Electrical response of molecular chains and the exact exchange approach

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Outline

- (Hyper)polarizability of molecular chains
  - When LDA/GGA fails…
- Exact exchange within DFT
  - Optimized effective potential
- The real space approach - PARSEC
  - Calculations with exact exchange
  - The electrical response
- Results
  - Problem solved
  - Why it works
- Conclusions
Electrical response of molecular chains

Organic oligomers and polymers possess large and directional linear and non-linear electrical response for optical applications!

e.g., polyacetylene

\[ \text{C}_{2n}\text{H}_{2n+2} \]

Many electrons

DFT should be method of choice
Static limit

Linear response – polarizability ($\mathcal{P}$)

Non-linear response – $2^{nd}$ hyperpolarizability ($\mathcal{G}$)

\[
\mathcal{P} \equiv \frac{\partial \mathcal{P}}{\partial \mathcal{F}} = \frac{\partial^2 E}{\partial \mathcal{F}^2} \\
\mathcal{G} \equiv \frac{\partial^3 \mathcal{G}}{\partial \mathcal{F}^3} = \frac{\partial^4 E}{\partial \mathcal{F}^4}
\]

$\mathcal{F}$ - dipole

$E$ - Total energy

$F$ – electric field

(semi) local functionals (LDA/GGA) make large errors in linear and **huge errors** in non-linear response in the direction of the chain

$C_{20}H_{22}$: $\mathcal{P}_{\text{LDA}} = 2$

$C_{44}H_{46}$: $\mathcal{P}_{\text{LDA}} = 60$

... but Hartree-Fock surprisingly good!

Problems with (semi) local xc functionals

1. Asymptotic decay is wrong – exponential vs. \( \sim 1/r \)

… but not the problem!

2. Self-interaction error:

\[
\frac{1}{2} \frac{\langle \vec{r} \rangle \langle \vec{r}' \rangle}{|\vec{r} \cdot \vec{r}'|} d^3\vec{r} d^3\vec{r}' + E_{xc}^{1\text{electron}} \neq 0
\]

Hartree-Fock is self-interaction free!

What’s the DFT equivalent?
Exact exchange within DFT

\[ E_{x}^{ex} = \frac{1}{2} \sum_{\sigma=\uparrow,\downarrow}^{N_{\sigma}} \int_{\sigma} \int_{\sigma'} \frac{d^{3}r d^{3}r'}{|\vec{r} \cdots \vec{r}'|} \left( \frac{1}{\rho_{i}^{*}(\vec{r}) \rho_{j}^{*}(\vec{r}') \rho_{i}(\vec{r}) \rho_{j}(\vec{r}')} \right) \]

**Advantages:**

- Self interaction free
- One more ingredient treated exactly – a “third generation functional”
- Correct asymptotic form, derivative discontinuity

**Disadvantages:**

- Correlation? Lack of “fortunate error cancellation”.
- **Orbital** dependence. Density dependence implicit.
The optimized effective potential

\[ V_{xc\square}(\vec{r}) = \frac{\nabla E_{xc}[\{\square j\square\}]}{\nabla n_{\square}(\vec{r})} = \sum_{i=1}^{N_\square} \frac{\nabla E_{xc}[\{\square j\square\}]}{\nabla n_{\square}(\vec{r}')} \frac{\nabla_{i\square}(\vec{r}')}{\nabla n_{\square}(\vec{r})} d^3\vec{r}' + c.c. = \ldots \]

The OEP integral equation:

\[ \sum_{i=1}^{N_\square} \nabla_{i\square}(\vec{r}') [V_{xc\square}(\vec{r}')] \nabla_{uci\square}(\vec{r}') \nabla_{i\square}(\vec{r}) \frac{\nabla_{j\square}(\vec{r}') \nabla_{j\square}^*(\vec{r})}{\nabla_{i\square} \nabla_{j\square}} d^3\vec{r}' + c.c = 0 \]

Where

\[ u_{xci\square}(\vec{r}) = \frac{1}{\nabla_{i\square}^*(\vec{r}) \nabla_{i\square}(\vec{r})} \frac{\nabla E_{xc}[\{\square j\square\}]}{\nabla n_{\square}(\vec{r})} \]

A local potential.

Not Hartree-Fock!!

The KLI approximation

\[ V_{xc\square}(\vec{r}) = \frac{1}{2n(\vec{r})} \sum_{i=1}^{N} \left\{ \Box_i^*(\vec{r}') [V_{xc\square}(\vec{r}') \Box u_{xc\square}(\vec{r}')] \Box_j^* \Theta_{ij} \right\} + c.c \]

Where

\[ \Box_i^*(\vec{r}) = \Box \sum_{j=1\atop j \neq i} \frac{\Box_i^*(\vec{r}') [V_{xc\square}(\vec{r}') \Box u_{xc\square}(\vec{r}')] \Box_j^* \Theta_{ij}}{\Box^*_i(\vec{r})} \]

\[ \bar{u}_{xc\square} = \Box_i^* (\vec{r}) u_{xc\square}(\vec{r}) \Box_i (\vec{r}) d^3 r \]

\[ \bar{V}_{xc\square} = \Box_i^* (\vec{r}) V_{xc\square}(\vec{r}) \Box_i (\vec{r}) d^3 r \]

Very accurate for ground state properties!

