

Exchange-Correlation Functionals for Strong Correlation

André Mirtschink

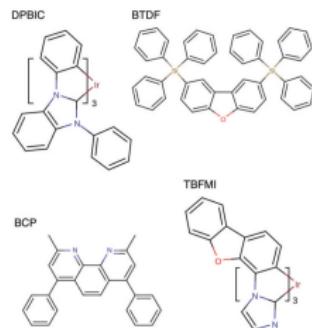
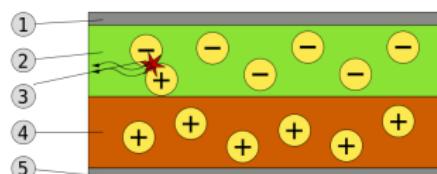
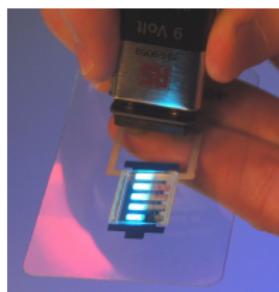
Nano-bio Spectroscopy Group, Donostia-San Sebastian, Spain

November 19, 2015
Group Seminar Theoretical Chemistry
TU Dresden

Introduction: Charge Transfer in Practice

CT: transfer of electronic charge among spatially separated regions by transitions between ground and excited states

e.g. in photosynthesis, organic photovoltaics, Organic Light Emitting Diodes (OLEDs)



- conductance of holes (4.) established by charge transfer in polymers

“During the past years simulation methods have been developed to compute the properties of OLEDs from their chemical composition. This allows for a cost efficient pre selection of molecules without elaborate synthesis and experimental characterization.” (wikipedia)

Introduction: Simulating OLEDs

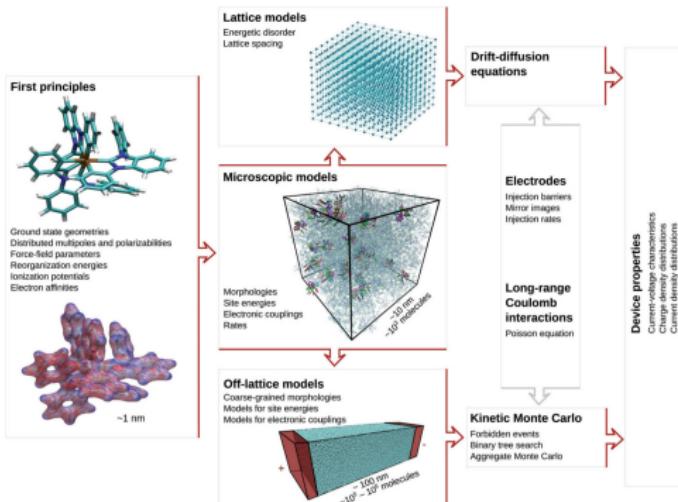


Figure 2. Possible workflows of parameter-free OLED simulations: polarizable force-fields and electronic properties of isolated molecules obtained from first principles are used to generate amorphous morphologies and evaluate charge transfer rates in small systems (microscopic models). Coarse-grained models are parametrized either by matching macroscopic observables, e.g., charge mobility, of the microscopic and coarse-grained (lattice) models. The resulting analytical expressions for mobility are then used to solve drift-diffusion equations for the entire device, after incorporating long-range electrostatic effects and electrodes. Alternatively, off-lattice models can be developed by matching distributions and correlations of site energies, electronic couplings, and positions of molecules. The master equations for this model can be solved using the kinetic Monte Carlo algorithm, yielding macroscopic characteristics of a device.

P Kordt et al., Adv. Funct. Mater. 25 (2015) 1955

Bridging the scales with DFT

- highly inhomogeneous compounds \rightarrow simulation boxes with 10^7 atoms
- functional approximations fail in the CT description

- QM: a resting atomic system is described by solutions to the many-body SE

$$\hat{H}\Psi(\mathbf{x}_1 \dots \mathbf{x}_N) = E\Psi(\mathbf{x}_1 \dots \mathbf{x}_N)$$

- ▶ wavefunction Ψ function of $(D + 1) \times N$ coordinates
 - ▶ expensive to compute
- HK theorem: Observables expressed as functional of ρ , in particular energy

$$E[\rho] = F[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) v_{ext}(\mathbf{r})$$

