Charge-transfer features in the exact Kohn-Sham potential of ensemble density functional theory

האוניברסיטה העברית בירושלים
THE HEBREW UNIVERSITY OF JERUSALEM

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The Hebrew University of Jerusalem, Jerusalem, Israel
ETH Zürich, Zürich, Switzerland

Charge transfer in a molecule

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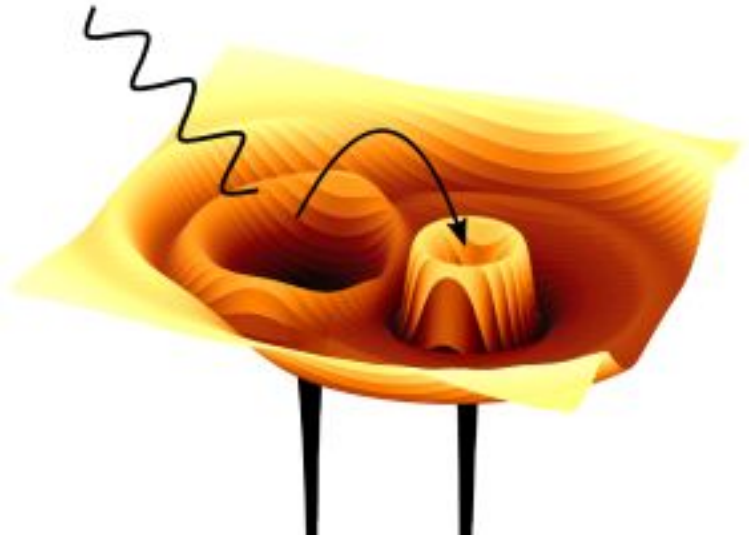

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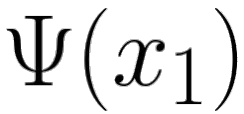
The more electrons you have, the more interactions...

...the exact, full-correlated many-body wavefunction quickly becomes impossible to calculate



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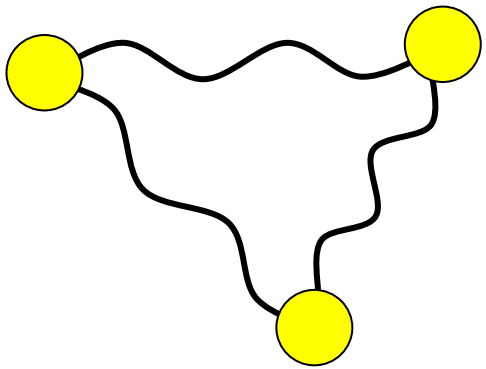

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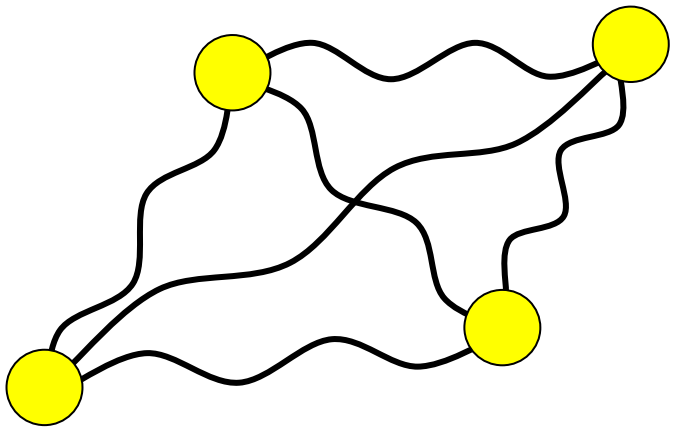

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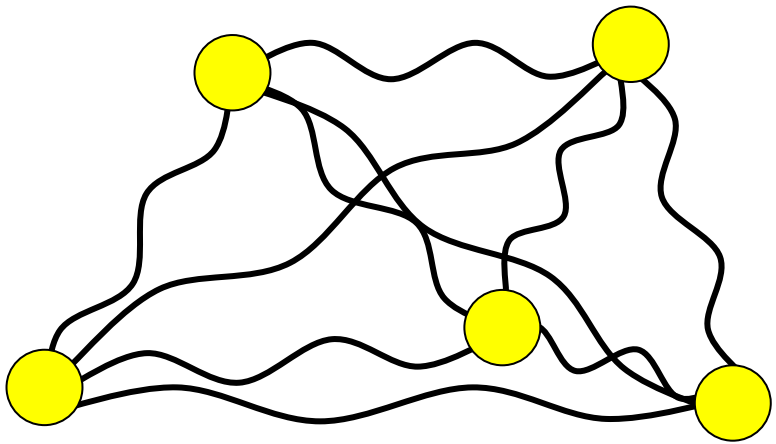
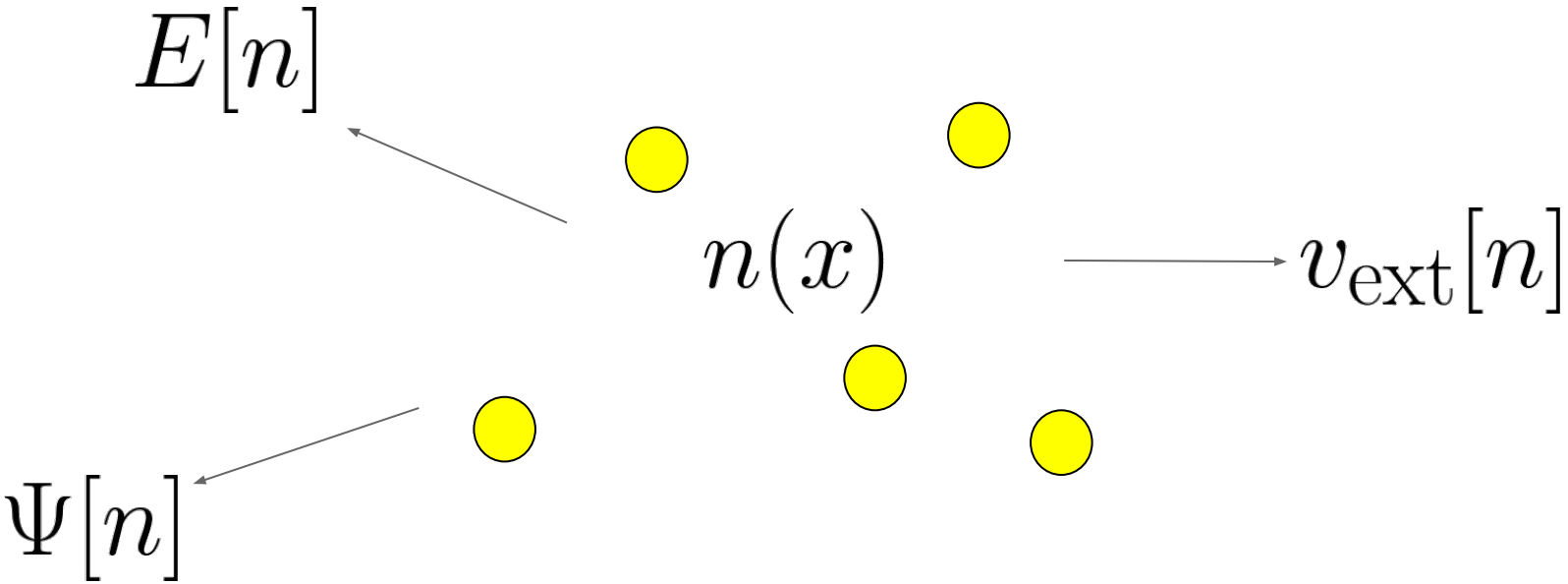


Density functional theory

Replace the wavefunction with the *density* – P. Hohenberg and W. Kohn Phys. Rev. **136**, B864



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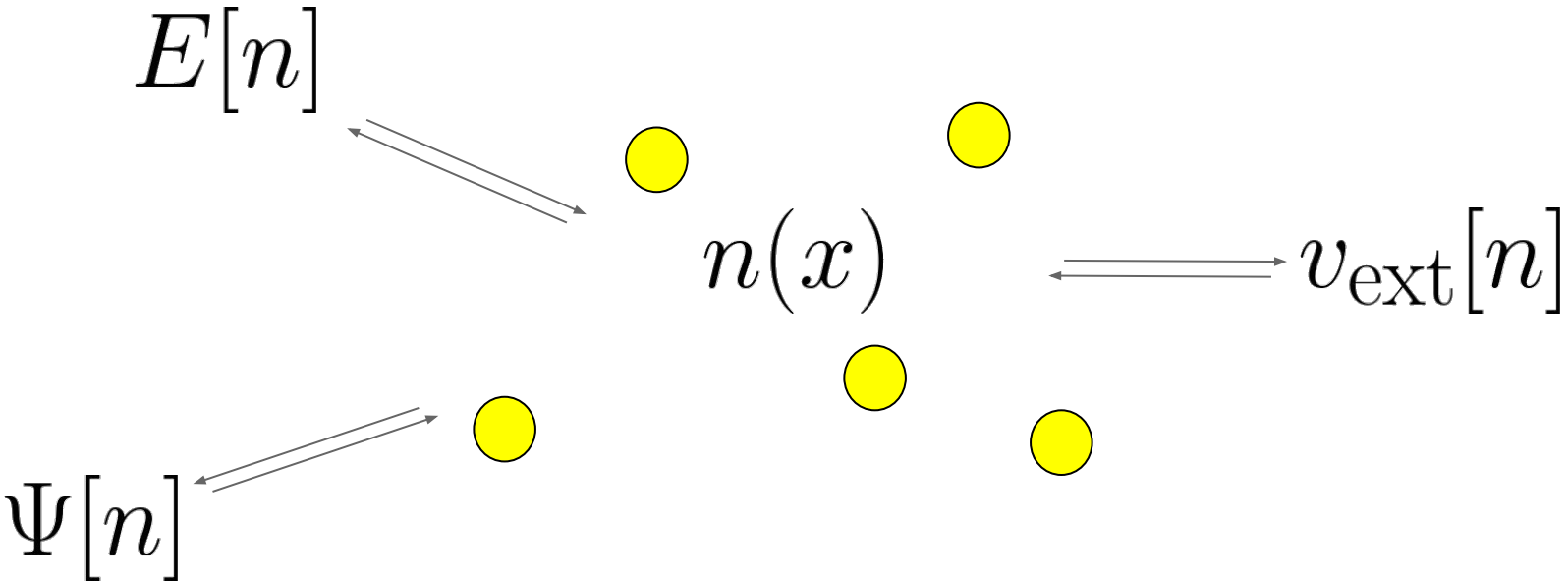

