Ensemble-generalization approach:

addressing some long-standing problems in DFT

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DFT2016 summer school, Los Angeles, August 2016

Acknowledgements

Prof. Leeor Kronik (WIS, Israel)

Prof. Stephan Kümmel (Bayreuth Univ., Germany)

Dr. Tobias Schmidt (Bayreuth Univ., Germany)

Outline

Presenting the problems

- Properties of the exact exchange-correlation (xc) functional:
  - Piecewise-linearity of the energy
  - Ionization potential (IP) theorem
  - Derivative Discontinuity (DD)
  - Principle of integer preference in dissociation
- Common xc approximations and their failures

Mel's lectures

John's lectures

Possible solution

- Ensemble-generalization procedure — *PRL 110, 126403 (2013)*
  - Kohn-Sham system: ensemble state
  - Generalization for: Hartree, exchange, correlation
  - Potential shift and Derivative Discontinuity — *JCP 140, 18A540 (2014)*, *JCP 143, 104105 (2015)*
  - Improvement in piecewise-linearity, IP, fundamental gap, dissociation — *PRA 91, 032504 (2015)*
- Conclusions

Piecewise-linearity

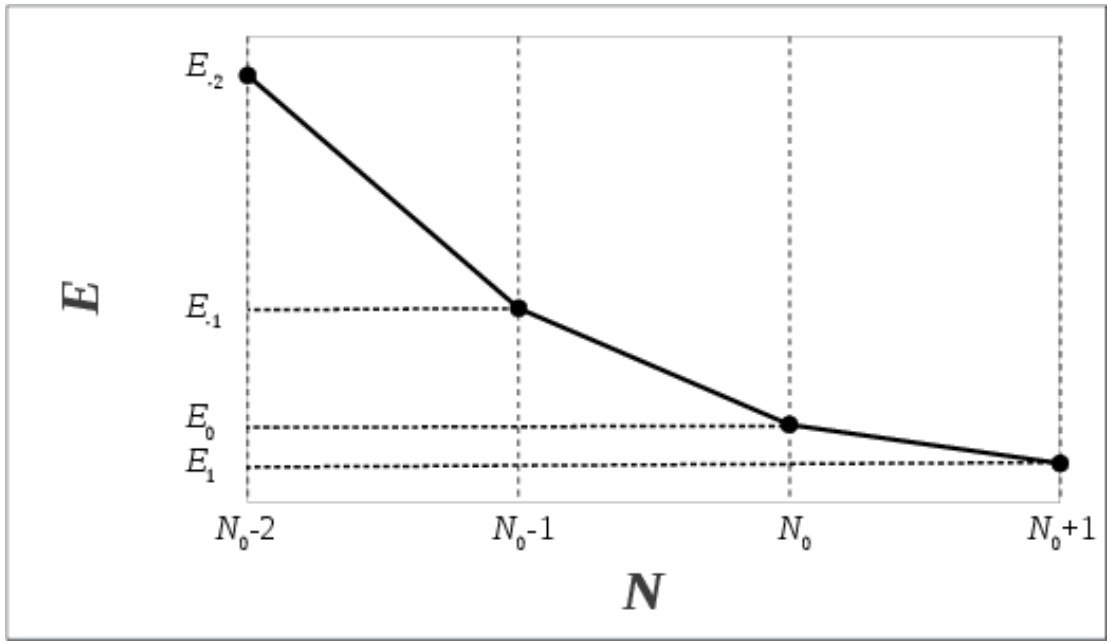
- If $N \in \mathbb{N}$, the ground state can be a pure state: $|\Psi\rangle$
- If $N = N_0 + \alpha$, where $N_0 \in \mathbb{N}$ and $\alpha \in [0,1]$, the ground state is definitely an ensemble.

Carlos' 3rd lecture

- For Coulomb systems:

$$\hat{\Lambda} = (1-\alpha)|\Psi_{N_0}\rangle\langle\Psi_{N_0}| + \alpha|\Psi_{N_0+1}\rangle\langle\Psi_{N_0+1}|$$

- Energy: $E(N) = \mathrm{Tr}\{\hat{\Lambda}\hat{H}\} = (1-\alpha)E_0 + \alpha E_1$

