g. \( v_{x}^{LDA}(\rho; r) = c \rho^{1/3}(r) \), integral equation for \( v_{x}(r) \) has to be solved.

Localized Hartree-Fock method

Approximation of average magnitudes of eigenvalue differences \( \Delta = |\varepsilon_{a} - \varepsilon_{s}| \)

\[ v_{x}(r) = 2 \sum_{a} \frac{\phi_{a}(r) [\hat{v}_{x}^{NL} \phi_{a}](r)}{\rho(r)} + 2 \sum_{a,b}^{occ.} \frac{\phi_{a}(r)\phi_{b}(r)}{\rho(r)} \langle \phi_{b} | \hat{v}_{x} - \hat{v}_{x}^{NL} | \phi_{a} \rangle \]

The localized Hartree-Fock method requires only occupied orbitals and is efficient and numerically stable.
Rydberg orbitals of ethene

LHF

+12Å  \( \pi (2p) \)
-12Å  -10.22 eV

BL YP

+12Å  \( \pi (2p) \)
-12Å  -6.58 eV

HF

+12Å  \( \pi (2p) \)
-12Å  -10.23 eV

+12Å  \( \pi (3p) \)
+2500Å  -2.03 eV

+12Å  \( \pi (4p) \)
+2500Å  -1.02 eV

+12Å  \( \pi (3p) \)
-2500Å  +0.0001 eV
Adsorption of tetralactam macrocycles on gold(111)

Investigation of electronic situation of adsorption
for interpretation of scanning tunneling microscopy data

Calculation of STM images via energy-filtered electron densities
Response properties
More accurate response properties with exact treatment of KS exchange
Example: NMR chemical shifts for organo-iron-complexes

<table>
<thead>
<tr>
<th>System</th>
<th>BP86\textsuperscript{a}</th>
<th>BPW91\textsuperscript{b,c}</th>
<th>LHF\textsuperscript{b}</th>
<th>Exp.\textsuperscript{c}</th>
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</thead>
<tbody>
<tr>
<td>Ferrocene</td>
<td>166</td>
<td>657</td>
<td>969</td>
<td>1532</td>
</tr>
<tr>
<td>Fe(CO)\textsubscript{3}(C\textsubscript{4}H\textsubscript{6})</td>
<td>-123</td>
<td>-105</td>
<td>12</td>
<td>4</td>
</tr>
<tr>
<td>CpFe(CO)\textsubscript{2}CH\textsubscript{3}</td>
<td>–</td>
<td>336</td>
<td>594</td>
<td>684</td>
</tr>
<tr>
<td>Fe(CO)\textsubscript{4}C\textsubscript{2}H\textsubscript{3}CN</td>
<td>90</td>
<td>120</td>
<td>170</td>
<td>303</td>
</tr>
</tbody>
</table>

\textsuperscript{a}SOS-IGLO, M. Bühl et al., J. Comp. Chem. \textbf{20}, 91 (1999).
\textsuperscript{b}BPW91\textsuperscript{a,b,c}
\textsuperscript{c}GIAO.
Band gaps of semiconductors

EXX band gaps agree with experimental band gaps
Cohesive energies of semiconductors

Accurate cohesive energies with combination of exact exchange and GGA correlation
EXX-bandstructure of polyacetylene

Band gaps
LDA: 0.76 eV
EXX: 1.62 eV
GW: 2.1 eV
Exp: ≈ 2 eV
Current Spin-Density-Functional Theory

Treatment of magnetic effects (magnetic fields, magnetism etc.)

\[ \hat{T} + \hat{v}_s + \hat{H}_s^{mag} \leftrightarrow \Phi_0 \leftrightarrow \rho_0, j_0, \sigma_0 \leftrightarrow \Psi_0 \leftrightarrow \hat{T} + \hat{V}_{ee} + \hat{v}_{ext} + \hat{H}^{mag} \]

Vignale, Rasolt 87/88

Problem: lack of good current-depend functionals
Possible solution: exact treatment of exchange

