SAND2019-2951C

An Exchange-Correlation Functional Capturing Bulk, Surface, and Confinement Physics

Sandia National Laboratories

PRESENTED BY

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CECAM Workshop "Improving the Theory in Density Functional Theory"

Lausanne, Switzerland

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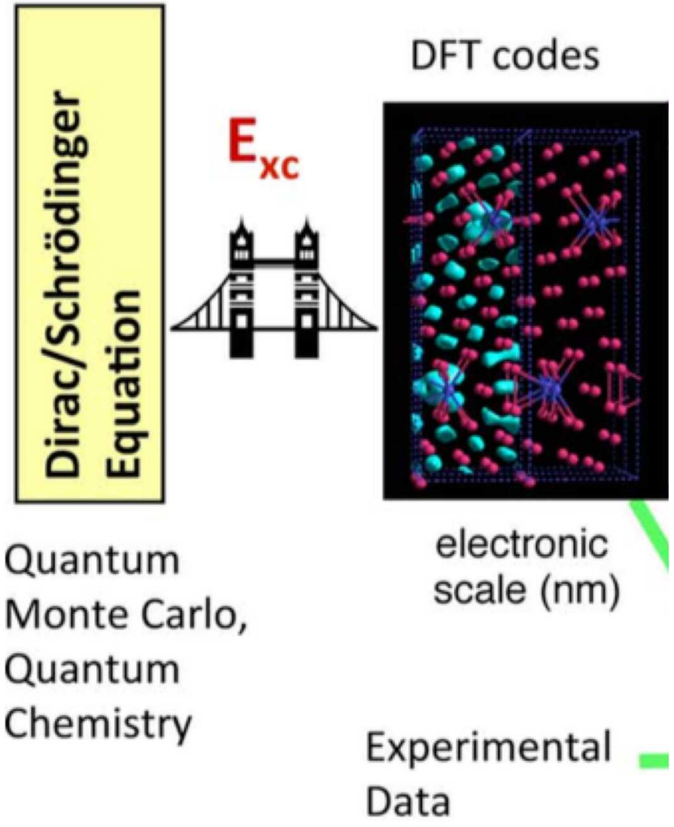
Why Another Functional?



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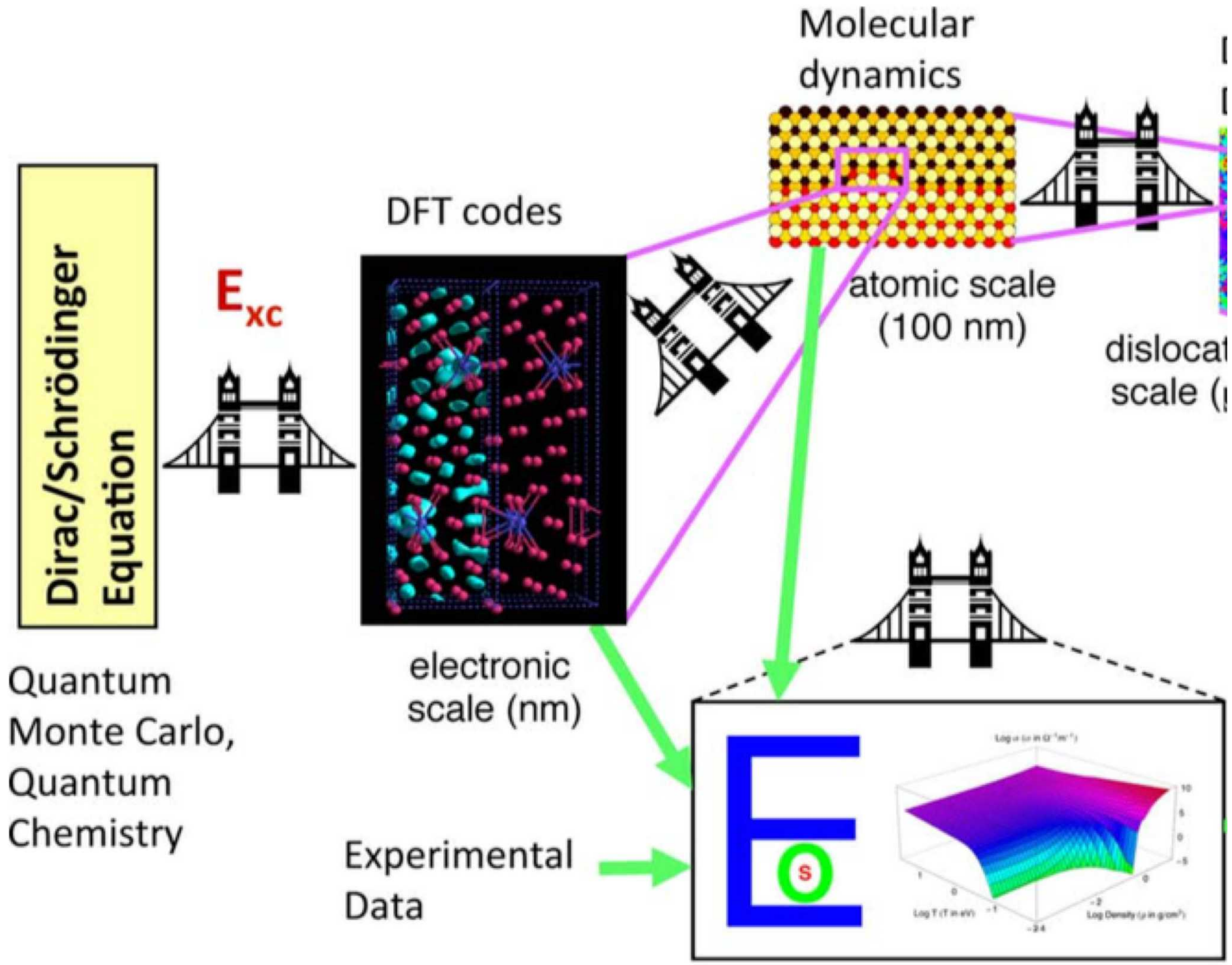

