The adiabatic strictly-correlated electrons functional

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Content/focus

Study the adiabatic approximation in TD DFT in the exact strong coupling limit

- Highly non-local spatial dependence (very different than conventional approximate functionals)
- Satisfaction of exact many-body constraints
- Analysis of the adiabatic kernel in this limit

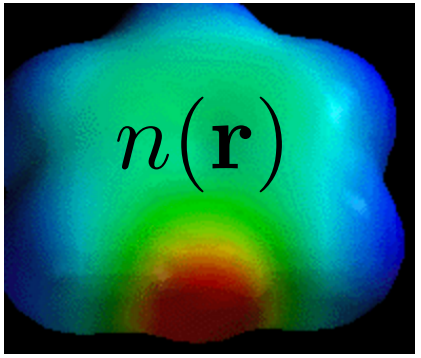
$$\mathcal{F}_{xc}(\mathbf{r},\mathbf{r}') = \frac{\delta^2 E_{xc}[n]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}$$

Get insight to build new approximations

Real time propagation

The strong-coupling limit of the HK functional

$$F\ [n] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \quad \hat{V}_{ee} | \Psi \rangle$$



$$\lim_{\lambda \to \infty} F_\lambda[n] = \lambda \min_{\Psi \to n} \langle \Psi | \hat{V}_{ee} | \Psi \rangle + O(\sqrt{\lambda})$$

semiclassical limit at **fixed density**

*Seidl, Gori-Giorgi & Savin, PRA **75**, 042511 (2007)*
*Gori-Giorgi, Vignale & Seidl, JCTC **5**, 743 (2009)*
*Gori-Giorgi, Seidl & Vignale, PRL **103**, 166402 (2009)*
Cotar, Friesecke, & Kluppelberg, Comm. Pure Appl. Math. 66, 548 (2013)

Strong coupling limit (SCE) of DFT

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

HK functional

$$T_s[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} | \Psi \rangle$$

KS kinetic energy

$$V_{ee}^{\mathrm{SCE}}[n] = \min_{\Psi \to n} \langle \Psi | \hat{V}_{ee} | \Psi \rangle$$

SCE functional

"strictly correlated electrons"

Hartree + xc functional tends asymptotically to SCE in the low-density or strong-coupling limit

$$E_{\mathrm{Hxc}}[n] = F[n] - T_s[n] \to V_{ee}^{\mathrm{SCE}}[n]$$

SCE functional (physical picture)

$$V_{ee}^{\mathrm{SCE}}[n] = \min_{\Psi \to n} \langle \Psi | \hat{V}_{ee} | \Psi \rangle$$

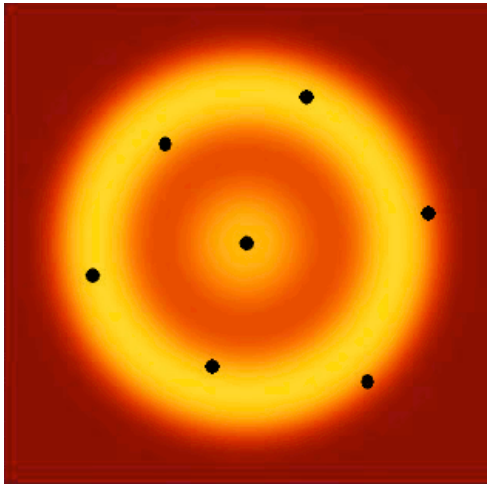
$$|\Psi_{\mathrm{SCE}}(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)|^2 = \int d\mathbf{s}\, \frac{n(\mathbf{s})}{N}\, \delta(\mathbf{r}_1 - \mathbf{f}_1(\mathbf{s}))\delta(\mathbf{r}_2 - \mathbf{f}_2(\mathbf{s}))...\delta(\mathbf{r}_N - \mathbf{f}_N(\mathbf{s}))$$

the wavefunction collapses to a 3D subspace of the full 3N-dimensional configuration space