Preliminary work on EXX-CSDFT with approximation of colinear spin

Helbig, Kurth, Gross
Spin-Current Density-Functional Theory I

Hamiltonian operator of real electron system

\[
\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{v}_{ext} + \hat{H}^{mag} + \hat{H}^{SO}
\]

\[
= \hat{T} + \hat{V}_{ee} + \sum_{i=1}^{N} \left[ v_{ext}(r_i) + p_i \cdot A(r_i) + A(r_i) \cdot p_i + \frac{1}{2} A(r_i) \cdot A(r_i) \right.
\]

\[
+ \frac{1}{2} \sigma \cdot B(r_i) + \frac{1}{4c^2} \sigma \cdot [(\nabla v_{ext})(r_i) \times p_i] \right]
\]

\[
= \hat{T} + \hat{V}_{ee} + \int dr \ \Sigma^T \ V(r) \ \hat{J}(r)
\]

\[
\Sigma_0 = 1 \quad \Sigma_1 = \sigma_x \quad \Sigma_2 = \sigma_y \quad \Sigma_3 = \sigma_z
\]

\[
\hat{J}_0(r) = \sum_{i=1}^{N} \delta(r - r_i) \quad \hat{J}_\nu(r) = \left( \frac{1}{2} \right) \sum_{i=1}^{N} p_{\nu,i} \ \delta(r - r_i) + \delta(r - r_i) \ p_{\nu,i}
\]

\[
V(r) = \begin{pmatrix}
V_{00}(r) & V_{01}(r) & V_{02}(r) & V_{03}(r) \\
V_{10}(r) & V_{11}(r) & V_{12}(r) & V_{13}(r) \\
V_{20}(r) & V_{21}(r) & V_{22}(r) & V_{23}(r) \\
V_{30}(r) & V_{31}(r) & V_{32}(r) & V_{33}(r)
\end{pmatrix} = \begin{pmatrix}
v_{ext}(r) + \frac{A^2(r)}{2} & A_x(r) & A_y(r) & A_z(r) \\
\frac{B_x(r)}{2} & 0 & -\frac{v_{ext,z}(r)}{4c^2} & \frac{v_{ext,y}(r)}{4c^2} \\
\frac{B_y(r)}{2} & \frac{v_{ext,z}(r)}{4c^2} & 0 & -\frac{v_{ext,x}(r)}{4c^2} \\
\frac{B_z(r)}{2} & -\frac{v_{ext,y}(r)}{4c^2} & \frac{v_{ext,x}(r)}{4c^2} & 0
\end{pmatrix}
\]
Spin-Current Density-Functional Theory II

Hamiltonian operator of real electron system

\[ \hat{H} = \hat{T} + \hat{V}_{ee} + \int dr \Sigma^T \mathbf{V}(\mathbf{r}) \mathbf{J}(\mathbf{r}) \]

Total energy

\[ E = T + V_{ee} + \sum_{\mu\nu} \int dr \mathbf{V}_{\mu\nu}(\mathbf{r}) \mathbf{\rho}_{\mu\nu}(\mathbf{r}) = T + V_{ee} + \int dr \mathbf{V}^T(\mathbf{r}) \mathbf{\rho}(\mathbf{r}) \]

\( \mathbf{V}(\mathbf{r}) \) treated as matrix or as vector with superindex \( \mu\nu \)

Spin current density \( \mathbf{\rho}(\mathbf{r}) \) (treated as vector)
Density \( \rho_{00} \), spin density \( \rho_{\mu0} \), current density \( \rho_{0\nu} \), spin current density \( \rho_{\mu\nu} \)

Constrained search, Hohenberg-Kohn functional

\[ F[\mathbf{\rho}] = \text{Min} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \longrightarrow \Psi[\mathbf{\rho}] \]
Spin-Current Density-Functional Theory III

Kohn-Sham Hamiltonian operator

$$\hat{H} = \hat{T} + \int dr \ \Sigma^T V_s(r) \ \hat{J}(r)$$

Kohn-Sham potential

$$V_s(r) = V(r) + U(r) + V_{xc}(r)$$

$$U(r) + V_{xc}(r) = \begin{pmatrix}
u(r) + V_{xc,00}(r) & V_{xc,01}(r) & V_{xc,02}(r) & V_{xc,03}(r) \\
V_{xc,10}(r) & V_{xc,11}(r) & V_{xc,12}(r) & V_{xc,13}(r) \\
V_{xc,20}(r) & V_{xc,21}(r) & V_{xc,22}(r) & V_{xc,23}(r) \\
V_{xc,30}(r) & V_{xc,31}(r) & V_{xc,32}(r) & V_{xc,33}(r)
\end{pmatrix}$$

