Accurately predicting electron affinities with Koopmans spectral functionals

Edward Linscott, Nicola Colonna, Riccardo De Gennaro, and Nicola Marzari

Theory and Simulation of Materials, École Polytechnique Fédérale de Lausanne
APS March Meeting, 18 March 2021

How can we predict spectral properties?

[1] C.-O. Almbladh et al. *Phys. Rev. B* 31.6 (1985), 3231

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- reliable ground-state properties
- computationally inexpensive
- KS eigenvalues formally meaningless (except HOMO[1])
- self-interaction error, band gap too small, etc.

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Koopmans

- orbital-density-dependent corrective terms to semi-local DFT
- comparable computational cost to DFPT
- KS eigenvalues are meaningful
- Accuracy comparable to GW

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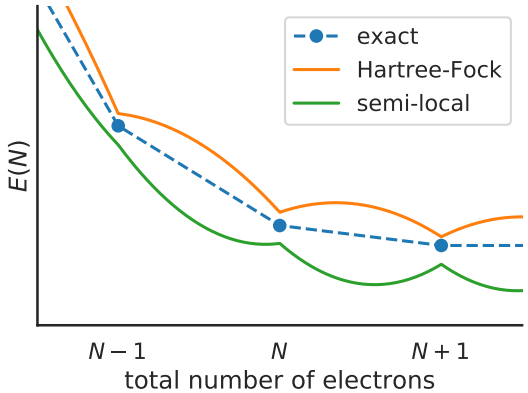
The absence of piecewise linearity

Edward Linscott
EPFL



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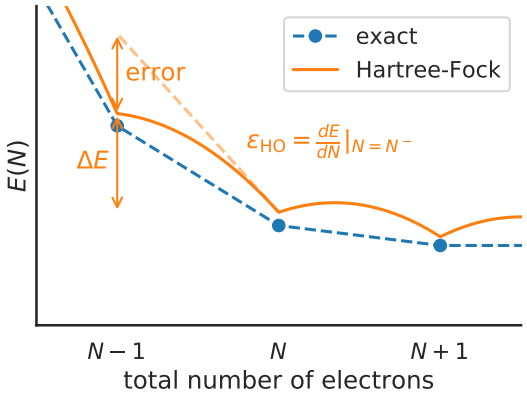

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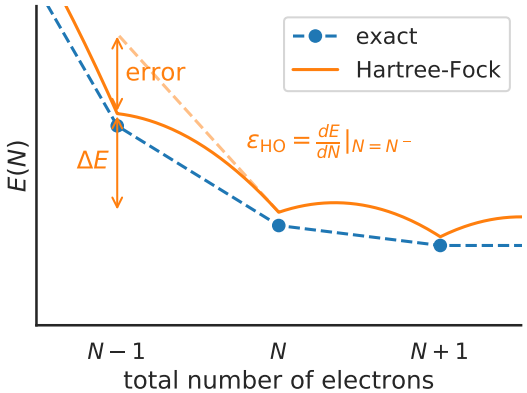

Consequences for ionisation potentials, electron affinities, band gaps, band widths...

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Restoring piecewise linearity to DFT

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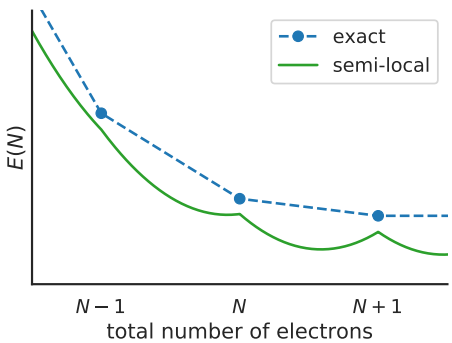

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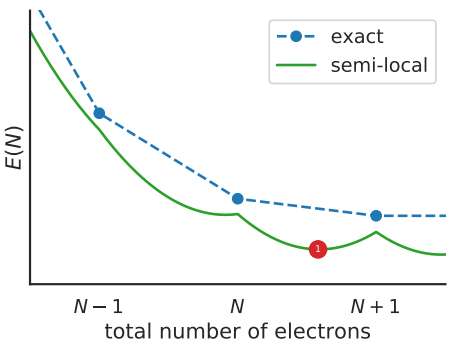