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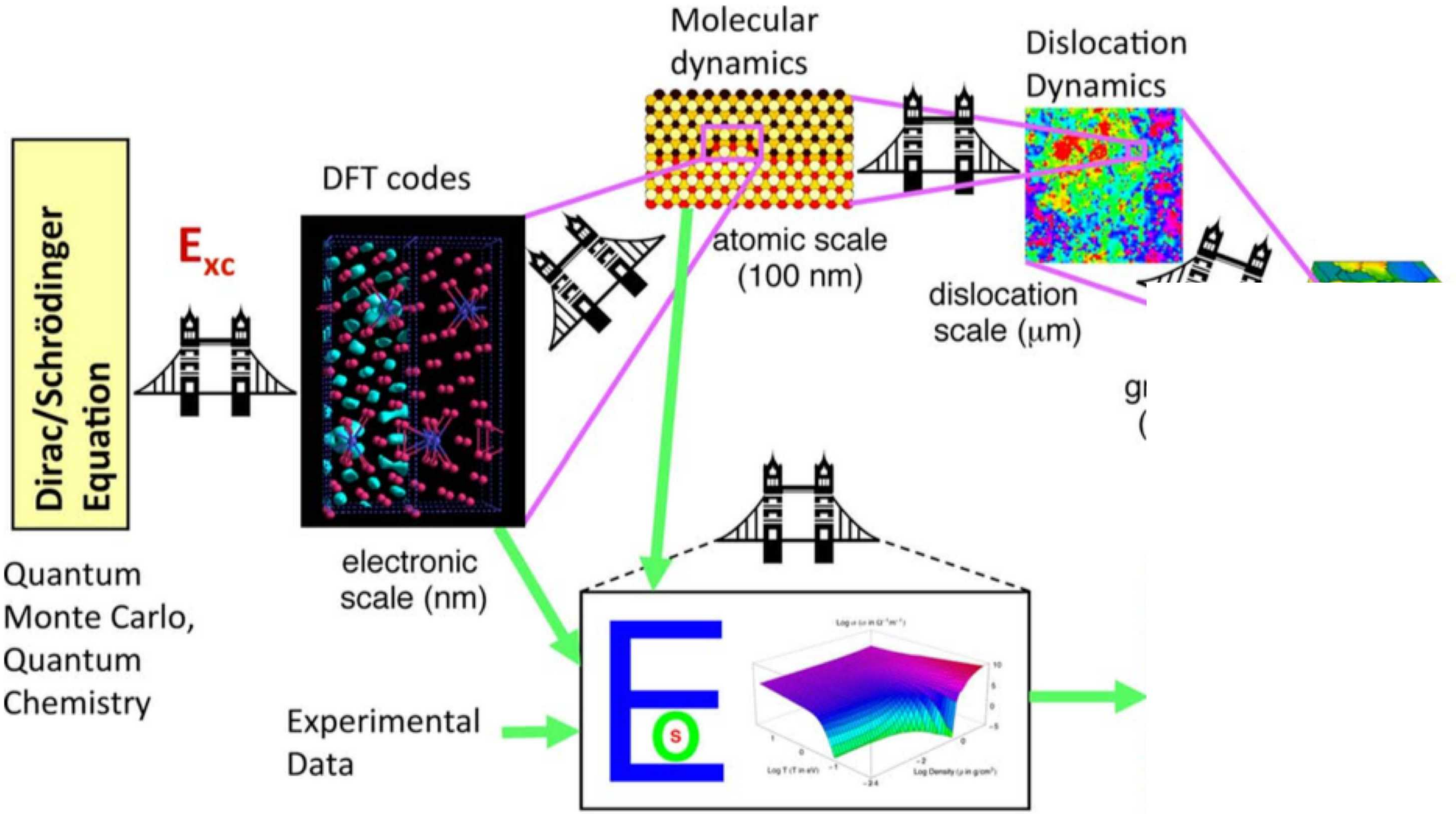

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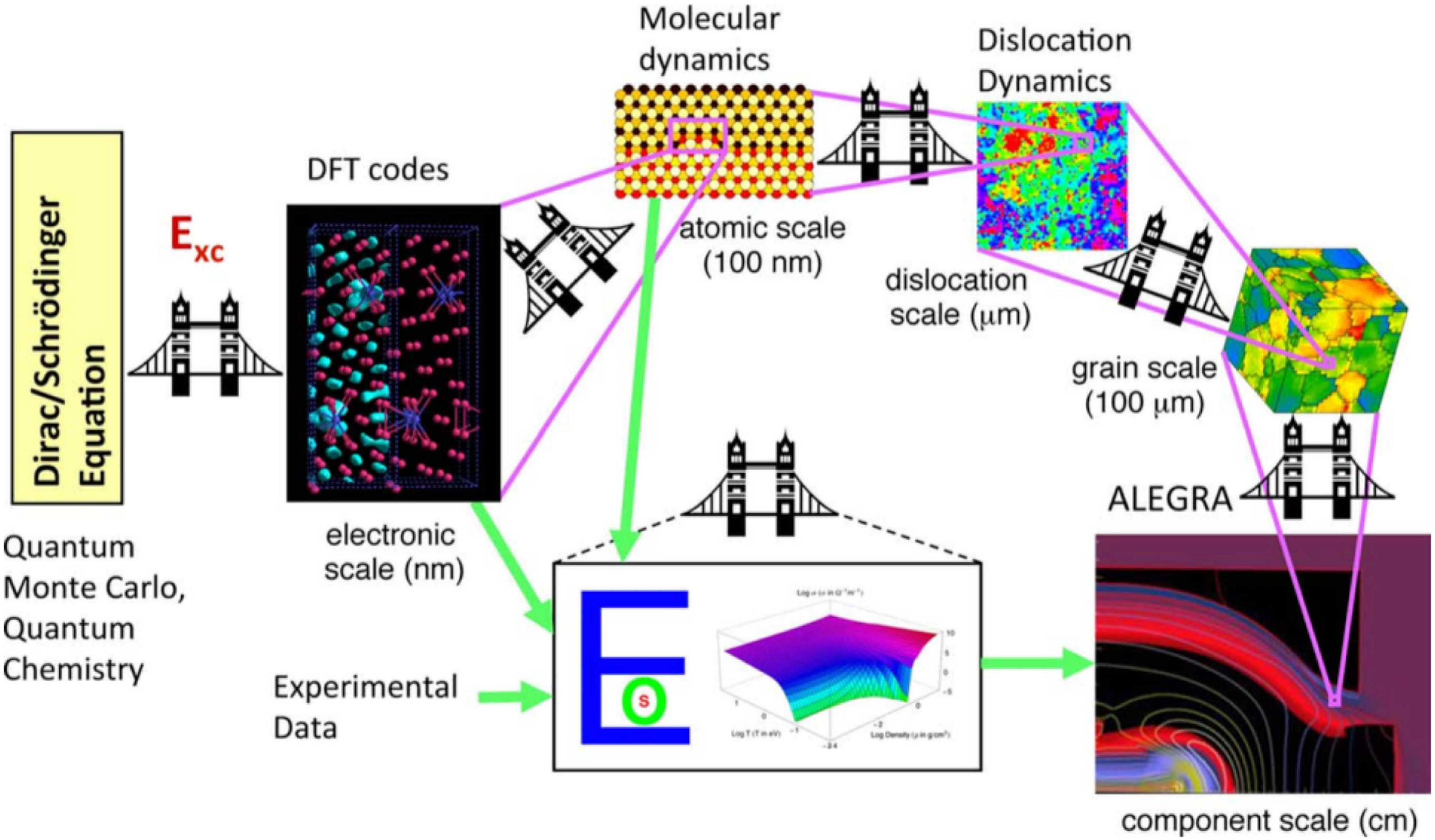
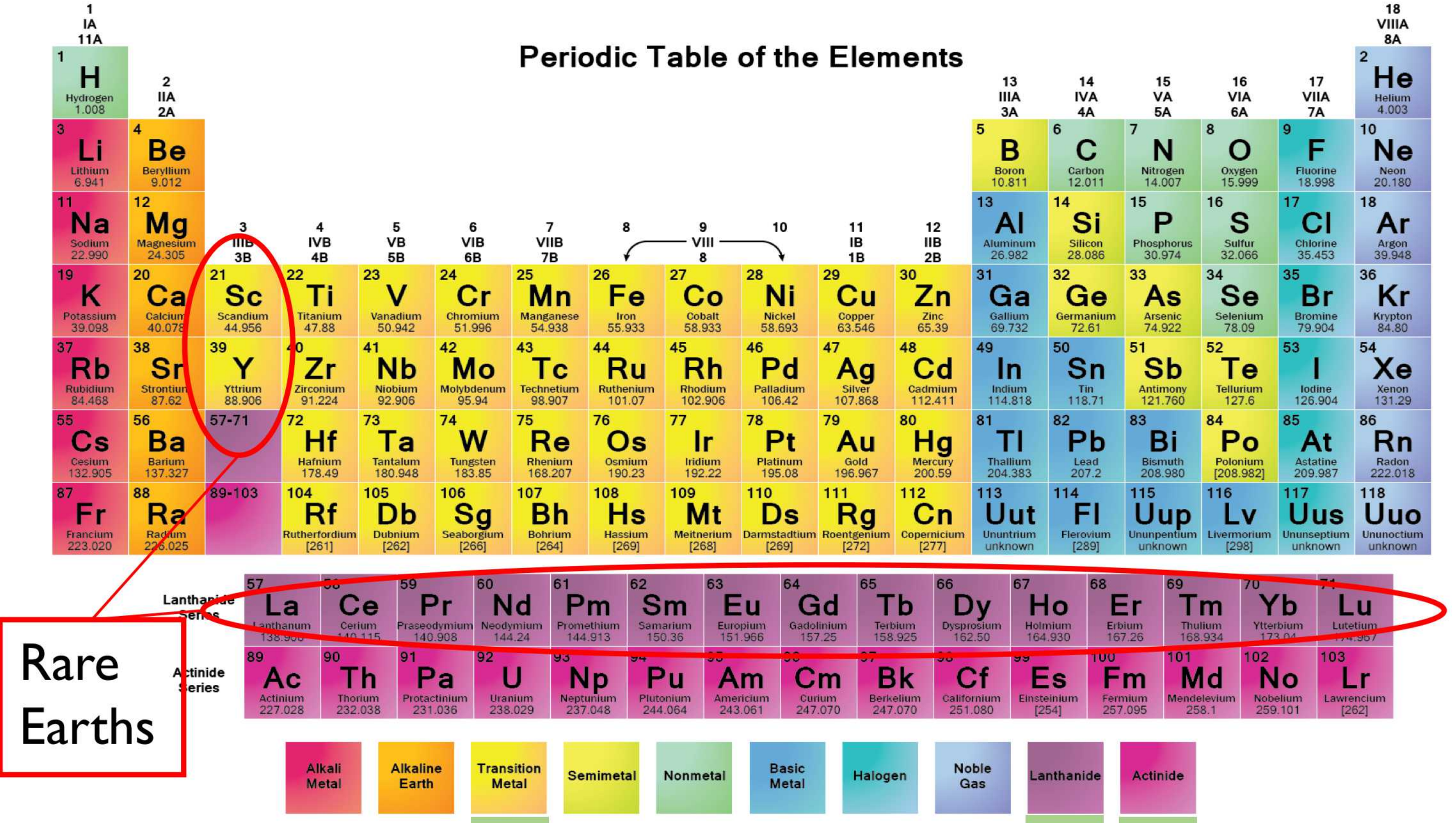