$$\mathbf{f}_i(\mathbf{r}, [n])$$

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

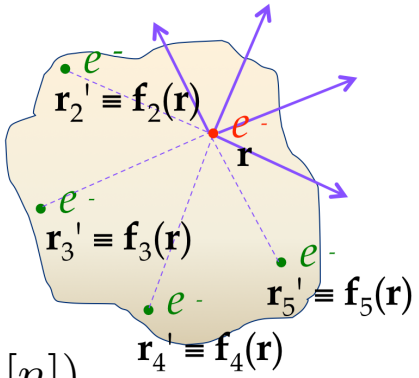
$$\mathbf{f}_1(\mathbf{r}) \equiv \mathbf{r},$$
$$\mathbf{f}_2(\mathbf{r}) \equiv \mathbf{f}(\mathbf{r}),$$
$$\mathbf{f}_3(\mathbf{r}) = \mathbf{f}(\mathbf{f}(\mathbf{r})),$$
$$\mathbf{f}_4(\mathbf{r}) = \mathbf{f}(\mathbf{f}(\mathbf{f}(\mathbf{r}))),$$
$$\vdots$$
$$\underbrace{\mathbf{f}(\mathbf{f}(\ldots\mathbf{f}(\mathbf{f}(\mathbf{r}))))}_{N \text{ times}} = \mathbf{r}.$$



Seidl, PRA 60, 4387 (1999)
*Seidl, Gori-Giorgi and Savin, PRA **75**, 042511 (2007)*
*Malet & Gori-Giorgi, PRL **109** 246402 (2012)*
*Malet, Mirtschink, Cremon, Reimann & Gori-Giorgi, PRB **87** 115146 (2013)*

SCE functional and functional derivative

$$V_{ee}^{\mathrm{SCE}}[n] = \frac{1}{2}\int d\mathbf{s}\, n(\mathbf{s}) \sum_{i=2}^{N} \frac{1}{|\mathbf{s} - \mathbf{f}_i(\mathbf{s};[n])|}$$



$$\frac{\delta V_{ee}^{\mathrm{SCE}}[n]}{\delta n(\mathbf{r})} = v_{\mathrm{SCE}}(\mathbf{r};[n])$$

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

shortcut to the functional derivative

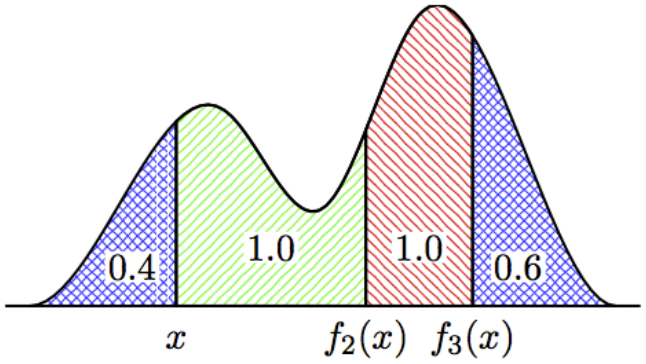
$v_{\mathrm{Hxc}}(\mathbf{r};[n]) \to v_{\mathrm{SCE}}(\mathbf{r};[n])$ in the low-density (strong-interaction) limit

*Seidl, Gori-Giorgi and Savin, PRA **75**, 042511 (2007)*

*Malet & Gori-Giorgi, PRL **109** 246402 (2012)*

*Malet, Mirtschink, Cremon, Reimann & Gori-Giorgi, PRB **87** 115146 (2013)*

1D case is transparent



$$N_e(x) = \int_{-\infty}^{x} n(x')\,dx'$$

$$a_k = N_e^{-1}(k)$$

$$f_i(x) = \begin{cases} N_e^{-1}[N_e(x) + i - 1] & x \le a_{N+1-i} \\ N_e^{-1}[N_e(x) + i - 1 - N] & x > a_{N+1-i}, \end{cases}$$

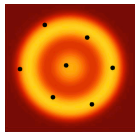
Written on simple physical considerations: *M. Seidl, PRA **60**, 4387 (1999)*

Rigorous Proof: *M. Colombo, L. De Pascale, S. Di Marino, Can. J. Math. 67, 350 (2015)*

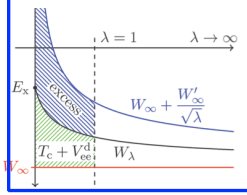
KS SCE applied to 1D physics: *Malet & Gori-Giorgi, PRL 109 246402 (2012);*
Malet, Mirtschink, Cremon, Reimann & Gori-Giorgi, PRB 87 115146 (2013)

Starting the investigation in TD DFT

A large amount of work has been done on the ground state



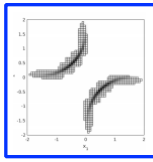
low-dimensional physics:
electrons, cold atoms..