Constrained search, noninteracting kinetic energy

$$T_s[\rho] = \text{Min} \ \langle \Psi | \hat{T} | \Psi \rangle \rightarrow \Phi[\rho]$$
Spin-Current Density-Functional Theory IV

\[
\hat{T} + \int dr \, \Sigma^T V_s(r) \hat{J}(r) \iff \Phi_0 \iff \rho_0 \iff \Psi_0 \iff \hat{T} + \hat{V}_{ee} + \int dr \, \Sigma^T V(r) \hat{J}(r)
\]

Energy functionals

Coulomb energy: \( U[\rho] = \int d\mathbf{r} d\mathbf{r}' \frac{\rho(r) \rho(r')}{|\mathbf{r} - \mathbf{r}'|} \)

Exchange energy: \( E_x[\rho] = \langle \Psi[\rho] | \hat{V}_{ee} | \Psi[\rho] \rangle - U[\rho] \)

Correlation energy: \( E_c[\rho] = F[\rho] - T_s[\rho] - U[\rho] - E_x[\rho] \)

Potentials

\[
V_{x,\mu\nu}(\mathbf{r}) = \frac{\delta E_x}{\delta \rho_{\mu\nu}(\mathbf{r})} \quad V_{c,\mu\nu}(\mathbf{r}) = \frac{\delta E_c}{\delta \rho_{\mu\nu}(\mathbf{r})}
\]

In the formalism that is actually applied components of \( \rho_0 \) are omitted

Spin-current density-functionals required

Here, exact treatment of exchange: EXX spin-current DFT
Exact exchange spin-current density-functional theory

Integral equation for $v_{x,\mu\nu}$ by taking derivative $\frac{\delta E_x}{\delta \rho_{s,\kappa\lambda}(r)}$ in two ways

$$
\sum_{\mu\nu} \int dr' \frac{\delta E_x}{\delta \rho_{\mu\nu}(r')} \frac{\delta \rho_{\mu\nu}(r')}{\delta V_{s,\kappa\lambda}(r)} = \sum_a \int dr' \frac{\delta E_x}{\delta \phi_a(r')} \frac{\delta \phi_a(r')}{\delta V_{s,\kappa\lambda}(r)}
$$

Spin current EXX equation

$$
\int dr' \ X_s(r, r') \ V_x(r') = t(r)
$$

KS response function

$$
X_s^{\mu\nu,\kappa\lambda}(r, r') = \sum_{a} \sum_{s} (\text{occ. unocc.}) \ \langle \phi_a | \sigma_{\mu} \hat{J}_{\nu}(r') | \phi_s \rangle \langle \phi_s | \sigma_{\kappa} \hat{J}_{\lambda}(r') | \phi_a \rangle \frac{\varepsilon_a - \varepsilon_s}{\varepsilon_a - \varepsilon_s}
$$

Right hand side $t(r)$

$$
t^{\mu\nu}(r) = \sum_{a} \sum_{s} (\text{occ. unocc.}) \ \langle \phi_a | \sigma_{\mu} \hat{J}_{\nu}(r) | \phi_s \rangle \langle \phi_s | \hat{v}_{NL}^{x} | \phi_a \rangle \frac{\varepsilon_a - \varepsilon_s}{\varepsilon_a - \varepsilon_s}
$$

16-component vectors $V_{x}(r)$ and $t(r)$, 16x16-dimensional matrix $X_s(r, r')$
Plane wave implementation of EXX-SCDFT

Introduction of plane-wave basis set turns spin current EXX equation

$$\int dr' \ X_s(r, r') \ V_x(r') = t(r)$$

into matrix equation

$$X_s \ V_x = t$$

$V_x$ and $t$ consist, at first, of 16 subvectors, $X_s$ of 16x16 submatrices

Transformation of $V_x$, $X_s$, and $t$ on transversal and longitudinal contributions

Removal of subvectors in $V_x$ and $t$ and of rows and columns of submatrices in $X_s$ yields, e.g., pure current DFT, pure spin DFT etc.