Ann E. Mattson *et al.*, International Journal of Quantum Chemistry (2016), DOI: 10.1002/qua.25097.

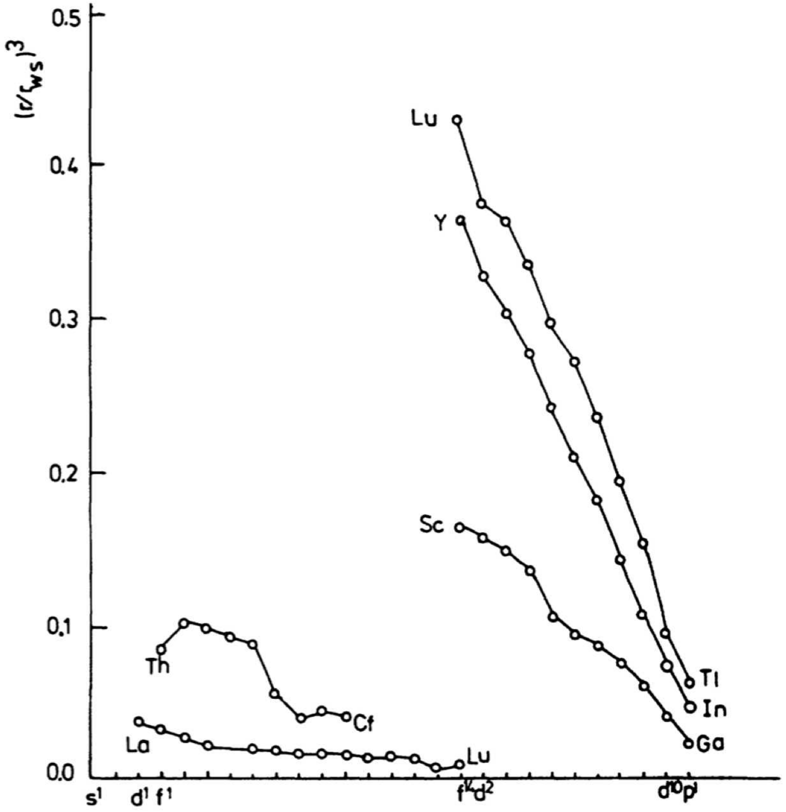
Failure of Semi-Local Functionals for Transition Metals



s sp d sp sp sp p - f f

Type of electrons governing properties

Ratio of d and f shell volume to Wigner-Seitz volume of transition elements



Phys. Rev. B **37**, 10674 (1988).

Develop an exchange-correlation functional that takes electron confinement into account.