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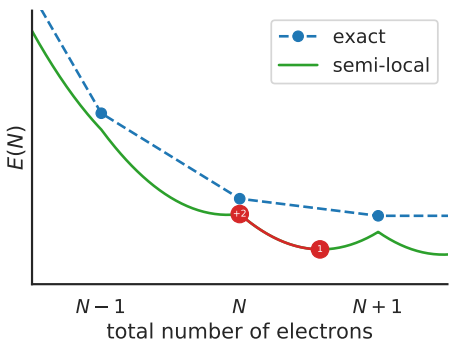

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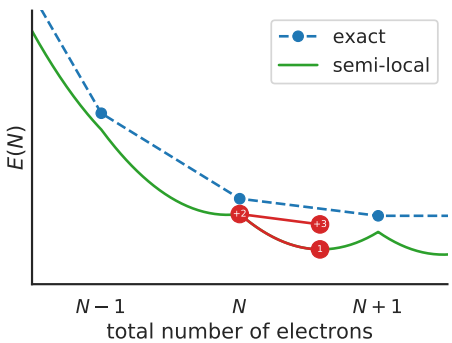

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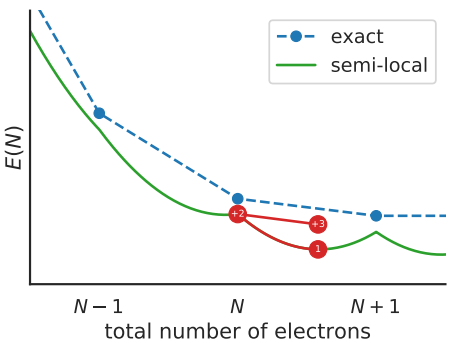

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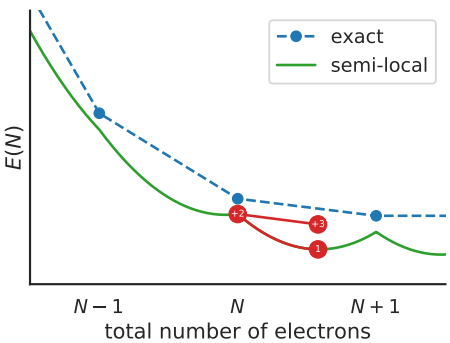

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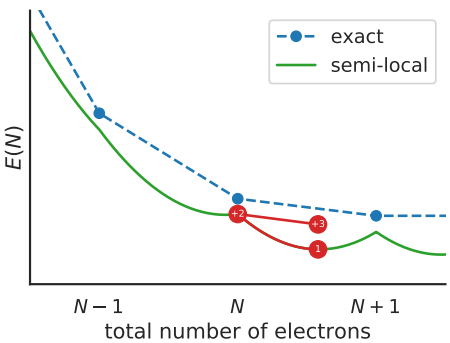

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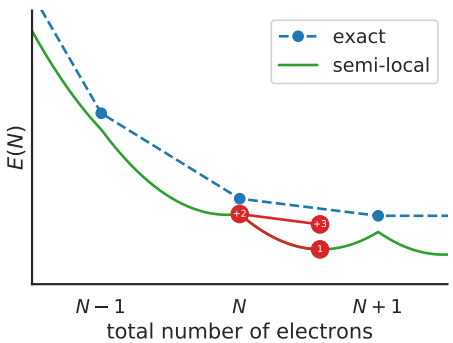

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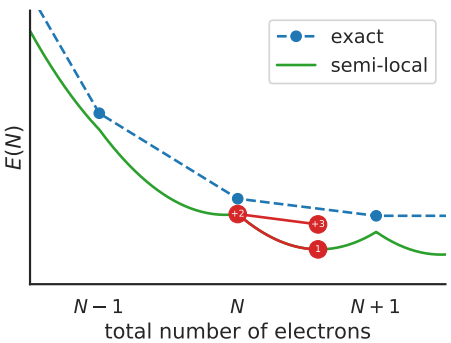

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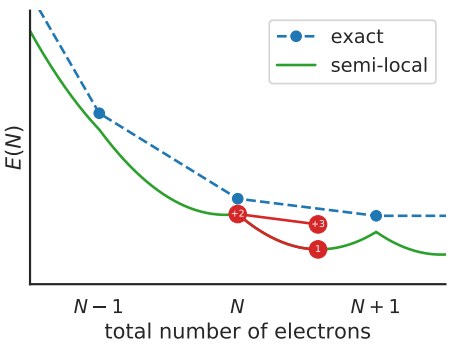

