(Some) wrap up

1) KS SCE

what it does right for models in physics (lattice hamiltonians?)

serious limitations (hopeless) for chemistry

2) beyond KS SCE

next leading orders: do they contain the right physics? too difficult?

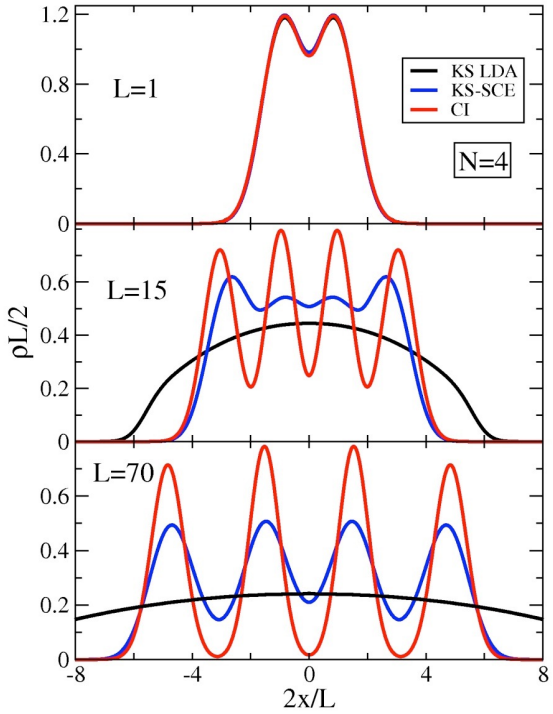
spin

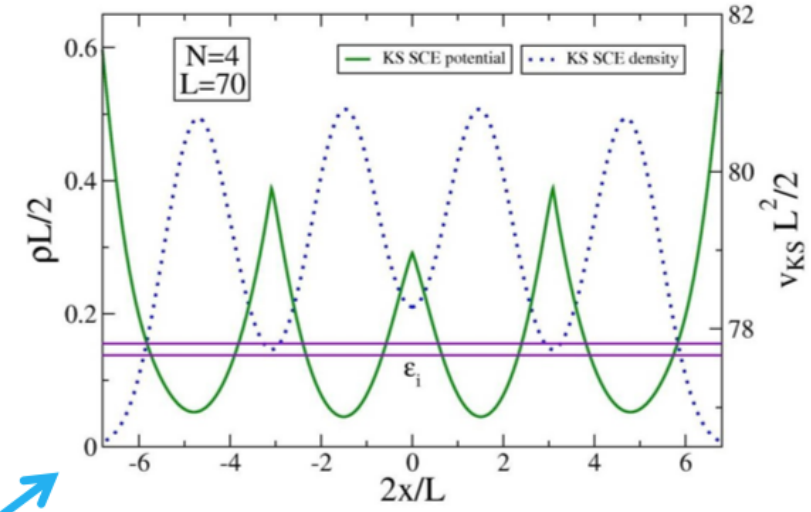
3) chemistry/solid state physics

how to turn what we have learned into useful approximations?

KS SCE in 1D: $2k_F$ - $4k_F$ crossover without magnetic order

1D harmonic confinement: $v_{\rm ext}(x) = \frac{1}{2}\omega^2 x^2 \quad \omega = \frac{4}{L^2}$ *L*: effective length





Previous attempts include self-interaction corrections (SIC) and GGA:

S. H. Abedinpour, M. Polini, G. Xianlong, and M. P. Tosi, Eur. Phys. J. B 56, 127 (2007)

D. Vieira and K. Capelle, J. Chem. Theory Comput. 6, 3319 (2010)

D. Vieira, Phys. Rev. B 86, 075132 (2012)

Spherically symmetric systems

ansatz: 1D solution for the radial part + relative angles minimization

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

not always the lowest solution (it depends on the density)

Colombo & Stra, arXiv:1507.08522

Seidl, Di Marino, Gerolin, Nenna, Giesbertz & Gori-Giorgi, arXiv:1702.05022

however, the 1D-like solution is very close to the true minimum, and the potential computed from it is the functional derivative of the 1D-like SCE functional

Seidl, Di Marino, Gerolin, Nenna, Giesbertz & Gori-Giorgi, arXiv:1702.05022

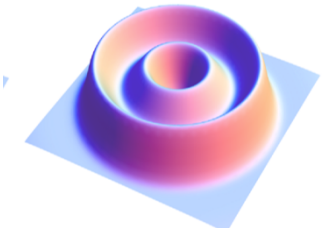
$$\nabla v_{\mathrm{SCE}}(\mathbf{r}) = -\sum_{i=2}^{N} \frac{\mathbf{r} - \mathbf{f}_i(\mathbf{r})}{|\mathbf{r} - \mathbf{f}_i(\mathbf{r})|^3}$$

Example: 10 electrons in 2D harmonic potential

Self-consistent KS densities and potential with the SCE functional

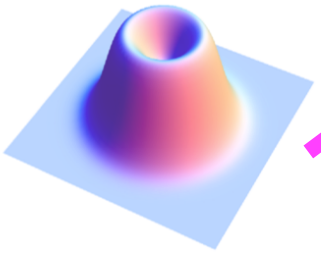
strong correlation
(Wigner rings)