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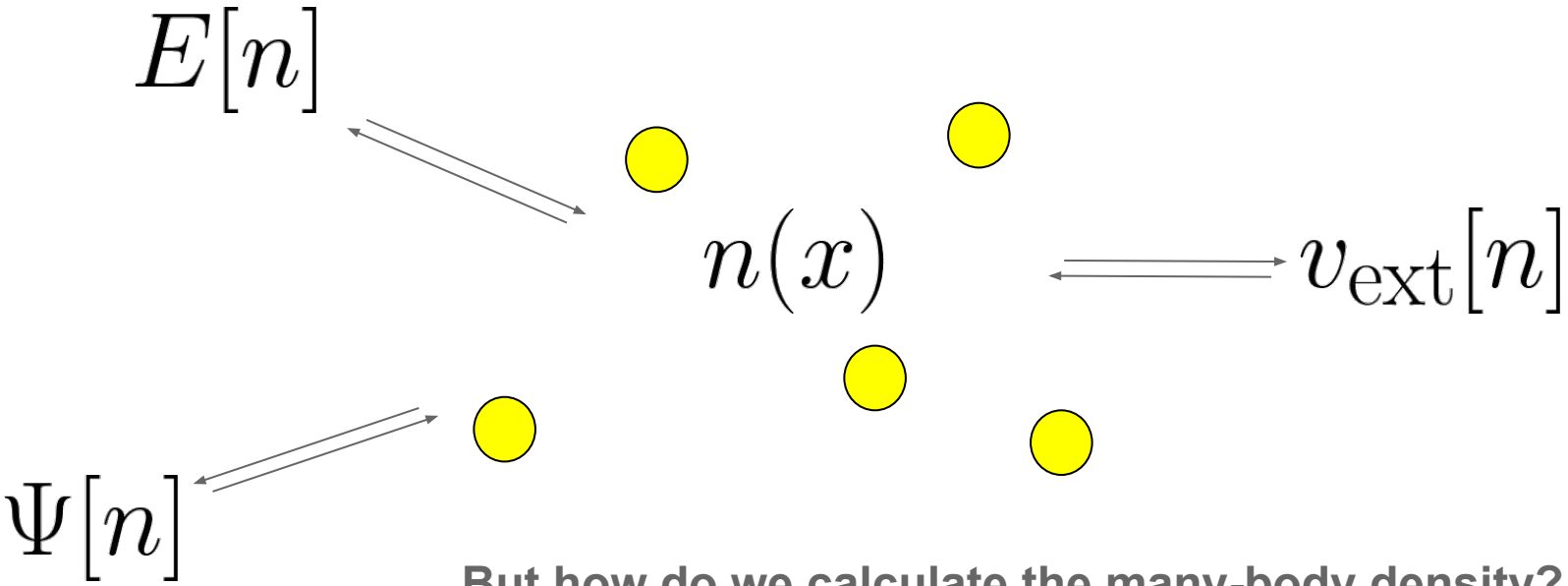
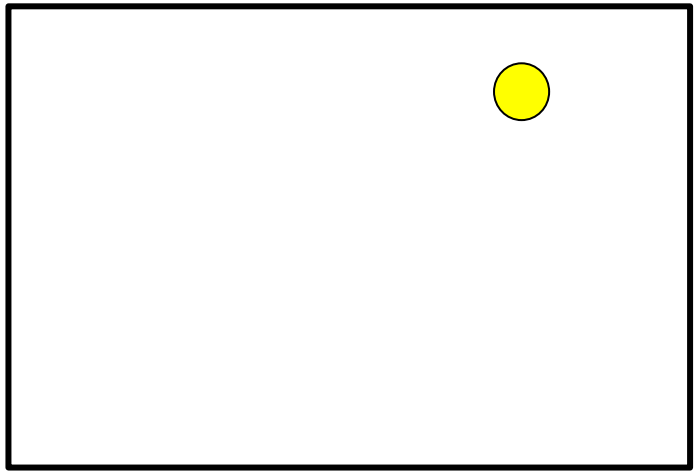
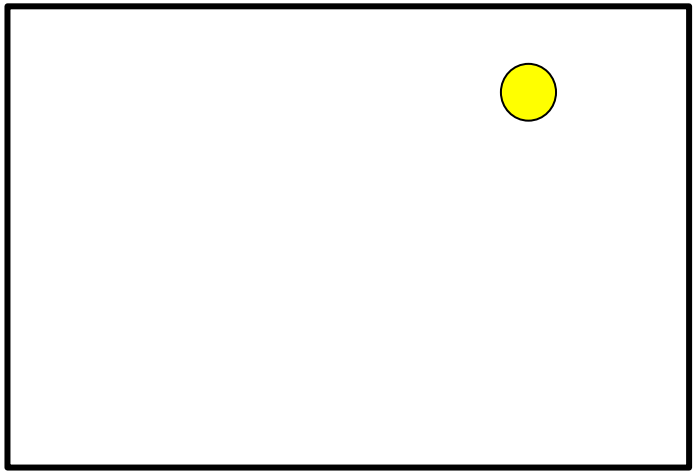


But how do we calculate the many-body density?

Many-body system



Kohn-Sham system



The electron densities are the same

Computational scaling: k^1

Computational scaling: $1 \cdot k$

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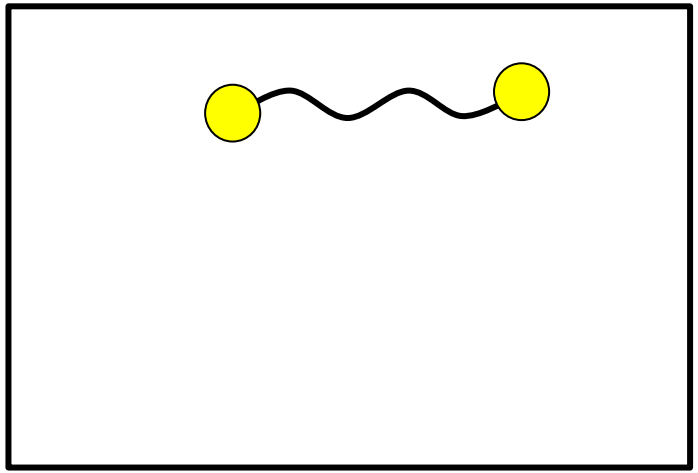

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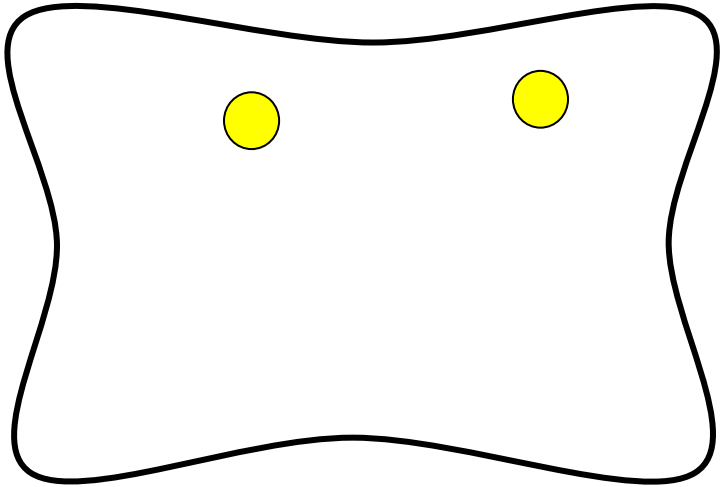

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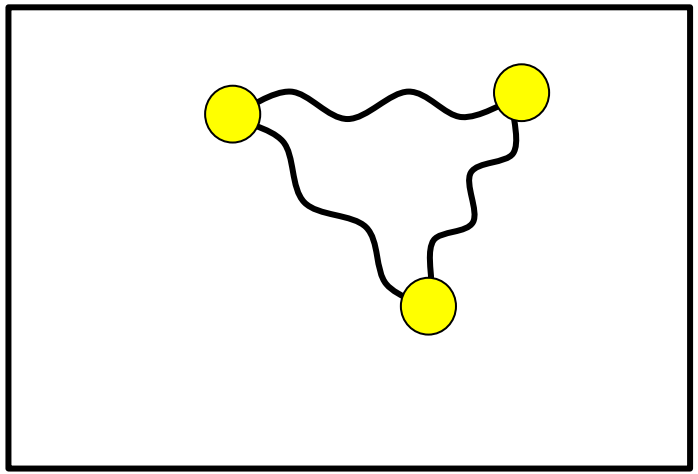

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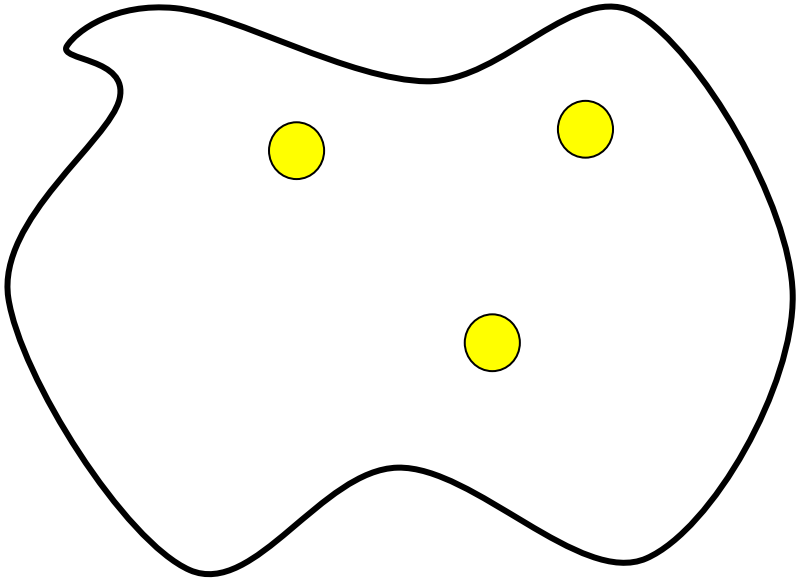

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Computational scaling: $3 \cdot k$

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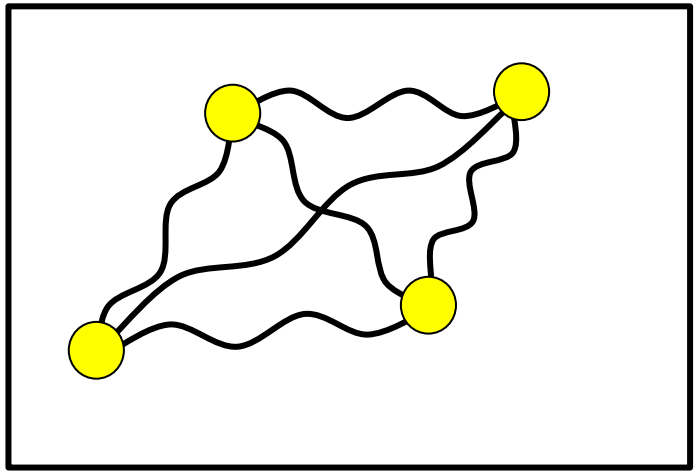

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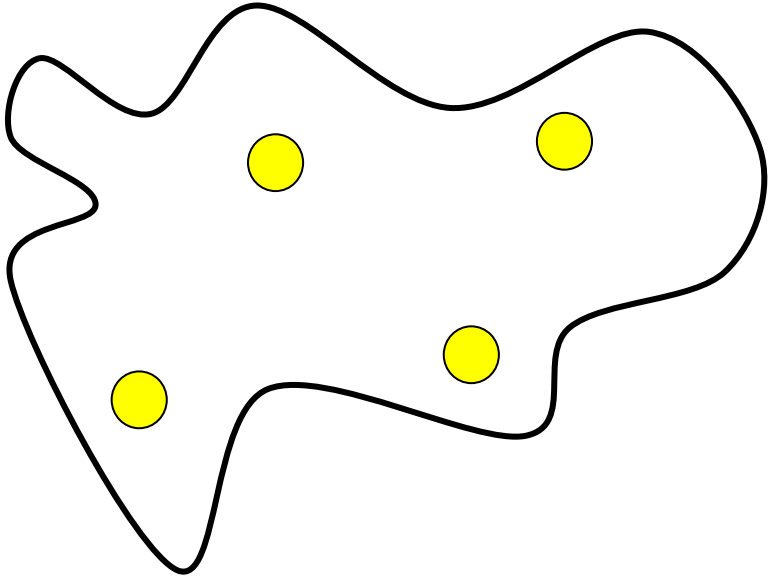

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Computational scaling: $4 \cdot k$