- ▶ ρ is a function of D coordinates
- ▶ ground state computation by variation of density
- ▶ exact expressions for the universal functional are computationally not efficient

Density Functional Theory

- HK theorem: Observables expressed as functional of ρ , in particular energy $E[\rho]$

$$E[\rho] = F[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) v_{ext}(\mathbf{r})$$

- ▶ unique mapping $\rho(\mathbf{r}) \leftrightarrow v(\mathbf{r})$
- ▶ uniqueness holds also beyond the physical $e^\ominus e^\ominus$ interaction

$$\{\rho(\mathbf{r}), \hat{V}_{ee}\} \leftrightarrow v_{ext}(\mathbf{r}) \leftrightarrow \Psi$$

$$\{\rho(\mathbf{r}), \hat{W}_{ee}\} \leftrightarrow \tilde{v}(\mathbf{r}) \leftrightarrow \tilde{\Psi}$$

- ▶ Levy-Lieb: \tilde{v} guarantees $\tilde{\Psi} \rightarrow \rho$ constraint

$$\tilde{F}[\rho] = \min_{\tilde{\Psi} \rightarrow \rho} \langle \tilde{\Psi} | \hat{T} + \hat{W}_{ee} | \tilde{\Psi} \rangle$$

- KS: introduce non-interacting reference system

$$\{\rho(\mathbf{r}), \hat{W}_{ee} = 0\} \leftrightarrow v_s(\mathbf{r}) \leftrightarrow \Phi$$

- ▶ which ground state WF is a Slater determinant $\tilde{\Psi} \rightarrow \Phi$
- the ground state energy of the physical system is

$$E[\rho] = \langle \Phi[\rho] | \hat{T} | \Phi[\rho] \rangle + U_H[\rho] + E_{xc}[\rho] + \int v_{ext}(\mathbf{r})\rho(\mathbf{r})$$

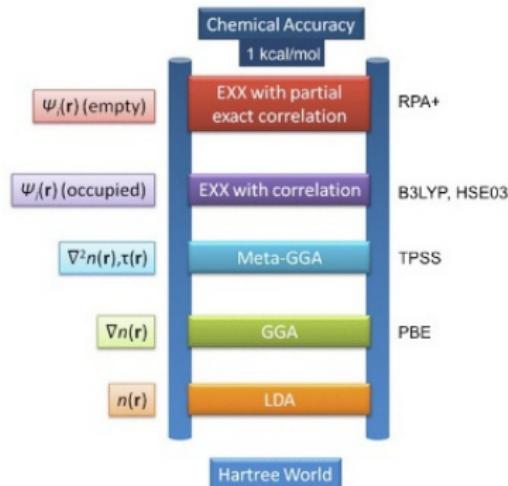
- Φ is obtained from the single-particle equations with the effective KS potential v_s

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

- ▶ $v_s(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})$
- ▶ v_{xc} accounts for many-body effects
- ▶ $v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \Big|_{\rho=\rho_0}$
- ▶ in principle exact, practical implementations use approximations

E_{xc} in Practice

traditional approximations
according to Jacob's ladder



- suitable if kinetic energy dominates
 - ▶ weak electronic correlation
- fail for strong correlation
 - ▶ electron localization due to dominating electronic repulsion
 - ▶ need of a non-local functional
- for higher rungs
 - ▶ rigor is lost (symmetry breaking)
 - ▶ computational effort increases
 - ▶ physical meaning of orbitals mitigated

<http://www.sas.upenn.edu/~jianmin/Research/>

- problematic:
 - ▶ long-range charge transfer
 - ▶ bond stretching
 - ▶ Coulomb blockade
- alternative strategies for the construction of approximations: *adiabatic connection*

Adiabatic Connection of DFT

- HK theorem: unique mapping for any $e^\Theta e^\Theta$ interaction

$$\{\rho(\mathbf{r}), \hat{W}_{ee}\} \leftrightarrow \tilde{v}(\mathbf{r}) \leftrightarrow \tilde{\Psi}$$