Model hydrogen molecular chains

--- H — H — H — H — H --- H — H ---

**Same problem! e.g. \( H_{12} \)**

<table>
<thead>
<tr>
<th>method</th>
<th>( g ) [a.u.]</th>
<th>( g^* ) [a.u.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CI</td>
<td>127</td>
<td>179,000</td>
</tr>
<tr>
<td>HF</td>
<td>138</td>
<td>147,000</td>
</tr>
<tr>
<td>xKLI</td>
<td>157</td>
<td>277,000</td>
</tr>
<tr>
<td>LDA</td>
<td>211</td>
<td>( 1.27 \times 10^6 )</td>
</tr>
</tbody>
</table>

Why does KLI fail?

Option 1: DFT exact exchange too different from HF.
If so: Correlation??

Option 2: KLI response too different from that of OEP.
If so: why??

Need to do exact OEP!
OEPs made simple

A simple iterative procedure towards an exact OEP solution

\[
(\hat{h}_{KS} \square \square_i \square^* \square^i (\mathbf{r})) = \square \left[ V_{xc} (\mathbf{r}) \square u_{xci} (\mathbf{r}) \square (\overline{V}_{xci} \square \overline{u}_{xci}) \right] \square^* (\mathbf{r})
\]

\[
V_{xc}^{\text{new}} (\mathbf{r}) = V_{xc}^{\text{old}} (\mathbf{r}) + c \sum_{i=1}^{N_i} \square \square_i^* (\mathbf{r}) \square \square_i (\mathbf{r}) + c.c
\]


Calls for an all-purpose 3d implementation

(hyper)polarizabilities \( \square \) real space !!
The Real Space Approach

- System of interest placed in large domain and wave functions evaluated only at fixed grid points.
- Grid need not be cubic.

PARSEC:
Using *high order* finite differencing to approximate the Laplacian operator

\[ \frac{\partial^2 \Box}{\partial x^2} \bigg|_{x=x_0} = \frac{1}{h^2} \sum_{m=0}^{M} C_m \Box (x_0 + mh) \]
Real Space Approach (2)

• Advantages:
  The “basis” is objective
  Convergence is trivial
  Easy to implement
  No recurring basis setup and no spurious forces
  Natural, massive parallelization
  Resulting secular equation involves sparse matrices, which are never stored explicitly
  Can examine very large systems
Computing  
(hyper)polarizabilities

\[ \frac{\hbar^2}{2m} \langle n \rangle^2 + V_{\text{eff}} \langle \vec{F} \cdot \vec{r} \rangle_n = E_n \langle n \rangle_n \]

\[ \langle n \rangle \equiv \frac{\partial \langle n \rangle}{\partial \vec{F}} = \frac{\partial^2 E}{\partial \vec{F}^2} \]

\[ \langle n \rangle \equiv \frac{\partial^3 \langle n \rangle}{\partial \vec{F}^3} = \frac{\partial^4 E}{\partial \vec{F}^4} \]

- F=0.0015 a.u., 0.003 a.u., … , 0.012 a.u.
- Polynomial fit
- Accuracy: \( \langle n \rangle \) to better than 1\%, \( \langle n \rangle \) to a few %. 

**xOEP works!**

--- H — H — H — H — H ---

<table>
<thead>
<tr>
<th></th>
<th>Polarizability [a.u.]</th>
<th>Hyperpolarizability [a.u.] 10⁻³</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>H₄</td>
<td>H₆</td>
</tr>
<tr>
<td>LDA</td>
<td>37.6</td>
<td>72.2</td>
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<tr>
<td>xKLI</td>
<td>33.1</td>
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<tr>
<td>xOEP</td>
<td>32.2</td>
<td>56.6</td>
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<tr>
<td>HF</td>
<td>---</td>
<td>56.4</td>
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<tr>
<td>CC/Ci</td>
<td>---</td>
<td>50.5</td>
</tr>
</tbody>
</table>
Field Counteracting behavior

LDA – follows the field (via density)
xKLI, xOEP – counteract the field
Different barriers!
Hardly affects ground state
xOEP vs. xKLI with $F=0.005$ a.u.

Exchange hole

Response exchange

Exchange response drastically different!
What’s at work?

- Functional derivative discontinuity – response to fractional charge
- Orbital mixing and orbital averages
The KLI approximation

\[
V_{\text{xc}}(\vec{r}) = \frac{1}{2n(\vec{r})} \sum_{i=1}^{N} \left\{ \left| \nabla_i(\vec{r}) \right|^2 [u_{\text{xc}}(\vec{r}) + \nabla_{\text{xc}} \cdot \nabla u_{\text{xc}}] - \nabla \cdot \left[ \nabla_i^* \nabla_i(\vec{r}) \right] \right\} + \text{c.c}
\]

Where

\[
\square_i^* (\vec{r}) = \sum_{j=1}^{N} \frac{[V_{\text{xc}}(\vec{r}') \nabla u_{\text{xc}}(\vec{r}')] \nabla_j (\vec{r}') d^3 \vec{r}'}{\nabla_i \square_j (\vec{r})}
\]

\[
\overline{u}_{\text{xc}} = \sum_{i} \nabla_i^* (\vec{r}) u_{\text{xc}}(\vec{r}) \nabla_i (\vec{r}) d^3 r \quad \overline{V}_{\text{xc}} = \sum_{i} \nabla_i^* (\vec{r}) V_{\text{xc}}(\vec{r}) \nabla_i (\vec{r}) d^3 r
\]

Very accurate for ground state properties!

Conclusions

- Optimized effective potentials implemented simply and robustly within a real space high order finite difference approach. **An all-purpose tool!**

- Hyperpolarizabilities of molecular chains computed for the first time using xOEP. Quality comparable to HF. **Kohn-Sham exact exchange works!**

- xOEP works when xKLI fails because it sets higher barriers between units. **Functional derivative discontinuity!**