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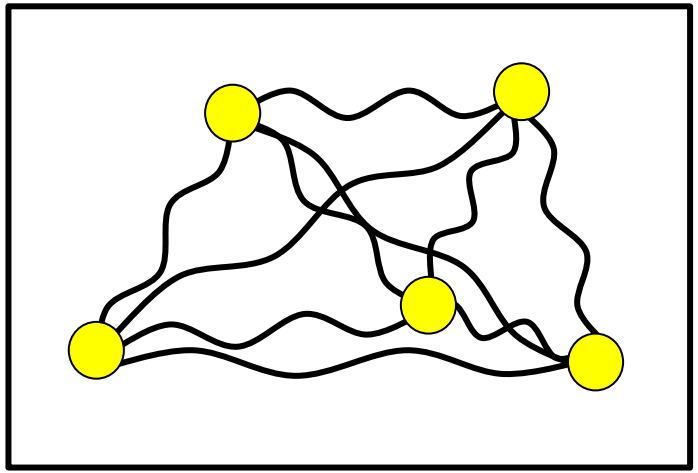

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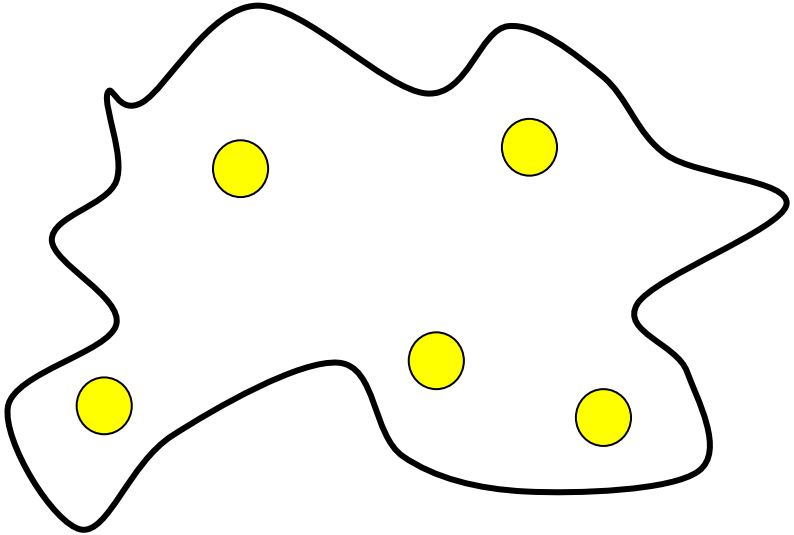

The electron densities are the same

Computational scaling: k^5

Computational scaling: $5 \cdot k$

Kohn-Sham theory

Auxiliary system of fully non-interacting electrons which experience a local effective potential – the Kohn-Sham potential

$$\left(-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2}+v_\mathrm{s}(x)\right)\phi_i(x)=\varepsilon_i\phi_i(x) \qquad n(x)=\sum_i|\phi_i(x)|^2$$

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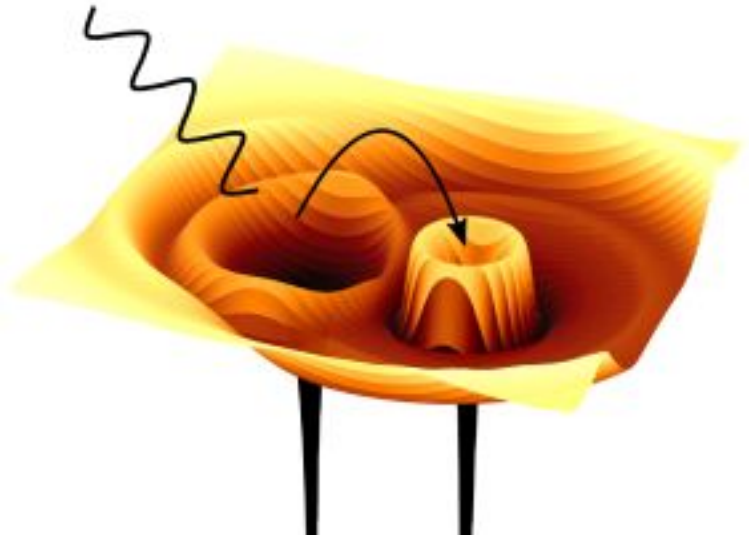

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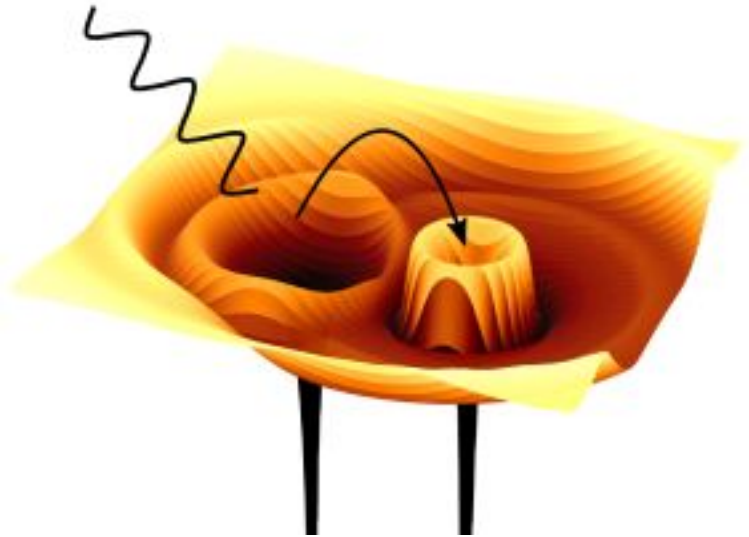

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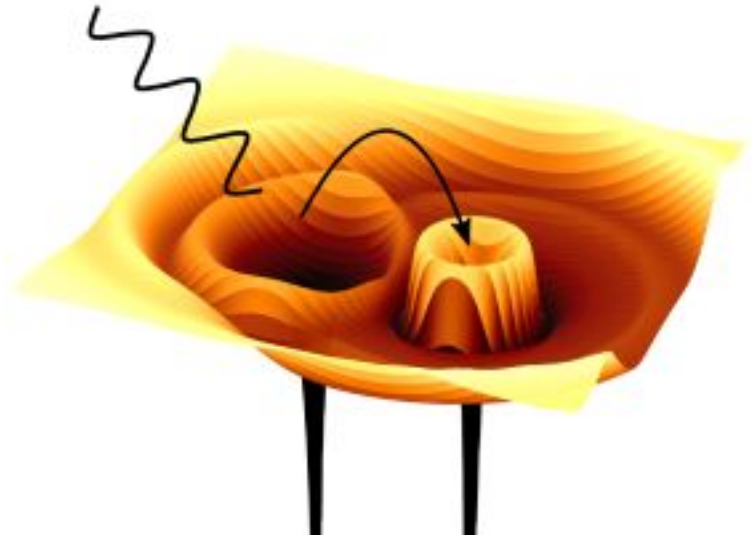
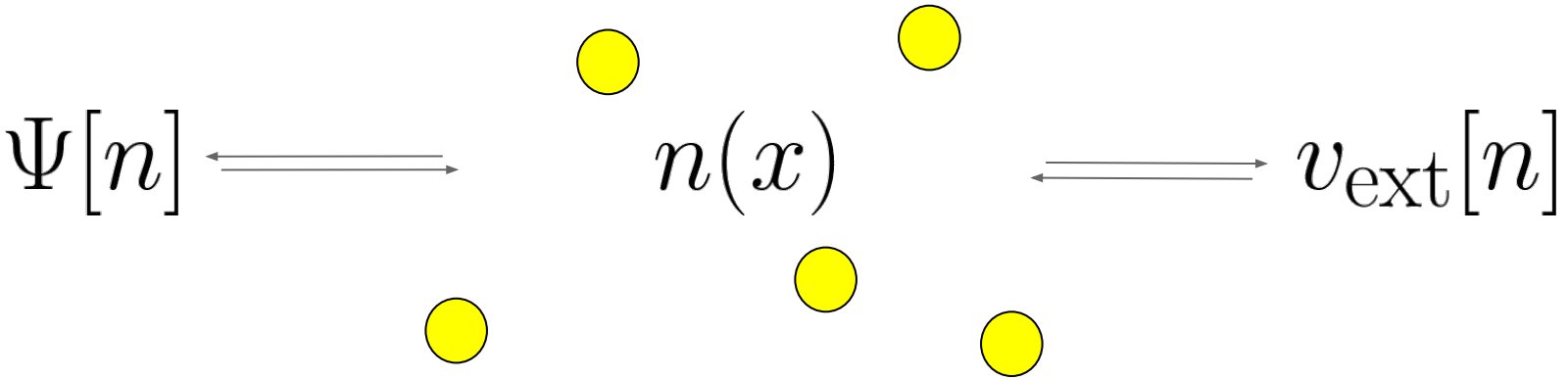


Ensemble density functional theory

Replace the **excited** wavefunction with the **excited** density –



E. K. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A **37**, 2809 (1988)

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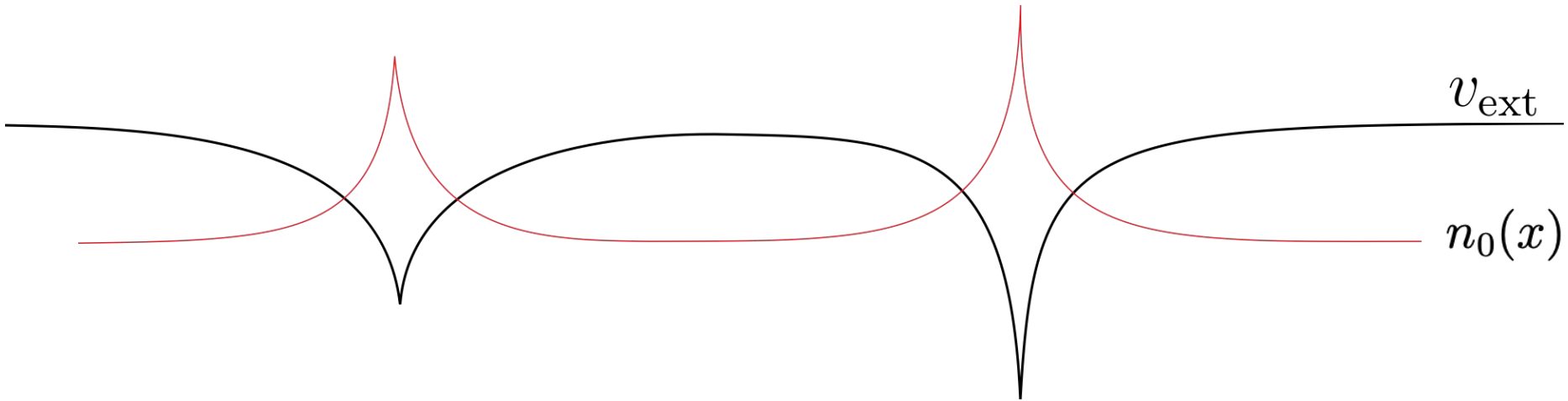

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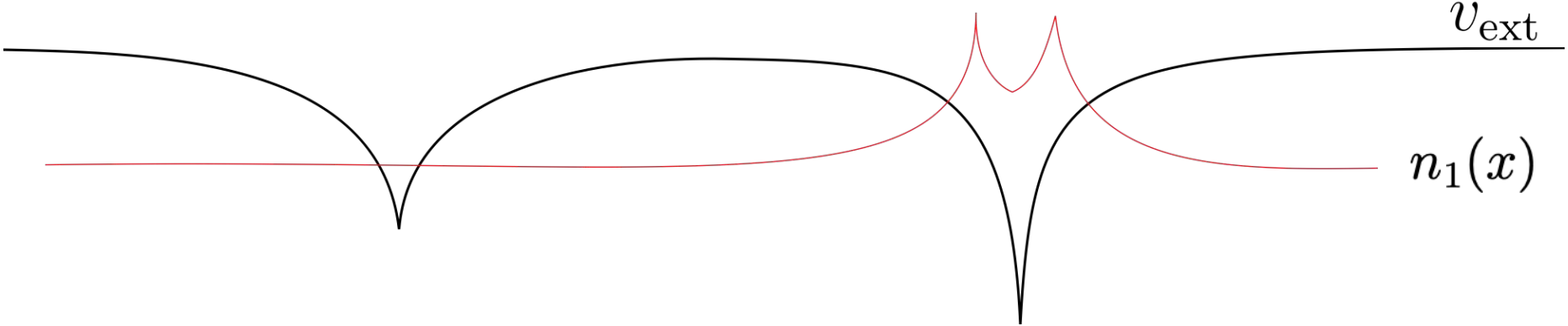