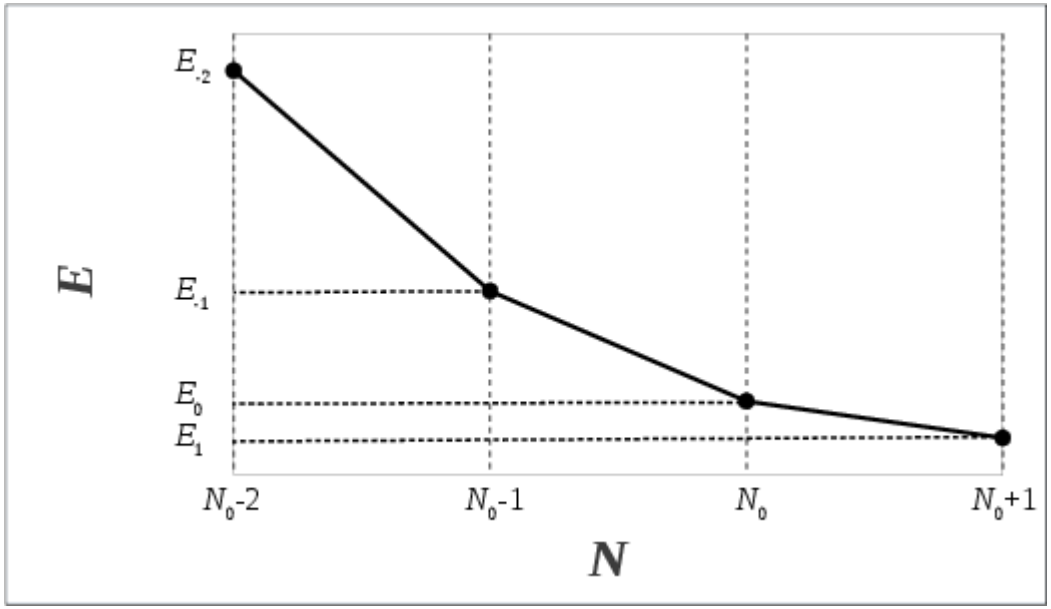


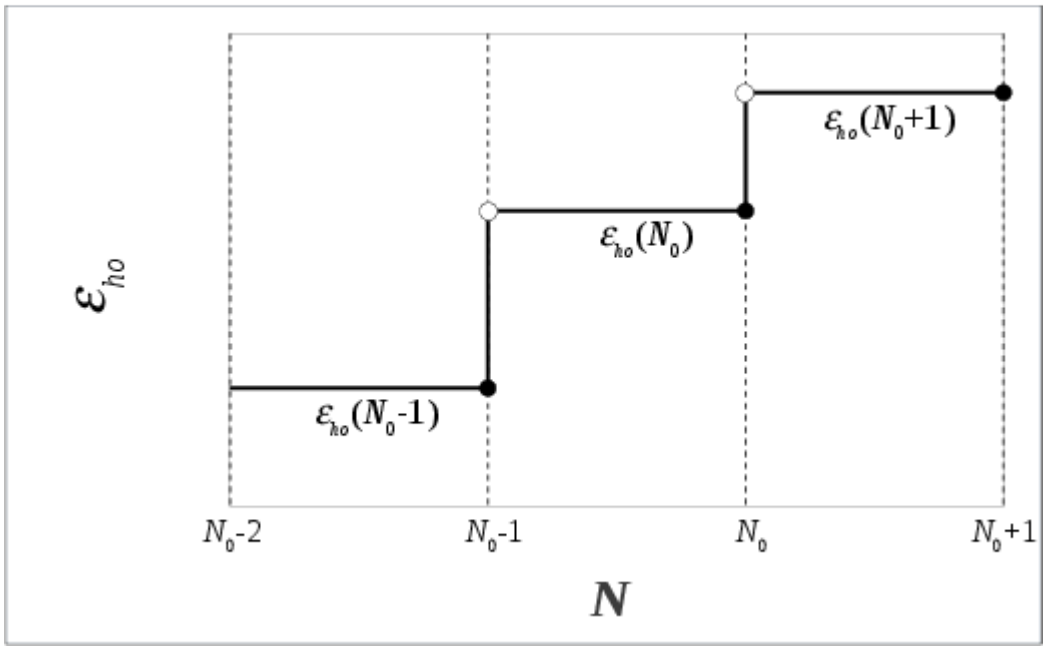
Convexity conjecture:

$(\ldots I_3 > I_2 > I_1 > A \ \ldots)$

Perdew *et al.* PRL 49, 1691 (1982)
Lieb, IJQC 24, 243 (1983)
Cohen *et al.*, Chem. Rev. 112, 289 (2012)

Ionization Potential Theorem





Piecewise-linearity

Janak's theorem:

$$\varepsilon_i = \partial E / \partial f_i$$

in particular,

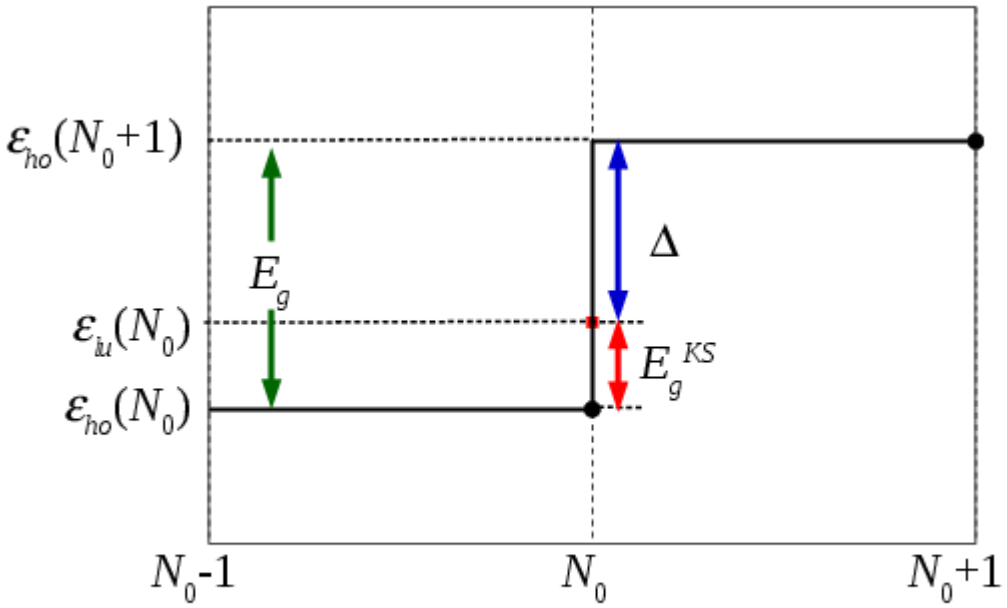
$$\varepsilon_{ho} = \partial E / \partial N$$

IP theorem:

$$\varepsilon_{ho} = -I$$

Almbladh, von Barth, PRB 31, 3231 (1985)
Levy *et al.*, PRA 30, 2745 (1984)
Perdew, Levy, PRB 56, 16021 (1997)
Harbola, PRB 60, 4545 (1999)
Janak, PRB 18, 7165 (1978)

Derivative Discontinuity, Δ



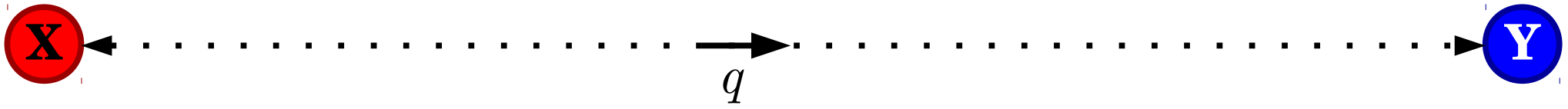
- Fundamental gap: $E_g = I - A$
- Two sources for the gap:
  - ⋆ occupying a new KS level
  - ⋆ $v_{KS}(\mathbf{r})$ "jumps" by a uniform constant:

    $v_S^+(\mathbf{r}) = v_S^-(\mathbf{r}) + \Delta$

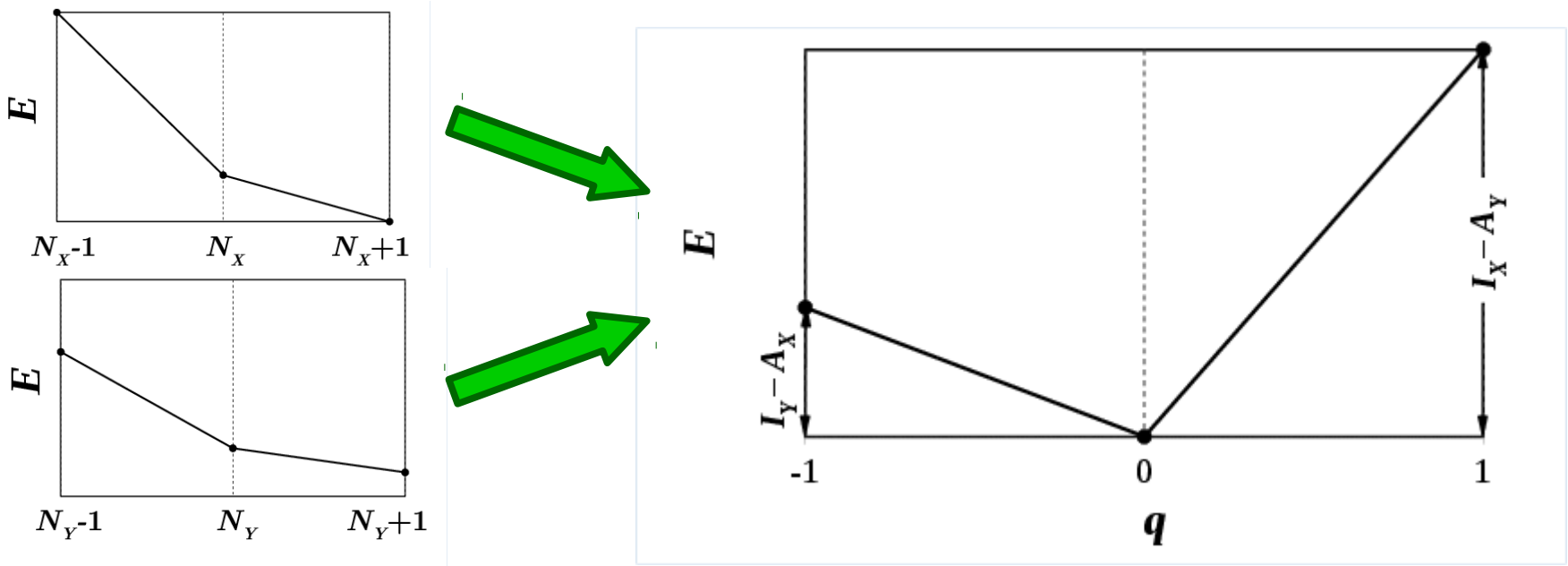
- $E_g = \underbrace{\varepsilon_{lu} - \varepsilon_{ho}}_{E_g^{KS}} + \Delta$

Godby *et al.*, PRB 36, 6497 (1987); Godby *et al.*, PRB 37, 10159 (1988); Chan, JCP 110, 4710 (1999);
Allen, Tozer, Mol.Phys. 100, 433 (2002); Teale *et al.*, JCP 129, 044110 (2008); Mosquera, Wasserman, PRA 89, 052506 (2014)
Perdew, Levy, PRL 51, 1884 (1983); Sham, Schlüter, PRL 51, 1888 (1983); Harbola, PRA 57, 4253 (1998); Yang *et al.*, JCP 136, 204111 (2012)

Dissociated system



- Consider a transfer of q electrons from X to Y
- At infinite distance: $E_{X\ldots Y}(q) = E_X(N_X^0 - q) + E_Y(N_Y^0 + q)$



- **Principle of integer preference:**

  dissociation into fragments with *integer* number of electrons

Perdew, Adv. Quantum Chem. 21, 113 (1990); Ruzsinszky *et al.*, JCP 126, 104102 (2007)

Approx. xc functionals: KS scheme

- Standard approach to a system with fractional $N = N_0 + \alpha$

$$\left(-\frac{1}{2}\nabla^2 + v_S^{app}[n](\mathbf{r})\right)\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r})$$

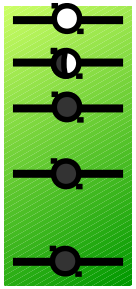
'as is'

$$n(\mathbf{r}) = \sum_{i=1}^{\infty} f_i\,|\varphi_i(\mathbf{r})|^2$$

'as is'

$$f_i = \begin{cases} 1 & : \quad i \leqslant N_0 \\ \alpha & : \quad i = N_0 + 1 \\ 0 & : \quad i > N_0 + 1 \end{cases}$$