- we consider

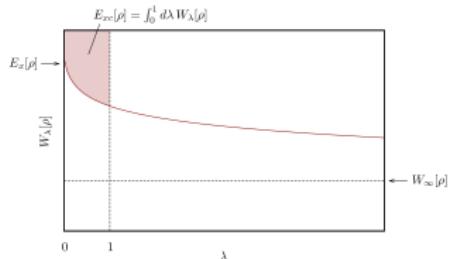
$$\hat{W}_{ee} = \lambda \hat{V}_{ee}, \quad \lambda \in [0, \infty)$$

- $\lambda = 1$... physical system, $\lambda = 0$... Kohn-Sham reference system
 $\lambda \rightarrow \infty$... reference system of strictly correlated electrons¹ (SCE)
- for a given ρ and λ a unique wavefunction $\Psi_\lambda[\rho]$ can be found from

$$\min_{\Psi_\lambda \rightarrow \rho} \langle \Psi_\lambda | \hat{T} + \lambda \hat{V}_{ee} | \Psi_\lambda \rangle$$

- $\Psi_\lambda[\rho]$ can be used to compute E_{xc}

$$\begin{aligned} E_{xc}[\rho] &= \int_0^1 d\lambda \langle \Psi_\lambda[\rho] | \hat{V}_{ee} | \Psi_\lambda[\rho] \rangle - U_H[\rho] \\ &= \int_0^1 d\lambda W_\lambda[\rho] \end{aligned}$$



¹M. Seidl, P. Gori-Giorgi, A. Savin, PRA **75** (2007) 042511

Approximate E_{xc} From the Adiabatic Connection

- we use an approximation for W_λ

- ▶ compute W_λ in the limits $\lambda \rightarrow 0, \infty$
 - ▶ obtain \tilde{W}_λ by interpolation
 - ▶ use \tilde{W}_λ to compute \tilde{E}_{xc}

- example: Seidl's ISI interpolation²

$$\tilde{W}_\lambda = W_\infty + \frac{W_0 - W_\infty}{\sqrt{1 + 2X\lambda}}$$

$$X = \frac{W'_0}{W_\infty - W_0}$$

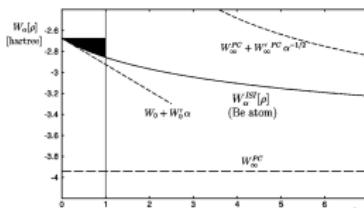
W'_0 from Görling-Lieb perturbation theory

W_∞ approximated from point-charge-plus-continuum model

- models interpolating between W_0 and $W_{\lambda \leq 1}$

- ▶ Becke: linear models for $\tilde{W}_\lambda \rightarrow$ half & half, (B3LYP)
 - ▶ Ernzerhof, Burke, Perdew: two legged models, curved models
 - ▶ Mori-Sanches, Cohen, Young: MCY functionals

$$\tilde{E}_{xc}[\rho] = \int_0^1 d\lambda \tilde{W}_\lambda[\rho]$$



²M. Seidl, PRA 60 (1999) 4387

Interpolations Along the Adiabatic Connection

- non-linear interpolation models for W_λ are not *size-consistent*
- interpolations performed locally are size-consistent

$$W_\lambda [\rho] = \int d\mathbf{r} \rho(\mathbf{r}) w_\lambda [\rho](\mathbf{r})$$

- $w_\lambda(\mathbf{r})$... energy density³

$$w_\lambda [\rho](\mathbf{r}) = \frac{1}{2\rho(\mathbf{r})} \int d\mathbf{r}' \frac{n_2(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

³AM, M. Seidl, P. Gori-Giorgi, JCTC **8** (2012) 3097

Ingredients for Local Interpolations of $w_\lambda(\mathbf{r})$

- $\lambda = 0$: non-interacting reference system

$$w_0(\mathbf{r}) = \frac{1}{2} \int d\mathbf{r}' \frac{\rho_x(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

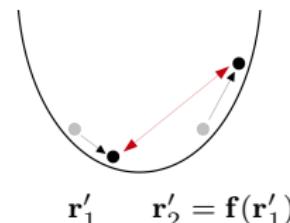
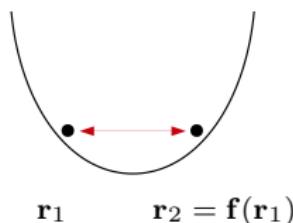
with the exchange hole ρ_x given in terms of KS orbitals ψ