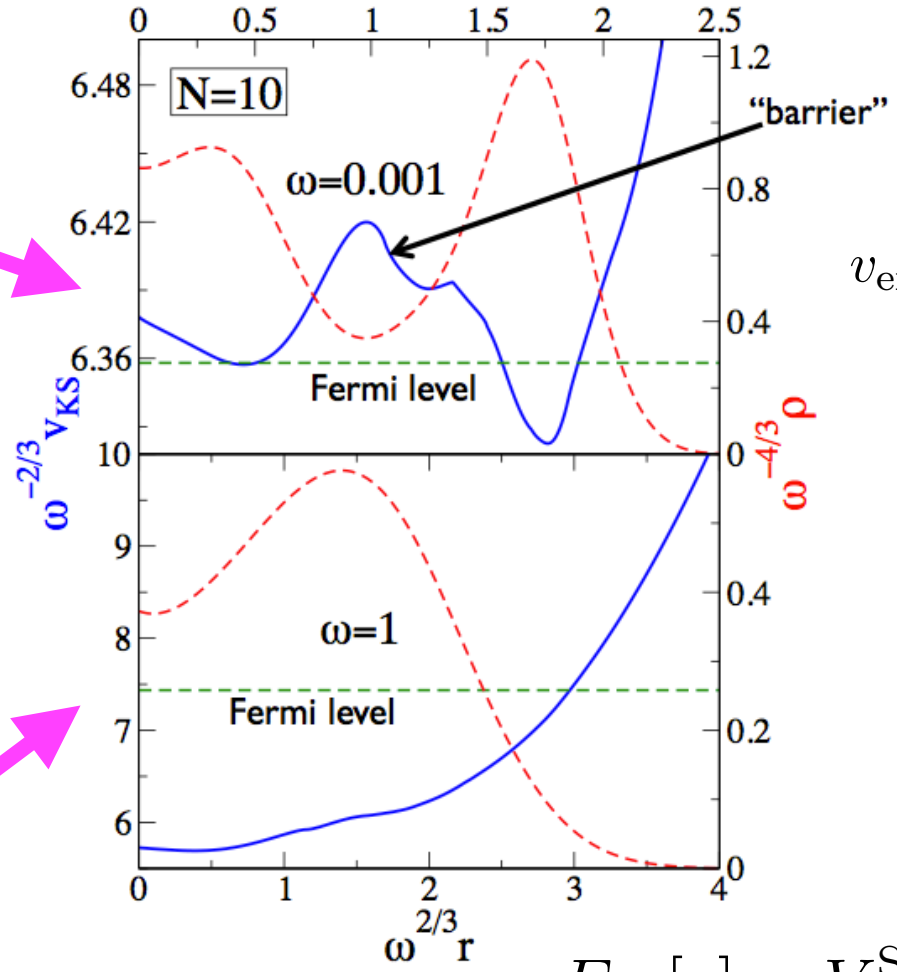
$\omega = 0.001$



weak correlation
(Fermi-liquid like)

$\omega = 1$



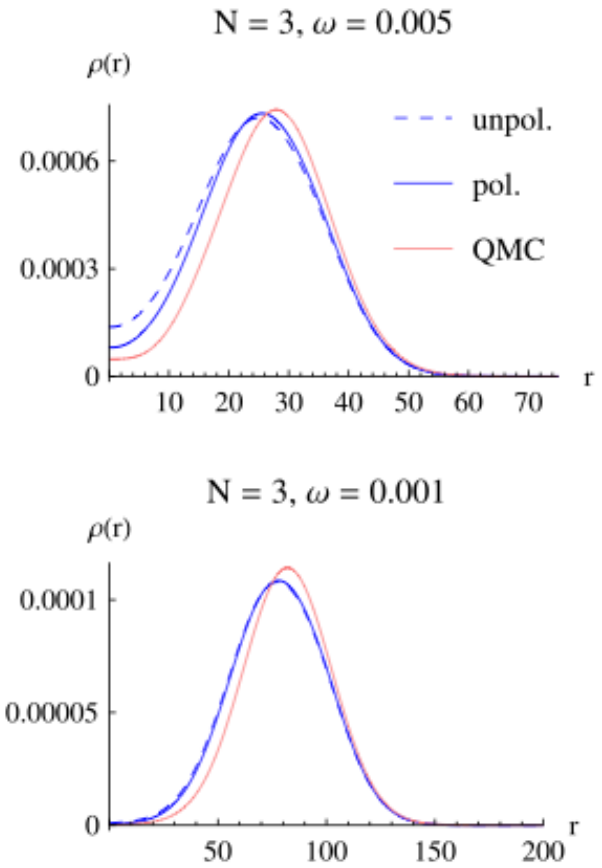


$$v_{\text{ext}}(\mathbf{r}) = \frac{1}{2}\omega^2 r^2$$

$$E_{xc}[\rho] \approx V_{ee}^{\text{SCE}}[\rho] - U[\rho]$$

*Mendl, Malet & Gori-Giorgi, PRB **89**, 125106 (2014)*

Accuracy of KS SCE for low-density



In this case the SGS maps are not optimal…
Approximate maps can be good enough…

energy accuracy
of ~ 1 mH* (~4%)

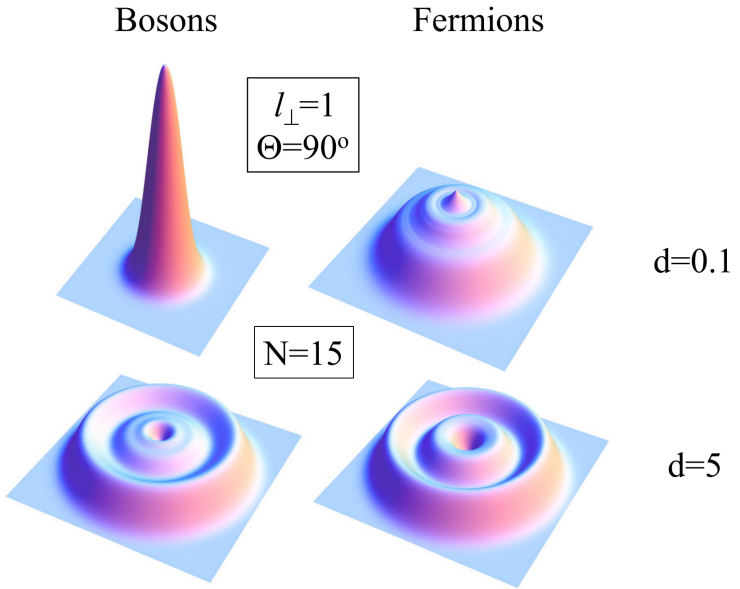
QMC: *D. Guclu and C.J. Umrigar*

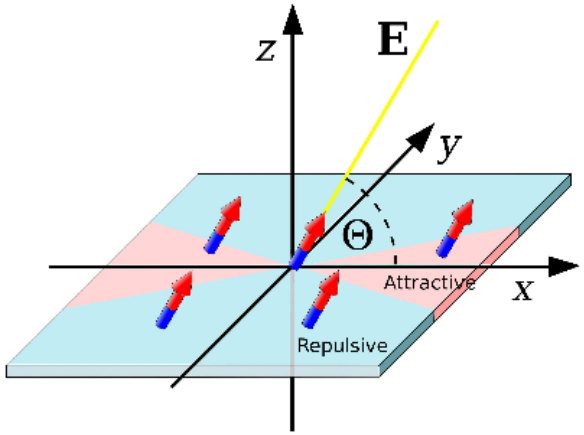
*Mendl, Malet & Gori-Giorgi, PRB **89**, 125106 (2014)*