xc functionals:
approximations, scaling
local interpolation, spin

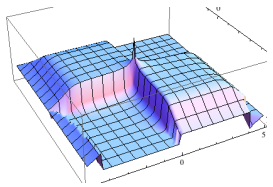
$$\Lambda[\rho] \equiv \max_{\Psi \to \rho} \lambda[\Psi]$$

Lieb-Oxford
bound



optimal transport theory:
algorithms, exact results

We start investigation in the TD framework



time-dependent:
adiabatic SCE kernel,
quantum transport

Adiabatic SCE: potential

The SCE potential has a highly non-local dependence on the density

if used in the adiabatic approximation for time propagation,
would it violate exact properties?

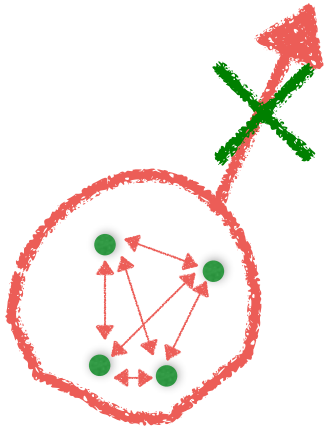
for example, KLI leads to spurious increased amplitude of dipole oscillations
[Mundt, Kummel, van Leeuwen, Reinhard, PRA 75, 050501 (2007)]

The xc potential should satisfy the generalised translational invariance

$$n'(\mathbf{r},t) = n(\mathbf{r} - \mathbf{R}(t),t) \qquad v_{xc}([n'];\mathbf{r},t) = v_{xc}([n];\mathbf{r} - \mathbf{R}(t),t)$$

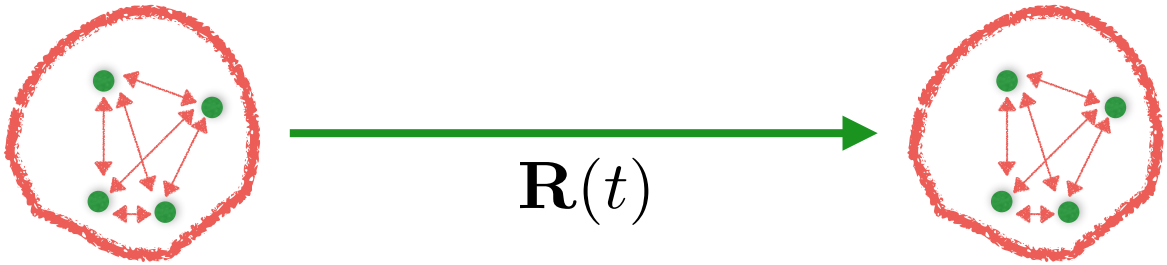
this also guarantees fulfilment of the zero-force theorem:

$$\int n(\mathbf{r},t)\, \nabla v_{xc}(\mathbf{r},t) d^3r = \mathbf{0}.$$



*Vignale, PRL **74**, 3233 (1995)*

The adiabatic SCE potential satisfies GTI



$$n'(\mathbf{r},t) = n(\mathbf{r} - \mathbf{R}(t),t) \qquad \mathbf{f}_i([n'];\mathbf{r}) = \mathbf{f}_i([n];\mathbf{r} - \mathbf{R}(t)) + \mathbf{R}(t).$$

$$\begin{aligned}\nabla v_{\mathrm{Hxc}}^{\mathrm{SCE}}([n'];\mathbf{r},t) &= -\sum_{i=2}^{N} \frac{\mathbf{r} - \mathbf{f}_i([n];\mathbf{r} - \mathbf{R}(t)) - \mathbf{R}(t)}{|\mathbf{r} - \mathbf{f}_i([n];\mathbf{r} - \mathbf{R}(t)) - \mathbf{R}(t)|^3} \\ &= \nabla v_{\mathrm{Hxc}}^{\mathrm{SCE}}([n];\mathbf{r} - \mathbf{R}(t),t).\end{aligned}$$

the adiabatic SCE potential satisfies the generalised translational invariance
(and thus the zero-force theorem)