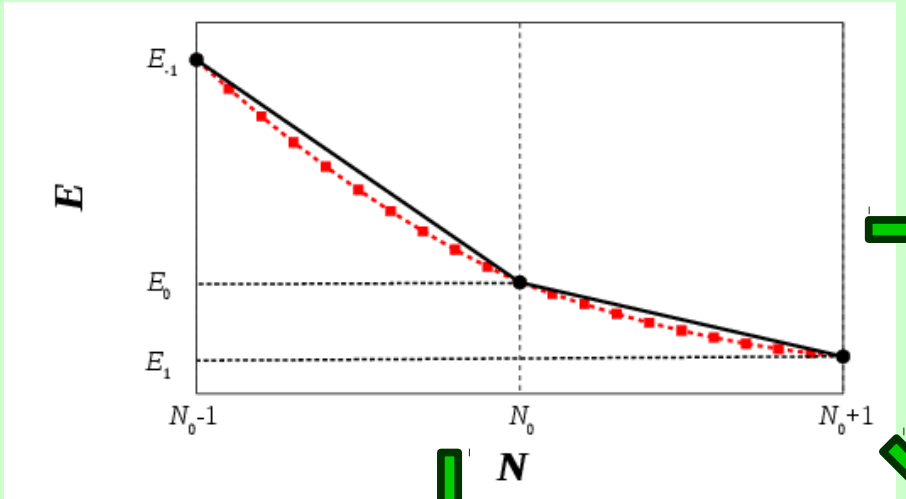
Kieron's 1st lecture



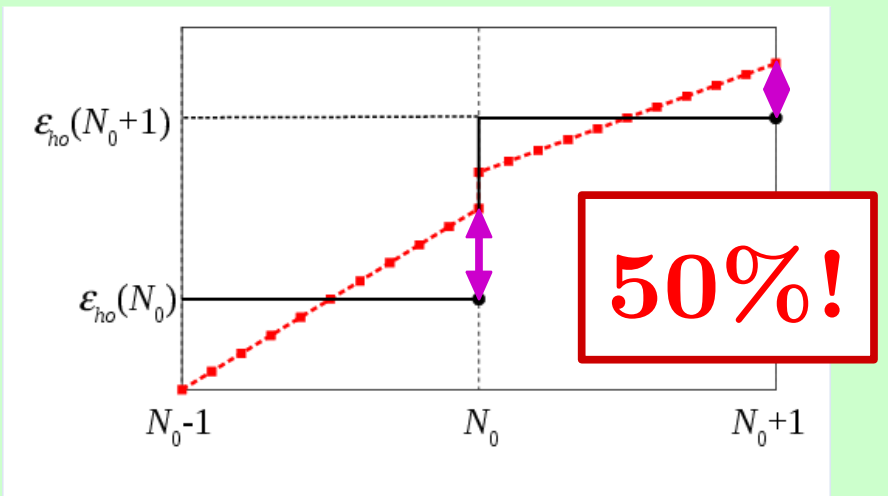
$$E[n] = T_S[n] + \int v_{ext}(\mathbf{r})\,n(\mathbf{r})d^3r + E_H[n] + E_{xc}^{app}[n]$$

Approx. xc functionals: failures

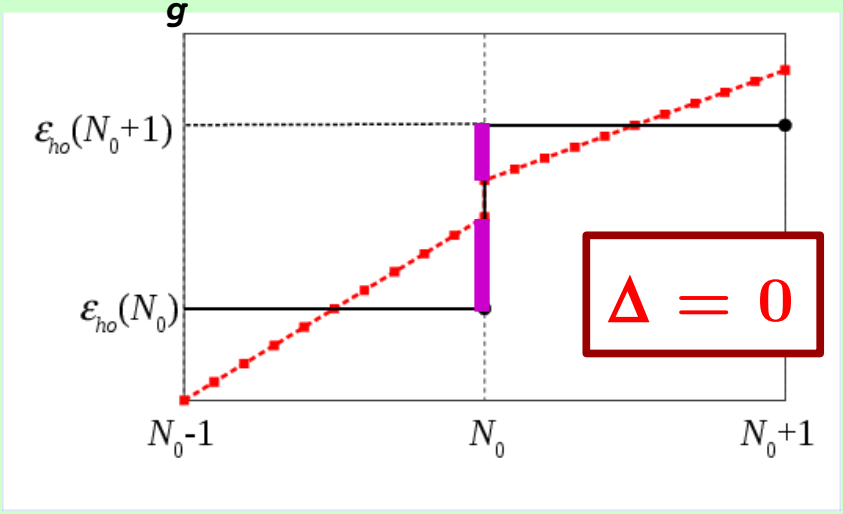
convex $E(N)$ curve



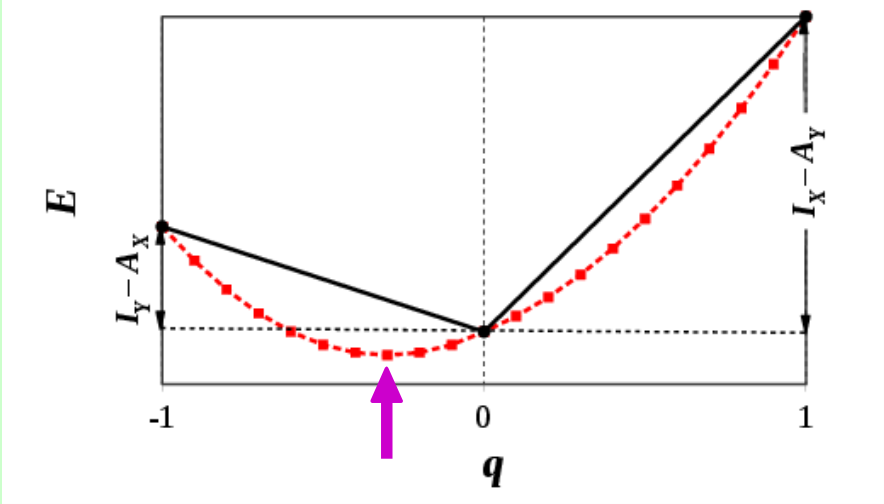
IP via ε_{ho} underestimated



E_g underestimated



Fractional dissociation



How to improve the situation?

- Compensate the convexity by amending E_{xc}

  Cococcioni, de Gironcoli, PRB 71, 035105 (2005)
  Lany, Zunger, PRB 80, 085202 (2009)
  Andrade, Aspuru-Guzik, PRL 107, 183002 (2011)
  Zheng *et al.*, PRL 107, 026403 (2011)
  Zheng *et al.*, JCP 138, 174105 (2013)
  Li *et al.*, PRL 114, 053001 (2015)
  Dabo et al., PRB 82, 115121 (2010)
  Dabo et al., Top. Curr. Chem. 347, 193 (2014)

- Tune to piecewise-linearity

  Stein et al., PRL 105, 266802 (2010)
  Kronik et al., JCTC 8, 1515 (2012)
  Sai et al., PRL 106, 226403 (2011)
  Refaely-Abramson, PRL 109, 226405 (2012)
  Imamura *et al.*, CPL 513, 130 (2011)
  Atalla et al., PRB 94, 035140 (2016)

- More methods

  Mosquera, Wasserman, PRA 89, 052506 (2014)
  Mosquera, Wasserman, Mol. Phys. 112, 2997 (2014)
  Vlček et al., JCP 142, 034107 (2015)
  Görling, PRB 91, 245120 (2015)

- Common implicit assumption:

  the functional for **fractional** N is the same as for **integer** N

- Our method: ensemble-generalization

  Kraisler, Kronik, PRL 110, 126403 (2013)
  Kraisler, Kronik, JCP 140, 18A540 (2014)

  ⋆ The KS system (defined by $v_S^{(\alpha)}(\mathbf{r})$) is in an ensemble state, too!