- $\lambda \rightarrow \infty$: strongly correlated reference system

$$w_{\lambda \rightarrow \infty}(\mathbf{r}) = \frac{1}{2} \sum_{i=2}^N \frac{1}{|\mathbf{r} - \mathbf{f}_i(\mathbf{r})|} - \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

where \mathbf{f} are the co-motion functions that give the positions of the *strictly correlated electrons* (point charges)

e.g. $2e^-$ in harmonic oscillator potential



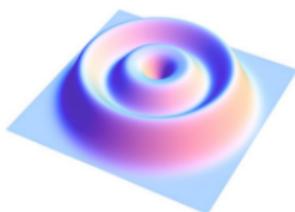
- SCE gives positions of e^\ominus for a given density

$$\rho(\mathbf{r}) \rightarrow \mathbf{f}_i(\mathbf{r})$$

- QM: probability of finding a e^\ominus in volume element $d\mathbf{r} =$

probability of finding another e^\ominus in volume element $d\mathbf{f}_i(\mathbf{r})$

$$\rho(\mathbf{r}) d\mathbf{r} = \rho(\mathbf{f}_i(\mathbf{r})) d\mathbf{f}_i(\mathbf{r})$$



density for 2D quantum dot, N=7

co-motion functions for 2D quantum dot,
N=7

Strictly Correlated Electrons

- the SCE wavefunction is obtained as sum of all allowed configurations $\{\mathbf{r}, \mathbf{f}_i(\mathbf{r})\}$

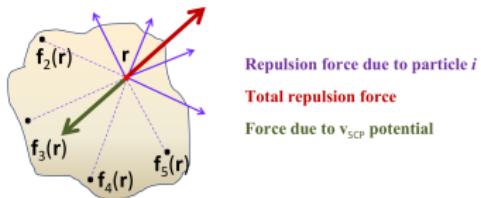
$$|\Psi_{SCE}(\mathbf{r}_1 \dots \mathbf{r}_N)|^2 = \frac{1}{N!} \sum_{\wp} \int d\mathbf{r} \frac{\rho(\mathbf{r})}{N} \delta(\mathbf{r}_1 - \mathbf{f}_{\wp(1)}(\mathbf{r})) \times \dots \times \delta(\mathbf{r}_N - \mathbf{f}_{\wp(N)}(\mathbf{r}))$$

- i.e. we must have that the potential energy for each configuration is the same - this is guaranteed by the SCE potential

$$E_{Pot} [\rho] (\mathbf{r}) = \sum_{i>j}^N \frac{1}{|\mathbf{f}_i(\mathbf{r}) - \mathbf{f}_j(\mathbf{r})|} + v_{SCE} [\rho] (\mathbf{r})$$

- the SCE potential can also be interpreted as the one that compensated the force of the other $N - 1$ exerted on a e^\ominus

$$\nabla v_{SCE} [\rho] (\mathbf{r}) = - \sum_{i=2}^N \frac{\mathbf{r} - \mathbf{f}_i(\mathbf{r})}{|\mathbf{r} - \mathbf{f}_i(\mathbf{r})|^3},$$



The SCE Functional

- total electrostatic energy for $\Psi_{SCE} \rightarrow$ SCE functional

$$V_{ee}^{SCE}[\rho] = \int d\mathbf{r} \frac{\rho(\mathbf{r})}{N} \sum_{i>j}^N \frac{1}{|\mathbf{f}_i(\mathbf{r}) - \mathbf{f}_j(\mathbf{r})|}$$

- the SCE wavefunction minimizes the scaled Levy-Lieb functional in the $\lambda \rightarrow \infty$ limit

$$\min_{\Psi_\lambda \rightarrow \rho} \langle \Psi_\lambda | \hat{T} + \lambda \hat{V}_{ee} | \Psi_\lambda \rangle \stackrel{\lambda \rightarrow \infty}{\approx} \min_{\Psi_\lambda \rightarrow \rho} \langle \Psi_\lambda | \lambda \hat{V}_{ee} | \Psi_\lambda \rangle = \lambda V_{ee}^{SCE}[\rho]$$

