

Electrical response of molecular chains and the exact exchange approach

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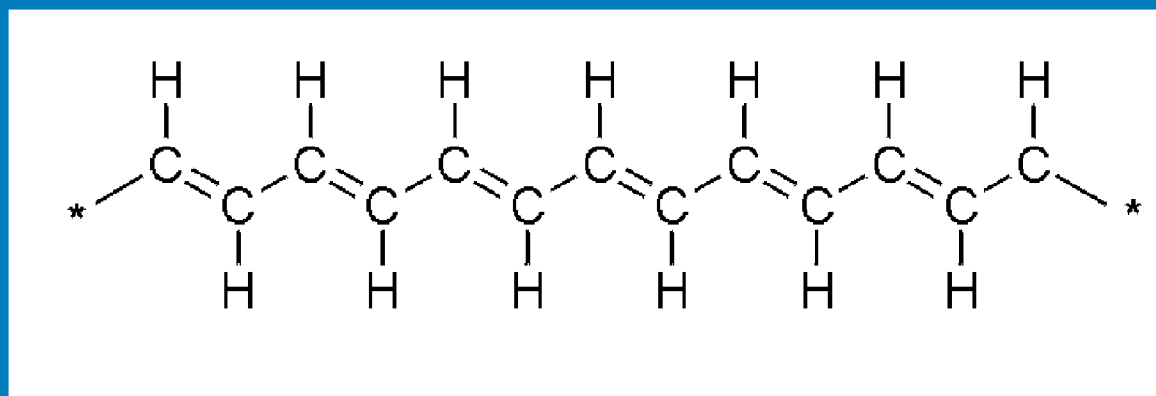
Outline

- **(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 \square optical applications!

e.g., polyacetylene



Many electrons \square

DFT should be method of choice

Static limit

Linear response – polarizability (α)

Non-linear response – 2nd hyperpolarizability (β)

$$\alpha \equiv \frac{\partial \langle \hat{\mu} \rangle}{\partial \vec{F}} = \frac{\partial^2 E}{\partial \vec{F}^2} \quad \beta \equiv \frac{\partial^3 \langle \hat{\mu} \rangle}{\partial \vec{F}^3} = \frac{\partial^4 E}{\partial \vec{F}^4}$$

$\langle \hat{\mu} \rangle$ - 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



... but Hartree-Fock surprisingly good!

Gisbergen et al., *Phys. Rev. Lett.* 83, 694 (1999).

Problems with (semi) local xc functionals

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

... but not the problem!

2. Self-interaction error:

$$\frac{1}{2} \int \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3\vec{r} d^3\vec{r}' + E_{xc}[\rho] \stackrel{1 \text{ electron}}{\neq} 0$$

Hartree-Fock is self-interaction free!

What's the DFT equivalent?

Exact exchange within DFT

$$E_x^{ex} \equiv \frac{1}{2} \sum_{\sigma=\uparrow,\downarrow} \sum_{i,j=1}^{N_{\sigma}} \iint d^3\vec{r} d^3\vec{r}' \frac{\psi_{i\sigma}^*(\vec{r}) \psi_{j\sigma}^*(\vec{r}') \psi_{j\sigma}(\vec{r}) \psi_{i\sigma}(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

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

$$V_{xc\sigma}(\vec{r}) = \frac{E_{xc}[\{\phi_{j\sigma}\}]}{n_{\sigma}(\vec{r})} = \sum_{\substack{i=1 \\ \sigma=\uparrow,\downarrow}} \left[\frac{E_{xc}[\{\phi_{j\sigma}\}]}{n_{i\sigma}(\vec{r}')} \frac{\phi_{i\sigma}(\vec{r}')}{n_{\sigma}(\vec{r})} \right] d^3\vec{r}' + c.c. = \dots$$

The OEP integral equation:

$$\sum_{i=1}^{N_{\sigma}} \phi_{i\sigma}^*(\vec{r}') [V_{xc\sigma}(\vec{r}') - u_{xci\sigma}(\vec{r}')] \phi_{i\sigma}(\vec{r}) \sum_{\substack{j=1 \\ j \neq i}} \frac{\phi_{j\sigma}(\vec{r}') \phi_{j\sigma}^*(\vec{r})}{n_{i\sigma}(\vec{r}) n_{j\sigma}(\vec{r})} d^3\vec{r}' + c.c. = 0$$

Where

$$u_{xci\sigma}(\vec{r}) = \frac{1}{\phi_{i\sigma}^*(\vec{r})} \frac{E_{xc}[\{\phi_{j\sigma}\}]}{n_{i\sigma}(\vec{r})}$$

A local potential.