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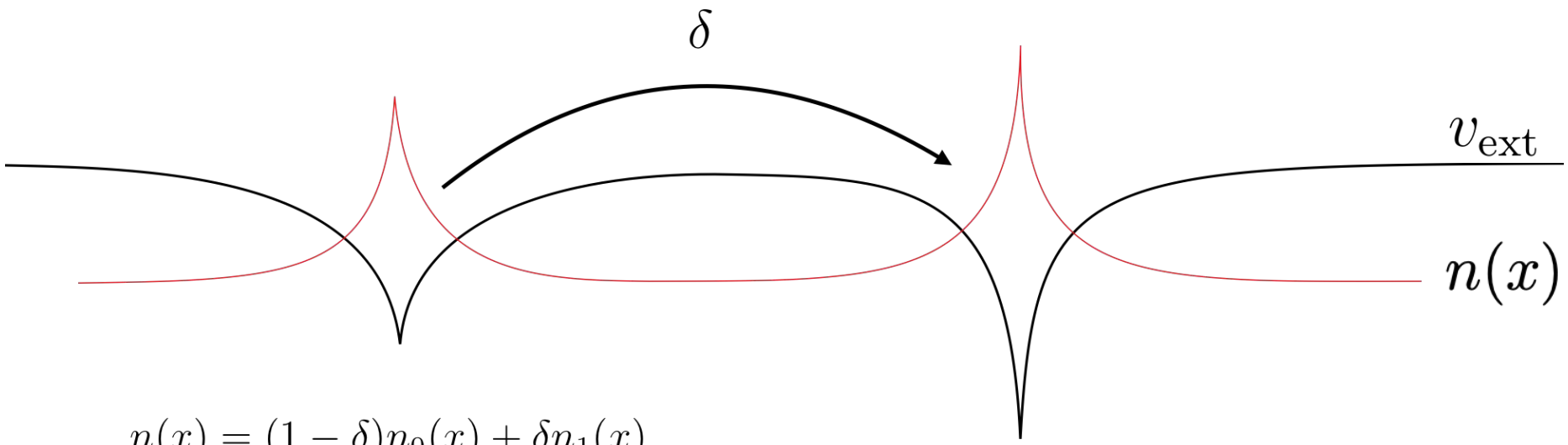

$$n(x) = (1-\delta)n_0(x) + \delta n_1(x)$$

$$0 < \delta << 1$$

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Available approximations:

- No interacting
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- Hybrid functionals
- Many-body perturbation theory (HF, G0W0, GW0, COHSEX, scGW, GW+ssc)

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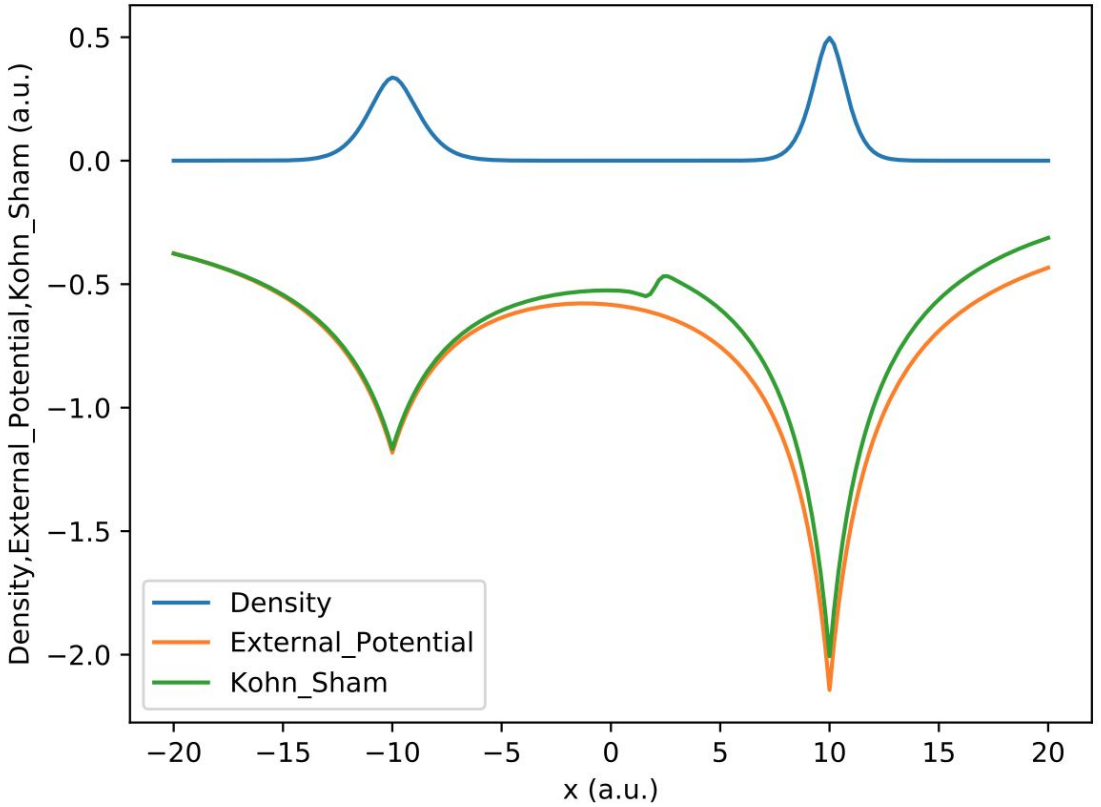

M. J. P. Hodgson *et al.*, PRB 93, 155146 (2016)

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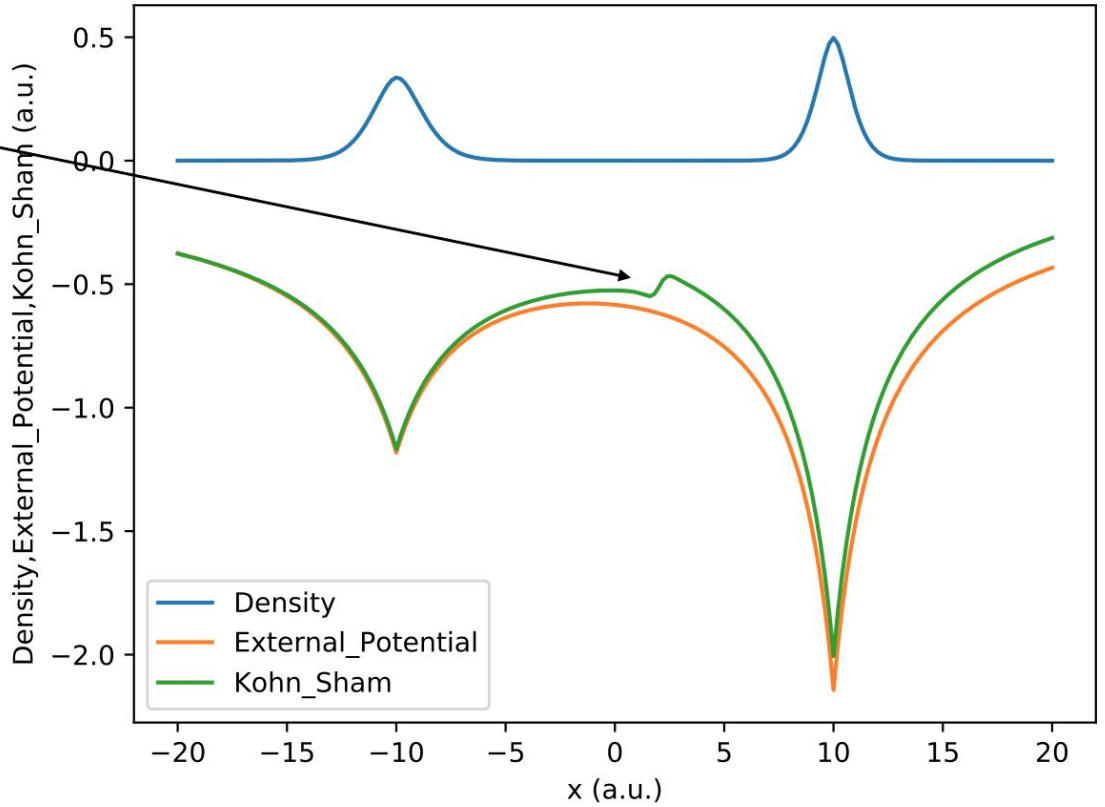

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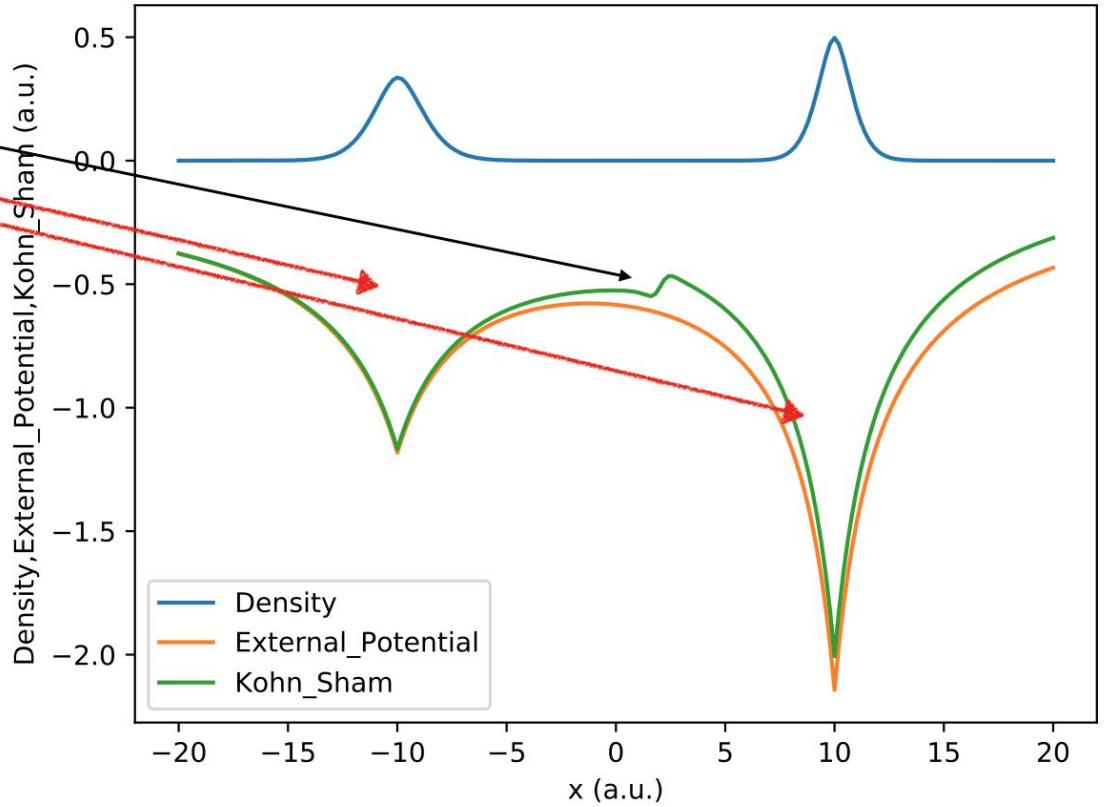