- the potential $v_\lambda [\rho](\mathbf{r})$ satisfying the $\Psi_\lambda \rightarrow \rho$ constraint in the $\lambda \rightarrow \infty$ limit is related to the SCE potential

$$\lim_{\lambda \rightarrow \infty} \frac{v_\lambda [\rho](\mathbf{r})}{\lambda} = v_{SCE} [\rho](\mathbf{r})$$

- furthermore it can be shown that the functional derivative of the SCE functional is the SCE potential

$$\left. \frac{\delta V_{ee}^{SCE}[\tilde{\rho}]}{\delta \tilde{\rho}(\mathbf{r})} \right|_{\tilde{\rho}=\rho} = -v_{SCE} [\rho](\mathbf{r})$$

the SCE functional is highly *non-local*,
but its functional derivative is still a
multiplicative potential

KS-DFT for Strong Correlation⁵

- $\tilde{v}_{SCE}[\rho] = -v_{SCE}[\rho]$ can be used as approximation for the electronic interaction in the KS reference system

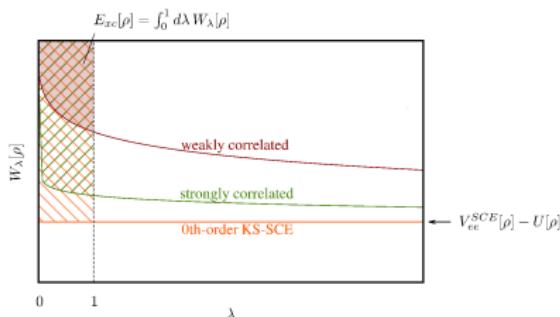
$$v_H[\rho] + v_{xc}[\rho] \approx \tilde{v}_{SCE}[\rho]$$

- i.e. we approximate the Hohenberg-Kohn functional

$$F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$$

$$\approx \min_{\Phi \rightarrow \rho} \langle \Phi | \hat{T} | \Phi \rangle + \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{V}_{ee} | \Psi \rangle$$

- always a lower bound
- exact in the weak- and strong-correlation regime, approximate in between
- strong correlation in KS-DFT

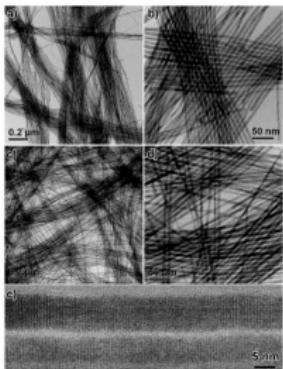


⁵F. Malet, P. Gori-Giorgi, PRL 109 (2012) 246402

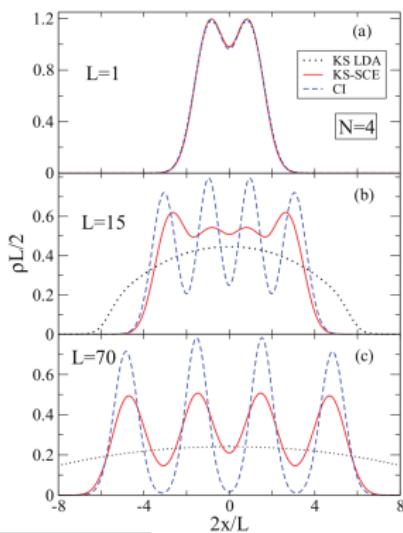
Systems with Tuneable Correlation

$$F^{KS-SCE}[\rho] = \min_{\Phi \rightarrow \rho} \langle \Phi | \hat{T} | \Phi \rangle + \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{V}_{ee} | \Psi \rangle$$

- evaluation by the use of semiconductor quantum wires
- show conductance quantization with transverse dimensions < 100 nm
- correlation regime controlled by wire length
- can be modeled with 1D harmonic oscillator and renormalized coulomb interaction^{6,7}



CdTe quantum wire,
Liu et al., J Am Chem Soc
134 18797 (2014)



self-consistent restricted KS-DFT

$2k_f \rightarrow 4k_f$
quantum phase transition

Coulomb blockade in DFT
requires quantum transport
simulation^a

L	CI	KS-SCE	$\Delta(\%)$
1	28.42	25.08	2.3
15	0.541	0.491	9.2
70	0.0602	0.06291	4.5