Not Hartree-Fock !!

Grabo et al., *Mol. Eng.* 7, 20 (1997).

The KLI approximation

$$V_{xc\sigma}(\vec{r}) = \frac{1}{2n_{\sigma}(\vec{r})} \sum_{i=1}^{N_{\sigma}} \left\{ |\phi_{i\sigma}(\vec{r})|^2 \left[u_{xc\sigma}(\vec{r}) + \bar{V}_{xc\sigma} - \bar{u}_{xc\sigma} \right] \cdot \left[\phi_{i\sigma}^*(\vec{r}) \phi_{i\sigma}(\vec{r}) \right] \right\} + c.c.$$

KLI

Where

$$\phi_{i\sigma}^*(\vec{r}) = \sum_{\substack{j=1 \\ j \neq i}}^{N_{\sigma}} \frac{\phi_{i\sigma}^*(\vec{r}') [V_{xc\sigma}(\vec{r}') - u_{xc\sigma}(\vec{r}')] \phi_{j\sigma}(\vec{r}') d^3 \vec{r}'}{\sum_{i\sigma} \sum_{j\sigma}} \phi_{j\sigma}^*(\vec{r})$$

$$\bar{u}_{xc\sigma} = \sum_{i\sigma} \phi_{i\sigma}^*(\vec{r}) u_{xc\sigma}(\vec{r}) \phi_{i\sigma}(\vec{r}) d^3 r \quad \bar{V}_{xc\sigma} = \sum_{i\sigma} \phi_{i\sigma}^*(\vec{r}) V_{xc\sigma}(\vec{r}) \phi_{i\sigma}(\vec{r}) d^3 r$$

Very accurate for ground state properties!

Krieger, Li, and Lafrate, *Phys. Rev. A* 46, 5453 (1992)

Model hydrogen molecular chains



Same problem! e.g. H_{12}

method	\square [a.u.]	\square [a.u.]
CI	127	179,000
HF	138	147,000
xKLI	157	277,000
LDA	211	$1.27 \cdot 10^6$

Grüning et al., *J. Chem. Phys.* 116, 6440 (2002).

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

$$(\hat{h}_{KS} + \sum_i u_{xi}) \psi_i^*(\vec{r}) = \sum_i \left[V_{xc}(\vec{r}) + u_{xci}(\vec{r}) + (\bar{V}_{xci} + \bar{u}_{xci}) \right] \psi_i^*(\vec{r})$$

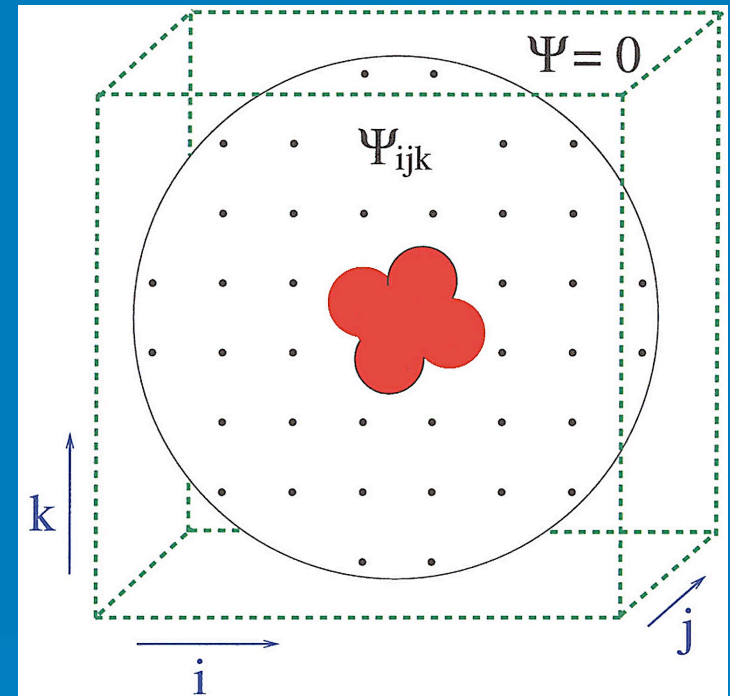
$$V_{xc}^{\text{new}}(\vec{r}) = V_{xc}^{\text{old}}(\vec{r}) + c \underbrace{\sum_{i=1}^{N_{\sigma}} \psi_i^*(\vec{r}) \psi_i(\vec{r})}_{0 \text{ when exact}} + c.c$$