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Constructing Exchange-Correlation Functionals

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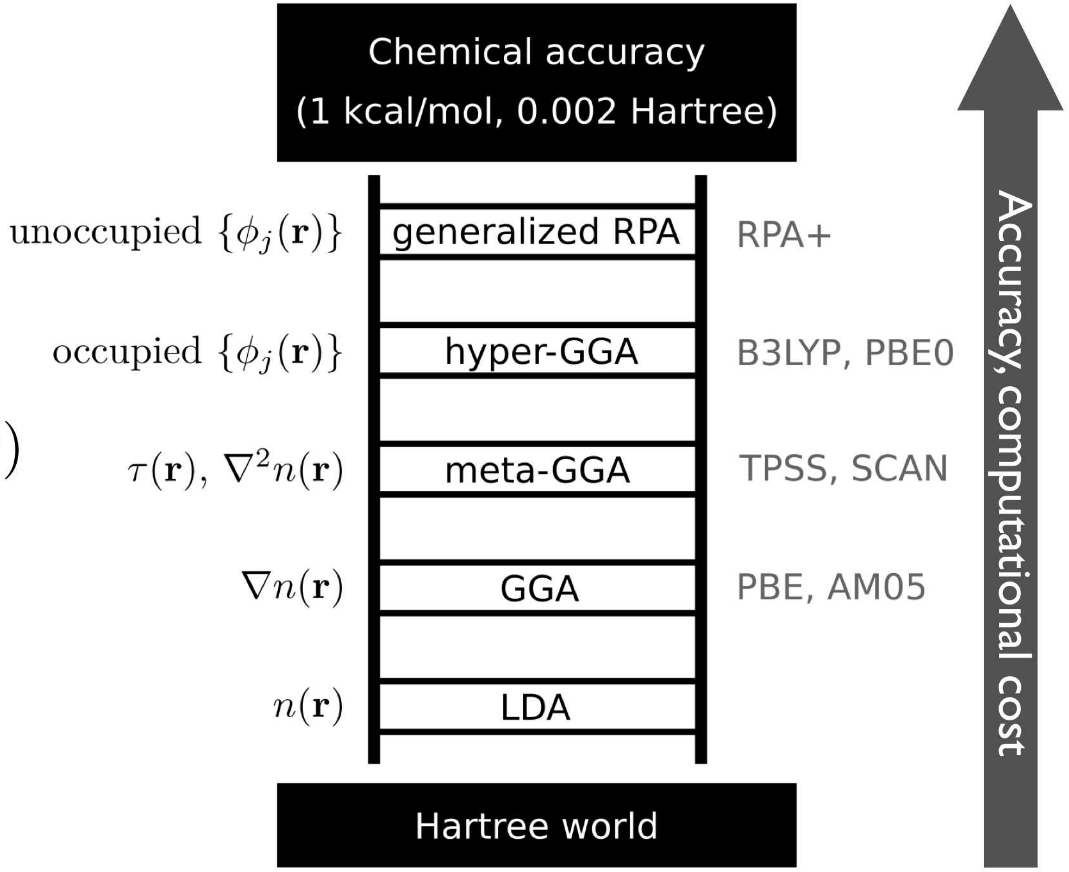
$$E_{\mathrm{XC}} = \int_{\Omega} d\mathbf{r}\; n(\mathbf{r})\, \epsilon_{\mathrm{XC}}$$

$$\epsilon_{\mathrm{XC}} = \begin{cases} \dots \\ \epsilon_{\mathrm{XC}}(n, \nabla n, \nabla^2 n, \tau) \\ \epsilon_{\mathrm{XC}}(n, \nabla n) \\ \epsilon_{\mathrm{XC}}(n) \end{cases}$$



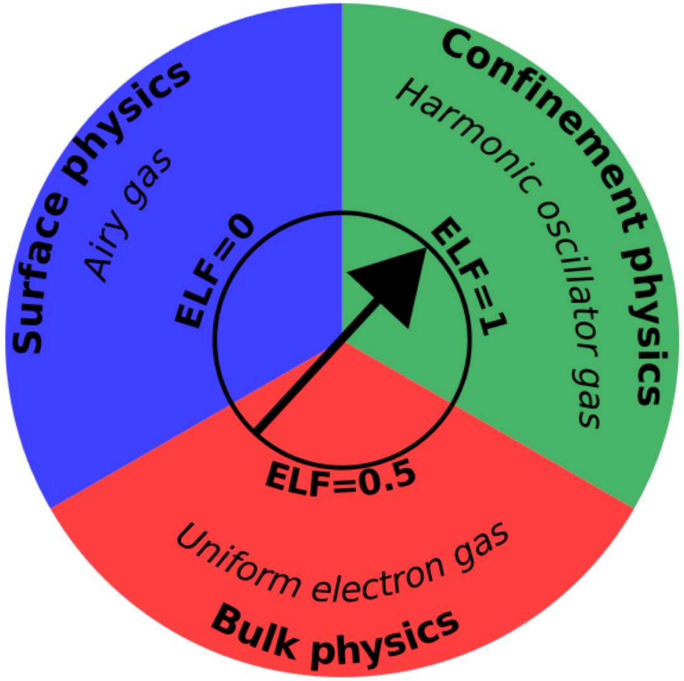
- Exactly solvable reference systems
- Exact constraints
- Chemical intuition

$$E_{\mathrm{XC}} = \int_{\Omega} d\mathbf{r}\; n(\mathbf{r})\, \epsilon_{\mathrm{XC}}[n, \nabla n, \tau; \{\gamma_j, \eta_j\}](\mathbf{r})$$

Divide domain into subsystems

Specialized functionals in different subsystems

Universal interpolation through the electron localization function



Exactly known subsystems

- Uniform electron gas
- Airy gas

$$\hat{H} = \hat{T} + \hat{V}_{\mathrm{ext}} \begin{cases} = -F\,z & -\infty < z < L \\ = \infty & z \geq L \end{cases}, \quad \phi_j(z) \propto Ai(z)$$

- Harmonic oscillator gas $\hat{H} = \hat{T} + \dfrac{\omega^2}{2} z^2, \quad \phi_j(\mathbf{r}) \propto e^{i(k_1\,x + k_2\,y)} H_j(z)\, e^{-z^2/2}$

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Exchange from the Harmonic Oscillator Gas

$$\left[-\frac{1}{2}\nabla^2 + \frac{\omega^2}{2}z^2\right]\psi_\nu(\mathbf{r}) = E_\nu\,\psi_\nu(\mathbf{r})\,,\;\; \psi_\nu(\mathbf{r}) = \frac{1}{\sqrt{L_1 L_2}}e^{i(k_1 x + k_2 y)}\phi_j(z)$$

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Exchange from the Harmonic Oscillator Gas

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$$\phi_j(z) = \left(\frac{1}{2^j j! l \sqrt{\pi}}\right)^{1/2} H_j(\bar{z}) e^{-\bar{z}^2/2}\,,\ \ \epsilon_j = \frac{j + 1/2}{l^2}$$

$$n(z) = 2\sum_j w_j \phi_j^*(z)\phi_j(z)\,,\quad w_j = \frac{1}{2\pi}(\mu - \epsilon_j)\,,\quad \mu = \frac{\alpha + 1/2}{l^2}$$

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$$\epsilon_{\mathrm{X}}^{\mathrm{HOG}} = -\frac{1}{2\pi n(z)}\int dz'\sum_{jj'}\frac{\phi_j(z)\phi_j(z')\phi_{j'}(z)\phi_{j'}(z')}{|z-z'|^3}g(k_j\Delta z, k_{j'}\Delta z)$$

$$g(s,s') = ss'\int_0^\infty dt\frac{J_1(st)J_1(s't)}{t\sqrt{1+t^2}}\,,\ \Delta z = |z - z'|$$