ASCE kernel for 1D systems

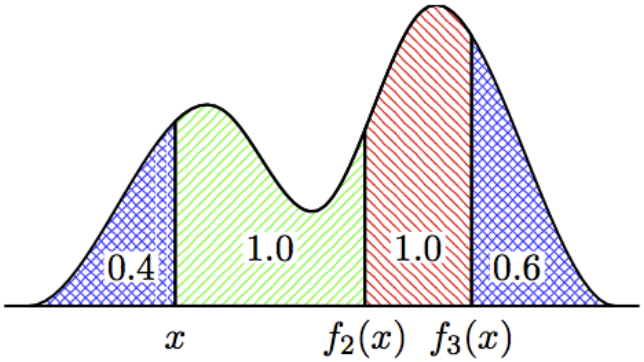
$$\mathcal{F}_{\mathrm{Hxc}}^{\mathrm{SCE}}([n];\mathbf{r},\mathbf{r}') = \frac{\delta^2 V_{ee}^{\mathrm{SCE}}[n]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}$$

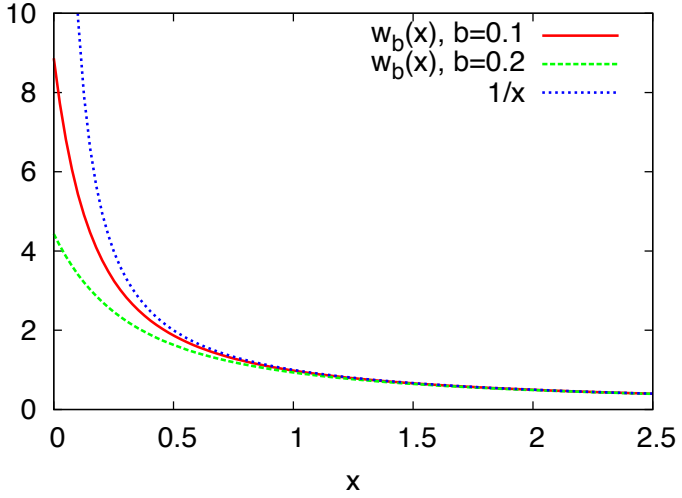
Intense amount of work has been done in identifying exact features of the kernel

SCE allows us to see how some of these features appear from the density dependence

1D hamiltonians

$$H_{1D} = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\frac{\partial^2}{\partial x_i^2} + \sum_{i=1}^{N}\sum_{j>i}^{N} w_b(|x_i - x_j|) + \sum_{i=1}^{N} v_{\text{ext}}(x_i)$$





$$v_{\text{Hxc}}^{\text{SCE}}([n];x) = -\sum_{i=2}^{N}\int_{x}^{\infty} w'(|\,y - f_i([n];y)|) \times \text{sgn}(\,y - f_i([n];y))\text{d}y.$$

$$\mathcal{F}_{\text{Hxc}}^{\text{SCE}}([n];x,x') = \frac{\delta v_{\text{Hxc}}^{\text{SCE}}([n];x)}{\delta n(x')}$$

we can analyse the kernel analytically

1D ASCE kernel

$$v_{\mathrm{Hxc}}^{\mathrm{SCE}}([n];x) = -\sum_{i=2}^{N}\int_{x}^{\infty} w'(|\,y - f_i([n];y)|) \times \mathrm{sgn}(\,y - f_i([n];y))\mathrm{d}y.$$

$$\mathcal{F}_{\mathrm{Hxc}}^{\mathrm{SCE}}([n];x,x') = \frac{\delta v_{\mathrm{Hxc}}^{\mathrm{SCE}}([n];x)}{\delta n(x')}$$

for densities that are non zero on the whole real line:

$$\mathcal{F}_{\mathrm{Hxc}}^{\mathrm{SCE}}([n];x,x') = \sum_{i=2}^{N}\int_{x}^{\infty} \frac{w''(|y - f_i([n];y)|)}{n(f_i([n];y))}\left[\theta(y-x') - \theta(f_i([n];y)-x')\right] dy$$

for densities with compact support there is an extra boundary term:

$$\mathcal{F}_{\mathrm{Hxc}}^{\mathrm{boundary}}([n];x,x') = \sum_{i=i}^{N}\theta(a_i - x)\theta(a_i - x')\frac{w'(|a_i - n^{+}|) + w'(|a_i - n^{-}|)}{n(a_i)}$$

$$\int_{-\infty}^{a_i} n(x)dx = i \in \mathbb{N}$$

*Lani, Di Marino, Gerolin, van Leeuwen & Gori-Giorgi, PCCP, **18**, 21092 (2016)*