Kümmel and Perdew, *Phys. Rev. Lett.* 90, 43004 (2003)

**Calls for an all-purpose 3d implementation
(hyper)polarizabilities in 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

$$\left. \frac{\partial^2 \square}{\partial x^2} \right|_{x=x_0} = \frac{1}{h^2} \sum_{m=-M}^M C_m \square(x_0 + mh)$$

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

$$\left[\frac{\hbar^2}{2m} \nabla^2 + V_{eff} \right] \underline{\vec{F}} \cdot \underline{\vec{r}} \psi_n = E_n \psi_n$$

$$\alpha \equiv \frac{\partial \langle \psi | \underline{\vec{F}} | \psi \rangle}{\partial \vec{F}} = \frac{\partial^2 E}{\partial \vec{F}^2} \quad \beta \equiv \frac{\partial^3 \langle \psi | \underline{\vec{F}} | \psi \rangle}{\partial \vec{F}^3} = \frac{\partial^4 E}{\partial \vec{F}^4}$$

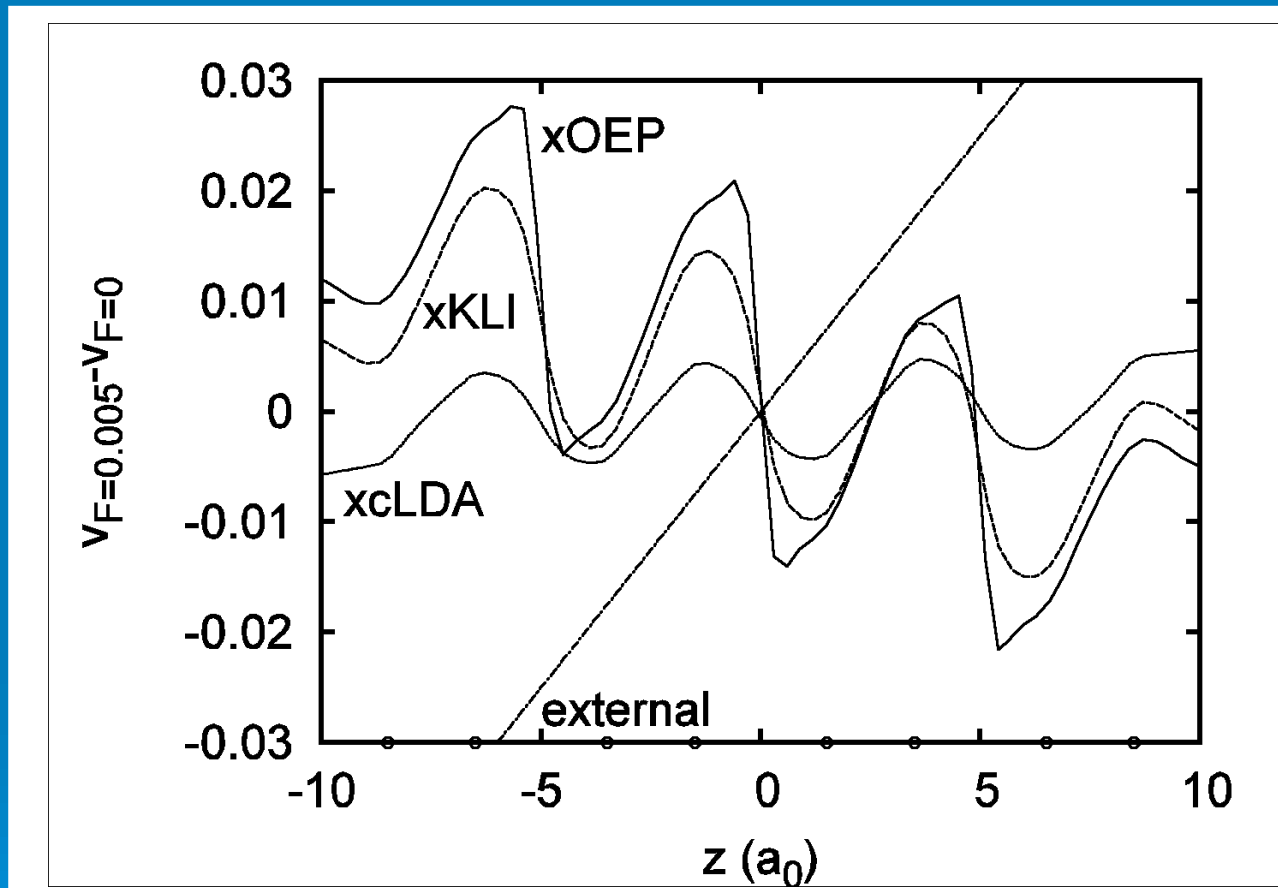
- $F=0.0015$ a.u., 0.003 a.u., ... , 0.012 a.u.
- Polynomial fit
- Accuracy: α to better than 1%, β to a few %.

xOEP works!



