Exact-exchange methods as examples of density-functional approaches 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
  – Plane wave and Gaussian basis set implementations
  – Examples of applications

• Exact exchange TDDFT

• Symmetrized KS formalism leading to state-dependent functionals

• DFT beyond the Hohenberg-Kohn theorem

• Concluding remarks
Shortcomings of standard Kohn-Sham methods I

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
Shortcomings of standard Kohn-Sham methods II

Shortcomings due to the Kohn-Sham formalism

- Treatment of open-shell systems problematic; inconsistencies for states which are lowest of their symmetry but not ground states
- Excited states can not be treated self-consistently

New KS approaches to treat open-shell systems and excited states lead to state-dependent functionals
Reconsidering of the Kohn-Sham formalism

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

$\Phi_m, \phi_j, \epsilon_j, \Phi_0 \leftarrow \hat{T} + \hat{v}_s \leftarrow \rho_0 \rightarrow \hat{T} + \hat{V}_{ee} + \hat{v}_{\text{ext}} \rightarrow \Psi_0, E_0, \Psi_n, E_n$

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
$\hat{v}_{\text{ext}} \rightarrow \rho_0 \rightarrow E_0[\rho_0]$

Conventional view on KS method
$\hat{v}_{\text{ext}} \rightarrow \hat{T} + \hat{v}_{\text{ext}} + \hat{u}[\rho_0] + \hat{v}_{xc}[\rho_0] \rightarrow \phi_j \rightarrow \rho_0 \rightarrow E_0[\rho_0]$

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

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

Examples for orbital-dependent functionals

Exchange energy

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

meta-GGA functionals

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

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

\[ \Phi_m, \phi_j, \varepsilon_j, \Phi_0 \leftarrow \hat{T} + \hat{\nu}_s \rightarrow \rho_0 \rightarrow \hat{T} + \hat{V}_{ee} + \hat{\nu}_{ext} \rightarrow \Psi_0, E_0, \Psi_n, E_n \]

- KS system is meaningful model system associated with real electron system, electron density mediates this association
- KS potential \( \nu_s \) defines physical situation as well as it does \( \nu_{ext} \)
- Depending on situation quantities like \( E_0 \) or \( E_{xc} \) are considered as
  - functionals \( E_0[\nu_s] \) or \( E_{xc}[\nu_s] \) of \( \nu_s \)
  - 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 \( \frac{\delta E_x}{\delta v_s(\mathbf{r})} \) 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

\[
\sum_{\text{occ.}} \sum_{\text{unocc.}} \frac{\phi_a(r) \phi_s(r) \langle \phi_s | \hat{v}_x | \phi_a \rangle}{\varepsilon_a - \varepsilon_s} = \sum_{\text{occ.}} \sum_{\text{unocc.}} \frac{\phi_a(r) \phi_s(r) \langle \phi_s | \hat{v}_x^{NL} | \phi_a \rangle}{\varepsilon_a - \varepsilon_s}
\]

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 \(\Delta = |\varepsilon_a - \varepsilon_s|\)

\[
v_x(r) = 2 \sum_a \frac{\phi_a(r) \left[ \hat{v}_x^{NL} \phi_a \right](r)}{\rho(r)} + 2 \sum_{\text{occ.}} \sum_{a,b \neq (N,N)} \frac{\phi_a(r) \phi_b(r)}{\rho(r)} \langle \phi_b | \hat{v}_x - \hat{v}_x^{NL} | \phi_a \rangle
\]

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

BLYP

+2500Å  \(\pi(3p)\)  -2500Å  +0.0001 eV

HF

-12Å  -10.23 eV

+2500Å  \(\pi(3p)\)  -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
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: \( \approx 2 \) eV
## Excitation energies of molecules