$$\hat{\Lambda}_{KS}^{(\alpha)} = (1-\alpha)|\Phi_{N_0}^{(\alpha)}\rangle\langle\Phi_{N_0}^{(\alpha)}| + \alpha|\Phi_{N_0+1}^{(\alpha)}\rangle\langle\Phi_{N_0+1}^{(\alpha)}|$$

  ⋆ Any quantity defined via an operator can be ensemble-generalized:

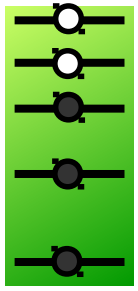
$$O = \mathrm{Tr}\{\hat{\Lambda}_{KS}^{(\alpha)}\hat{O}\} = (1-\alpha)\langle\Phi_{N_0}^{(\alpha)}|\hat{O}|\Phi_{N_0}^{(\alpha)}\rangle + \alpha\langle\Phi_{N_0+1}^{(\alpha)}|\hat{O}|\Phi_{N_0+1}^{(\alpha)}\rangle$$

Ensembles in the KS system

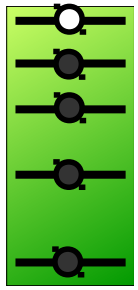
$$O = \mathrm{Tr}\{\hat{\Lambda}^{(\alpha)}_{KS}\hat{O}\} = (1-\alpha)\langle\Phi^{(\alpha)}_{N_0}|\hat{O}|\Phi^{(\alpha)}_{N_0}\rangle + \alpha\langle\Phi^{(\alpha)}_{N_0+1}|\hat{O}|\Phi^{(\alpha)}_{N_0+1}\rangle$$

- Density: $\hat{n}(\mathbf{r}) = \sum_i \delta(\mathbf{r}-\mathbf{r}_i)$

$$n^{(\alpha)}(\mathbf{r}) = \mathrm{Tr}\{\hat{\Lambda}^{(\alpha)}_{KS}\hat{n}(\mathbf{r})\} = (1-\alpha)\rho^{(\alpha)}_0(\mathbf{r}) + \alpha\rho^{(\alpha)}_1(\mathbf{r}) = \sum_{i=1}^{\infty} f_i\,|\varphi^{(\alpha)}_i(\mathbf{r})|^2$$

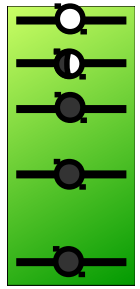


$$\rho^{(\alpha)}_0(\mathbf{r}) = \sum_{i=1}^{N_0}|\varphi^{(\alpha)}_i(\mathbf{r})|^2$$



as before

$$\rho^{(\alpha)}_1(\mathbf{r}) = \sum_{i=1}^{N_0+1}|\varphi^{(\alpha)}_i(\mathbf{r})|^2$$



$$f_i = \begin{cases} 1 & : \quad i \leqslant N_0 \\ \alpha & : \quad i = N_0+1 \\ 0 & : \quad i > N_0+1 \end{cases}$$

- KS kinetic energy: $\hat{T} = -\frac{1}{2}\sum_i \nabla^2_i$

$$T_S[n^{(\alpha)}] = (1-\alpha)T_S[\rho^{(\alpha)}_0] + \alpha\,T_S[\rho^{(\alpha)}_1] = -\frac{1}{2}\sum_{i=1}^{\infty} f_i\,\langle\varphi^{(\alpha)}_i|\nabla^2|\varphi^{(\alpha)}_i\rangle$$

as before

- External potential energy: $\hat{V} = \sum_i v_{ext}(\mathbf{r}_i) = \int v_{ext}(\mathbf{r})\hat{n}(\mathbf{r})d^3r$

$$V[n^{(\alpha)}] = (1-\alpha)V[\rho^{(\alpha)}_0] + \alpha\,V[\rho^{(\alpha)}_1] = \int v_{ext}(\mathbf{r})n^{(\alpha)}(\mathbf{r})d^3r$$

as before

Ensemble generalization

- Hartree and Exchange: $\hat{V}_{ee} = \frac{1}{2}\sum_i \sum_{j\neq i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$

Reminder: for a pure state
$\langle\Phi|\hat{V}_{ee}|\Phi\rangle = E_H[n] + E_x[n]$

  - ⋆ Ensemble-generalized Hartree:

Kraisler, Kronik, PRL 110, 126403 (2013)

$$E_{e-H}[n^{(\alpha)}] = (1-\alpha)E_H[\rho_0^{(\alpha)}] + \alpha\, E_H[\rho_1^{(\alpha)}]$$

not the same as

$$E_H\left[(1-\alpha)\rho_0^{(\alpha)} + \alpha\rho_1^{(\alpha)}\right]$$

See also:
Gidopoulos *et al*, PRL 88, 033003 (2002)
Zheng *et al*., JCP 138, 174105 (2013)

  - ⋆ Ensemble-generalized exchange:

Kraisler, Kronik, PRL 110, 126403 (2013)

$$E_{e-x}[n^{(\alpha)}] = (1-\alpha)E_x[\rho_0^{(\alpha)}] + \alpha\, E_x[\rho_1^{(\alpha)}]$$

See also:
Gould, Dobson, JCP 138, 014103 (2013)

    - ◦ correct for exact exchange. The same is required for approx. exchange

- Correlation: we suggest the same form:

Kraisler, Kronik, PRL 110, 126403 (2013)

$$E_{e-c}[n^{(\alpha)}] = (1-\alpha)E_c[\rho_0^{(\alpha)}] + \alpha\, E_c[\rho_1^{(\alpha)}]$$

  - ⋆ this is an approximation!

See also: Mosquera, Wasserman, PRA 89, 052506 (2014); Mol. Phys. 112, 2997 (2014)
Görling, PRB 91, 245120 (2015)

Properties of ensemble-functionals

$$E_{e-Hxc}[n^{(\alpha)}(\mathbf{r})] = (1-\alpha)E_{Hxc}[\rho_0^{(\alpha)}(\mathbf{r})] + \alpha\, E_{Hxc}[\rho_1^{(\alpha)}(\mathbf{r})]$$

- Applicable for any underlying xc functional, e.g., LSDA $\rightarrow$ eLSDA
- For pure states, E remains unchanged.
- All e-functionals are orbital-dependent and α-dependent.
  - ⋆ To obtain $v_{e-S}[n](\mathbf{r})$, we need the optimized-effective-potential (OEP) method (or approx's, e.g. KLI).
    Numerically expensive.
    Weitao's lecture
  - ⋆ Some results can be obtained free-of-charge.