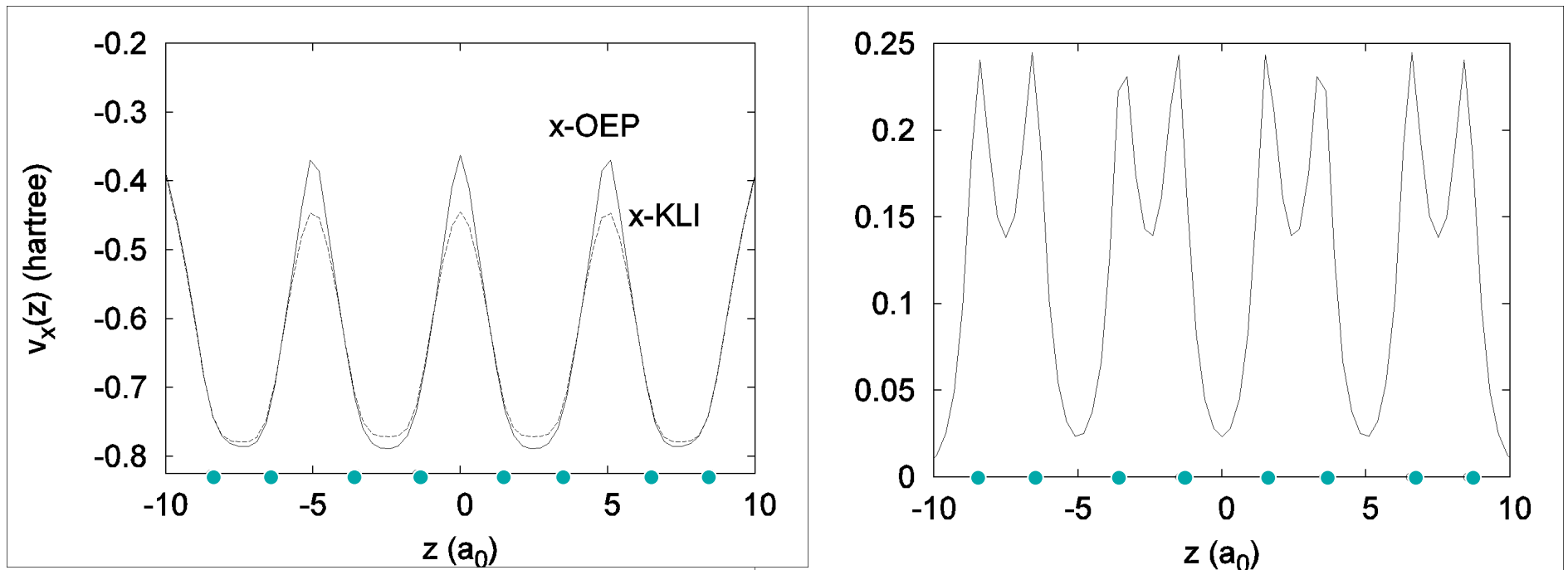
	Polarizability α				Hyperpolarizability β			
	[a.u.]				[a.u.] 10^{-3}			
	H ₄	H ₆	H ₈	H ₁₂	H ₄	H ₆	H ₈	H ₁₂
LDA	37.6	72.2	114.6	210.5	23.5	101	280	1200
xKLI	33.1	60.2	90.6	156.3	10.7	36	90	300
xOEP	32.2	56.6	84.2	138.1	9.3	30	68	144
HF	---	56.4	---	137.6	---	29.7	---	147
CC/CI	---	50.5	---	123.6	---	31.3	---	179