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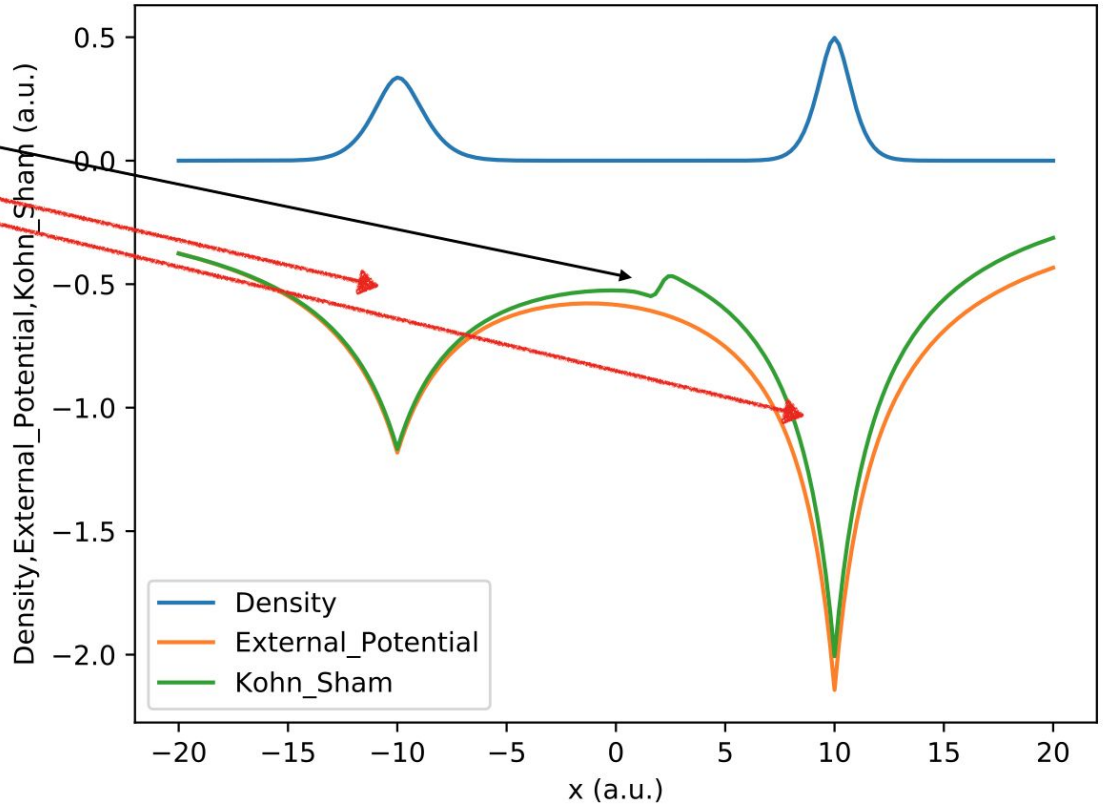

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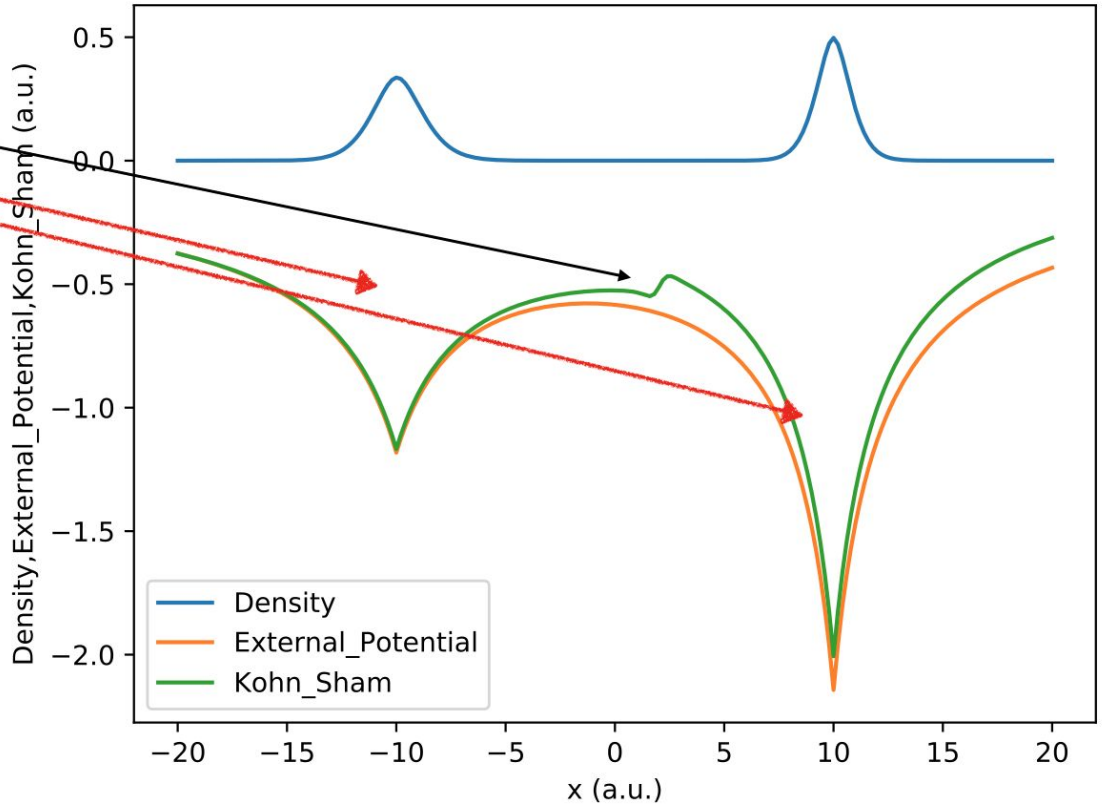
Bonded case: $\eta_R^{\mathrm{ho}} = \eta_L^{\mathrm{ho}}$



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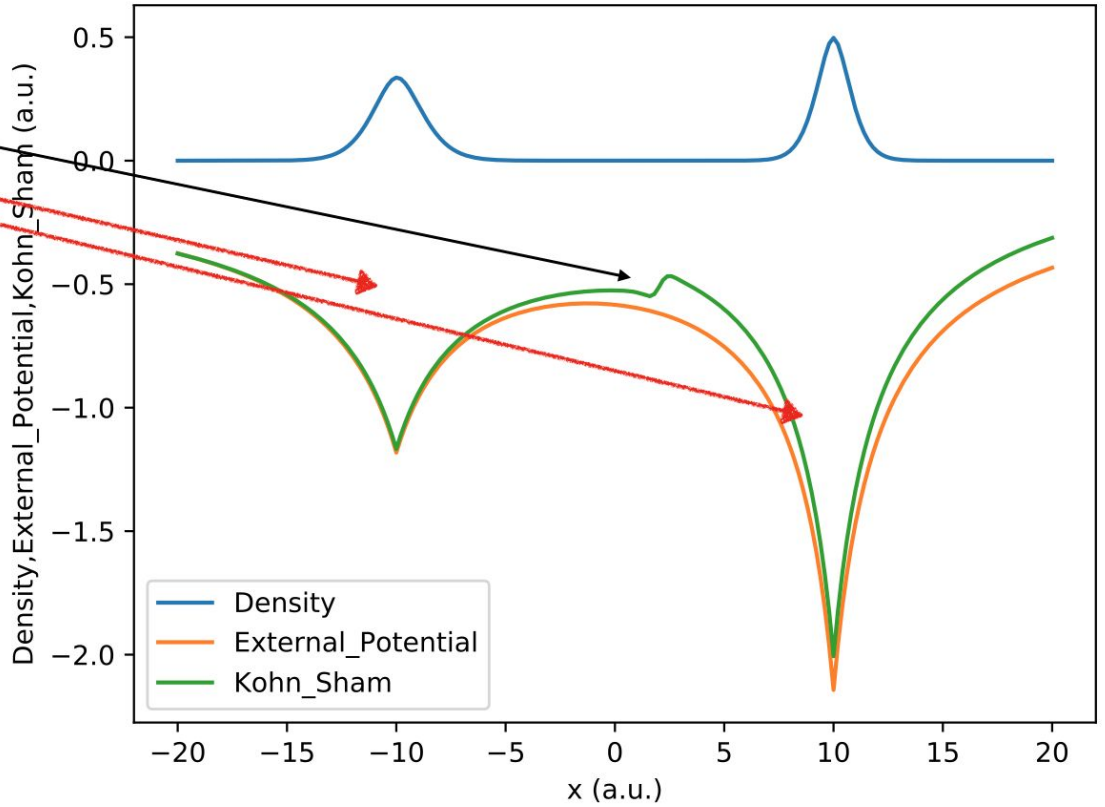
$$\Rightarrow S = I_R - I_L$$



Almbladh, C. O.; von Barth, U. In Density Functional Methods in Physics; Dreizler, R. M., da Providência, J., Eds.; NATO ASI Series; Plenum Press, 1985; Vol. 123, pp 209–231.

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The ‘local number of electrons’ of the right atom will increase by δ

J. Perdew *et al.*, PRL 49, 1691 (1982)

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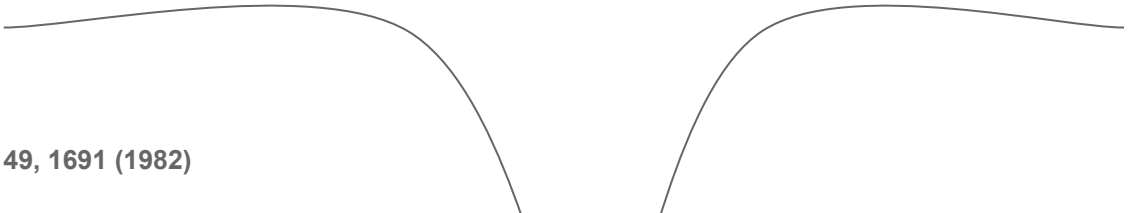

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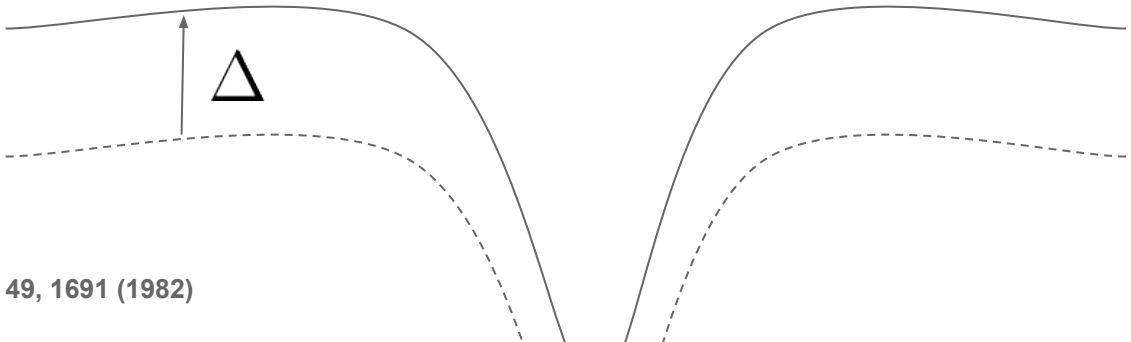
$$\Delta = I - A - (\varepsilon^{\mathrm{lu}} - \varepsilon^{\mathrm{ho}})$$



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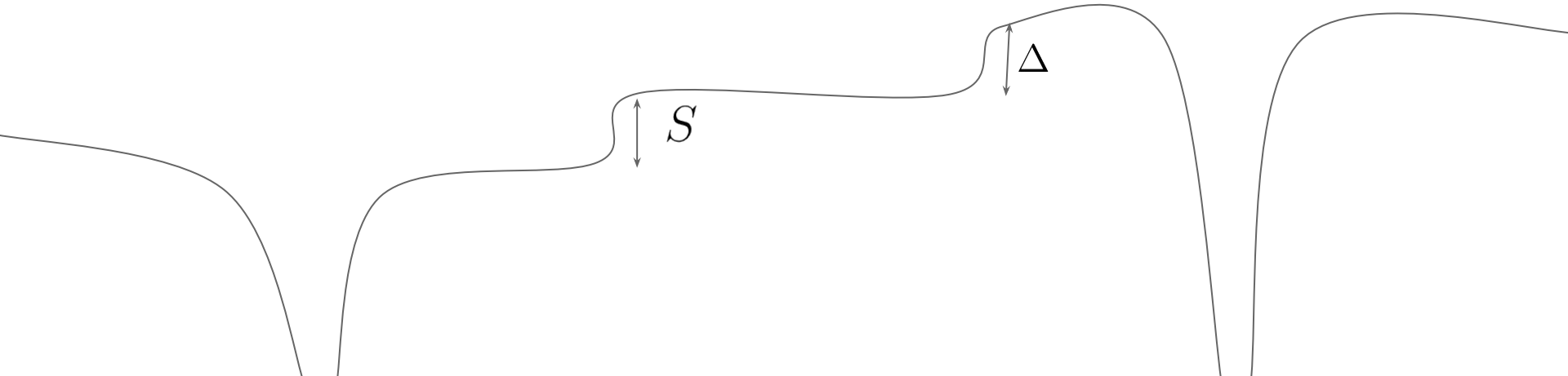
When charge is transferred what do we expect?