Ensemble-generalized potential

- In general, for fractional N, $v_S[n](\mathbf{r})$ is obtained with OEP
- In the limit $N \to N_0^-$, $v_{e-S}^-[n](\mathbf{r}) = v_S[n](\mathbf{r}) + v_0$

$$v_0 = E_{Hxc}[n] - E_{Hxc}[n - |\varphi_{ho}|^2] - \int v_{Hxc}[n](\mathbf{r})|\varphi_{ho}(\mathbf{r})|^2 d^3r$$

$$\Longrightarrow \varepsilon_{e-i} = \varepsilon_i + v_0$$

Kraisler, Kronik, PRL 110, 126403 (2013)

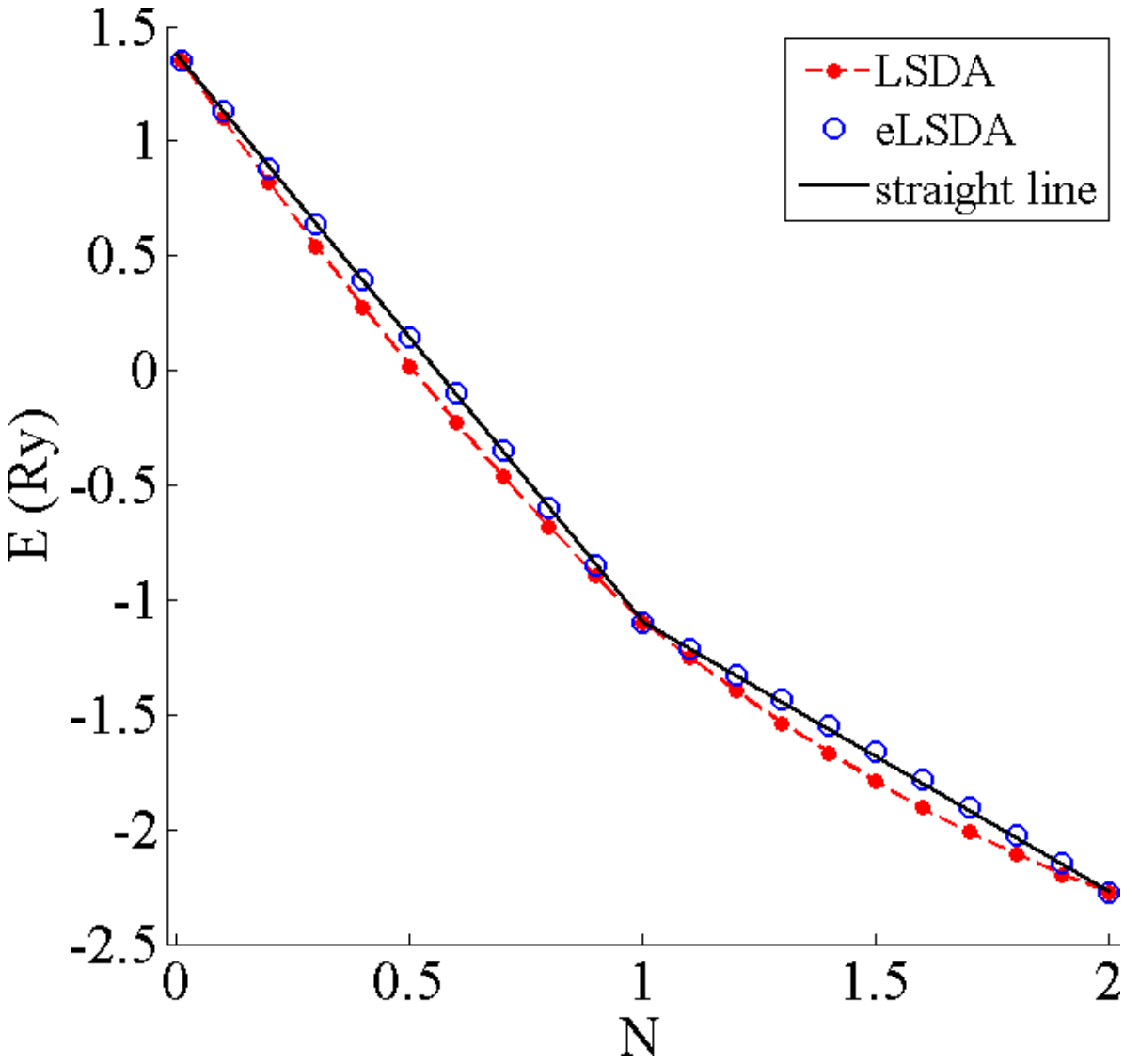
- In the limit $N \to N_0^+$, $v_{e-S}^+[n](\mathbf{r}) = v_{e-S}^-[n](\mathbf{r}) + \Delta$

$$\Delta = E_{Hxc}\left[n + |\varphi_{lu}|^2\right] - 2E_{Hxc}[n] + E_{Hxc}\left[n - |\varphi_{ho}|^2\right] - \int v_{Hxc}[n](\mathbf{r})(|\varphi_{lu}(\mathbf{r})|^2 - |\varphi_{ho}(\mathbf{r})|^2) d^3r$$

Kraisler, Kronik, JCP 140, 18A540 (2014)

- The DD is naturally introduced
- Easy to calculate. OEP machinery not required.