1D ASCE kernel

for densities that are non zero on the whole real line:

$$\mathcal{F}_{\rm Hxc}^{\rm SCE}([n];x,x') = \sum_{i=2}^{N} \int_{x}^{\infty} \frac{w''(|y-f_i([n];y)|)}{n(f_i([n];y))} \left[\theta(y-x') - \theta(f_i([n];y)-x')\right] dy$$

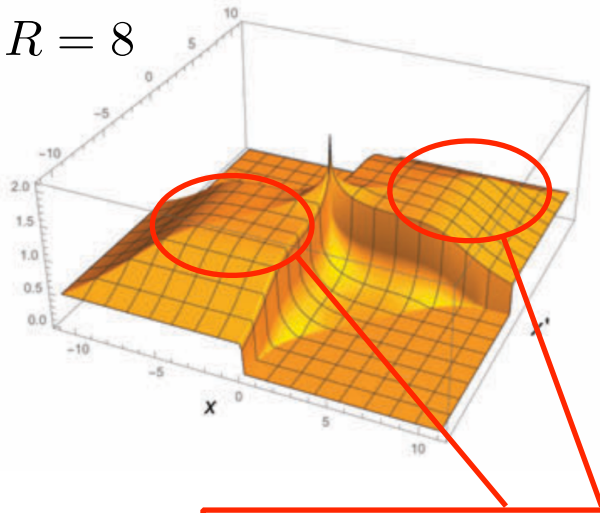
example: model homonuclear dissociation $n(x) = \frac{a}{2}\left(\mathrm{e}^{-a\left|x-\frac{R}{2}\right|} + \mathrm{e}^{-a\left|x+\frac{R}{2}\right|}\right)$

1D ASCE kernel

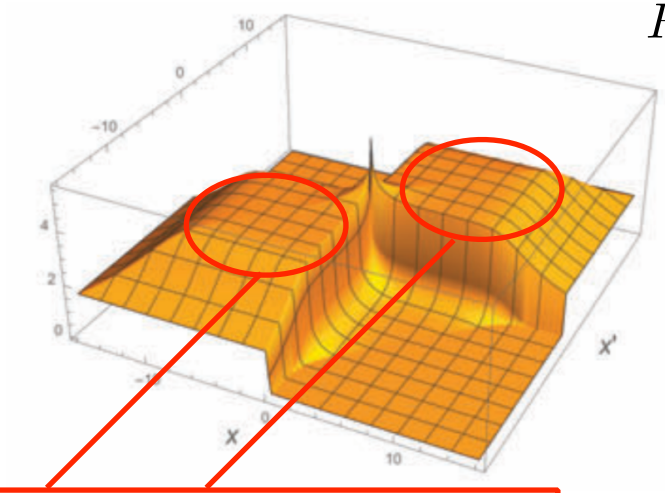
$$\mathcal{F}_{\rm Hxc}^{\rm SCE}([n];x,x') = \sum_{i=2}^{N} \int_{x}^{\infty} \frac{w''(|y - f_i([n];y)|)}{n(f_i([n];y))} \left[\theta(y-x') - \theta(f_i([n];y) - x')\right] dy$$

example: model homonuclear dissociation $n(x) = \frac{a}{2}\left(\mathrm{e}^{-a\left|x-\frac{R}{2}\right|} + \mathrm{e}^{-a\left|x+\frac{R}{2}\right|}\right)$

$R = 8$



$R = 12$



plateau regions around each atom of size $\approx R \times R$

plateau height:

$$\approx \frac{1}{n(0)(R - 1/a)^2}$$

density in the midbond: the height diverges as R increases

*Lani, Di Marino, Gerolin, van Leeuwen & Gori-Giorgi, PCCP, **18**, 21092 (2016)*