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$$\epsilon_{\mathrm{X}}^{\mathrm{BSC}} = \epsilon_{\mathrm{X}}^{\mathrm{surf}}\left\{1+[X_{\mathrm{conf}}-1][1+X_{\mathrm{conf}}\left(X_{\mathrm{surf},2}-1\right)]X_{\mathrm{surf},2}\right\} + \epsilon_{\mathrm{X}}^{\mathrm{conf}}\ \left\{1+X_{\mathrm{conf}}[X_{\mathrm{surf},2}-1]\right\}[1-X_{\mathrm{conf}}X_{\mathrm{surf},2}]$$

Exchange from the Harmonic Oscillator Gas

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$$\epsilon_{\rm X}^{\rm BSC} = \epsilon_{\rm X}^{\rm surf}\left\{1 + [X_{\rm conf}-1][1+X_{\rm conf}\left(X_{\rm surf,2}-1\right)]X_{\rm surf,2}\right\} + \epsilon_{\rm X}^{\rm conf}\;\left\{1 + X_{\rm conf}[X_{\rm surf,2}-1]\right\}[1 - X_{\rm conf}X_{\rm surf,2}]$$

$$\epsilon_{\rm X}^{\rm conf} = \epsilon_{\rm X}^{\rm LDA}[n, |\nabla n|, \tau](\mathbf{r})\,F_{\rm X}^{\rm HOG}[n,|\nabla n|,\tau]$$

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Enhancement Factor of HOG Exchange

$$F_{\mathrm{X}}^{\mathrm{HOG}}[n, |\nabla n|, \tau] = \frac{[l\, \epsilon_{\mathrm{X}}\, (n(\mathbf{r}), |\nabla n(\mathbf{r})|, \mathrm{ELF}(\mathbf{r}))]^{\mathrm{conf}}}{[l\, \epsilon_{\mathrm{X}}\, (n(\mathbf{r}), |\nabla n(\mathbf{r})|, ELF(\mathbf{r}))]^{\mathrm{LDA}}}$$

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Enhancement Factor of HOG Exchange

$$F_{\mathrm{X}}^{\mathrm{HOG}}[n,|\nabla n|,\tau] = \frac{[l\,\epsilon_{\mathrm{X}}\,(n(\mathbf{r}),|\nabla n(\mathbf{r})|,\mathrm{ELF}(\mathbf{r}))]^{\mathrm{conf}}}{[l\,\epsilon_{\mathrm{X}}\,(n(\mathbf{r}),|\nabla n(\mathbf{r})|,ELF(\mathbf{r}))]^{\mathrm{LDA}}}$$

$$[l\,\epsilon_{\mathrm{X}}\,(n(\mathbf{r}),|\nabla n(\mathbf{r})|,ELF(\mathbf{r}))]^{\mathrm{LDA}} = -\frac{3}{4\pi}\left(3\sqrt{\pi}\exp[-\bar{z}^2]\alpha\,(n(\mathbf{r}),|\nabla n(\mathbf{r})|,\mathrm{ELF}(\mathbf{r}))\right)^{1/3}$$

$$[l\,\epsilon_{\mathrm{X}}\,(n(\mathbf{r}),|\nabla n(\mathbf{r})|,\mathrm{ELF}(\mathbf{r}))]^{\mathrm{conf}} = \frac{a_0(\alpha)+a_2(\alpha)\bar{z}^2+a_4(\alpha)\bar{z}^4+a_6(\alpha)\bar{z}^6-\bar{z}^8}{-\bar{z}^8/[2\sqrt{2\alpha}\,l\,\epsilon_{\mathrm{X}}^{>}\,(2\sqrt{2\alpha}\,\bar{z})]+1}$$

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Enhancement Factor of HOG Exchange

$$F_{\mathrm{X}}^{\mathrm{HOG}}[n, |\nabla n|, \tau] = \frac{[l\, \epsilon_{\mathrm{X}}\,(n(\mathbf{r}), |\nabla n(\mathbf{r})|, \mathrm{ELF}(\mathbf{r}))]^{\mathrm{conf}}}{[l\, \epsilon_{\mathrm{X}}\,(n(\mathbf{r}), |\nabla n(\mathbf{r})|, ELF(\mathbf{r}))]^{\mathrm{LDA}}}$$

$$[l\, \epsilon_{\mathrm{X}}\,(n(\mathbf{r}), |\nabla n(\mathbf{r})|, ELF(\mathbf{r}))]^{\mathrm{LDA}} = -\frac{3}{4\pi}\left(3\sqrt{\pi}\exp[-\bar{z}^2]\alpha\,(n(\mathbf{r}), |\nabla n(\mathbf{r})|, \mathrm{ELF}(\mathbf{r}))\right)^{1/3}$$

$$[l\, \epsilon_{\mathrm{X}}\,(n(\mathbf{r}), |\nabla n(\mathbf{r})|, \mathrm{ELF}(\mathbf{r}))]^{\mathrm{conf}} = \frac{a_0(\alpha) + a_2(\alpha)\bar{z}^2 + a_4(\alpha)\bar{z}^4 + a_6(\alpha)\bar{z}^6 - \bar{z}^8}{-\bar{z}^8/[2\sqrt{2\alpha}\, l\, \epsilon_{\mathrm{X}}^{>}\,(2\sqrt{2\alpha}\,\bar{z})] + 1}$$

$$\epsilon_{\mathrm{X}}^{>}(t) = \frac{1}{t}\left[\frac{1}{2} - \frac{I_1(t)}{t} + \frac{L_1(t)}{t}\right]$$

$$a_0(\alpha) = 2\,A(\alpha)\,,\ a_2(\alpha) = \frac{B(\alpha)}{2(\alpha)} - 2\,A(\alpha)$$

$$a_4(\alpha) = \frac{C(\alpha)}{48\alpha^2} - \frac{B(\alpha)}{2\alpha} + A(\alpha)\,,\ a_6(\alpha) = \frac{D(\alpha)}{2880\alpha^3} - \frac{C(\alpha)}{48\alpha^2} + \frac{B(\alpha)}{4\alpha} - \frac{A(\alpha)}{3}$$

Enhancement Factor of HOG Exchange

$$F_{\mathrm{X}}^{\mathrm{HOG}}[n, |\nabla n|, \tau] = \frac{[l\,\epsilon_{\mathrm{X}}\,(n(\mathbf{r}), |\nabla n(\mathbf{r})|, \mathrm{ELF}(\mathbf{r}))]^{\mathrm{conf}}}{[l\,\epsilon_{\mathrm{X}}\,(n(\mathbf{r}), |\nabla n(\mathbf{r})|, ELF(\mathbf{r}))]^{\mathrm{LDA}}}$$

$$[l\,\epsilon_{\mathrm{X}}\,(n(\mathbf{r}), |\nabla n(\mathbf{r})|, ELF(\mathbf{r}))]^{\mathrm{LDA}} = -\frac{3}{4\pi}\left(3\sqrt{\pi}\exp[-\bar{z}^2]\alpha\,(n(\mathbf{r}), |\nabla n(\mathbf{r})|, \mathrm{ELF}(\mathbf{r}))\right)^{1/3}$$

$$[l\,\epsilon_{\mathrm{X}}\,(n(\mathbf{r}), |\nabla n(\mathbf{r})|, \mathrm{ELF}(\mathbf{r}))]^{\mathrm{conf}} = \frac{a_0(\alpha) + a_2(\alpha)\bar{z}^2 + a_4(\alpha)\bar{z}^4 + a_6(\alpha)\bar{z}^6 - \bar{z}^8}{-\bar{z}^8/[2\sqrt{2\alpha}\,l\,\epsilon_{\mathrm{X}}^{>}(2\sqrt{2\alpha}\,\bar{z})] + 1}$$