Ultracold dipolar quantum gases

Bosons and fermions: change the kinetic energy functional

Easy to treat tunable interactions with the SCP functional





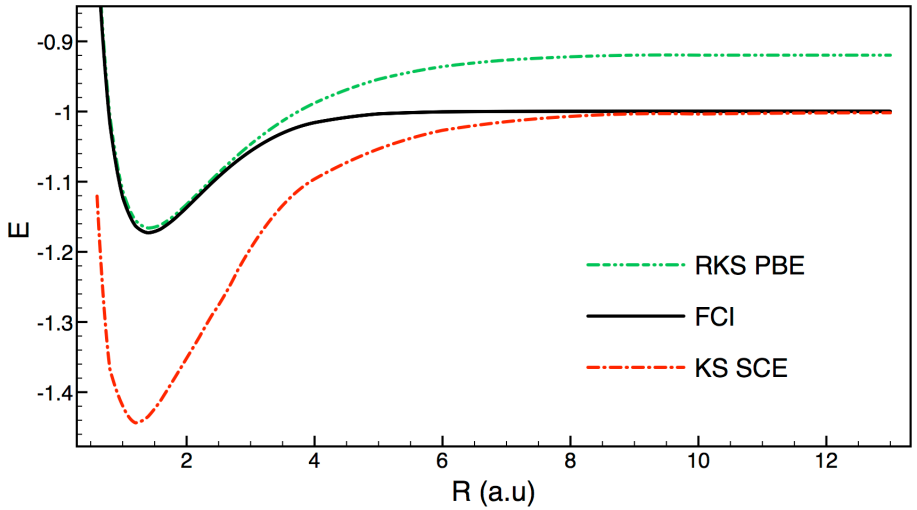
$$V_{\rm int}^{\rm SCP}[n] = \frac{1}{2}\int d\mathbf{r} n(\mathbf{r}) \sum_{i=2}^{N} v_{\rm int}(\mathbf{r} - \mathbf{f}_i(\mathbf{r}))$$

$$\nabla v_{\rm SCP}([n];\mathbf{r}) = \sum_{i=2}^{N} \nabla v_{\rm int}(\mathbf{r} - \mathbf{f}_i(\mathbf{r}))$$

KS SCE on a lattice interesting for (model many-body) physics?

*Malet, Mirtschink, Mendl, Bjerlin, Karabulut, Reimann & PG-G, PRL **115**, 033006 (2015)*

H_2 molecule (SCE from Kantorovich formulation)



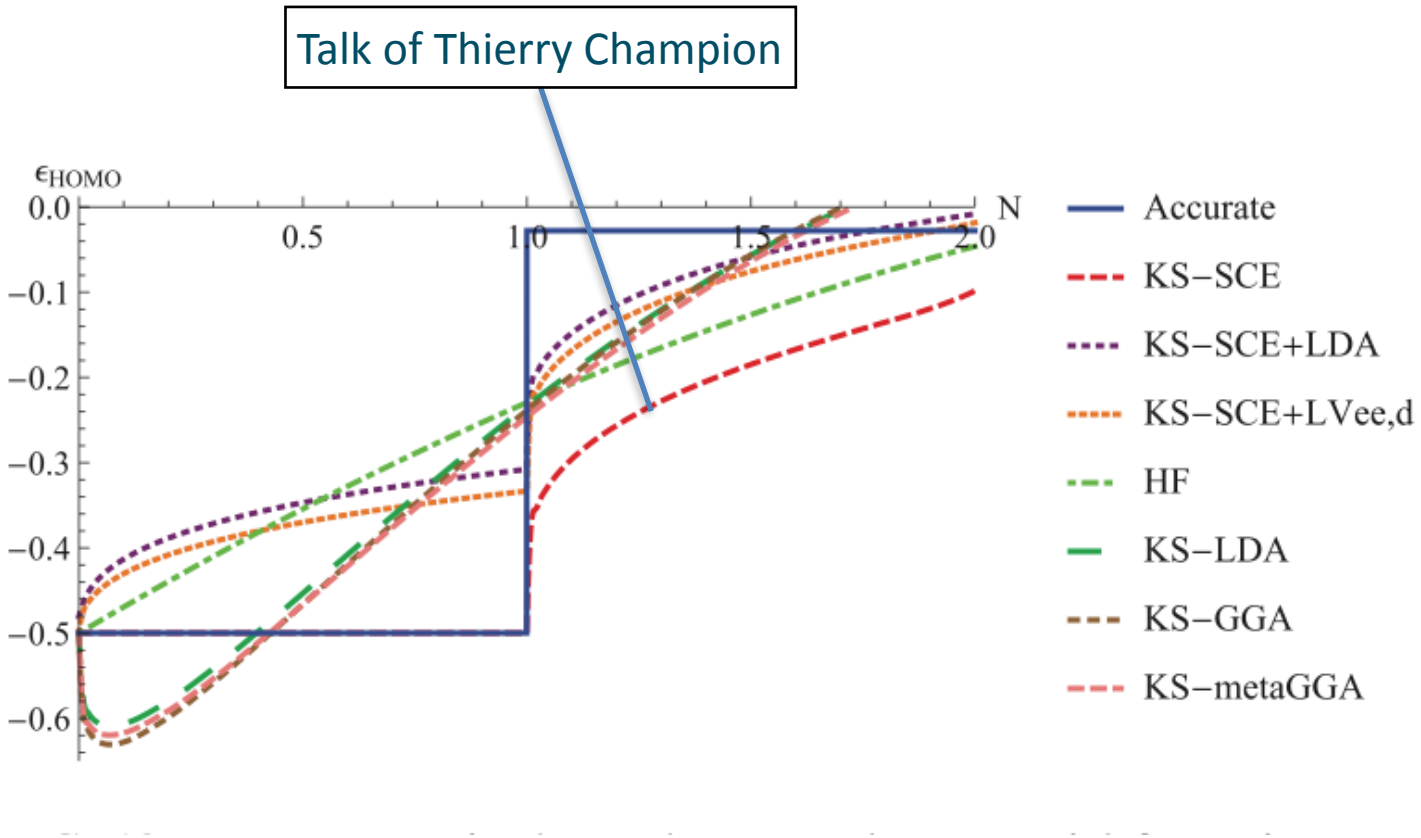
-KS SCE dissociates correctly
-horrible at equilibrium and beyond
-higher order terms improve the results

$$F[\rho] = T_s[\rho] + V_{ee}^{\mathrm{SCE}}[\rho]$$

Chen, Friesecke, Mendl, JCTC 10, 4360 (2014)

Vuckovic, Wagner, Mirtschink & Gori-Giorgi, JCTC 11, 3153 (2015)

