Excitations in finite systems

pragmatic improvements of DFT and fundamental questions in TDDFT

Stephan Kümmel
Theoretische Physik IV, University of Bayreuth

- not in Dresden since 2005 😊

Benasque 2010: Time-Dependent Density-Functional Theory
Benasque, January 11, 2010
Outline

1. “simple” excitations
   photoelectron spectroscopy and interpreting Kohn-Sham eigenvalues – the self-interaction issue

2. “true” excitations
   reconstructing the exact kernel $f_{xc}$ – first steps and insights
1. Organic semiconductors

Conjugated organic molecules can be semiconductors. Great interest because of use for

- light emitting diodes (OLEDs), displays, lasers
- antistatic foils, contacts in and screening of electronic devices, RFID tags
- organics solar cells
1. Organic semiconductors

typical molecules:

- Pentacene
- PTCDA
- NTCDA

Questions:

- Structure, e.g. gas phase vs. film?
- Electronic states? Excitations?
- Charge transfer mechanism?

⇒ Input from electronic structure theory needed
⇒ Many electrons → (TD)DFT
1. Photoelectron spectroscopy

Photoelectron spectroscopy frequently used for experimental investigation

\[ h\omega \rightarrow e^- \]
Photoelectron spectroscopy frequently used for experimental investigation
1. Photoelectron spectroscopy

- single particle interpretation:
  - measure binding energy of one electron
  - several electrons at same energy ⇒ higher peak
  - i.e., measure density of states (DOS)

*how to define single particle energies for interacting electrons?*
1. Photoelectron spectroscopy

- **single particle interpretation:**
  - measure binding energy of one electron
  - several electrons at same energy $\Rightarrow$ higher peak
  - i.e., measure density of states (DOS)

  *how to define single particle energies for interacting electrons?*

- **many-particle interpretation:**

  $|\psi_N\rangle + \hbar \omega \rightarrow |\psi_{N-1}\rangle^* + e^- |_{\text{detector}}$

  *calculating excited states of many-particle system accurately?*
1. Photoelectron spectroscopy

- **single particle interpretation:**
  - measure binding energy of one electron
  - several electrons at same energy \( \Rightarrow \) higher peak
  - i.e., measure density of states (DOS)

  *how to define single particle energies for interacting electrons?*

- **many-particle interpretation:**
  \[
  |\psi_N\rangle + \hbar \omega \rightarrow |\psi_{N-1}\rangle^* + e^-|_{\text{detector}}
  \]

  *calculating excited states of many-particle system accurately?*

- **DFT ideal (in principle): “optimal” single particle energies**

  KS DOS:
  - eigenvalues \( \leftrightarrow \) binding energies
  - degeneracies \( \leftrightarrow \) peak heights usually with broadening by hand

  *how good do \( \varepsilon_i \) describe the excitations that are measured in PES?*
1. Kohn-Sham DFT and PES

Kohn-Sham framework:
\[
\left[-\frac{\hbar^2}{2m} \nabla^2 + v_{KS}(\mathbf{r})\right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})
\]
Kohn-Sham equations

\[v_{KS}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d^3r' + v_{xc}(\mathbf{r})\]
Kohn-Sham potential

\[v_{xc}(\mathbf{r}) : \text{exchange-correlation potential}\]
*standard approximations LDA, GGA, ...*

What is known:

- eigenvalues \(\varepsilon_i\) can be interpreted as approximations to relaxed vertical ionization potentials
  
  *Perdew, Zunger, PRB 23, 5048 (1981); Chong, Gritsenko, Baerends, JCP 116, 1760 (2002)*

- approximation most reliable for outer valence levels

- approximation accurate if \(v_{xc}\) is “accurate enough”
1. Some examples

Examples 1: “Working”

**Si$_6^-$**

![Graph 1: Binding energy vs. intensity for Si$_6^-$](image1.png)

**Na$_5^-$**

![Graph 2: Binding energy vs. intensity for Na$_5^-$](image2.png)

Kronik, Fromherz, Ko, Ganteför, Chelikowsky, Nat. Mat. 1, 49 (2002)

1. More examples

Example 2: “Not working” PTCDA

typical result: \( \varepsilon_i \) peak where true spectrum has HOMO – HOMO-1 “gap”

\[\text{Dori, Menon, Kilian, Sokolowskim, Kronik, Umbach, 73, 195208 (2006)}\]
1. Findings so far

- $\varepsilon_i$ from LDA, GGAs – if “rigidly shifted” – describe PES quite reasonably for many systems (e.g. Na clusters, Si clusters, $\text{Si}_x\text{D}^-$, Pentacene, ...)