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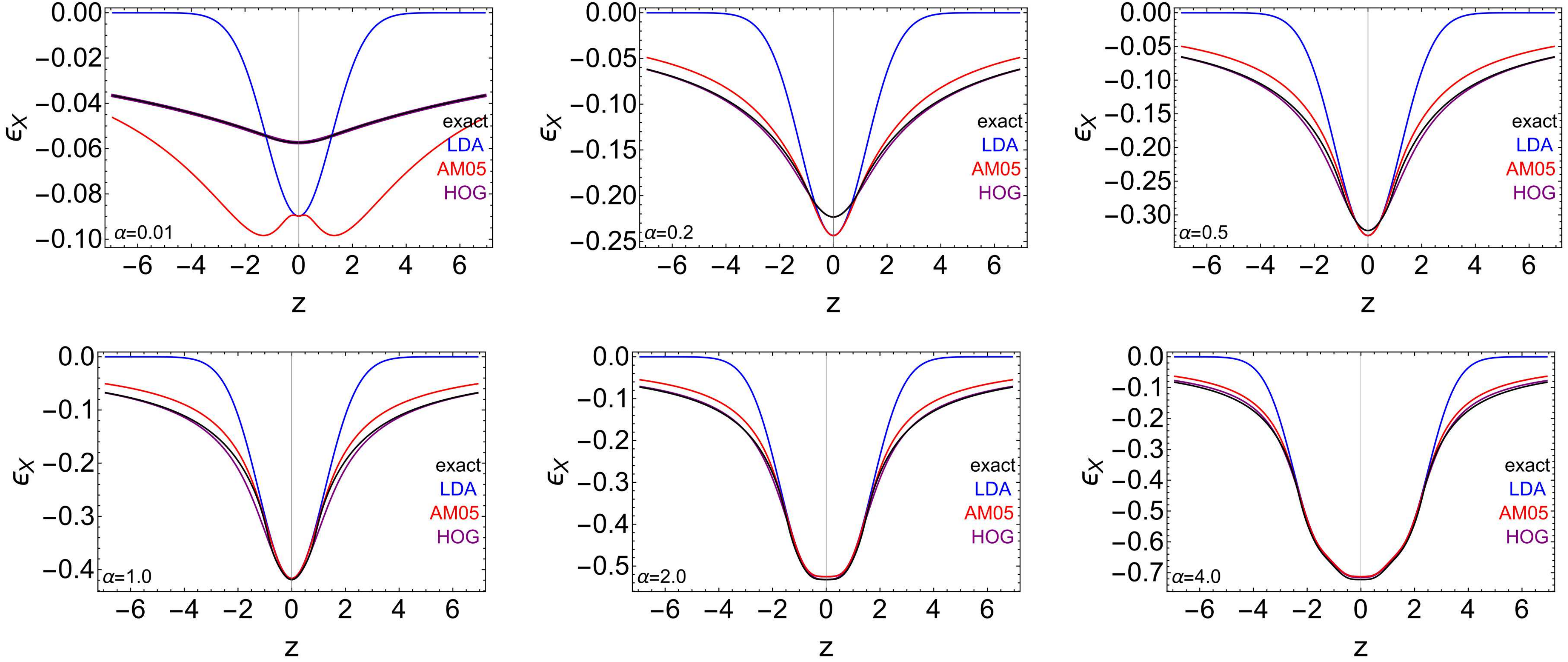
$$A(\alpha) = \frac{1 - \gamma - \ln(-2\alpha) - \Gamma(0, -2\alpha)}{4\sqrt{\pi}} - \frac{2\sqrt{2\alpha}}{3\pi} + \frac{1 - e^{2\alpha}}{8\sqrt{\pi}\alpha} - \frac{4(2\alpha)^{3/2}}{45\pi}\,{}_2F_2\left(1, \frac{3}{2}; \frac{5}{2}, \frac{7}{2}; 2\alpha\right)$$

$$B(\alpha) = \frac{e^{2\alpha}\,\mathrm{erfc}(\sqrt{2\alpha}) - 2\alpha - 1}{\sqrt{\pi}} + \frac{2\sqrt{2\alpha}}{\pi}\,,\;\; C(\alpha) = \frac{16\alpha^2}{\sqrt{\pi}}\left[e^{2\alpha}\,\mathrm{erfc}(\sqrt{2\alpha}) - 1\right]$$

$$D(\alpha) = \frac{128\alpha^3}{\sqrt{\pi}}\left[2(1+\alpha)\,e^{2\alpha}\,\mathrm{erfc}(\sqrt{2\alpha}) - \sqrt{2\alpha/\pi} - 2\right]$$

Parametrization of HOG Exchange

Accurate parametrization across a wide range of confinement parameters



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Bulk-Surface-Confinement Exchange-Correlation Functional

$$\epsilon_{\mathrm{XC}}^{\mathrm{BSC}}[n, |\nabla n|, \tau](\mathbf{r}) = \epsilon_{\mathrm{X}}^{\mathrm{BSC}}[n, |\nabla n|, \tau](\mathbf{r}) + \epsilon_{\mathrm{C}}^{\mathrm{HOG}}[n, |\nabla n|](\mathbf{r})$$

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Bulk-Surface-Confinement Exchange-Correlation Functional

$$\epsilon_{\mathrm{XC}}^{\mathrm{BSC}}[n,|\nabla n|,\tau](\mathbf{r}) = \epsilon_{\mathrm{X}}^{\mathrm{BSC}}[n,|\nabla n|,\tau](\mathbf{r}) + \epsilon_{\mathrm{C}}^{\mathrm{HOG}}[n,|\nabla n|](\mathbf{r})$$

$$\epsilon_{\mathrm{X}}^{\mathrm{BSC}} = \epsilon_{\mathrm{X}}^{\mathrm{surf}}\left\{1+[X_{\mathrm{conf}}-1][1+X_{\mathrm{conf}}\left(X_{\mathrm{surf},2}-1\right)]X_{\mathrm{surf},2}\right\} + \epsilon_{\mathrm{X}}^{\mathrm{conf}}\ \left\{1+X_{\mathrm{conf}}[X_{\mathrm{surf},2}-1]\right\}[1-X_{\mathrm{conf}}X_{\mathrm{surf},2}]$$