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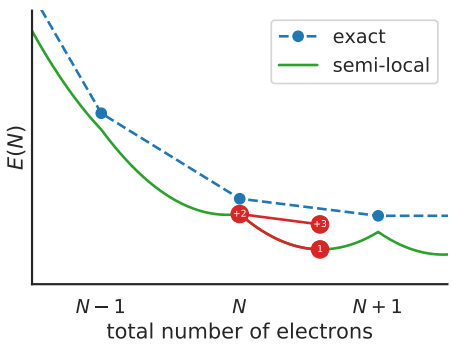

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Koopmans spectral functionals

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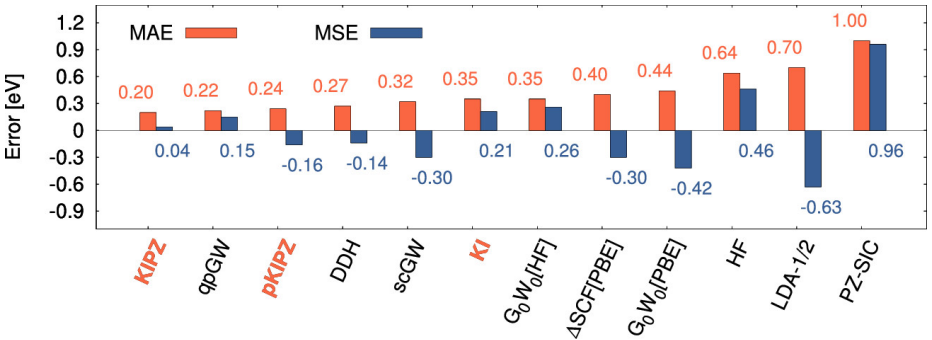
Ionisation potentials $= E(N-1) - E(N) \stackrel{?}{=} -\varepsilon_{HO}$ of 100 molecules (the GW100 set) cf. CCSD(T)



N. Colonna et al. *JCTC* 14.5 (2018), 2549; M. J. Van Setten et al. *JCTC* 11.12 (2015), 5665

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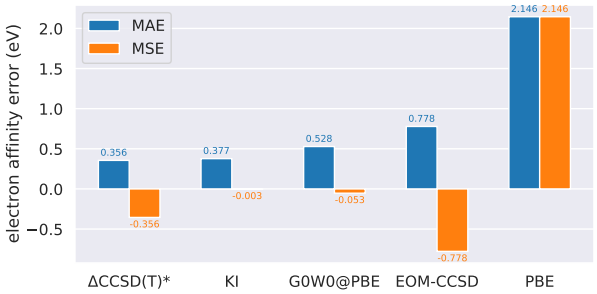
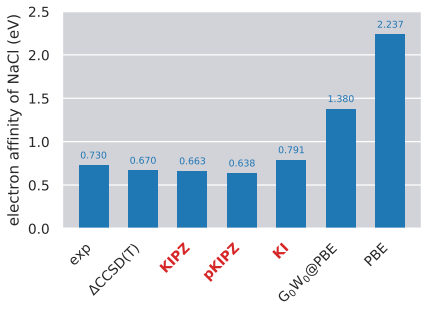
Electron affinities $= E(N) - E(N+1) \stackrel{?}{=} -\varepsilon_{LU}$ of molecules cf. CCSD(T)/exp

For 15 of the GW100 molecules with bound LUMOs



For the NaCl molecule



Figures from Linscott et al. (in prep)

N. L. Nguyen et al. *JCTC* 12.8 (2016), 3948

Calculating screening parameters

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Screening coefficients $\{\alpha_i\}$ must be determined first, either...

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paper in preparation

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Look out for our papers & code release later this year! (Follow @ed_linscott for updates)

Slides can be found at `elinscott.github.io/resources.html`

For further reading, see I. Dabo et al. *Phys. Rev. B* 82.11 (2010), 115121; G. Borghi et al. *Phys. Rev. B* 90.7 (2014), 075135; N. Colonna et al. *JCTC* 14.5 (2018), 2549; N. L. Nguyen et al. *Phys. Rev. X* 8.2 (2018), 021051; N. Colonna et al. *JCTC* 15.3 (2019), 1905