Results: total energy



H_2 molecule

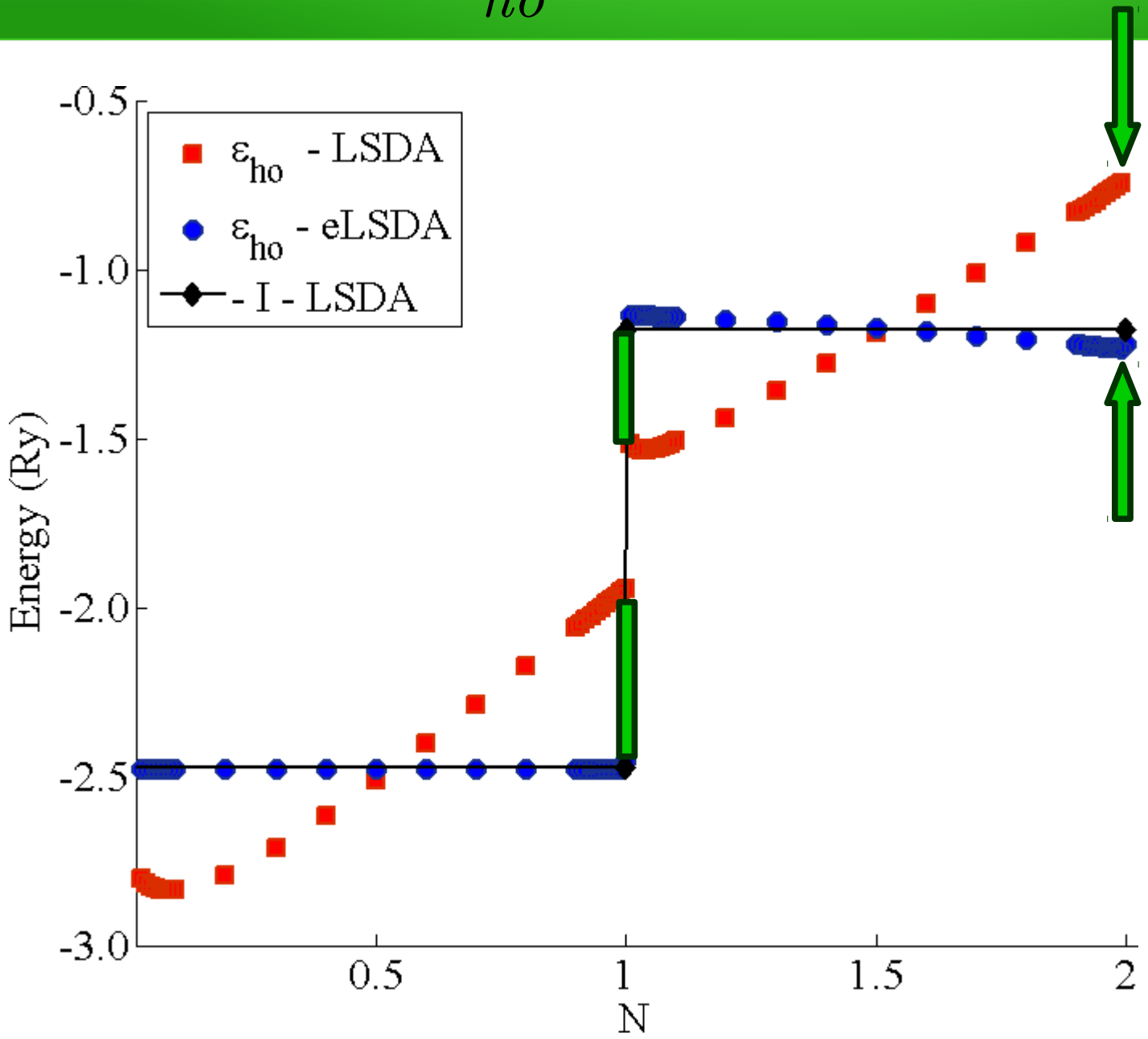
LSDA: convex curve, as expected

Connecting the points of integer N

The proposed ensemble-LSDA helps to restore piecewise-linearity

Kraisler, Kronik, PRL 110, 126403 (2013)

Results: ε_{ho} vs $-I$



H_2 molecule

Error in ε_{ho}:

LSDA: -37%

eLSDA: +6%

H_2^+ ion

Error in E_g:

LSDA: -67%

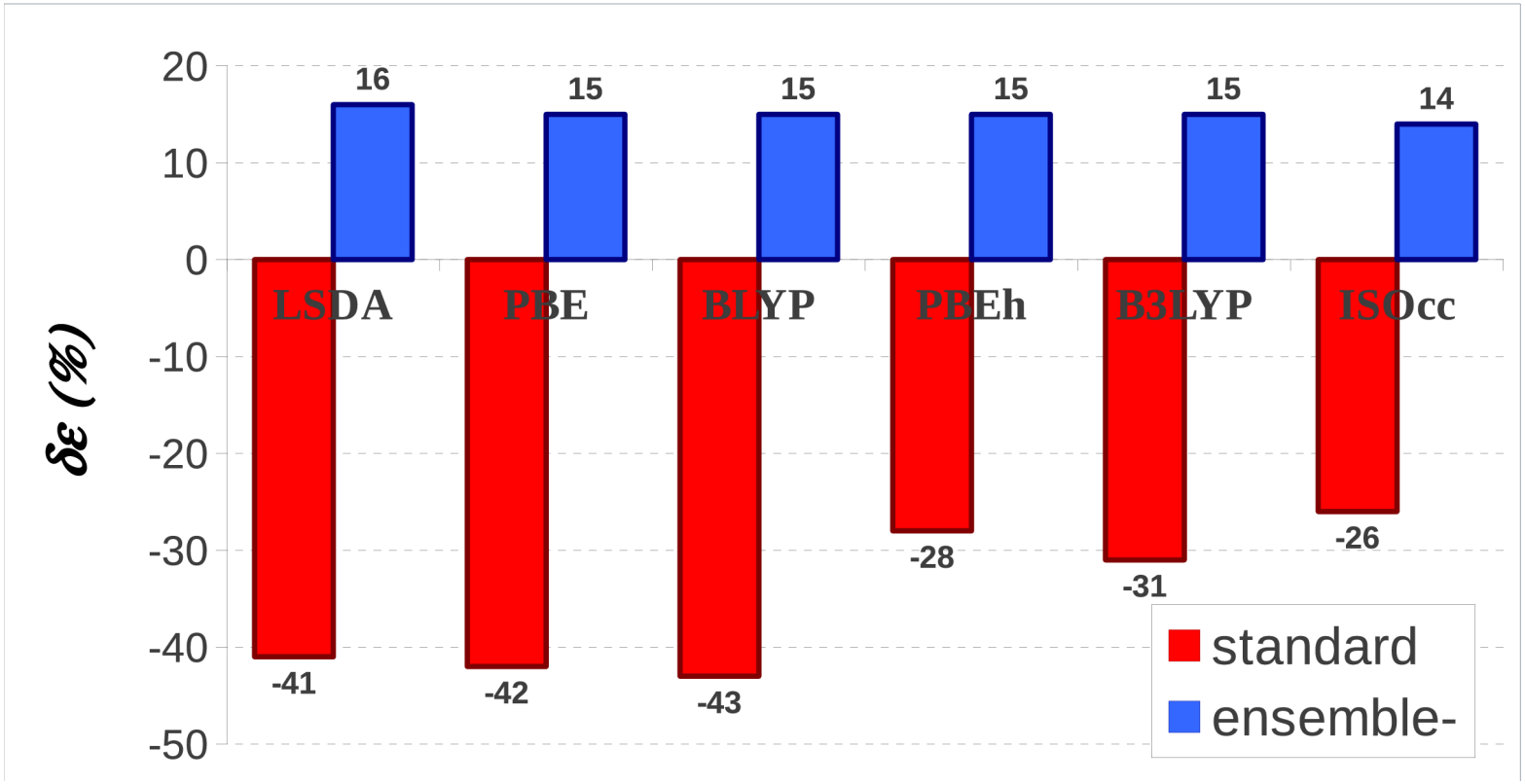
eLSDA: +3%

Kraisler, Kronik, PRL 110, 126403 (2013)

ε_{ho} vs experimental -I: statistics

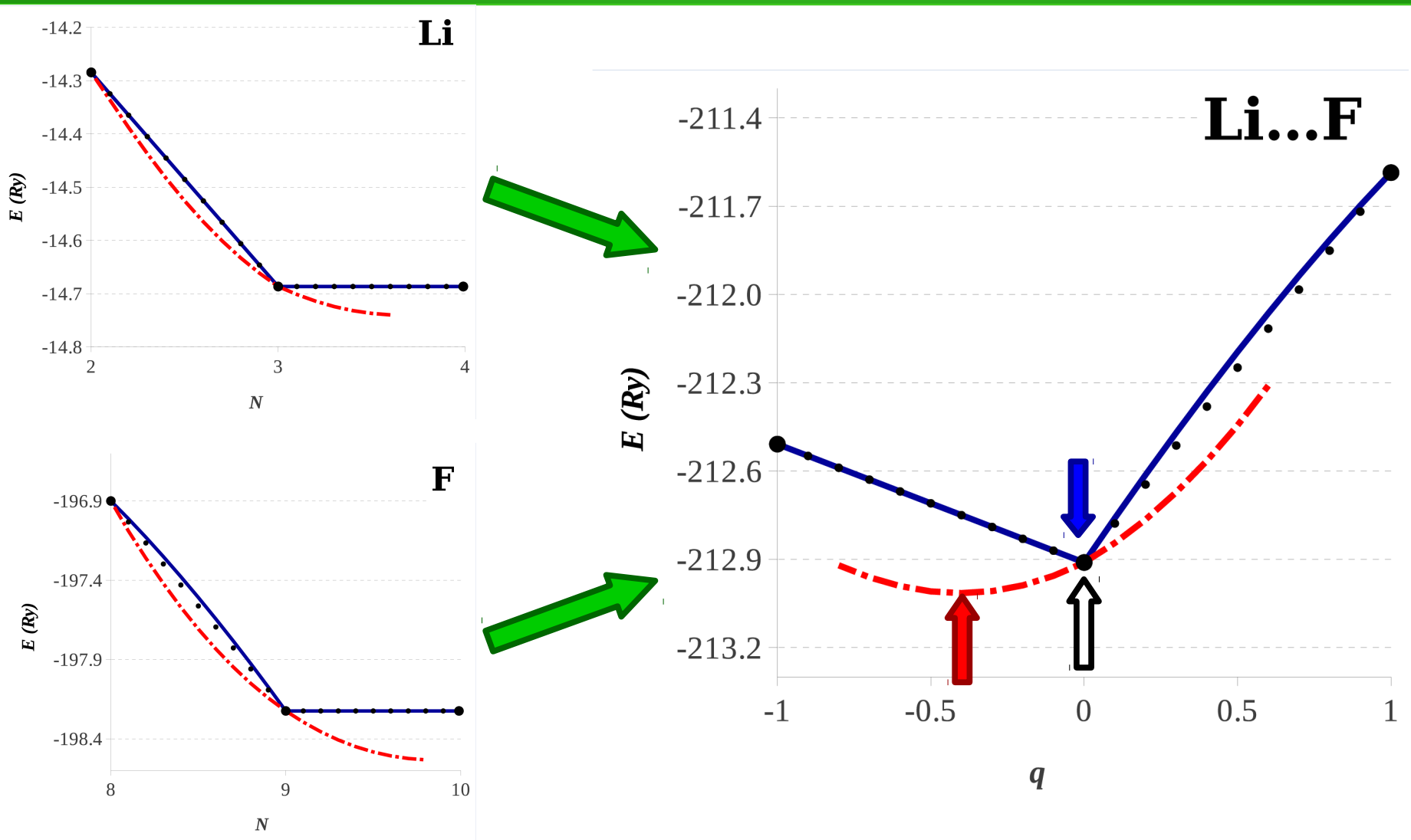
26 light atoms and diatomic molecules:

H, Li, Be, B, C, N, O, F, H_2, LiH, Li_2, LiF, BeH, BH, BO, BF, CH, CN, CO, NH, N_2, NO, OH, O_2, FH, F_2



Kraisler, Schmidt, Kümmel, Kronik, JCP 143, 104105 (2015)

Dissociation: Li...F molecule



- Asymptotic fractional dissociation problem eliminated

Kraisler, Kronik, PRA 91, 032504 (2015)

Conclusions

- With the ensemble approach much (not all) of the **piecewise-linearity problem** in DFT can be **removed**
- **Meaning:** better prediction of electronic properties with existing functionals, without compromise on energetics
  - ⋆ **Prediction of IP** via ε_{ho} is systematically **improved**
    - ◦ Non-negligible overestimation of ~15%, irrespective of the xc approximation, remains
  - ⋆ All xc functionals have a **derivative discontinuity**, Δ.
    - ◦ It can be revealed with the ensemble approach and affect E_g
  - ⋆ Asymptotic **fractional dissociation** problem is **eliminated**.

Kraisler, Kronik, PRL 110, 126403 (2013)
Kraisler, Kronik, JCP 140, 18A540 (2014)
Kraisler, Schmidt, Kümmel, Kronik, JCP 143, 104105 (2015)
Kraisler, Kronik, PRA 91, 032504 (2015)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