H atom (and chemistry) is far from SCE limit

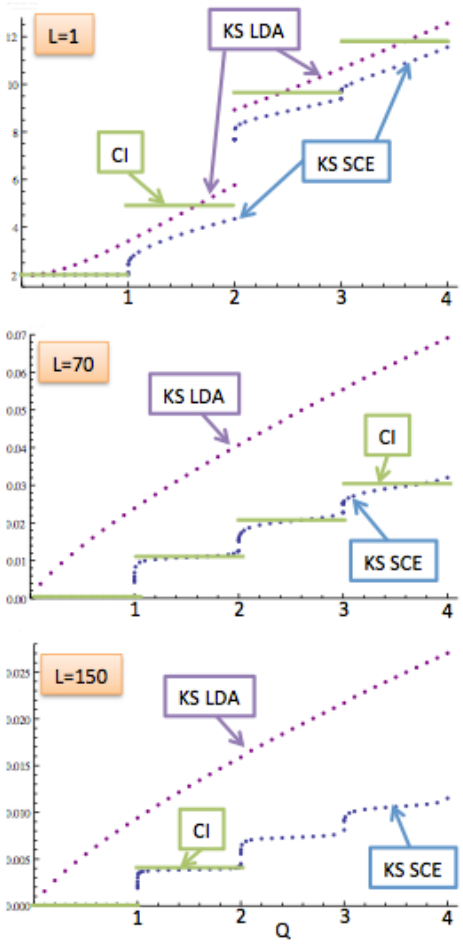


*Mirtschink, Umrigar, Morgan III & PG-G, JCP **140** 18A532 (2014)*

KS SCE behaves well only at extreme low density

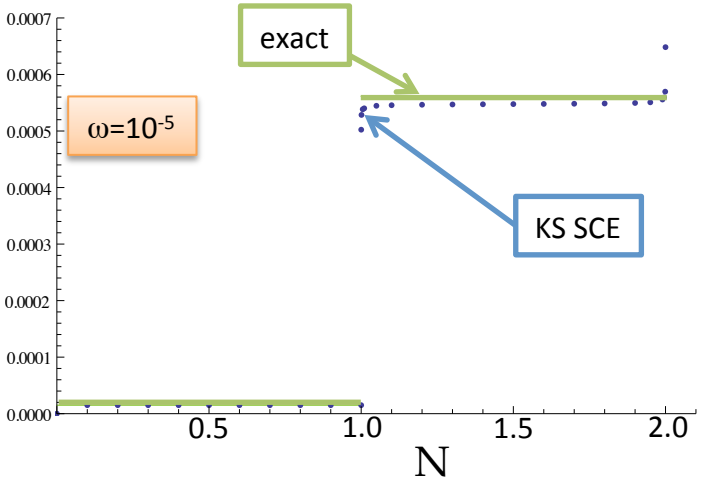
Highest occupied eigenvalue as a function of N

quasi 1D



$$v_{\text{ext}}(x) = \frac{1}{2}\omega^2 x^2 \qquad \omega = \frac{4}{L^2}$$

3D (Hooke's atom)



*Mirtschink, Seidl & Gori-Giorgi, PRL **111**, 126402 (2013)*

SCE and chemistry

-SCE itself must be approximated (too expensive for routine calculations)

[but local or semi-local approximations of SCE miss the right physics;
we need some non-locality]

non-local radius (NLR) model

*Wagner & PG-G, PRA **90**, 052512 (2014)*

*Zhou, Bahmann & Ernzerhof, JCP **143**, 124013 (2015)*

shell model

*Bahmann, Zhou & Ernzerhof, JCP **145**, 124014 (2016)*

- use input from the weakly correlated regime

local interpolation along the adiabatic connection?

Matthias Ernzerhof's talk

how to retain the usual limits of successful xc functionals?

Kieron Burke's review

- build approximations for the physical coupling strength rescaling SCE

multi-radii functional (MRF)

*Vuckovic & PG-G, J. Phys. Chem. Lett. **8**, 2799 (2017)*

Functionals inspired to the SCE form

Full non-locality compatible with the exact exchange energy density

$$w_\infty(\mathbf{r}) = \frac{1}{2}\sum_{i=2}^{N} \frac{1}{|\mathbf{r} - \mathbf{f}_i([\rho];\,\mathbf{r})|} - \frac{1}{2}v_{\mathrm{H}}(\mathbf{r})$$

from SCE theory

$R_i^{\mathrm{SCE}}([\rho];\mathbf{r})$ distances (or radii)

$$w_\lambda^{\mathrm{MRF}}(\mathbf{r}) = \frac{1}{2}\sum_{i=2}^{N} \frac{1}{R_i^{\lambda}([\rho];\,\mathbf{r})} - \frac{1}{2}v_{\mathrm{H}}(\mathbf{r})$$

$$W_\lambda[\rho] = \int \rho(\mathbf{r})\, w_\lambda([\rho];\mathbf{r})\, d\mathbf{r}$$

key ingredients:

$$\tilde{\rho}(\mathbf{r},\,u) = \int \frac{1}{4\pi}\rho(\mathbf{r}+\mathbf{u})\, \mathrm{d}\Omega_{\mathbf{u}}$$

$$N_{\mathrm{e}}(\mathbf{r},\,u) = \int_0^u 4\pi x^2 \tilde{\rho}(\mathbf{r},\,x)\, \mathrm{d}x$$

Vuckovic & PG-G, J. Phys. Chem. Lett. ***8****, 2799 (2017)*

Coordinate Scaling

$$\rho_\gamma(\mathbf{r}) = \gamma^3 \rho(\gamma\,\mathbf{r})$$

$$\lim_{\gamma\to\infty} E_{xc}[\rho_\gamma] \to \gamma E_x[\rho]$$

$$\lim_{\gamma\to 0} E_{xc}[\rho_\gamma] \to \gamma W_\infty[\rho]$$

$$N_e(\mathbf{r},\, u) = \int_0^u 4\pi x^2 \tilde{\rho}(\mathbf{r},\, x)\, \mathrm{d}x$$

$$w_\lambda^{\mathrm{MRF}}(\mathbf{r}) = \frac{1}{2}\sum_{i=2}^{N} \frac{1}{R_i^\lambda([\rho];\,\mathbf{r})} - \frac{1}{2} v_{\mathrm{H}}(\mathbf{r})$$

$$\tilde{\rho}(\mathbf{r},\, u) = \int \frac{1}{4\pi} \rho(\mathbf{r}+\mathbf{u})\, \mathrm{d}\Omega_{\mathbf{u}}$$