Spin-orbit-dependent pseudopotentials from relativistic atomic OEP program

Höck, Engel 98
Test of pseudopotentials and of implementation of fields

Oxygen orbital eigenvalues with bare pseudopotential in magnetic field

Zeemann splitting: $\Delta E = \beta g_J B m_J$

Paschen-Back splitting: $\Delta E = \beta B (m_\ell + 2m_s)$
Example of oxygen atom in magnetic field

Eigenvalues of oxygen KS orbitals $s_{m\ell,m_s}$ and $p_{m\ell,m_s}$
Spin-orbit effects in semiconductor band structures

Bandstructures of Germanium without and with spin-orbit

Spin-orbit splitting energies in [meV] (preliminary results)

<table>
<thead>
<tr>
<th></th>
<th>Germanium</th>
<th>Silicon</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta(\Gamma_{7v} - \Gamma_{8v})$</td>
<td>$\Delta(\Gamma_{25v})$</td>
</tr>
<tr>
<td>Spin current</td>
<td>258.097</td>
<td>42.481</td>
</tr>
<tr>
<td>Spin current+SO</td>
<td>258.084</td>
<td>42.587</td>
</tr>
</tbody>
</table>
| Experiment | 297 | 200$^a$
|          | $\Delta(\Gamma_{6c} - \Gamma_{8c})$ |               |
| Spin current | 173.255 |               |
| Spin current+SO | 173.221 |               |
| Experiment | 200$^a$ |               |

$^a$Madelung, Semiconductor Data Handbook
Spin-current densities and potentials for Germanium

\[
\begin{align*}
\rho_{12} &= \rho_{23} = -\rho_{13} = -\rho_{21} = -\rho_{32} = \rho_{31} \\
\rho_{0\mu} &= \rho_{\mu0} = \rho_{\mu\mu} = 0 \quad \text{for} \quad \mu = 1, 2, 3
\end{align*}
\]
Summary spin-current density-functional theory

- Treatment of magnetic and spin effects
- Spin-orbit can be included
- Flexible choice of considered interactions
- Exchange can be handled exactly, no approximate exchange functional needed
- Promising first results
Time-dependent DFT

Electronic system with periodic perturbation \( w(\omega, r) \cos(\omega t)e^{\varepsilon t}, \varepsilon \to 0^+ \)

\[
\hat{T} + \hat{V}_{ee} + \hat{v}_{ext} + \hat{w}(\omega) \cos(\omega t)
\]

Linear response \( \rho^L(\omega, r) \) of electron density

\( w(\omega, r) \cos(\omega t) \to \rho^L(\omega, r) \cos(\omega t) \)

Kohn-Sham Hamilton operator

Original Kohn-Sham state: \( \Phi(-\infty) = \Phi_0 \)

\[
\hat{T} + \hat{v}_{ext} + \hat{u} + \hat{v}_{xc} + \left[ \hat{w}(\omega) + \hat{w}_{uxc}(\omega) \right] \cos(\omega t) + O
\]

Linear response \( \rho(\omega, r) \)

\[
\rho^L(\omega) = X_s(\omega) \ w_s(\omega)
\]

\[
\rho^L(\omega) = X_s(\omega) \ [w(\omega) + F_{uxc}(\omega) \rho^L(\omega)]
\]

\[
[\mathbf{1} - X_s(\omega)F_{uxc}(\omega)] \ \rho^L(\omega) = X_s(\omega) \ w(\omega)
\]

Poles of response function: excitation frequencies
Density-matrix-based coupled Kohn-Sham equation I

Response of density as product of occupied and unoccupied orbitals

\[ \rho^L(\omega, r) = \int d\mathbf{r}' \chi_s(\omega, \mathbf{r}, \mathbf{r}') w_s(\omega, \mathbf{r}') \]

\[ = \sum_{\text{occ}} \sum_{\text{unocc}} \phi_a(\mathbf{r}) \phi_s(\mathbf{r}) \frac{4\epsilon_{sa}}{\omega^2 - \epsilon_{sa}^2} \langle \phi_s | \hat{\omega}_s(\omega) | \phi_a \rangle \]

\[ = \sum_{\text{occ}} \sum_{\text{unocc}} \phi_a(\mathbf{r}) \phi_s(\mathbf{r}) x_{as} \]