Vertical excitation energies of ethylene, in eV

<table>
<thead>
<tr>
<th>Sym.</th>
<th>V/R</th>
<th>LHFX</th>
<th>BP</th>
<th>SOAP</th>
<th>EXP</th>
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</thead>
<tbody>
<tr>
<td>$^3B_{1u}$</td>
<td>V</td>
<td>4.57</td>
<td>4.68</td>
<td>4.64</td>
<td>4.36</td>
</tr>
<tr>
<td>$^3B_{3u}$</td>
<td>R</td>
<td>7.10</td>
<td>6.51</td>
<td>7.18</td>
<td>6.98</td>
</tr>
<tr>
<td>$^1B_{3u}$</td>
<td>R</td>
<td>7.38</td>
<td>6.53</td>
<td>7.29</td>
<td>7.15</td>
</tr>
<tr>
<td>$^1B_{1u}$</td>
<td>V</td>
<td>7.80</td>
<td>7.43</td>
<td>7.62</td>
<td>7.66</td>
</tr>
<tr>
<td>$^3B_{1g}$</td>
<td>R</td>
<td>8.16</td>
<td>7.09</td>
<td>7.91</td>
<td>7.79</td>
</tr>
<tr>
<td>$^1B_{1g}$</td>
<td>R</td>
<td>8.29</td>
<td>7.10</td>
<td>8.00</td>
<td>7.83</td>
</tr>
<tr>
<td>$^1B_{2g}$</td>
<td>R</td>
<td>8.28</td>
<td>6.95</td>
<td>7.94</td>
<td>8.00</td>
</tr>
<tr>
<td>$^3A_{g}$</td>
<td>R</td>
<td>7.97</td>
<td>7.36</td>
<td>8.70</td>
<td>8.15</td>
</tr>
<tr>
<td>$^1A_{g}$</td>
<td>R</td>
<td>8.27</td>
<td>7.36</td>
<td>8.91</td>
<td>8.29</td>
</tr>
<tr>
<td>$^3B_{3u}$</td>
<td>R</td>
<td>8.62</td>
<td>7.61</td>
<td>8.96</td>
<td>8.57</td>
</tr>
<tr>
<td>$^1B_{3u}$</td>
<td>R</td>
<td>8.83</td>
<td>7.64</td>
<td>9.03</td>
<td>8.62</td>
</tr>
</tbody>
</table>

MAE: 0.20 0.71 0.27
Max.: 0.46 1.05 0.62

LHF compared to BP orbitals and eigenvalues lead to strong improvement

LHF orbitals solve problem of TDDFT in treatment of Rydberg states
Response properties
More accurate response properties with exact treatment of KS exchange
Example: NMR chemical shifts for organo-iron-complexes

Fe(CO)$_5$  |  Ferrocene  |  Fe(CO)$_3$(C$_4$H$_6$)  |  CpFe(CO)$_2$CH$_3$  |  Fe(CO)$_4$C$_2$H$_3$CN

<table>
<thead>
<tr>
<th>System</th>
<th>BP86$^a$</th>
<th>BPW91$^b,c$</th>
<th>LHF$^b$</th>
<th>Exp.$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrocen</td>
<td>166</td>
<td>657</td>
<td>969</td>
<td>1532</td>
</tr>
<tr>
<td>Fe(CO)$_3$(C$_4$H$_6$)</td>
<td>-123</td>
<td>-105</td>
<td>12</td>
<td>4</td>
</tr>
<tr>
<td>CpFe(CO)$_2$CH$_3$</td>
<td>–</td>
<td>336</td>
<td>594</td>
<td>684</td>
</tr>
<tr>
<td>Fe(CO)$_4$C$_2$H$_3$CN</td>
<td>90</td>
<td>120</td>
<td>170</td>
<td>303</td>
</tr>
</tbody>
</table>

$^a$SOS-IGLO, M. Bühl et al., J. Comp. Chem. 20, 91 (1999).  
$^c$GIAO.
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
Absorption spectrum of silicon

Realistic spectrum only if exchange is treated exactly
Description of excitonic effects with DFT methods possible
Symmetrized KS formalism for open-shell systems

Totally symmetric contribution to the spin density takes role of spin density

$$
\phi_{j}^{\Lambda,\lambda}, \varepsilon_{j}^{\Lambda}, \Phi_{0}^{\Gamma,\gamma} \leftarrow \hat{T} + \hat{v}_s(\Gamma) \quad \overset{HK}{\longrightarrow} \quad \bar{\rho}(\Gamma) \quad \overset{HK}{\rightarrow} \quad \hat{T} + \hat{V}_{ee} + \hat{v}_{\text{ext}} \rightarrow \Psi_{0}^{\Gamma,\gamma}, E_{0}^{\Gamma,\gamma}
$$

KS equations for symmetrized KS formalism

$$
\left[ \hat{T} + \hat{v}_{\text{ext}} + \hat{u}[\bar{\rho}] + \hat{v}_{xc}[\bar{\rho}, \Gamma] \right] \phi_{j}^{\Lambda,\lambda} = \varepsilon_{j}^{\Lambda} \phi_{j}^{\Lambda,\lambda}
$$

KS Hamiltonian operator is always non-spin-polarized and exhibits same symmetry as real Hamiltonian operator

Functionals $E_{xc}[\bar{\rho}, \Gamma]$ and $v_{xc}[\bar{\rho}, \Gamma]$ evaluated as state-dependent functionals $E_{xc}[\Phi_{0}^{\Gamma,\gamma}]$ and corresponding functional derivative for $v_{xc}$
Open-shell LHF: Results for carbon