What about the interatomic step, S?

If $S \rightarrow S + \Delta$ then the density will not be distributed correctly through the molecule!



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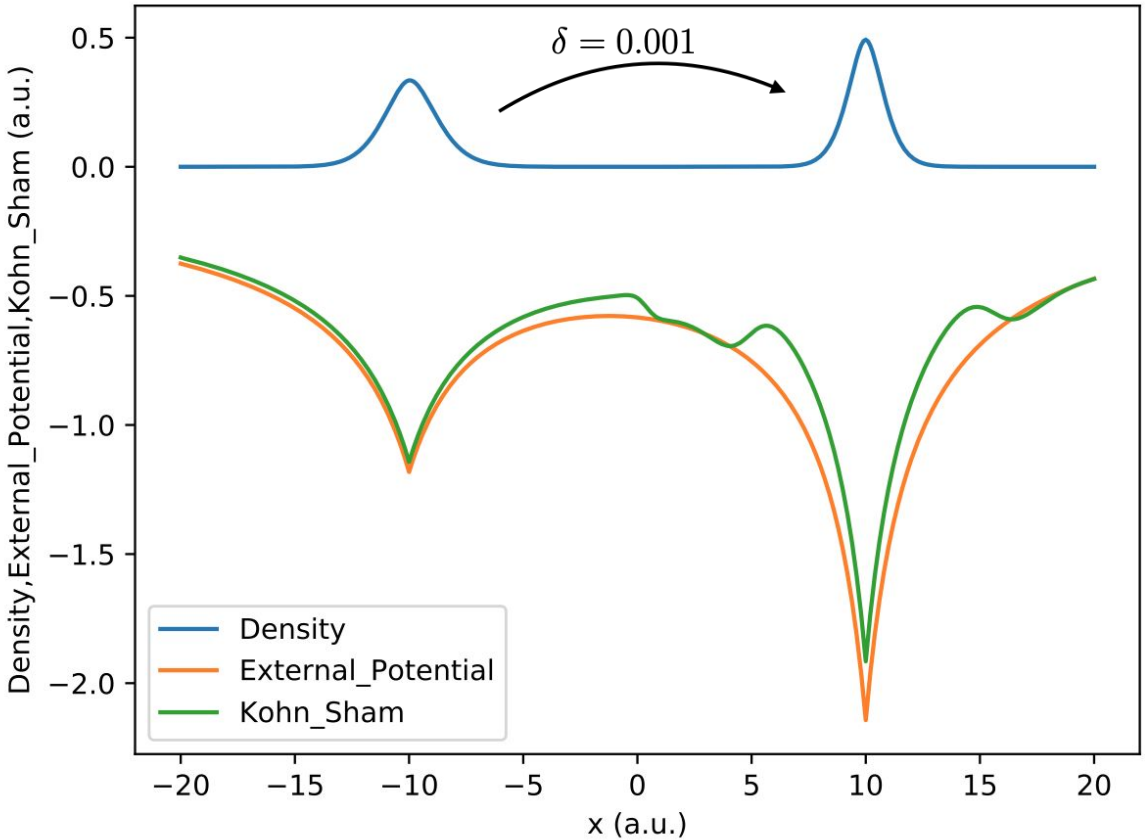

M. J. P. Hodgson*, E. Kraisler*, *et al.*, *J Phys. Chem. Lett.* 2017, *8* (24), 5974–5980.

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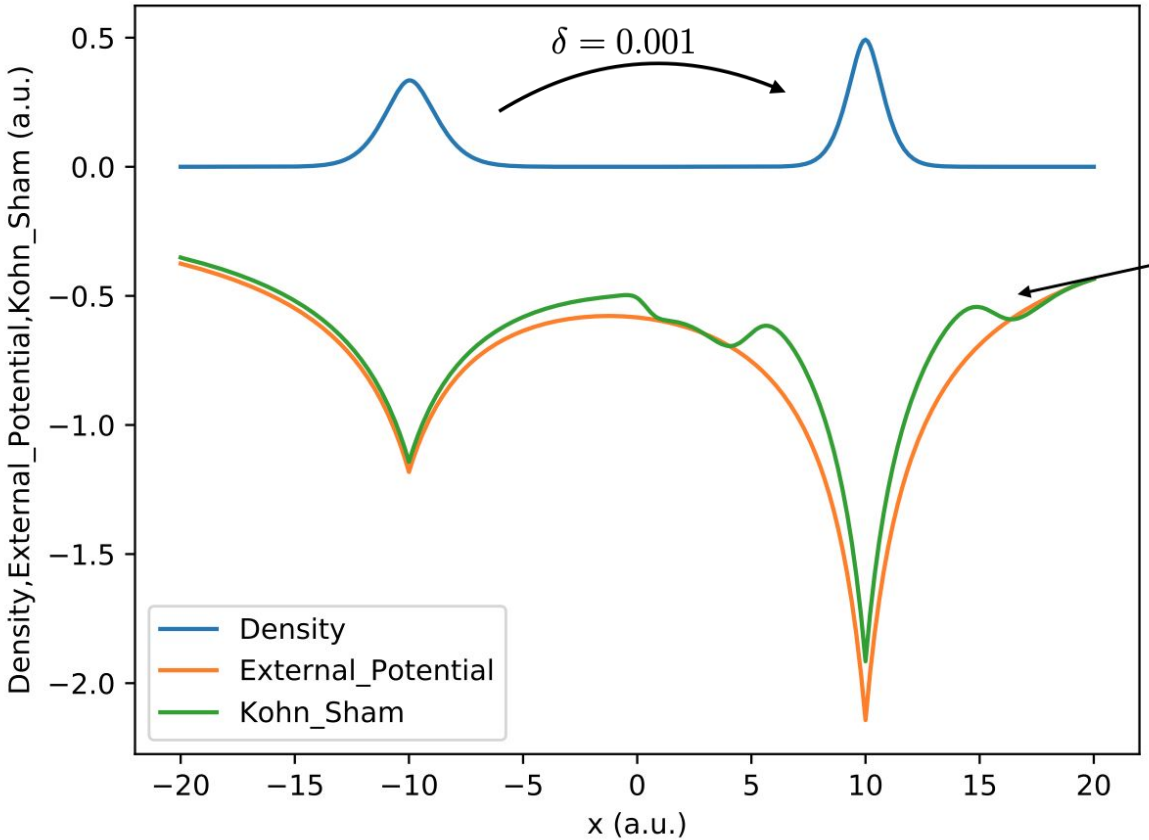
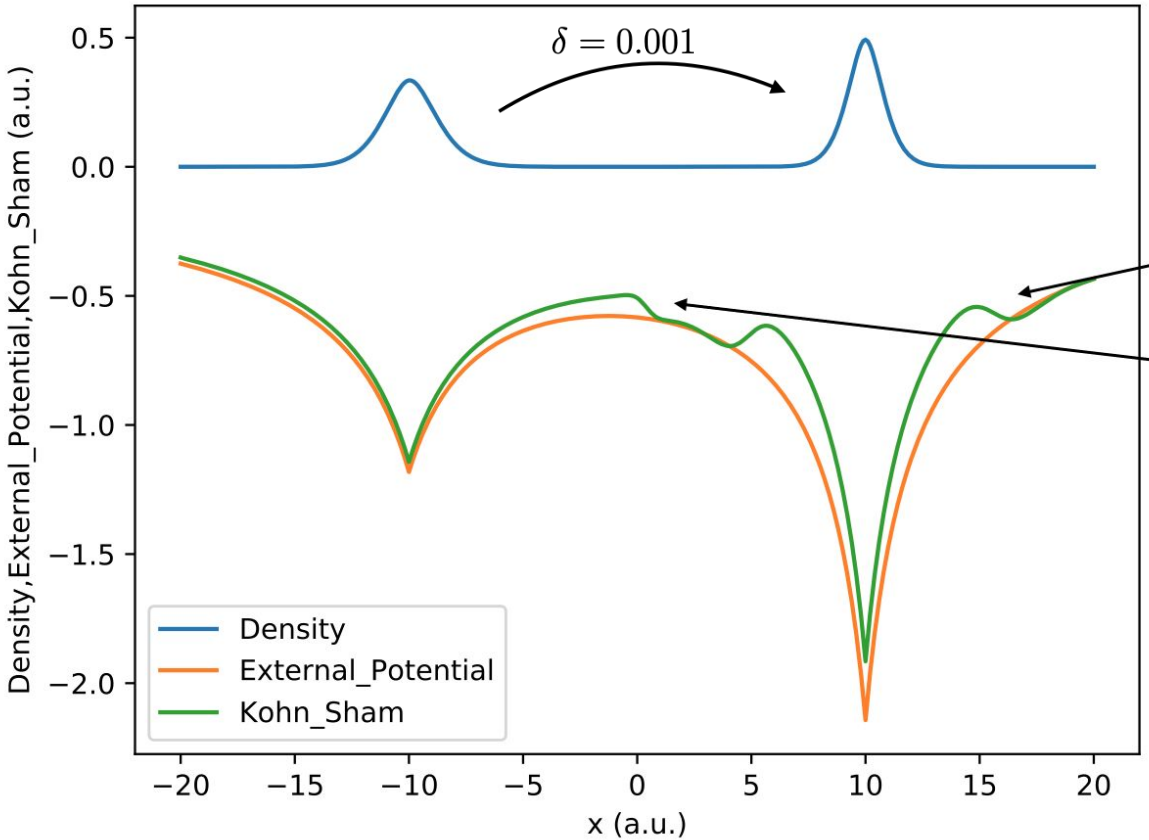


Derivative discontinuity of Atom R:

$$\Delta_R = I_R - A_R + \varepsilon_R^{\mathrm{ho}} - \varepsilon_R^{\mathrm{lu}}$$

M. J. P. Hodgson*, E. Kraisler*, *et al.*, *J Phys. Chem. Lett.* 2017, *8* (24), 5974–5980.

Charge transfer excitation in a 1D molecule



Derivative discontinuity of Atom R:

$$\Delta_R = I_R - A_R + \varepsilon_R^{\mathrm{ho}} - \varepsilon_R^{\mathrm{lu}}$$

$$\Delta_{L\to R}^{\mathrm{CT}} = I_L - A_R + \eta_L^{\mathrm{ho}} - \eta_R^{\mathrm{lu}}$$

What's this?