- $\varepsilon_i$ from LDA, GGAs fail qualitatively to describe PES of many organic semiconductors (PTCDA, NTCDA, ...)

pragmatic and fundamental – p.10
1. Findings so far

- $\varepsilon_i$ from LDA, GGAs – if “rigidly shifted” – describe PES quite reasonably for many systems (e.g. Na clusters, Si clusters, Si$_x$D$^-$, Pentacene, ...)
- $\varepsilon_i$ from LDA, GGAs fail qualitatively to describe PES of many organic semiconductors (PTCDA, NTCDA, ...)

**Aims:**

- i) understand why $\varepsilon_i$ map DOS reliably for some systems but not for others
- ii) develop a better approach to determine DOS theoretically
1. What is going wrong - the SI problem

i) When are commonly used approximations “accurate enough”?

The self-interaction problem in the Kohn-Sham energy functional

\[ E[n] = \text{kinetic energy} + \text{interaction with nuclei} + \]

\[ \frac{e^2}{2} \int \int \frac{n(r)n(r')}{|r - r'|} d^3r d^3r' + E_{\text{xc}}[n] \]

Hartree-energy \( E_H \): spurious electrostatic interaction of each orbital density with itself

\( \uparrow \) \hspace{2cm} \text{xc-energy } E_{\text{xc}}: \)

\( \uparrow \)

must exactly compensate the Hartree error

(Semi-)local \( E_{\text{xc}} \) approximations suffer from spurious electron self-interaction: \( E_H[n_1] + E_{\text{xc}}^{\text{sl}}[n_1] \neq 0 \)
1. Defining SIE per orbital

Self-interaction in energy carries over to the potential:

\[ v_{KS}(r) = v_{\text{ext}}(r) + \frac{\delta}{\delta n(r)} (E_H[n] + E_{xc}[n]) \]

\[ = v_{\text{ext}}(r) + v_H[n](r) + v_{xc}[n](r) \]
1. Defining SIE per orbital

Self-interaction in energy carries over to the potential:

\[ v_{KS}(r) = v_{ext}(r) + \frac{\delta}{\delta n(r)} (E_H[n] + E_{xc}[n]) \]
\[ = v_{ext}(r) + v_H[n](r) + v_{xc}[n](r) \]

Define self-interaction error \( e_i \) for each orbital:

\[ e_i = \langle \varphi_i | v_H[|\varphi_i|^2] | \varphi_i \rangle + \langle \varphi_i | v_{xc}[|\varphi_i|^2] | \varphi_i \rangle \]
1. Evaluate self-interaction error per orbital

Compare $e_i$ for different systems ($e_i$ relative to $e_{\text{HOMO}}$)

- PENTACENE
- PTCDA
- NTCDA
- $\text{Si}_4\text{D}^-$
1. A criterion for $\varepsilon_i$-PES reliability

Conclusions so far:

- self-interaction error different for different orbitals $\Rightarrow$ contorted, unreliable eigenvalue spectrum

- **Result 1:** $e_i$ is an easy-to-evaluate criterion to predict reliability of KS-eigenvalue DOS!

How to get rid of SI error?
1. Self-interaction correction

**Basic idea:** subtract self-interaction orbital-by-orbital

\[
E_{xc}^{\text{SIC}} = E_{xc}^{\text{app}} - \sum_{i=1}^{N} \left( E_H[|\varphi_i|^2] + E_{xc}^{\text{app}}[|\varphi_i|^2] \right)
\]

old idea ... \textit{Perdew, Zunger, PRB 23, 5048 (1981)}
1. **Self-interaction correction**

**Basic idea:** subtract self-interaction orbital-by-orbital

\[
E_{xc}^{\text{SIC}} = E_{xc}^{\text{app}} - \sum_{i=1}^{N} \left( E_{H}[|\varphi_i|^2] + E_{xc}^{\text{app}}[|\varphi_i|^2] \right)
\]

old idea ... *Perdew, Zunger, PRB 23, 5048 (1981)*

... posing problems:

- how to calculate \( v_{xc} = \frac{\delta}{\delta n} E_{xc}[\{|\varphi_i|^2\}] \) ?