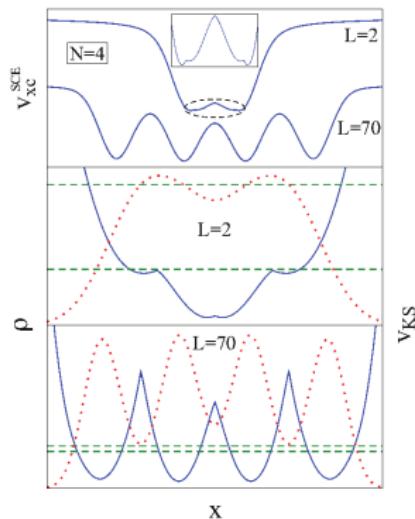
^aAM, S. Kurth, P. Gori-Giorgi, A. Rubio,
in preparation

⁶F. Malet et al., PRL 109 (2012) 246402

⁷F. Malet, AM et al., PRB 87 (2013) 115146

Features of the SCE Potential

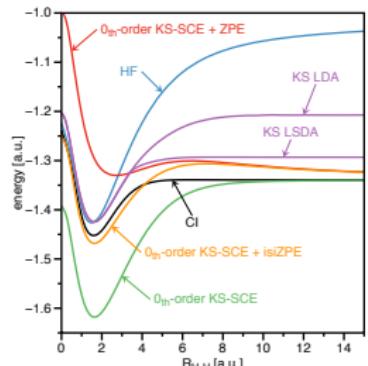
- $2k_f \rightarrow 4k_f$: strong correlation in DFT without symmetry breaking



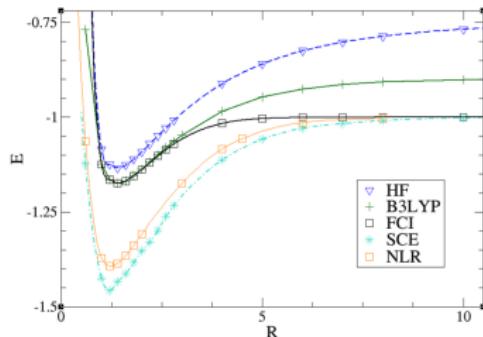
- bump in v_{xc} localizes electrons → essential feature for bond dissociation⁸

⁸M.A. Buijse, E.J. Baerends, J.G. Snijders, PRA **40** 4190 (1989)

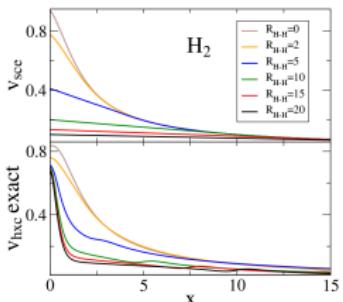
H_2 bond dissociation⁹



1D H_2 molecule
KS-SCE self consistent



3D H_2 molecule
KS-SCE on post-functional level



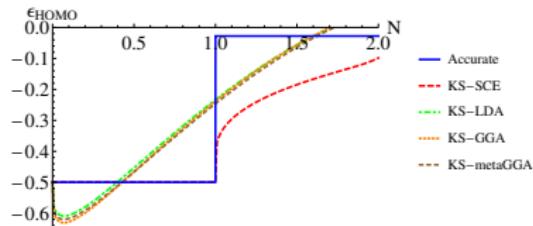
1D H_2 molecule

- bump in bond mid point vanishes for large separations
- even a small bump localizes electrons
- bump is energetically not important for large separations

⁹S. Vuckovic, L. O. Wagner, AM, P. Gori-Giorgi, JCTC 11 (2015) 3153

DFT for He Isoelectronic Series¹⁰

- H^- unbound with traditional DFT functionals ($\varepsilon_{\text{HOMO}} > 0$)



- KS-SCE *overbinds* H^- anion
 - ▶ SCE potential has correct $N^{-1/r}$ decay $\rightarrow \varepsilon_{\text{HOMO}}^{H^-} < 0$
 - ▶ SCE functional is SI free $E_H^{\text{SCE}} = E_H^{\text{exact}}$
 - ▶ SCE functional gives a lower bound to the energy $E_{H^-}^{\text{SCE}} < E_{H^-}^{\text{exact}}$
- note also: the SCE functional shows a *smooth derivative discontinuity*