Excitation energies [eV]

<table>
<thead>
<tr>
<th>Open shells</th>
<th>State</th>
<th>ROHF</th>
<th>OSLHF</th>
<th>Exp.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2p^2$</td>
<td>$^1D$</td>
<td>1.559</td>
<td>1.539</td>
<td>1.26</td>
</tr>
<tr>
<td>$2s^1, 2p^3$</td>
<td>$^5S$</td>
<td>2.433</td>
<td>2.429</td>
<td>4.18</td>
</tr>
<tr>
<td>$2p^2$</td>
<td>$^1S$</td>
<td>3.783</td>
<td>3.771</td>
<td>2.68</td>
</tr>
<tr>
<td>$2p^1, 3s^1$</td>
<td>$^1P$</td>
<td>7.402</td>
<td>7.439</td>
<td>7.68</td>
</tr>
<tr>
<td>$2s^1, 2p^3$</td>
<td>$^3D$</td>
<td>8.007</td>
<td>7.990</td>
<td>7.94</td>
</tr>
</tbody>
</table>

*) NIST atomic spectra database
## Open-shell LHF: Results

### Total energies [eV]

<table>
<thead>
<tr>
<th>System</th>
<th>Open-Sh.</th>
<th>Sy.</th>
<th>HF</th>
<th>ΔLHF</th>
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</thead>
<tbody>
<tr>
<td>Thiophene</td>
<td>closed-sh.</td>
<td>$^1A_1$</td>
<td>-15003.744</td>
<td>+0.750</td>
</tr>
<tr>
<td></td>
<td>$1a_{2}^1$, $4b_{2}^1(U)$</td>
<td>$^3B_1$</td>
<td>-14996.632</td>
<td>+0.854</td>
</tr>
<tr>
<td></td>
<td>$1a_{2}^1$, $4b_{2}^1$</td>
<td>$^3B_1$</td>
<td>-15000.403</td>
<td>+1.155</td>
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<tr>
<td></td>
<td>$1a_{2}^1$, $4b_{2}^1$</td>
<td>$^1B_1$</td>
<td>-14997.699</td>
<td>+1.873</td>
</tr>
<tr>
<td>$C_6H_6^+$†</td>
<td>$3e_{1g}^3$</td>
<td>$^2E_{1g}$</td>
<td>-6271.532</td>
<td>+0.639</td>
</tr>
<tr>
<td>$C_{10}H_8^+$</td>
<td>$3a_u^1(U)$</td>
<td>$^2A_u$</td>
<td>-10428.268</td>
<td>+1.451</td>
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<tr>
<td>$C_{10}H_8^+$</td>
<td>$3a_u^1$</td>
<td>$^2A_u$</td>
<td>-10427.891</td>
<td>+1.329</td>
</tr>
</tbody>
</table>

![Graph showing energy vs distance](image)
Generalized adiabatic connection KS approach

Self-consistent KS treatment of excited states

Based on general theorem relating electron densities with external potentials and Hamiltonian operators

Generalized adiabatic connection

\[
\begin{bmatrix}
\hat{T} + \alpha \hat{V}_{ee} + \hat{v}(\alpha, \nu)
\end{bmatrix} \Psi(\alpha, \nu) = E(\alpha, \nu) \Psi(\alpha, \nu)
\]

\[\Psi(\alpha = 0, \nu) = \Phi_m \quad \Psi(\alpha = 1, \nu) = \Psi_n \quad \rho(\nu) \text{ independent of } \alpha\]

Symmetrized generalized adiabatic connection KS scheme

\[
\phi_j^{\Lambda, \lambda}, \varepsilon_j^{\Lambda}, \Phi_{m}^{\Gamma, \gamma} \leftarrow \hat{T} + \hat{v}_s(\Gamma, \nu) \leftarrow \bar{\rho}(\Gamma, \nu) \rightarrow \hat{T} + \hat{V}_{ee} + \hat{v}_{ext} \rightarrow \Psi_{n}^{\Gamma, \gamma}, E_{n}^{\Gamma, \gamma}
\]

KS equations for symmetrized GAC-KS approach

\[
\begin{bmatrix}
\hat{T} + \hat{v}_{ext} + \hat{u}[\bar{\rho}] + \hat{v}_{xc}[\bar{\rho}, \Gamma, \nu] 
\end{bmatrix} \phi_j^{\Lambda, \lambda} = \varepsilon_j^{\Lambda} \phi_j^{\Lambda, \lambda}.
\]