- usual OEP is very tedious to calculate for SIC (much more tedious than EXX-OEP) *Körzdörfer, Mundt, Kümmler, PRL 100, 133004 (2008)*

- \( E_{xc}^{\text{SIC}} \) is not invariant under unitary transformation of \( \{\varphi_i\} \)
  \( \{\varphi_i\} \rightarrow \{\tilde{\varphi}_i\} \) while leaving \( n \) constant changes \( E \)!
New approach: Generalized Optimized Effective Potential

**basic idea:** take unitary variance of $E_{xc}^{SIC}$ into account by including a unitary transformation between two sets of orbitals into the OEP minimization

\[
v_{xc} = \frac{\delta E_{xc} \{ \tilde{\phi} \}}{\delta n} = \sum_{\alpha, \beta, \gamma = \uparrow, \downarrow} \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} \int dr' \int dr'' \int dr''' \frac{\delta E_{xc}[\{ \tilde{\phi} \}]}{\delta \tilde{\phi}_i^{\alpha}(r')} \frac{\delta \varphi_j^{\beta}(r'')}{\delta \varphi_j^{\beta}(r'')} \frac{\delta v_{ks, \gamma}(r''')}{\delta n_\sigma(r)}
\]


Calculations become numerically feasible

**Test:** problem of “peak in gap” resolved?
1. Eigenvalues vs. PES for SIC

1. A side-remark on the KLI approximation
1. A side-remark on the KLI approximation

For SIC-functional the KLI approximation to G-OEP works, but the usual KLI approximation does not work!
1. Summary for “simple” excitations

Results 2:

- spatial structure of orbitals has great influence on self-interaction
- DOS from LDA, GGAs o.k. for Si, Na, Pentacene ... because all relevant orbitals are (de-)localized on a similar level
- PTCDA, NTCDA, ... : orbitals of different spatial character, thus LDA, GGAs have problems
- self-interaction free DFT can predict DOS with reasonable accuracy

there is a “trick” to estimate main effect of SIC without actually doing a SIC calculation:

\[ \varepsilon_{i}^{\text{est}} = \varepsilon_{i}^{\text{LDA}} - 0.94 \int \left( |\varphi_{i}|^2 \right)^{\frac{4}{3}} d^3r - \langle \varphi_{i} | v_{c}^{\text{LDA}} [ |\varphi_{i}|^2, 0 ] | \varphi_{i} \rangle \]

2. “True” excitations

Going beyond the $\varepsilon_i$ is mandatory

- when single-particle interpretation breaks down (e.g. in strong fields)
- for calculating optical absorption
- in case of collective resonances
- ...

**TDDFT**

e.g., in the Casida-formalism

$$\Omega_{ij} = \delta_{ij}(\varepsilon_i - \varepsilon_0)^2 + 4 \sqrt{(\varepsilon_i - \varepsilon_0)(\varepsilon_j - \varepsilon_0)}F_{ij}$$

where

$$F_{ij} = \int \int \varphi_0 \varphi_i f_{\text{hxc}}(\omega) \varphi_0 \varphi_j \, d^3r \, d^3r',$$

allows to calculate the exact (in principle) excitation energies

if the exact xc-kernel $f_{xc} = \frac{\delta v_{xc}}{\delta n}$ is known
2. Reconstructing $f_{xc}$

Can we get insight into the exact kernel?