Field Counteracting behavior



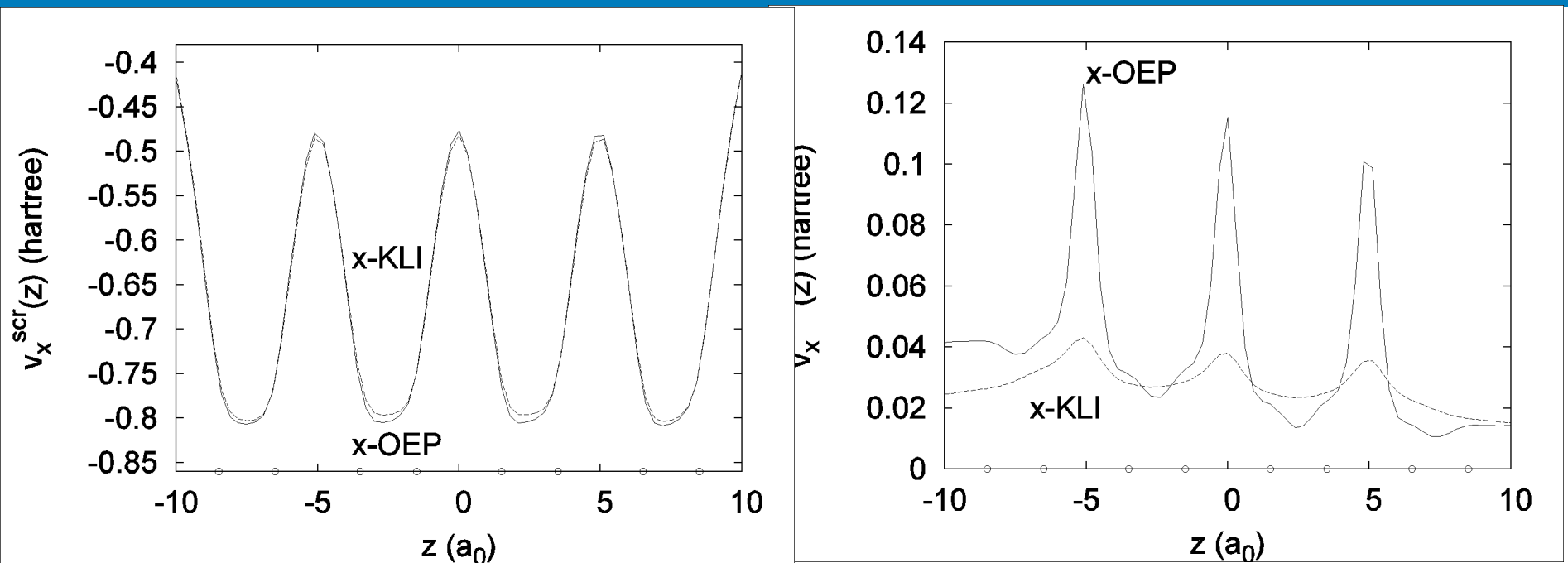
LDA – follows the field (via density)
xKLI, xOEP – counteract the field

xOEP vs. xKLI – no 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

$$V_{xc\sigma}(\vec{r}) = \frac{1}{2n_{\sigma}(\vec{r})} \sum_{i=1}^{N_{\sigma}} \left\{ |\phi_{i\sigma}(\vec{r})|^2 \left[u_{xc\sigma}(\vec{r}) + \bar{V}_{xc\sigma} - \bar{u}_{xc\sigma} \right] \cdot \left[\phi_{i\sigma}^*(\vec{r}) \phi_{i\sigma}(\vec{r}) \right] \right\} + c.c.$$

KLI

Where

$$\phi_{i\sigma}^*(\vec{r}) = \sum_{\substack{j=1 \\ j \neq i}}^{N_{\sigma}} \frac{\phi_{i\sigma}^*(\vec{r}') [V_{xc\sigma}(\vec{r}') - u_{xc\sigma}(\vec{r}')] \phi_{j\sigma}(\vec{r}') d^3 \vec{r}'}{\sum_{i\sigma} \sum_{j\sigma}} \phi_{j\sigma}^*(\vec{r})$$

$$\bar{u}_{xc\sigma} = \sum_{i\sigma} \phi_{i\sigma}^*(\vec{r}) u_{xc\sigma}(\vec{r}) \phi_{i\sigma}(\vec{r}) d^3 r \quad \bar{V}_{xc\sigma} = \sum_{i\sigma} \phi_{i\sigma}^*(\vec{r}) V_{xc\sigma}(\vec{r}) \phi_{i\sigma}(\vec{r}) d^3 r$$

Very accurate for ground state properties!

Krieger, Li, and Iafrate, *Phys. Rev. A* 46, 5453 (1992)

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!**