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$$\epsilon_{\mathrm{X}}^{\mathrm{BSC}} = \epsilon_{\mathrm{X}}^{\mathrm{surf}} \left\{1 + [X_{\mathrm{conf}} - 1][1 + X_{\mathrm{conf}} \left(X_{\mathrm{surf},2} - 1\right)]X_{\mathrm{surf},2}\right\} + \epsilon_{\mathrm{X}}^{\mathrm{conf}} \left\{1 + X_{\mathrm{conf}}[X_{\mathrm{surf},2} - 1]\right\} [1 - X_{\mathrm{conf}} X_{\mathrm{surf},2}]$$

$$\epsilon_{\mathrm{C}}^{\mathrm{HOG}}[n, |\nabla n|](\mathbf{r}) = \epsilon_{\mathrm{C}}^{\mathrm{LDA}}[n](\mathbf{r}) \left\{X_{\mathrm{surf},1}(\mathbf{r}; \eta_1) + [1 - X_{\mathrm{surf},1}(\mathbf{r}; \eta_1)](\gamma_1 + \gamma_2\, r_{\mathrm{S}})\right\}$$

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Bulk-Surface-Confinement Exchange-Correlation Functional

$$\epsilon_{\mathrm{XC}}^{\mathrm{BSC}}[n, |\nabla n|, \tau](\mathbf{r}) = \epsilon_{\mathrm{X}}^{\mathrm{BSC}}[n, |\nabla n|, \tau](\mathbf{r}) + \epsilon_{\mathrm{C}}^{\mathrm{HOG}}[n, |\nabla n|](\mathbf{r})$$

$$\epsilon_{\mathrm{X}}^{\mathrm{BSC}} = \epsilon_{\mathrm{X}}^{\mathrm{surf}} \{1 + [X_{\mathrm{conf}} - 1][1 + X_{\mathrm{conf}} (X_{\mathrm{surf},2} - 1)] X_{\mathrm{surf},2}\} + \epsilon_{\mathrm{X}}^{\mathrm{conf}} \{1 + X_{\mathrm{conf}}[X_{\mathrm{surf},2} - 1]\} [1 - X_{\mathrm{conf}} X_{\mathrm{surf},2}]$$

$$\epsilon_{\mathrm{C}}^{\mathrm{HOG}}[n, |\nabla n|](\mathbf{r}) = \epsilon_{\mathrm{C}}^{\mathrm{LDA}}[n](\mathbf{r}) \{X_{\mathrm{surf},1}(\mathbf{r}; \eta_1) + [1 - X_{\mathrm{surf},1}(\mathbf{r}; \eta_1)](\gamma_1 + \gamma_2 \, r_{\mathrm{S}})\}$$

$$X_{\mathrm{conf}}(\mathbf{r}; \eta_2) = 1 - \frac{\eta_2 \, [\mathrm{ELF}(\mathbf{r}) - 1/2]^4}{1 + \eta_2 \, [\mathrm{ELF}(\mathbf{r}) - 1/2]^4}$$

$$X_{\mathrm{surf},2}(\mathbf{r}; \eta_3) = \frac{2}{1 + e^{2\,\eta_3\, s^2(\mathbf{r})}}$$

$$X_{\mathrm{surf},1}(\mathbf{r}; \eta_1) = 1 - \frac{\eta_1 \, s^2(\mathbf{r})}{1 + \eta_1 \, s^2(\mathbf{r})}$$

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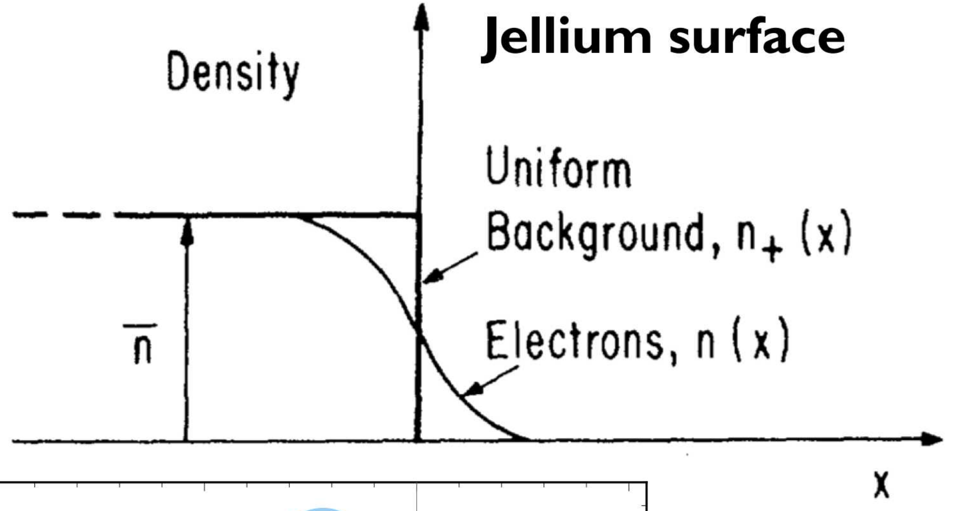
Constraining the Functional Form with the Jellium Surface

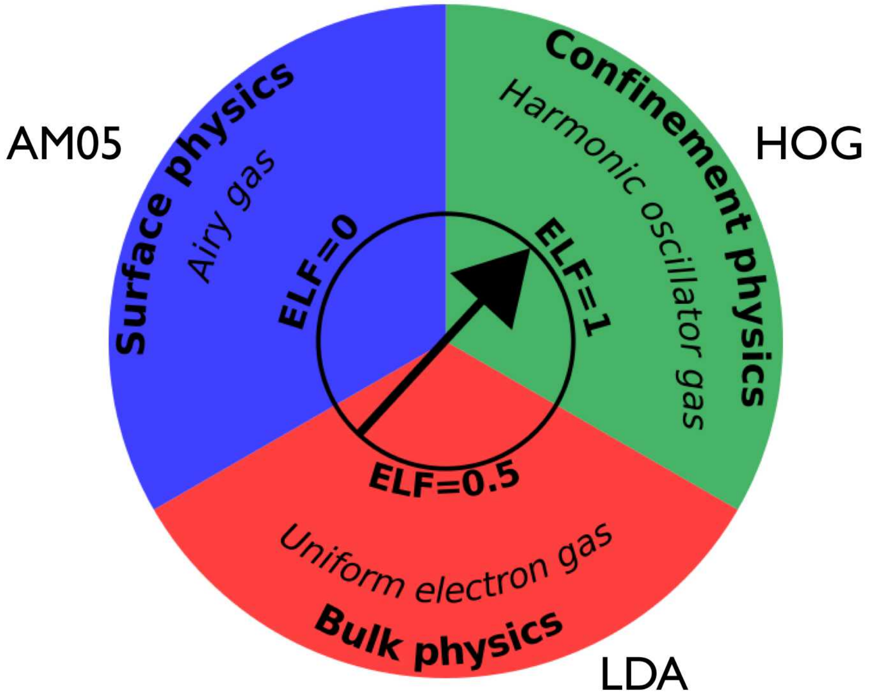
$$E_{\mathrm{XC}} = \int_\Omega d\mathbf{r}\; n(\mathbf{r})\, \epsilon_{\mathrm{XC}}[n, \nabla n, \tau; \{\gamma_j, \eta_j\}](\mathbf{r})$$