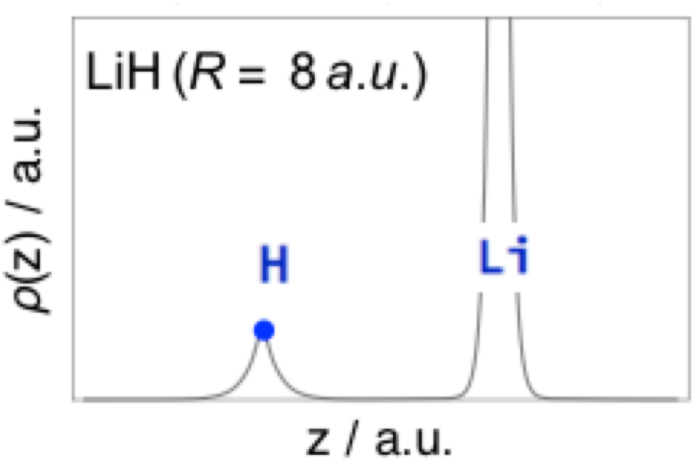
$$\nu_i^\lambda[\rho] = i - 1 + \sigma_i^\lambda([\rho];\mathbf{r}) \qquad R_i^\lambda([\rho];\mathbf{r}) = N_e^{-1}(\mathbf{r}, \nu_i^\lambda[\rho])$$

if these are set to a constant, $\sigma_i^\lambda = \sigma$

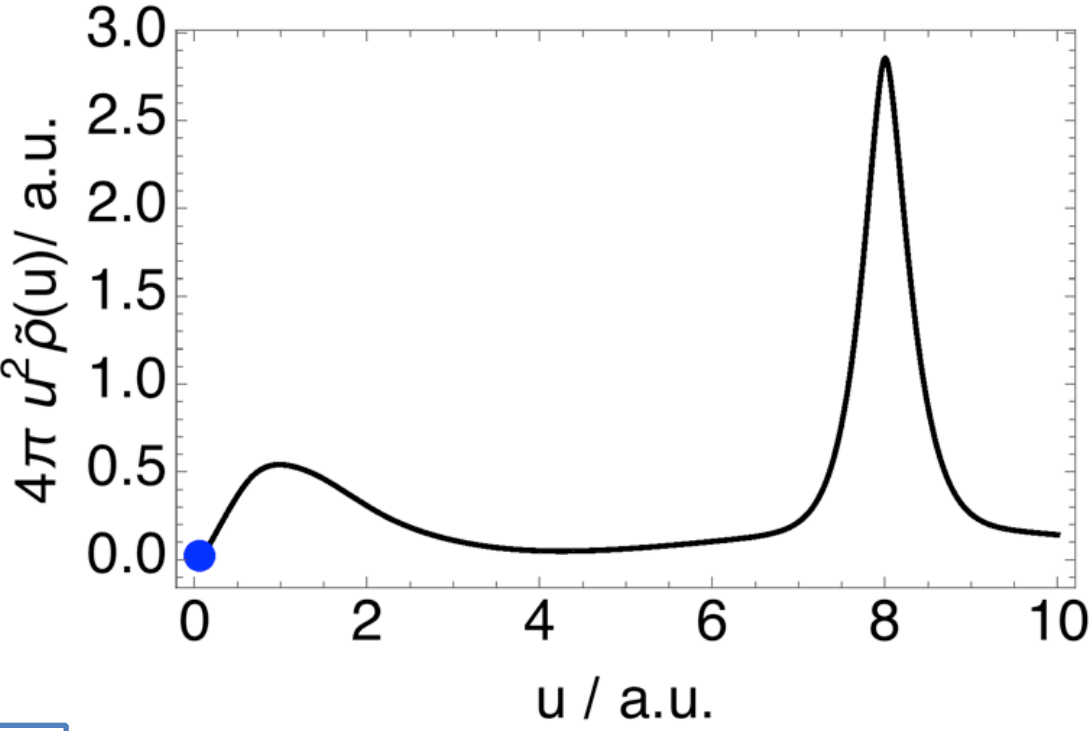
$$W_1^{\mathrm{MRF}}[\rho_\gamma] = \gamma\, W_1^{\mathrm{MRF}}[\rho]$$

with σ_i^λ varying between two constants we can cover the whole scaling

Full non-locality: MRF



- reference e⁻
- remaining (N-1) e⁻



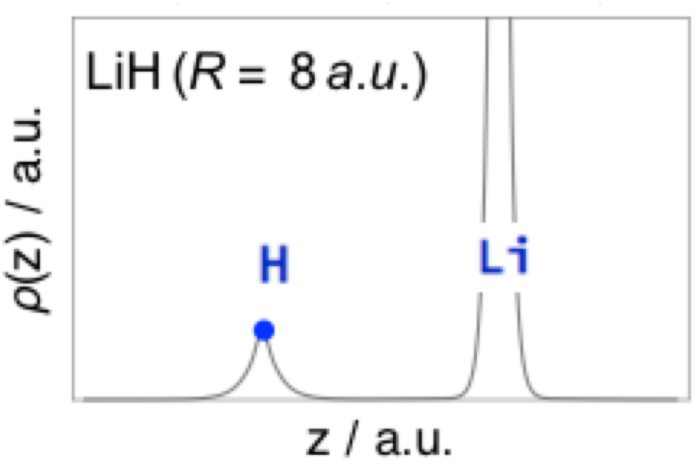
$$R_i^1(\mathbf{r}) = N_e^{-1}(\mathbf{r}, i - 1 + \sigma_i(\mathbf{r}))$$

$$\sigma_i(\mathbf{r}) = \frac{1}{2} e^{-bS_i(\mathbf{r})^2}$$

$$S_i(\mathbf{r}) = \frac{\partial N_e(\mathbf{r}, u)}{\partial u}\Big|_{u=N_e^{-1}(\mathbf{r},i-1)}$$

$$w_\lambda^{\mathrm{MRF}}(\mathbf{r}) = \frac{1}{2}\sum_{i=2}^{N} \frac{1}{R_i^\lambda([\rho]; \mathbf{r})} - \frac{1}{2} v_H(\mathbf{r})$$