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Charge-transfer derivative discontinuity

$$\Delta^{\mathrm{CT}}_{L\to R} = I_L - A_R + \eta^{\mathrm{ho}}_L - \eta^{\mathrm{lu}}_R$$

Derivative discontinuity of Atom R:

$$\Delta_R = I_R - A_R + \varepsilon^{\mathrm{ho}}_R - \varepsilon^{\mathrm{lu}}_R = I_R - A_R + \eta^{\mathrm{ho}}_R - \eta^{\mathrm{lu}}_R$$

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Charge-transfer derivative discontinuity

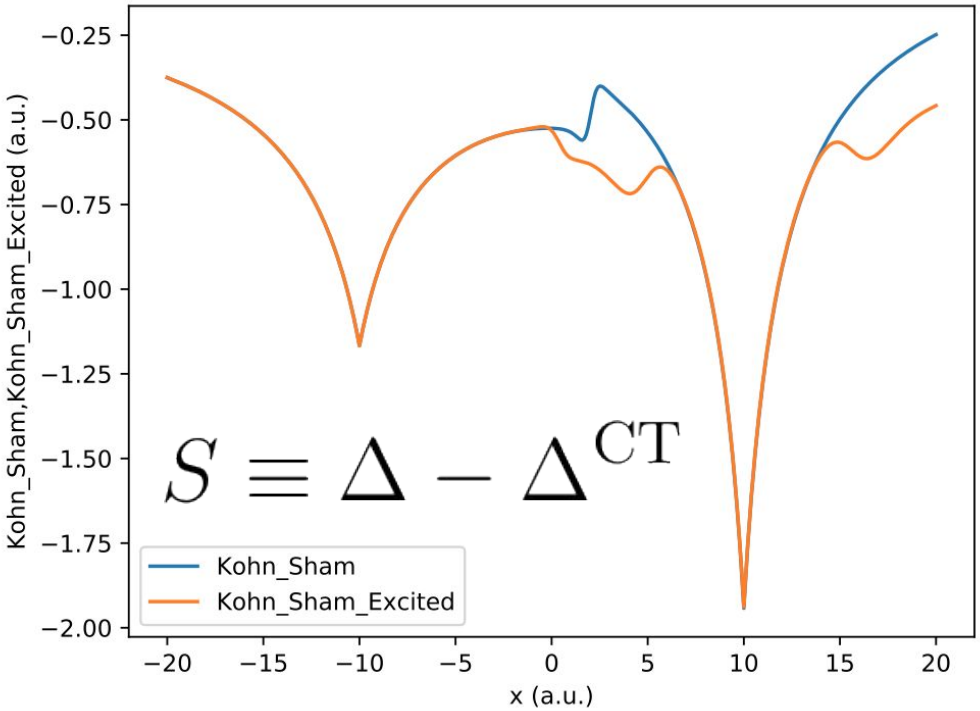
$$\Delta^{\mathrm{CT}}_{L\to R} = I_L - A_R + \eta^{\mathrm{ho}}_L - \eta^{\mathrm{lu}}_R$$

Derivative discontinuity of Atom R:

$$\Delta_R = I_R - A_R + \varepsilon^{\mathrm{ho}}_R - \varepsilon^{\mathrm{lu}}_R = I_R - A_R + \eta^{\mathrm{ho}}_R - \eta^{\mathrm{lu}}_R$$

$$S = S_1 + S_2 = \Delta_R - \Delta^{\mathrm{CT}}_{L\to R} = I_R - I_L + \eta^{\mathrm{ho}}_R - \eta^{\mathrm{ho}}_L$$

Charge-transfer derivative discontinuity



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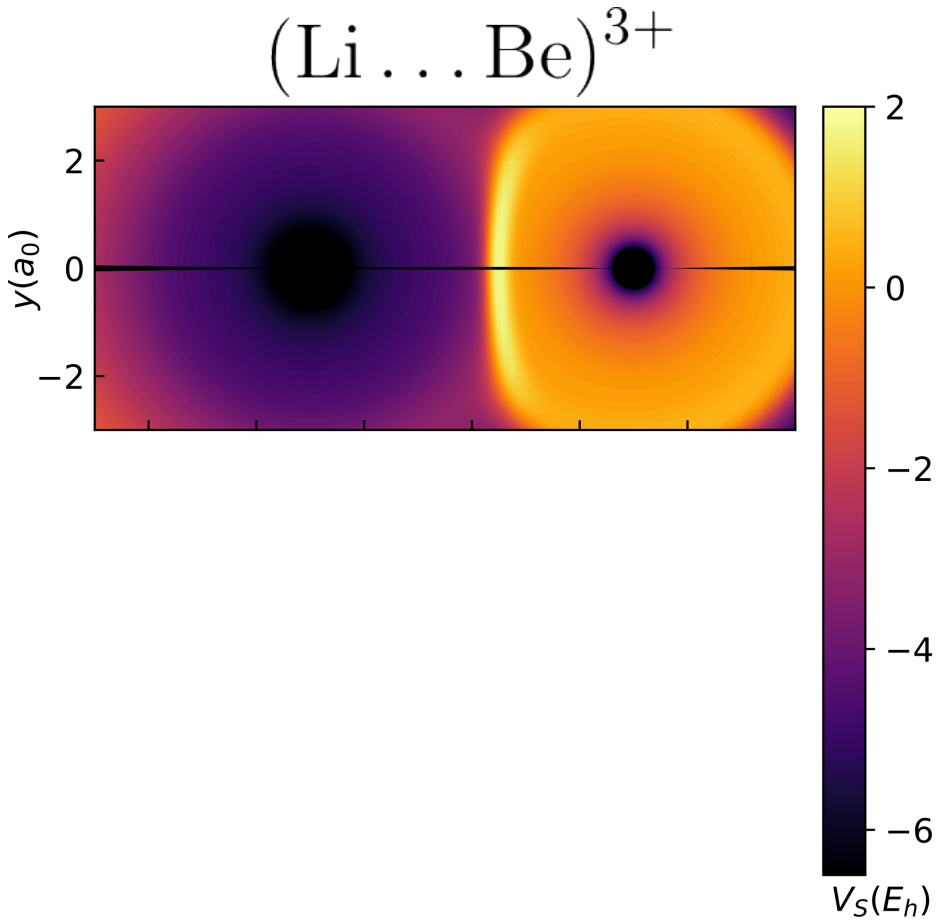
What about in 3D?



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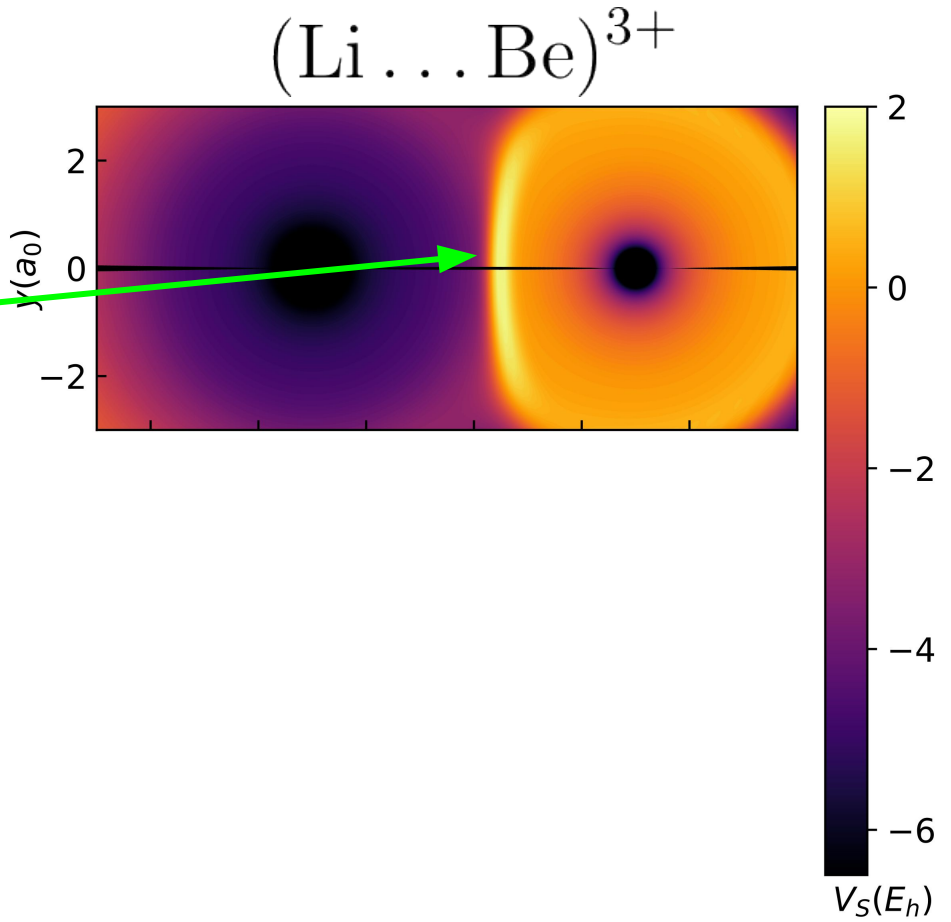
What about in 3D?

$$S = I_{\mathrm{Be}} - I_{\mathrm{Li}} + \eta^{\mathrm{ho}}_{\mathrm{Be}} - \eta^{\mathrm{ho}}_{\mathrm{Li}}$$



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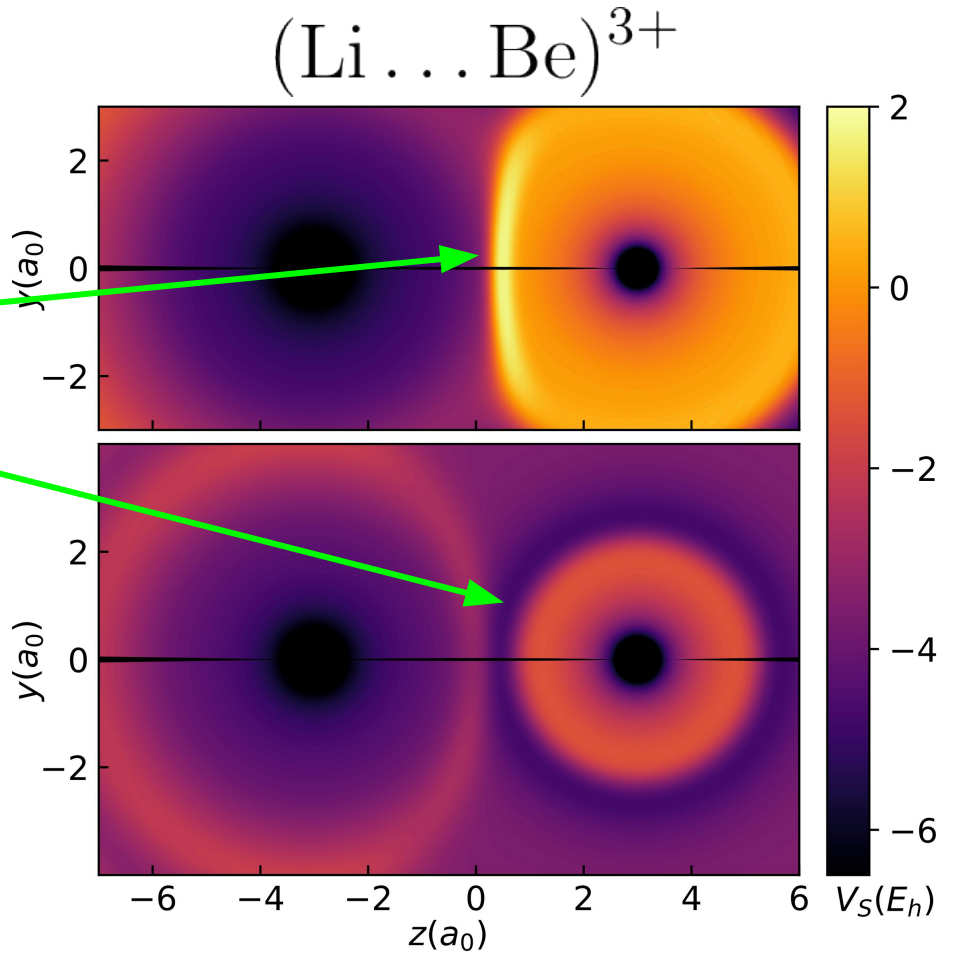
What about in 3D?