Substitution in density-matrix based coupled KS equation

\[ \rho^L(\omega, r) = \int d\mathbf{r}' \chi_s(\omega, \mathbf{r}, \mathbf{r}') \left[ w(\omega, \mathbf{r}') + \int d\mathbf{r}'' f_{u,xc}(\omega, \mathbf{r}', \mathbf{r}'') \rho^L(\omega, \mathbf{r}'') \right] \]

yields

\[ \sum_{as} \phi_a(\mathbf{r}) \phi_s(\mathbf{r}) x_{as}(\omega) \]

\[ = \sum_{as} \phi_a(\mathbf{r}) \phi_s(\mathbf{r}) \frac{4\epsilon_{sa}}{\omega^2 - \epsilon_{sa}^2} \left[ w_{as}(\omega) + \sum_{bt} K_{as, bt} x_{bt}(\omega) \right] \]
Density-matrix-based coupled Kohn-Sham equation II

Sufficient and necessary [JCP 110, 2785 (1999)] condition for density-based CKS equation to hold is that density-matrix-based CKS equation holds

\[ x(\omega) = \lambda(\omega)[w(\omega) + K(\omega)x(\omega)] \]

\[ [1 - \lambda(\omega)K(\omega)]x(\omega) = \lambda(\omega)w(\omega) \]

with

\[ w_{as}(\omega) = \int dr \ w(\omega, r)\phi_a(r)\phi_s(r) \]
\[ \lambda_{bt,as}(\omega) = \delta_{bt,as} \frac{4\epsilon_{sa}}{\omega^2 - \epsilon_{sa}^2} \]

\[ K_{as,bt}(\omega) = \int dr \int dr' \phi_a(r)\phi_s(r)f_{u,xc}(\omega, r, r')\phi_b(r')\phi_t(r') \]

Derivation of time dependent DFT without invoking the quantum mechanical or the Keldysch formalism possible [IJQC 69, 265 (1998)]
Density-matrix-based coupled Kohn-Sham equation III

\[
[1 - \lambda(\omega)K(\omega)]x(\omega) = \lambda(\omega)w(\omega)
\]

Multiplication with \(\lambda^{-1}(\omega) = (1/4) \epsilon^{-\frac{1}{2}} [\omega^2 1 - \epsilon^2] \epsilon^{-\frac{1}{2}}\) yields

\[
(1/4) \epsilon^{-\frac{1}{2}} \left[ \omega^2 1 - \epsilon^2 - 4\epsilon^{\frac{1}{2}}K(\omega)\epsilon^{\frac{1}{2}} \right] \epsilon^{-\frac{1}{2}} x(\omega) = w(\omega)
\]

With adiabatic approximation \(K = K(\omega = 0)\) and spectral representation

\[
M = \epsilon^2 + 4\epsilon^{\frac{1}{2}}K\epsilon^{\frac{1}{2}} = \sum_i x_i \omega_i^2 x_i^T
\]

of symmetric, positive definite matrix \(M\)

Excitation energies from eigenvalues of \(M\)
Absorption spectra of solids and molecules

Molecules

Exact excitation energies for only a few transitions
Ideal for density-matrix-based methods

\[
\begin{bmatrix}
\epsilon^2 + 4\epsilon^{1/2} K \epsilon^{1/2}
\end{bmatrix}
\begin{bmatrix}
x_i
\end{bmatrix}
= \omega_i^2
\begin{bmatrix}
x_i
\end{bmatrix}
\]

Iterative eigensolvers for determination of excitation energies \( \omega_i \)

Solids

Involved one-particle states: occupied bands \( \times \) unoccupied bands \( \times \) \( k \)-points
Exact excitation energies depend on \( k \)-points and are meaningless
Oscillator strengths for large number of transitions required
Ideal for density-based methods considering frequencies \( \omega + i\eta \)

\[
X(\omega + i\eta) = \left[ 1 - X_s(\omega + i\eta)F_{uxc}(\omega + i\eta) \right]^{-1} X_s(\omega)
\]