¹⁰AM, C. J. Umrigar, J. D. Morgan III, P. Gori-Giorgi, JCP **140** (2014) 18A532

DFT for He Isoelectronic Series

- $2e^\ominus$ with decreasing nuclear charge $Z \rightarrow$ quantum phase transition to unbound system

$$Z_{crit}^{accurate} = 0.91, \quad Z_{crit}^{KS-SCE} = 0.73$$

- corrections are needed: KS-SCE + LDA

$$F[\rho] = T_s[\rho] + V_{ee}^{SCE}[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) (\epsilon_{xc}^{HEG}(\mathbf{r}) - \epsilon_{xc}^{SCE}(\mathbf{r}))$$

<hr/> <hr/> Z_{crit} <hr/>					
Accurate	0.91	KS-LDA	1.22	KS-SCE	0.73
		KS-GGA	1.23	KS-SCE+LDA	0.94
		KS-metaGGA	1.21	KS-SCE+LVee,d	0.90
		HF	1.03		
		B3LYP	1.14		

- KS-SCE+LDA is no more SI free

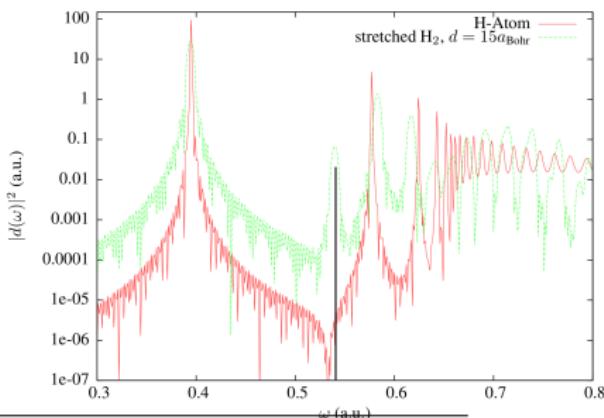
Charge Transfer in DFT¹¹

- Model: stretched H₂ in 1D



- Absorption spectra at large separation:
 - absorption spectra of isolated H atom
 - + CT transition at

$$\omega_{exact}^{CT} \approx I^H - A^H - 1/R$$



time propagation of time-dependent Schrödinger equation

$$\begin{aligned}\omega_{exact}^{CT} &\approx I^D - A^A - 1/R \\ &= 0.670 - 0.060 - 0.067 \\ &= 0.542 Ha\end{aligned}$$

¹¹AM, U. Giovannini, P. Gori-Giorgi, A. Rubio, in preparation

Charge Transfer in DFT

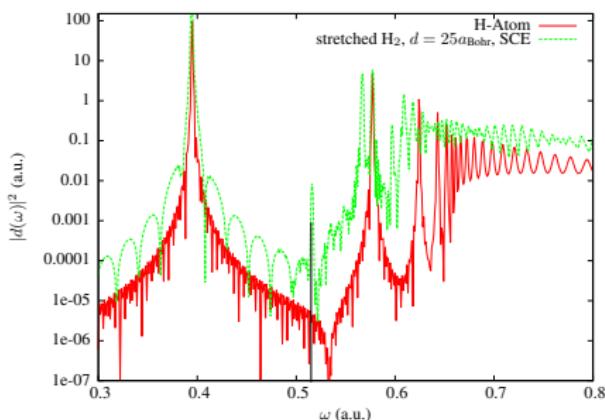
- CT transition in exact KS-DFT

$$\omega_{exDFT}^{CT} \approx -\epsilon_{HOMO}^D + \epsilon_{LUMO}^{A,N} + \Delta_{xc} - 1/R$$

- any approximation needs

- ▶ correct $1/r$ decay ϵ_{HOMO}^D
- ▶ derivative discontinuity Δ_{xc}
- ▶ non-local

- SCE functional has this features → adiabatic TD-DFT



time propagation of time-dependent
Kohn-Sham equation

$$\begin{aligned}\omega_{SCE}^{CT} &\approx -\epsilon_{HOMO}^H + \epsilon_{HOMO}^{H^-} - 1/R \\ &= 0.670 - 0.089 - 0.040 \\ &= 0.541 Ha\end{aligned}$$