Functionals \(E_{xc}[\bar{\rho}, \Gamma, \nu]\) and \(v_{xc}[\bar{\rho}, \Gamma, \nu]\) evaluated as state-dependent functional \(E_{xc}[\Phi_{m}^{\Gamma, \gamma}]\) and corresponding functional derivative for \(v_{xc}\)
**GAC-OSLHF: Excited States of Carbon**

Excitation energies [eV]

\[ ^3P (1s^2, 2s^2, 2p^2) \longrightarrow ^{1/3}P (1s^2, 2s^2, 2p^1, ns^1) \]

<table>
<thead>
<tr>
<th>State</th>
<th>OSLHF</th>
<th>OSEX</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^1P) ((2p \rightarrow 6s))</td>
<td>10.26</td>
<td>10.24</td>
<td>10.71</td>
</tr>
<tr>
<td>(^1P) ((2p \rightarrow 5s))</td>
<td>9.95</td>
<td>9.94</td>
<td>10.40</td>
</tr>
<tr>
<td>(^1P) ((2p \rightarrow 4s))</td>
<td>9.30</td>
<td>9.31</td>
<td>9.71</td>
</tr>
<tr>
<td>(^1P) ((2p \rightarrow 3s))</td>
<td>7.44</td>
<td>7.49</td>
<td>7.68</td>
</tr>
<tr>
<td>(^3P) ((2p \rightarrow 6s))</td>
<td>10.24</td>
<td>10.23</td>
<td>10.70</td>
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<tr>
<td>(^3P) ((2p \rightarrow 5s))</td>
<td>9.92</td>
<td>9.92</td>
<td>10.38</td>
</tr>
<tr>
<td>(^3P) ((2p \rightarrow 4s))</td>
<td>9.25</td>
<td>9.25</td>
<td>9.68</td>
</tr>
<tr>
<td>(^3P) ((2p \rightarrow 3s))</td>
<td>7.24</td>
<td>7.27</td>
<td>7.48</td>
</tr>
</tbody>
</table>

Self-consistent KS treatment of highly excited states (Rydberg states) possible with generalized adiabatic connection KS approach
GAC-OSLHF: Results for CO

Exchange potentials for various states

Experiment: $1^1\Pi(5\sigma \rightarrow 2\pi) \ 8.51\text{eV}; \ 2^1\Pi(5\sigma \rightarrow 3\pi) \ 11.53\text{eV}$
GAC-OSLHF: Results for ketene

C₂H₂O

Excitation energies [eV]

<table>
<thead>
<tr>
<th>Excitation</th>
<th>State</th>
<th>OSLHF</th>
<th>TDDFT</th>
<th>Exp.</th>
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</thead>
<tbody>
<tr>
<td>2b₂ → 6b₁</td>
<td>1A₂</td>
<td>8.24</td>
<td>9.18</td>
<td></td>
</tr>
<tr>
<td>2b₂ → 6b₁</td>
<td>3A₂</td>
<td>8.23</td>
<td>9.15</td>
<td></td>
</tr>
<tr>
<td>2b₂ → 5b₁</td>
<td>1A₂</td>
<td>8.00</td>
<td>8.96</td>
<td></td>
</tr>
<tr>
<td>2b₂ → 5b₁</td>
<td>3A₂</td>
<td>7.99</td>
<td>8.94</td>
<td></td>
</tr>
<tr>
<td>2b₂ → 4b₁</td>
<td>1A₂</td>
<td>7.02</td>
<td>7.69</td>
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</tr>
<tr>
<td>2b₂ → 4b₁</td>
<td>3A₂</td>
<td>6.99</td>
<td>7.62</td>
<td></td>
</tr>
<tr>
<td>2b₂ → 3b₁</td>
<td>1A₂</td>
<td>4.15</td>
<td>4.35</td>
<td>3.87</td>
</tr>
<tr>
<td>2b₂ → 3b₁</td>
<td>3A₂</td>
<td>3.82</td>
<td>3.95</td>
<td>3.35</td>
</tr>
</tbody>
</table>

![Graph showing excitation energies and positions](image)
Concluding remarks

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

- More information accessible than through electron density alone
- Formally as well as technically close relations to traditional quantum chemistry and many-body methods
- (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 (e.g. NMR data, Rydberg excitations accessible by TDDFT)
  - Anions accessible
  - TDDFT with exact-exchange kernel
- New KS approaches based on state-dependent functionals
  - Symmetrized KS method for open-shell systems
  - GAC-KS approach for self-consistent treatment of excited states (DFT beyond the Hohenberg-Kohn theorem)
- Development of new functionals desirable
  - Correlation functional for combination with exact exchange
  - Combined exchange-correlation functional with potential with correct asymptotic

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