Absorption spectrum from imaginary part of response function \( X \)
Shortcomings of present time-dependent DFT methods

- Charge-transfer excitations not correctly described
- Polarizability of chain-like conjugated molecules strongly overestimated
- Two-electron or generally multiple-electron excitations not included

\[
\left[ \epsilon^2 + 4\epsilon^{\frac{1}{2}} K \epsilon^{\frac{1}{2}} \right] = \omega_i^2 x_i
\]

\[
K_{as, bt}(\omega) = \int dr \int dr' \phi_a(r) \phi_s(r) f_{u, xc}(\omega, r, r') \phi_b(r') \phi_t(r')
\]
TDDFT

‘Charge-transfer’-problem also in symmetric systems

**Ethylene dimer excitations**

![Graph showing excitations vs. distance](image)
Time-dependent DFT with exact exchange kernel

Integral equation for exact frequency-dependent exchange kernel $f_x(\omega, \mathbf{r}_1, \mathbf{r}_2)$

$$\int d\mathbf{r}_3 d\mathbf{r}_4 \; X_s(\omega, \mathbf{r}_1, \mathbf{r}_3) \; f_x(\omega, \mathbf{r}_3, \mathbf{r}_4) \; X_s(\omega, \mathbf{r}_4, \mathbf{r}_2) = h(\omega, \mathbf{r}_1, \mathbf{r}_2)$$

The function $h(\omega, \mathbf{r}_1, \mathbf{r}_2)$ depends on KS orbitals and eigenvalue differences.

Implementation for solids using plane-wave basis sets leads to promising results.
Function $h_x$, matrix $H_x$

$$H_{x,GG'}(q; \omega) =$$

$$- \frac{2}{\Omega} \sum \sum \sum \left[ \frac{\langle ak|e^{-i(q+G)\cdot r}|sk+q\rangle\langle sk+q; bk'|tk'+q; ak\rangle\langle tk'+q|e^{i(q+G')\cdot r}|bk'\rangle}{(\epsilon_{ak} - \epsilon_{sk+q} + \omega + i\eta)(\epsilon_{bk'} - \epsilon_{tk'+q} + \omega + i\eta)} \right]$$

$$- \frac{2}{\Omega} \sum \sum \left[ \frac{\langle ak|e^{-i(q+G)\cdot r}|sk+q\rangle\langle bk|\hat{v}_{NL}^x \hat{v}_{x}^{NL} - \hat{v}_x|ak\rangle\langle sk+q|e^{i(q+G')\cdot r}|bk\rangle}{(\epsilon_{ak} - \epsilon_{sk+q} + \omega + i\eta)(\epsilon_{bk} - \epsilon_{sk+q} + \omega + i\eta)} \right]$$

$$+ \frac{2}{\Omega} \sum \sum \left[ \frac{\langle ak|e^{-i(q+G)\cdot r}|sk+q\rangle\langle sk+q|\hat{v}_{NL}^x \hat{v}_x^{NL} - \hat{v}_x|tk+q\rangle\langle tk+q|e^{i(q+G')\cdot r}|ak\rangle}{(\epsilon_{ak} - \epsilon_{sk+q} + \omega + i\eta)(\epsilon_{ak} - \epsilon_{tk+q} + \omega + i\eta)} \right]$$

$$+ \ldots$$
Absorption spectrum of silicon

Realistic spectrum only if exchange is treated exactly
Description of excitonic effects with DFT methods possible
Concluding remarks

State- and orbital-dependent functionals lead to new generation of DFT methods

- More information accessible than through electron density alone
- (Effective) exact exchange methods
  - Problem of Coulomb self-interactions solved
  - Improved orbital and eigenvalues spectra corresponding to basic chemical and physical concepts; improved response properties
- Exact exchange spin-current DFT
  - Access to magnetic properties
  - Inclusion of spin-orbit effects
- Exact exchange TDDFT
  - Includes frequency-dependent kernel
  - Might solve some of the present shortcomings of TDDFT
- New KS approaches based on state-dependent functionals
  - DFT beyond the Hohenberg-Kohn theorem
- Formally as well as technically close relations to traditional quantum chemistry and many-body methods
- Development of new functionals for correlation desirable

Further information: www.chemie.uni-erlangen.de/pctc/