$$S = I_{\mathrm{Be}} - I_{\mathrm{Li}} + \eta^{\mathrm{ho}}_{\mathrm{Be}} - \eta^{\mathrm{ho}}_{\mathrm{Li}}$$

$$\Delta_{\mathrm{Be}} = I_{\mathrm{Be}} - A_{\mathrm{Be}} + \eta^{\mathrm{ho}}_{\mathrm{Be}} - \eta^{\mathrm{lu}}_{\mathrm{Be}}$$



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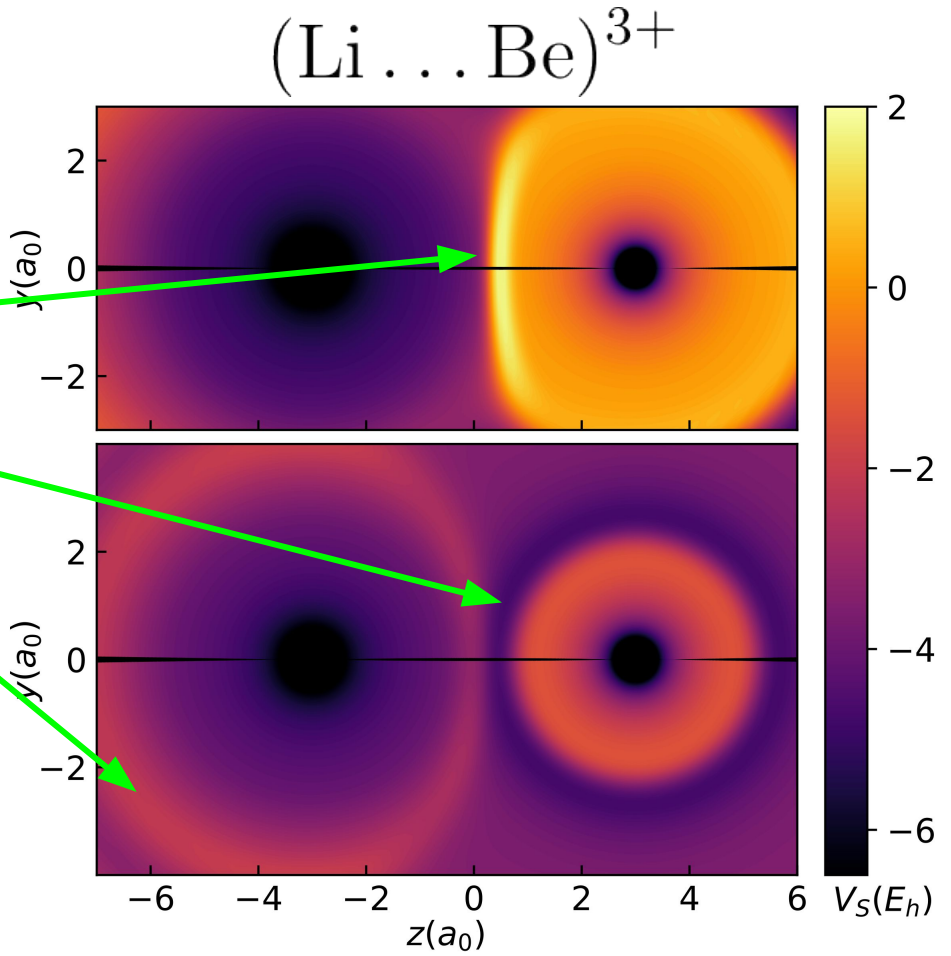
What about in 3D?

$$S = I_{\mathrm{Be}} - I_{\mathrm{Li}} + \eta^{\mathrm{ho}}_{\mathrm{Be}} - \eta^{\mathrm{ho}}_{\mathrm{Li}}$$

$$\Delta_{\mathrm{Be}} = I_{\mathrm{Be}} - A_{\mathrm{Be}} + \eta^{\mathrm{ho}}_{\mathrm{Be}} - \eta^{\mathrm{lu}}_{\mathrm{Be}}$$

$$\Delta^{\mathrm{CT}}_{\mathrm{Li}\to\mathrm{Be}} = I_{\mathrm{Li}} - A_{\mathrm{Be}} + \eta^{\mathrm{ho}}_{\mathrm{Li}} - \eta^{\mathrm{lu}}_{\mathrm{Be}}$$



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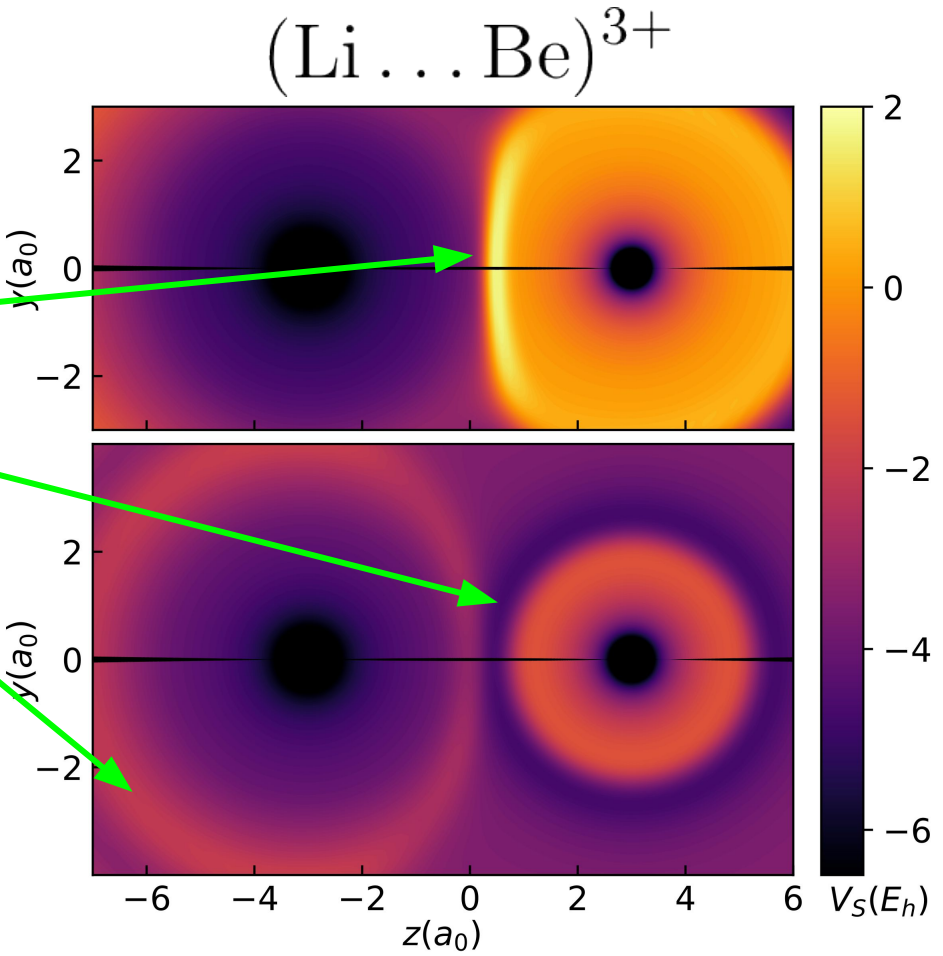
What about in 3D?

$$S = I_{\mathrm{Be}} - I_{\mathrm{Li}} + \eta^{\mathrm{ho}}_{\mathrm{Be}} - \eta^{\mathrm{ho}}_{\mathrm{Li}}$$

$$\Delta_{\mathrm{Be}} = I_{\mathrm{Be}} - A_{\mathrm{Be}} + \eta^{\mathrm{ho}}_{\mathrm{Be}} - \eta^{\mathrm{lu}}_{\mathrm{Be}}$$

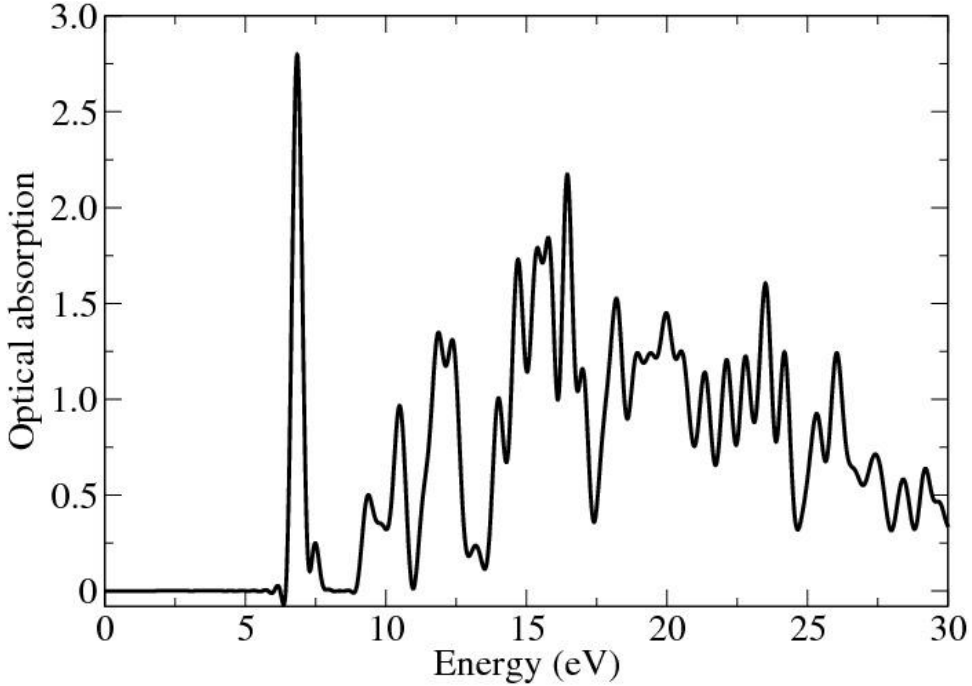
$$\Delta^{\mathrm{CT}}_{\mathrm{Li}\to\mathrm{Be}} = I_{\mathrm{Li}} - A_{\mathrm{Be}} + \eta^{\mathrm{ho}}_{\mathrm{Li}} - \eta^{\mathrm{lu}}_{\mathrm{Be}}$$

$$S \equiv \Delta_{\mathrm{Be}} - \Delta^{\mathrm{CT}}_{\mathrm{Li}\to\mathrm{Be}}$$



M. J. P. Hodgson*, E. Kraisler*, *et al.*, *J Phys. Chem. Lett.* 2017, *8* (24), 5974–5980.

What about time-dependent density functional theory?



$$f_{\mathrm{xc}}(x, x', t - t') = \frac{\delta v_{\mathrm{xc}}(x, t)}{\delta n(x', t')}$$

Conclusions

1. Charge transfer in molecules can be modelled via ensemble density functional theory

2. Discontinuities in the exchange-correlation energy lead to step features in the exact Kohn-Sham potential

3. Approximate density-functionals must capture these nonlocal features in order to yield accurate charge-transfer energies and densities (even in the ground state)

M. J. P. Hodgson*, Eli Kraisler*, Axel Schild, and E. K. U. Gross, *The Journal of Physical Chemistry Letters* 2017, *8* (24), 5974–5980.

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