Full non-locality: MRF

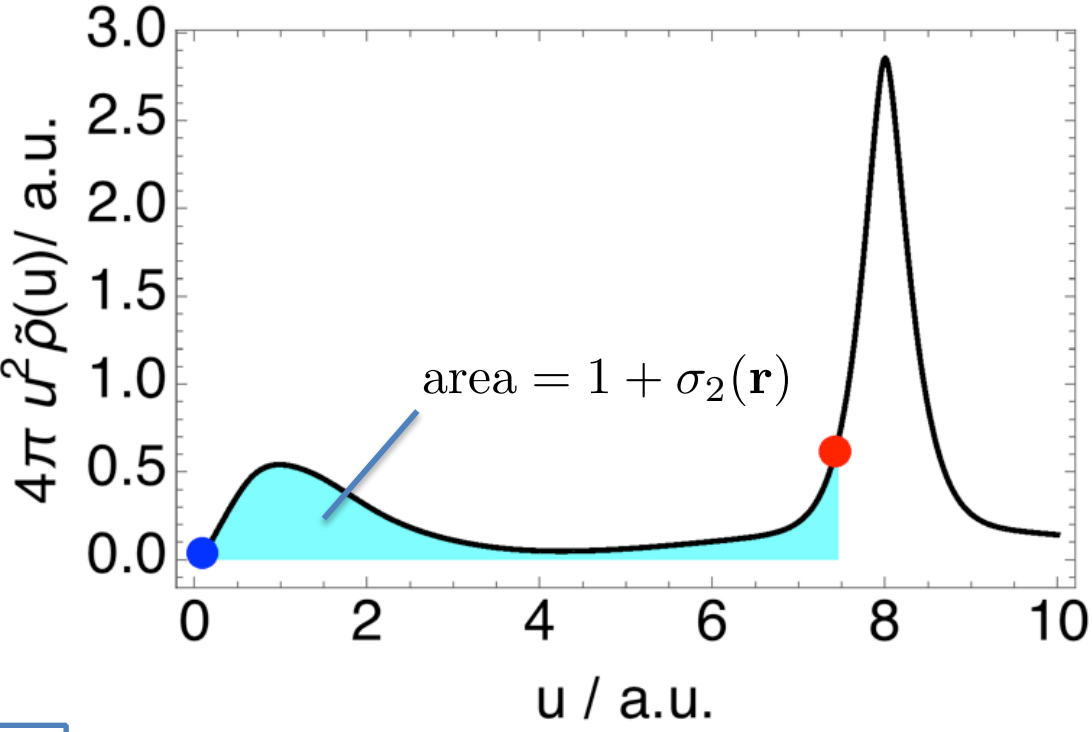


- reference e⁻
- remaining (N-1) e⁻

$$R_i^1(\mathbf{r}) = N_e^{-1}(\mathbf{r}, i - 1 + \sigma_i(\mathbf{r}))$$

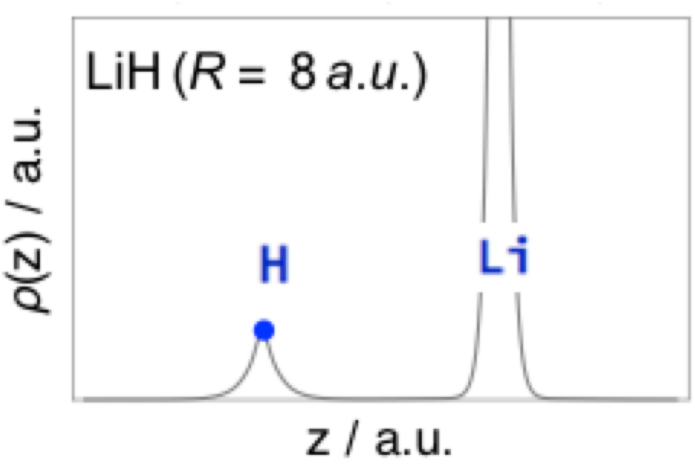
$$\sigma_i(\mathbf{r}) = \frac{1}{2} e^{-bS_i(\mathbf{r})^2}$$

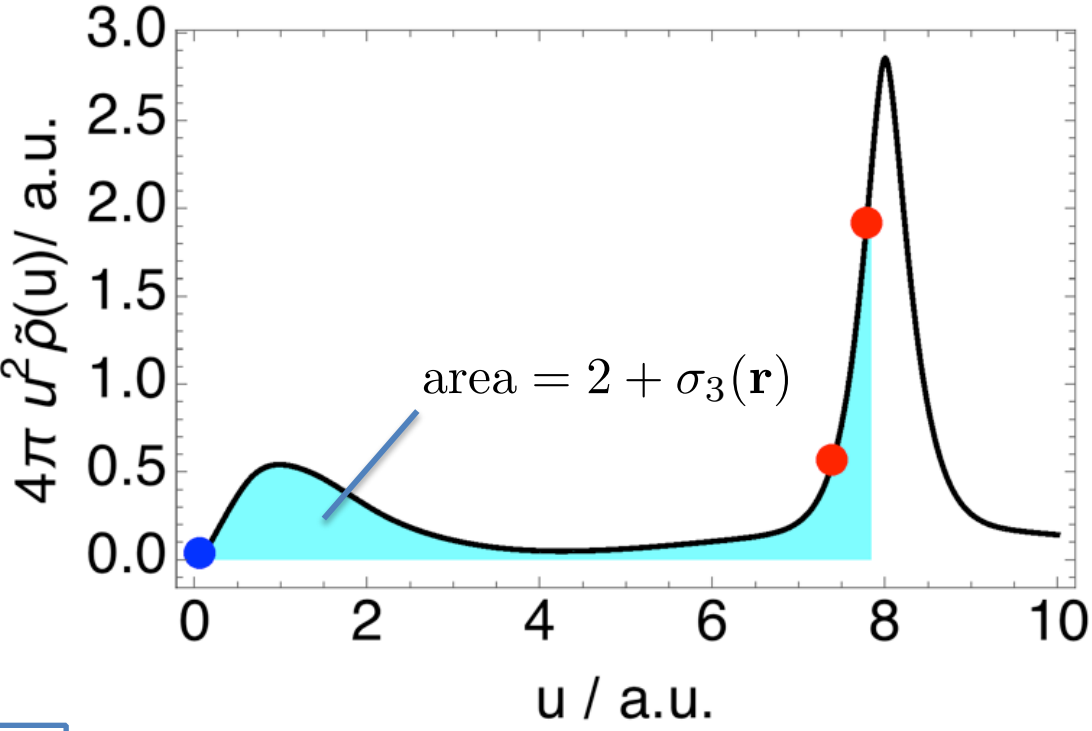
$$S_i(\mathbf{r}) = \frac{\partial N_e(\mathbf{r}, u)}{\partial u}\Big|_{u=N_e^{-1}(\mathbf{r},i-1)}$$



$$w_\lambda^{\mathrm{MRF}}(\mathbf{r}) = \frac{1}{2} \sum_{i=2}^{N} \frac{1}{R_i^\lambda([\rho]; \mathbf{r})} - \frac{1}{2} v_H(\mathbf{r})$$

