Pilot Applications of the SCE Functional for the Description of Strong Correlation in Adiabatic TDDFT

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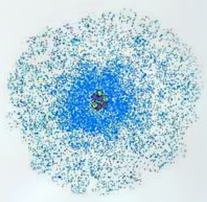
Kohn-Sham reference system

electrons are modeled as

- charge clouds (**quantum mechanical** picture)
- without interaction between them
- move in an external field chosen such that the physical density is obtained



- effectively the KS single-particle equations are solved

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

Adiabatic connection[1]

. . . is a formalism that allows for a rigorous construction of an approximate energy density functional where both reference systems are combined

$$E_{xc}[\rho] = \int_0^1 d\lambda\, \langle\Psi_\lambda[\rho]|\hat{V}_{ee}|\Psi_\lambda[\rho]\rangle - E_H[\rho] \equiv \int_0^1 d\lambda\, W_\lambda[\rho] \qquad (3)$$

where the wavefunction $\Psi_\lambda[\rho$ stems from the energy minimization

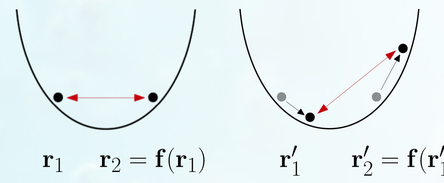
$$\min_{\Psi\to\rho}\langle\Psi|\hat{T} + \lambda\hat{V}_{ee}|\Psi\rangle \qquad \forall \quad \lambda \in \mathbb{R}$$

and for $\lambda \to 0$ the KS reference system is encountered and for $\lambda \to \infty$ we have the SCE reference system[2]

SCE reference system[2]

electrons are modeled as

- point charges (**classical** picture)
- no kinetic energy
- electronic positions are thus perfectly correlated (strictly correlated electrons, **SCE**)



- co-motion functions $\mathbf{f}_i(\mathbf{r})$ for all reference positions $\mathbf{r}$ follow from the SCE differential equation

$$\rho(\mathbf{r})\, d\mathbf{r} = \rho(\mathbf{f}_i(\mathbf{r}))\, d\mathbf{f}_i(\mathbf{r}) \qquad \forall \quad i \in 2\ldots N \qquad (2)$$

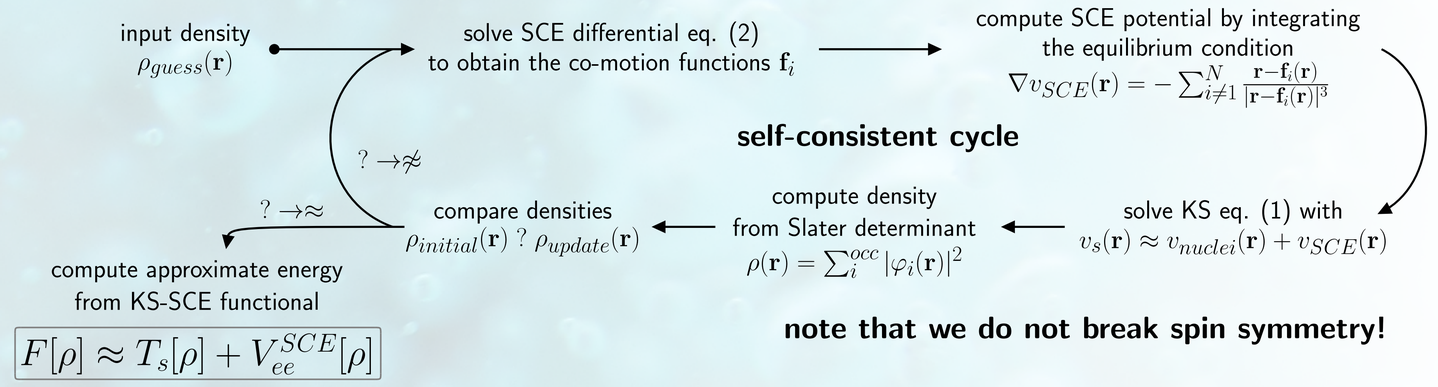
that is solved such that the potential energy for each electronic arrangement is the same

KS-SCE method[3,4]

we do now approximate the coupling constant integrand W_λ of eq. (3) for all λ by its value in the strong-interaction limit[5]

$$W_\lambda \approx V_{ee}^{SCE}[\rho] = \int d\mathbf{r}\, \frac{\rho(\mathbf{r})}{N}\sum_{i>2}^{N}\frac{1}{|\mathbf{r} - \mathbf{f}_i(\mathbf{r})|}$$

which is equivalent to a **linear interpolation on** W_λ, and a method results that is exact for weakly and strongly correlated systems and approximate in between these limits when solved self consistently



note that we do not break spin symmetry!