**Yes** if response functions can be constructed and inverted.

Interacting response function:

$$\chi^{-1} = \left. \frac{\delta v_{\text{ext}}}{\delta n} \right|_{n_0}$$

Kohn-Sham response function:

$$\chi_s^{-1} = \left. \frac{\delta v_s}{\delta n} \right|_{n_0}$$

Take $\frac{\delta}{\delta n}$ of $v_s = v_{\text{ext}} + v_h + v_{xc}$:

$$\chi_s^{-1} = \chi^{-1} + V_{ee} + f_{xc}$$
Constructing $\chi$ and $\chi_s$

The static $\chi = \frac{\delta n}{\delta v_{\text{ext}}}$ can be constructed according to the scheme:

1. Solve interaction Schrödinger equation for $v_{\text{ext}}$ on a grid $\rightarrow n$
2. Solve interaction Schrödinger equation for $v_{\text{ext}} + \delta v$ where

$$\Rightarrow \tilde{n}^k$$

3. $\delta n^k = \tilde{n}^k - n$

4. $\chi(i, k) = \frac{\delta n^k(z_i)}{c}$ real space matrix representation of $\chi$!
Constructing $\chi$ and $\chi_s$

The static $\chi = \frac{\delta n}{\delta v_{ext}}$ can be constructed according to the scheme:

1. Solve interaction Schrödinger equation for $v_{ext}$ on a grid $\rightarrow n$
2. Solve interaction Schrödinger equation for $v_{ext} + \delta v$ where

$$\delta v_{ext}$$

$\Rightarrow \tilde{n}^k$

3. $\delta n^k = \tilde{n}^k - n$
4. $\chi(i, k) = \frac{\delta n^k(z_i)}{c}$ \hspace{1cm} \text{real space matrix representation of $\chi$!}$

Same scheme applied to exact (reconstructed) $v_s \Rightarrow \chi_s(i, k)$
What is needed? Very accurate solutions of Schrödinger and KS equations!

i) linear response $\rightarrow$ $c$ must be small
division $\Rightarrow \tilde{\delta n}$ needed very accurately

Solve for 1 dimensional 2 electron singlet systems with

$$V_{ee} = \frac{e^2}{\sqrt{z^2+1}}$$

1D Helium atom: $v_{\text{ext}} = \frac{-2e^2}{\sqrt{z^2+1}}$

1D anharmonic Hooke’s atom: $v_{\text{ext}} = 0.05(z^2 + 0.01z^6)$
Looking at $\chi$ and $\chi_s$ for 1D Helium

Looking at $\chi$ and $\chi_s$ for A6-Hooke

The adiabatically exact $f_{xc}$ for 1 D Helium

Visualization: $f_{c,0}^{\text{scaled}} = \arctan(f_c)$

Reliability?

- Viewgraphs of $\chi$ and $\chi_s$ can be trusted, numerically stable
- Viewgraphs of $f_{xc}$ cannot be trusted – inversion of response functions is numerically critical
Reliability?

- Viewgraphs of $\chi$ and $\chi_s$ can be trusted, numerically stable.
- Viewgraphs of $f_{xc}$ cannot be trusted – inversion of response functions is numerically critical.

**Testing the reconstructed kernel via sumrule:**

$$\int f_{xc}(z, z') \frac{\partial n_0(z')}{\partial z'} \, dz' = \frac{\partial v_{xc,0}(z)}{\partial z}$$

TDDFT with exact static $f_{xc}$ for A6 Hooke

kernel numerics o.k., tested by comparing with propagation results

full: exact  broken: adiabatically exact
Results from the adiabatically exact kernel

- the static xc kernel can be constructed
- it can be accurate for some systems (1D Helium)
- but even though its adiabatically exact it fails badly for other systems – double excitations
- we need xc approximations with memory for TDDFT
Collaborators and thanks

- Thomas Körzdörfer, Bayreuth: SIC and photoelectron spectra
- Mark Thiele, Bayreuth: adiabatic kernel
- Leeor Kronik, Noa Marom, Weizmann Institute of Science: photoelectron spectra

Financial support from DFG Normalverfahren and German-Israeli Foundation
Estimating SIC eigenvalues shift

PTCDA

NTCDA
Dipole power spectrum of 1D Helium

\begin{center}
\begin{figure}
\begin{center}
\includegraphics[width=\textwidth]{dipole_power_spectrum.png}
\end{center}
\end{figure}
\end{center}

\textit{full: exact  broken: adiabatically exact}