Full non-locality: MRF





- reference e⁻
- remaining (N-1) e⁻

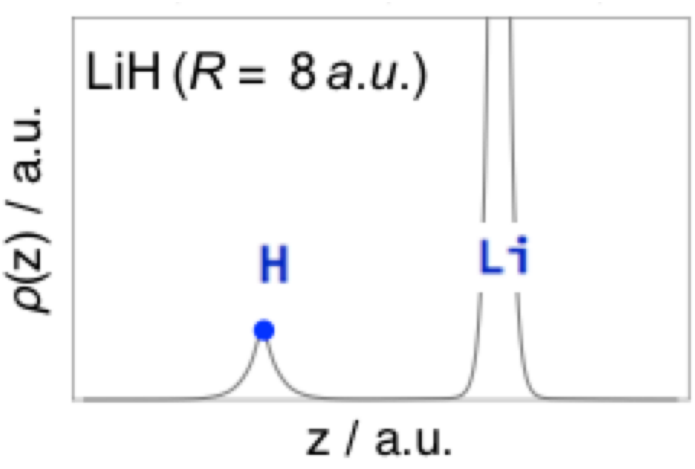
$$R_i^1(\mathbf{r}) = N_e^{-1}(\mathbf{r},\, i - 1 + \sigma_i(\mathbf{r}))$$

$$\sigma_i(\mathbf{r}) = \frac{1}{2} e^{-bS_i(\mathbf{r})^2}$$

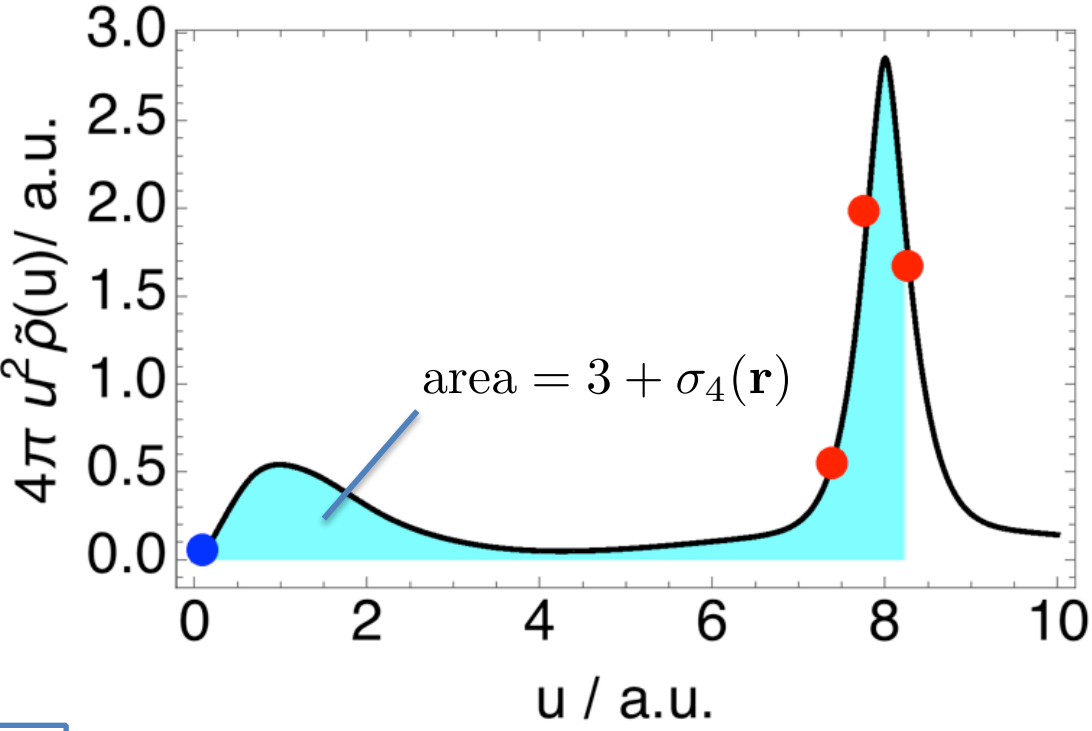
$$S_i(\mathbf{r}) = \frac{\partial N_e(\mathbf{r},\, u)}{\partial u}\Big|_{u=N_e^{-1}(\mathbf{r},i-1)}$$

$$w_\lambda^{\mathrm{MRF}}(\mathbf{r}) = \frac{1}{2}\sum_{i=2}^{N} \frac{1}{R_i^\lambda([\rho];\, \mathbf{r})} - \frac{1}{2} v_{\mathrm{H}}(\mathbf{r})$$

Full non-locality: MRF



- reference e⁻
- remaining (N-1) e⁻



$$R_i^1(\mathbf{r}) = N_e^{-1}(\mathbf{r},\, i - 1 + \sigma_i(\mathbf{r}))$$

$$\sigma_i(\mathbf{r}) = \frac{1}{2} e^{-bS_i(\mathbf{r})^2}$$

$$S_i(\mathbf{r}) = \frac{\partial N_e(\mathbf{r},\, u)}{\partial u}\Big|_{u=N_e^{-1}(\mathbf{r},i-1)}$$

$$w_\lambda^{\mathrm{MRF}}(\mathbf{r}) = \frac{1}{2}\sum_{i=2}^{N} \frac{1}{R_i^\lambda([\rho];\, \mathbf{r})} - \frac{1}{2} v_H(\mathbf{r})$$

Full non-locality: MRF for atoms

$$W_1[\rho] = \langle \Psi_1[\rho] | \hat{V}_{ee} | \Psi_1[\rho] \rangle - U[\rho]$$ (in Hartree)

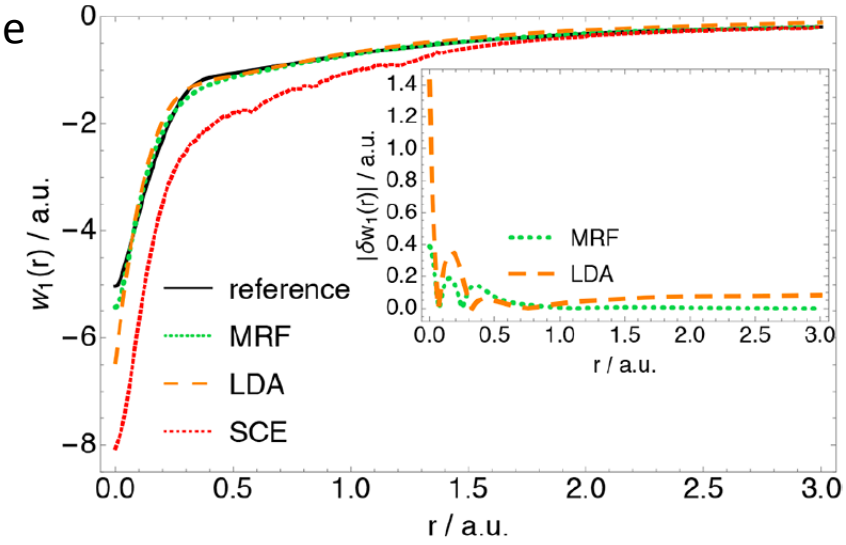
atom/ion	reference	MRF-1	PBE	SCE
He	−1.1029	−1.1844	−1.1047	−1.4982
H^-	−0.4532	−0.4681	−0.4413	−0.5689
Be	−2.8341	−2.8044	−2.8430	−4.0195
Li^-	−1.9462	−2.1170	−1.9617	−2.7308
F^-	−10.889	−10.741	−10.997	−16.940
Ne	−12.765	−12.823	−12.876	−20.041
Mg	−16.701	−16.365	−16.913	−26.709
Cl^-	−28.89	−28.48	−29.19	−47.26
Ar	−31.35	−31.19	−31.68	−51.49
Ca	−35.60	−35.92	−36.85	−60.34
MAE	-	0.17	0.24	-

$$W_1^{\mathrm{DFA}}[\rho] = E_{\mathrm{x}}^{\mathrm{DFA}}[\rho] + 2E_{\mathrm{c}}^{\mathrm{DFA}}[\rho] - \frac{\partial E_{\mathrm{c}}^{\mathrm{DFA}}[\rho_\gamma]}{\partial \gamma}\Big|_{\gamma=1}$$