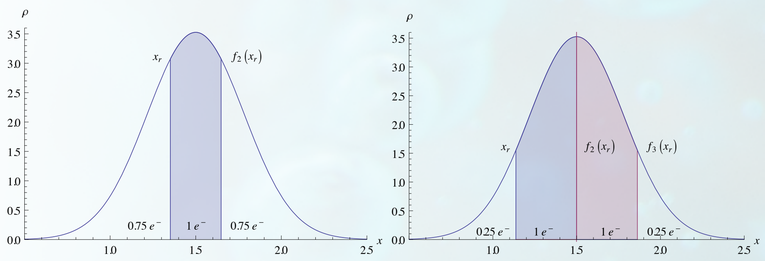
SCE functional for fractional electron numbers[6,7]

as the SCE functional models electrons as point charges, can we treat non-integer electron numbers $Q = N + \eta$[8]? **Yes!** Because a rigorous solution of the SCE differential eq. (2) is possible

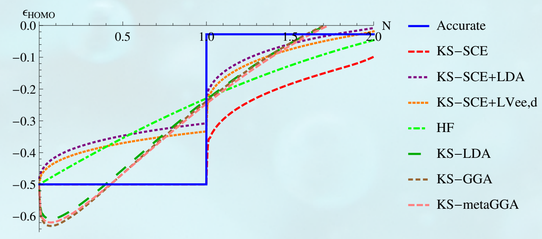
- e.g. in 1D we find that the density in between two electronic positions always integrates to 1

$$\int_{f_i(x)}^{f_{i+1}(x)} dy\, \rho(y) = 1$$

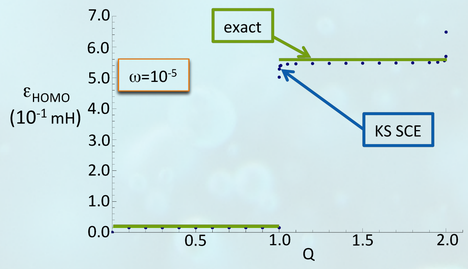
and for a Gaussian containing 2.5 e$^-$ we sometimes find two or three electrons inside the density



- let's check on the **derivative discontinuity** of the SCE functional in the Hydrogen nuclear field



we have it, although a sharp step structure is only obtained for very strongly correlated systems, e.g. Hooke's atom



- other good news: **KS-SCE binds** H^-
- KS-SCE+L. . . are local corrections to the SCE functional that derive from the homogeneous electron gas
  but: they are not self-interaction free
  though: we have ideas on how to cure this[10]
- for comparison we give the maximum number of electrons to be bound with the traditional functionals (also spin restricted):

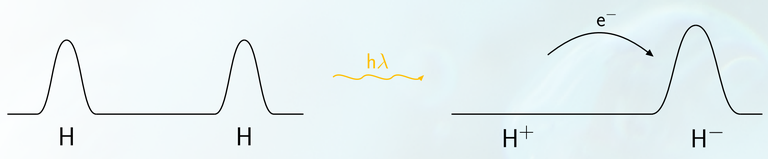
	Q_{max}
KS-LDA:	1.71
KS-GGA:	1.70
KS-metaGGA:	1.73
KS-hybrid:	1.75

in a *ET-QZ3P+3diffuse* basis set

KS-TDDFT with the adiabatic SCE functional[9]

the SCE functional exerts a smoothed derivative discontinuity – can we describe **charge transfer excitations** in adiabatic TDDFT?

- we did apply the KS-SCE method to a 1D model for the H_2 molecule and consider the electron hopping HH $\to$ H^+H^-



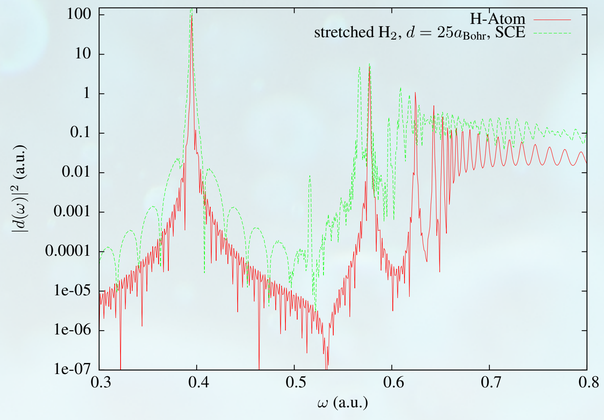
- at $R = 25\mathrm{a_{Bohr}}$ we estimate the exact CT peak from the total energies

$$\omega_{CT} \approx I_H - A_H - 1/R = 0.569\mathrm{Ha}$$

and an SCE estimate can be obtained from the orbital eigenvalues

$$\omega_{CT}^{SCE} \approx -\varepsilon_{HOMO}^{H} + \varepsilon_{\mathrm{HOMO}}^{H^-,SCE} - 1/R = 0.541\mathrm{Ha}$$

- precondition is of course that 1D H^- is bound - we do!



CT peak can be identified at $\omega \approx 0.516\mathrm{Ha}$

ω shows the right $1/R$ behavior upon further dissociation
excitation intensity vanishes too

Implications for applications

- promising for CT description of real-world matter by adiabatic TDDFT
  problem: SCE differential eq. (2) can so far be only solved for spherically symmetric 3D densities
  solution 1: construction of approximate co-motion functions $\mathbf{f}_i(\mathbf{r})$ by geometrical arguments
  $\to$ poster by S. Vuckovic *"Dissociating chemical bond in the strictly – correlated regime of density functional theory"*
  solution 2: non-local radius model to approximate SCE functional
  $\to$ poster by L. Wagner *"Capturing strong electron correlation with nonlocal density functionals"*
- promising for modeling of quantum transport in nano devices
  $\to$ G. Lani, A. Mirtschink, S. Kurth, P. Gori-Giorgi, in preparation
- poster on fundamental aspects of ASCE by G. Lani *"The SCE functional in the time domain: insights into its formal properties"*

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