Analysis of the divergence

$$^1\Sigma_g \rightarrow {}^1\Sigma_u$$

bond breaking excitation in H_2

Gritsenko, van Gisbergen, Gorling & Baerends, J. Chem. Phys., 113, 8478 (2000)
Giesbertz & Baerends Chem. Phys. Lett., 461, 338 (2008)

$$(\epsilon_u - \epsilon_g) \int dx \int dx' \sigma_g(x)\sigma_u(x)\mathcal{F}_{\mathrm{Hxc}}^{\mathrm{SCE}}([n];x,x')\sigma_g(x')\sigma_u(x')$$

goes to zero
as R gets larger

$$\int \mathrm{d}x \int \mathrm{d}x' |\phi_{\mathrm{A}}(x)|^2 \mathcal{F}_{\mathrm{Hxc}}^{\mathrm{SCE}}([n];x,x')|\phi_{\mathrm{A}}(x')|^2 \approx \frac{1}{n(0)(R-1/a)^2}.$$

the divergence appears in the atomic regions, due to the presence of another distant atom (highly non-local dependence on the density)

*Lani, Di Marino, Gerolin, van Leeuwen & Gori-Giorgi, PCCP, **18**, 21092 (2016)*

Analysis of the divergence

$$\int dx \int dx' |\phi_A(x)|^2 \mathcal{F}_{Hxc}^{SCE}([n]; x, x') |\phi_A(x')|^2 \approx \frac{1}{n(0)(R - 1/a)^2}.$$

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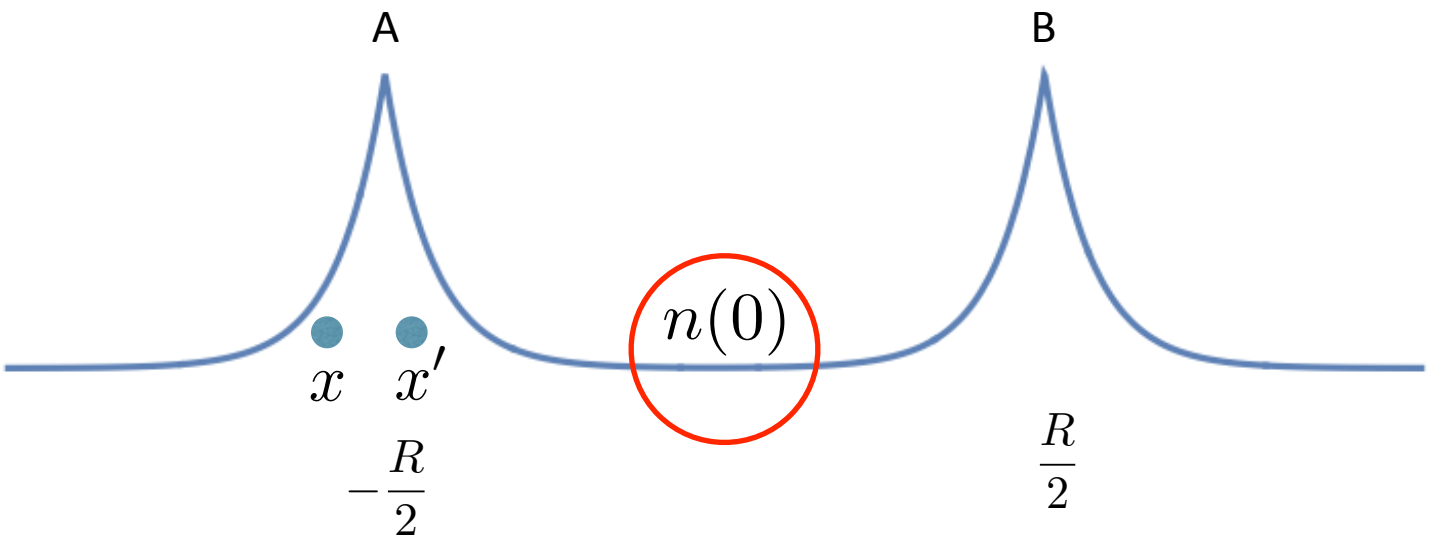

*Lani, Di Marino, Gerolin, van Leeuwen & Gori-Giorgi, PCCP, **18**, 21092 (2016)*

Conclusions & Perspectives TD part

- The adiabatic SCE potential does satisfy the zero-force theorem

  real time evolution for bosons/fermions in presence of disorder

  transport

- SCE kernel: mathematical and physical aspects

  Mott gap ?

  bond breaking excitations ?

  learn how to construct approximations

  next leading order

Acknowledgments

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Robert van Leeuwen

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Nederlandse Organisatie voor Wetenschappelijk Onderzoek

MARIE CURIE ACTIONS

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Thank you for your attention!