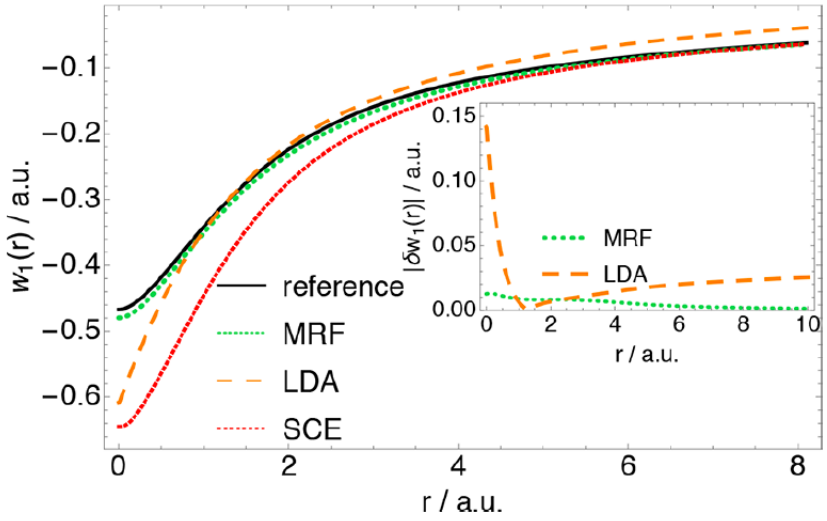
Vuckovic & PG-G, J. Phys. Chem. Lett. ***8****, 2799 (2017)*

MRF energy densities are locally accurate

Ne



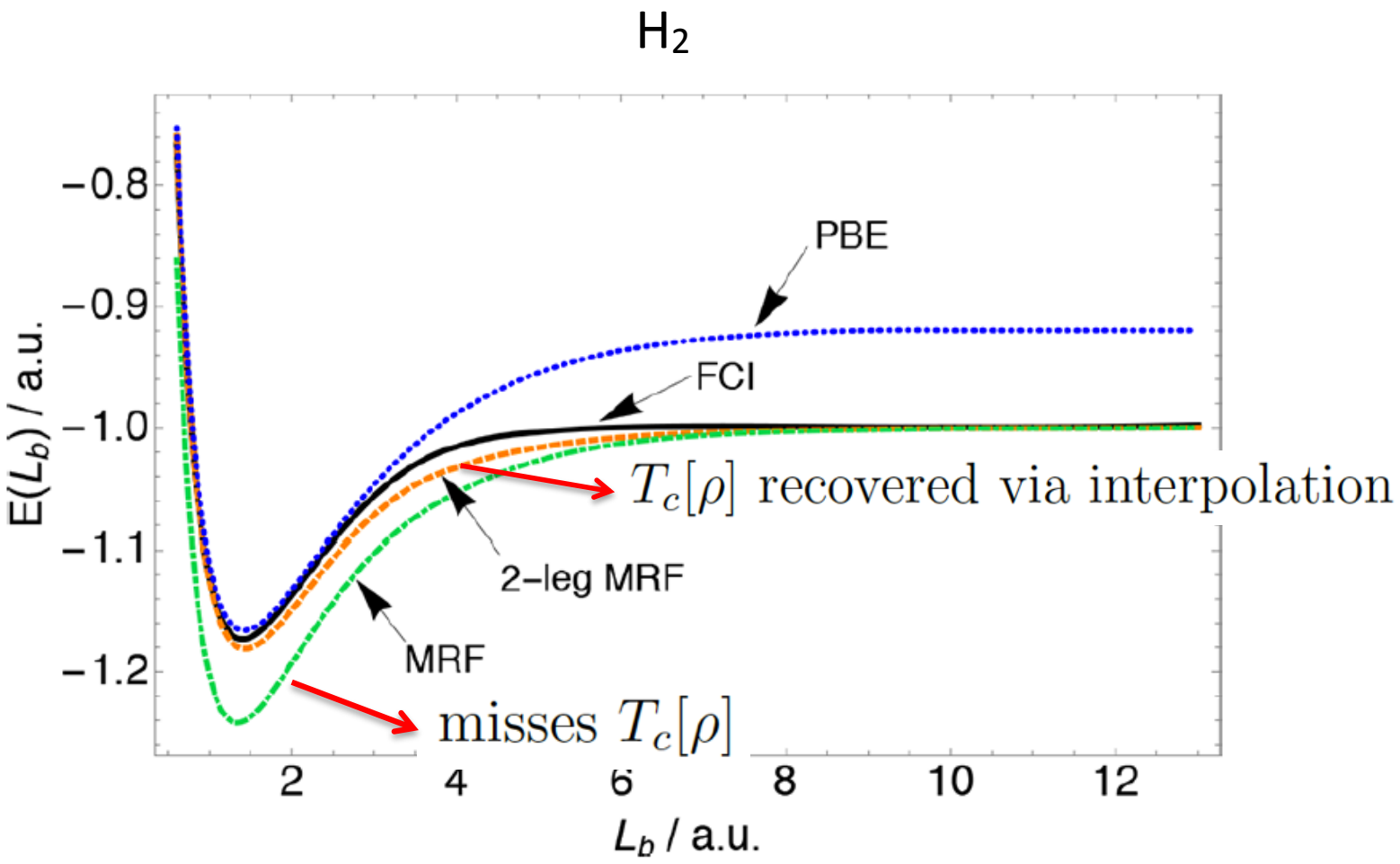
H$^-$



$$w_1(\mathbf{r}) = \frac{1}{2}\int \frac{h_{xc}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'$$

Vuckovic & PG-G, J. Phys. Chem. Lett. ***8****, 2799 (2017)*

Static correlation from MRF



MRF is exact for H_2^+

Vuckovic & PG-G, J. Phys. Chem. Lett. ***8****, 2799 (2017)*

(Some) wrap up

1) KS SCE

what it does right for models in physics (lattice hamiltonians?)

serious limitations (hopeless) for chemistry

2) beyond KS SCE

next leading orders: do they contain the right physics? too difficult?

spin

3) chemistry/solid state physics

how to turn what we have learned into useful approximations?