- for a formal explanation of the SCE results the SCE kernel needs to be considered within the Casida equations
- a 1s-1s model for the CT transition predicts the CT frequency at¹²

$$w^{CT} = \Delta\varepsilon_{\sigma\sigma^*} + \sqrt{2\Delta\varepsilon_{\sigma\sigma^*} K_{\sigma\sigma^*,\sigma\sigma^*}}$$
$$K_{\sigma\sigma^*,\sigma\sigma^*} = \int d\mathbf{r} \int d\mathbf{r}' \chi_\sigma(\mathbf{r}) \chi_{\sigma^*}(\mathbf{r}) f_{Hxc}(\mathbf{r}, \mathbf{r}') \chi_\sigma(\mathbf{r}') \chi_{\sigma^*}(\mathbf{r}')$$

- $\Delta\varepsilon \rightarrow 0$ for large R
- kernel in K-matrix for large R needs to cause
 - ▶ divergence in K to compensate for $\Delta\varepsilon \rightarrow 0$
 - ▶ give rise to $1/R$ term
- the SCE kernel in 1D

$$f_{Hxc}^{SCE}(x, x') = \sum_{i=2}^N \int_{-\infty}^x dy w''(|x - x'|) \frac{\theta(x' - y) - \theta(x' - f_i(y))}{\rho(f(y))}$$

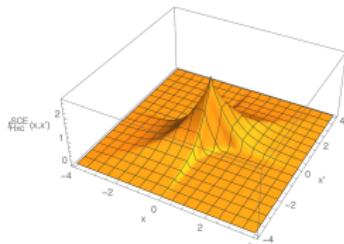
¹²O.V. Gritsenko, S.J.A. van Gisbergen, A. Görling, E.J. Baerends, JCP **113** (2000) 8478

SCE kernel 1D

- the SCE kernel in 1D

$$f_{Hxc}^{SCE}(x, x') = \sum_{i=2}^N \int_{-\infty}^x dy w''(|x - x'|) \frac{\theta(x' - y) - \theta(x' - f_i(y))}{\rho(f(y))}$$

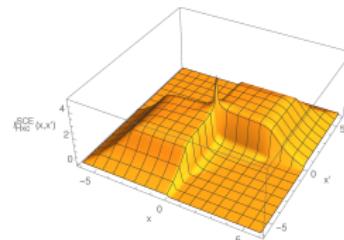
- for a model density out of two exponentials



$$R = 1$$

- for large R we have a plateau of high

$$f_{Hxc}^{SCE}\left(-\frac{R}{2}, -\frac{R}{2}\right) = \frac{1}{R} \frac{1}{\rho(0)}$$



$$R = 14$$

- for large R we have a peak of high

$$f_{Hxc}^{SCE}(0, 0) = \frac{2}{R} \frac{1}{\rho(0)}$$

- note: a local kernel shows a non-zero value only for $x = x'$

Conclusions

- a rigorous strategy for the construction of approximate E_{xc} has been presented
- the SCE reference system was introduced
- an approximate E_{xc} was constructed by combining the KS- with the SCE reference system
- the KS-SCE approximation is:
 - ▶ non-local
 - ▶ SI free
 - ▶ derivative discontinuity
 - ▶ accurate in the weak- and strong-correlation regime
 - ▶ universal (bosons with dipolar interaction¹³)
- can not be used for chemistry yet, because:
 - ▶ inaccurate in the intermediate-correlation regime
 - corrections of LDA kind, local interpolations or higher order corrections to SCE
 - ▶ the SCE functional can not be calculated for arbitrary 3D systems
 - co-motion functions are not unique in 3D
 - approximations to co-motion functions
 - model the strong-interacting limit (PC model, non-local radius model)
- future:
 - ▶ SCE in solids, esp. Mott insulator
 - ▶ SCE for diatomics → SCE-DFTB

The SCE functional can lead to improved functional approximations. Before realistic 3D systems can be tackled, however, the accuracy needs to be improved and a 3D implementation of the functional should be developed.

¹³F. Malet, AM et. al, PRL 115 (2015) 033006

Acknowledgments

- Angel Rubio
Stefan Kurth
and group members
(UPV San Sebastian)
- financial support: DFG research fellowship
- thank you for your attention!!!
- Paola Gori-Giorgi
Michael Seidl
Francesc Malet
and group members (VU Amsterdam)