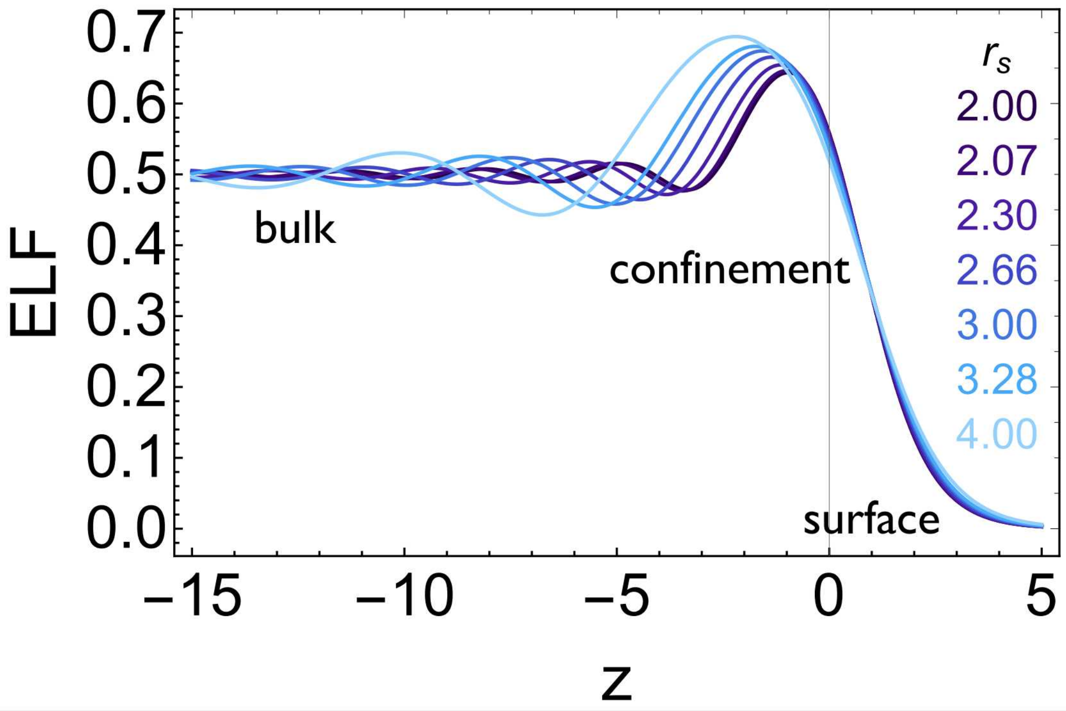
Divide domain into subsystems

Specialized functionals in different subsystems

Jellium surface







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Assessing the XC Enhancement Factor

Properties

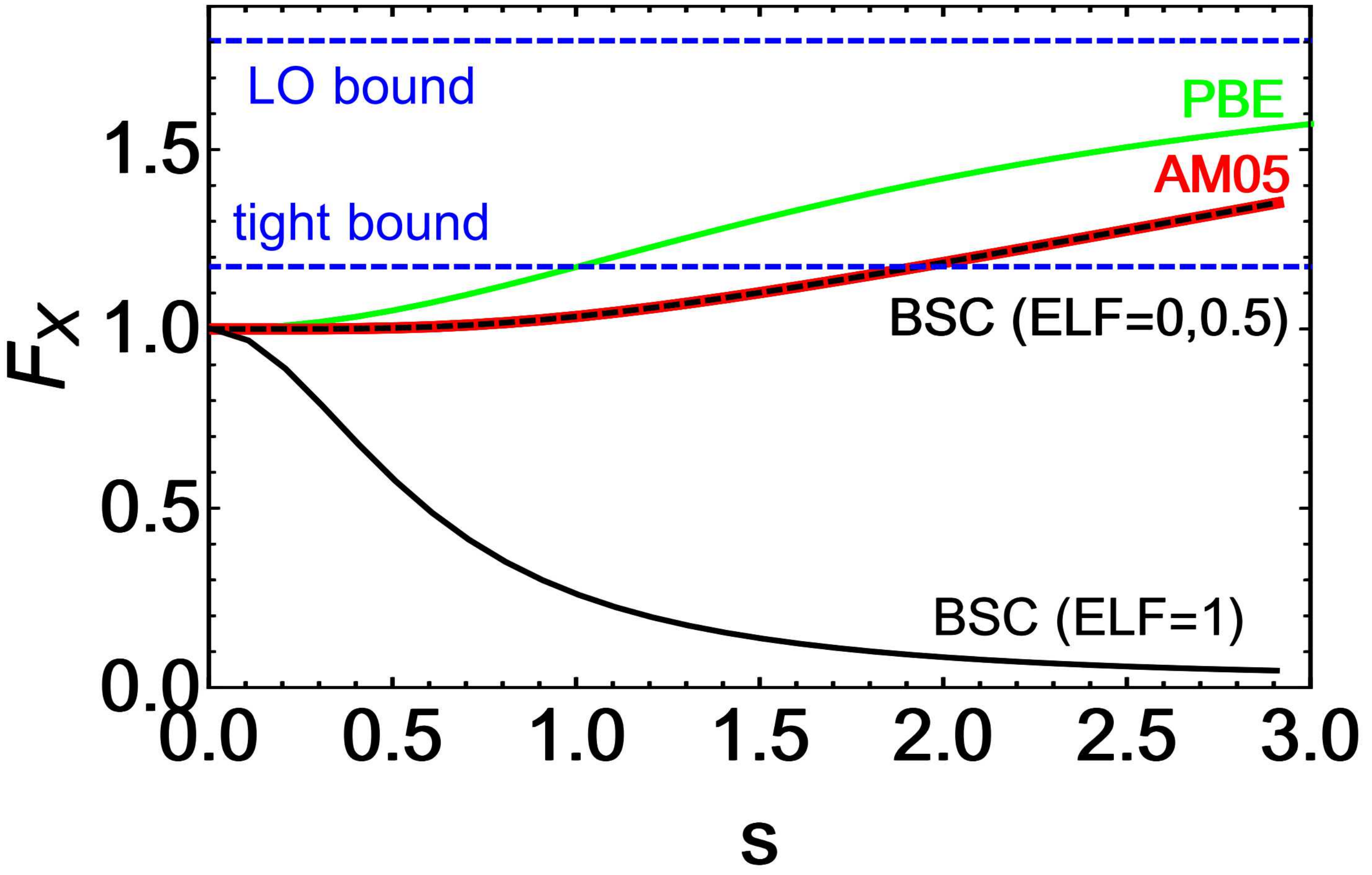
Exchange

- Recovers the correct uniform gas limit
- Satisfies linear response of the UEG (quadratic in the small s limit)
- Partially satisfies LO and tight bound

Correlation

- Recovers the correct uniform gas limit

$$E_{\mathrm{X}} = \int d\mathbf{r}\; n(\mathbf{r})\, \epsilon_{\mathrm{X}}^{\mathrm{unif}}(n)\, F_{\mathrm{X}}(n, |\nabla n|, \tau)$$



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Properties

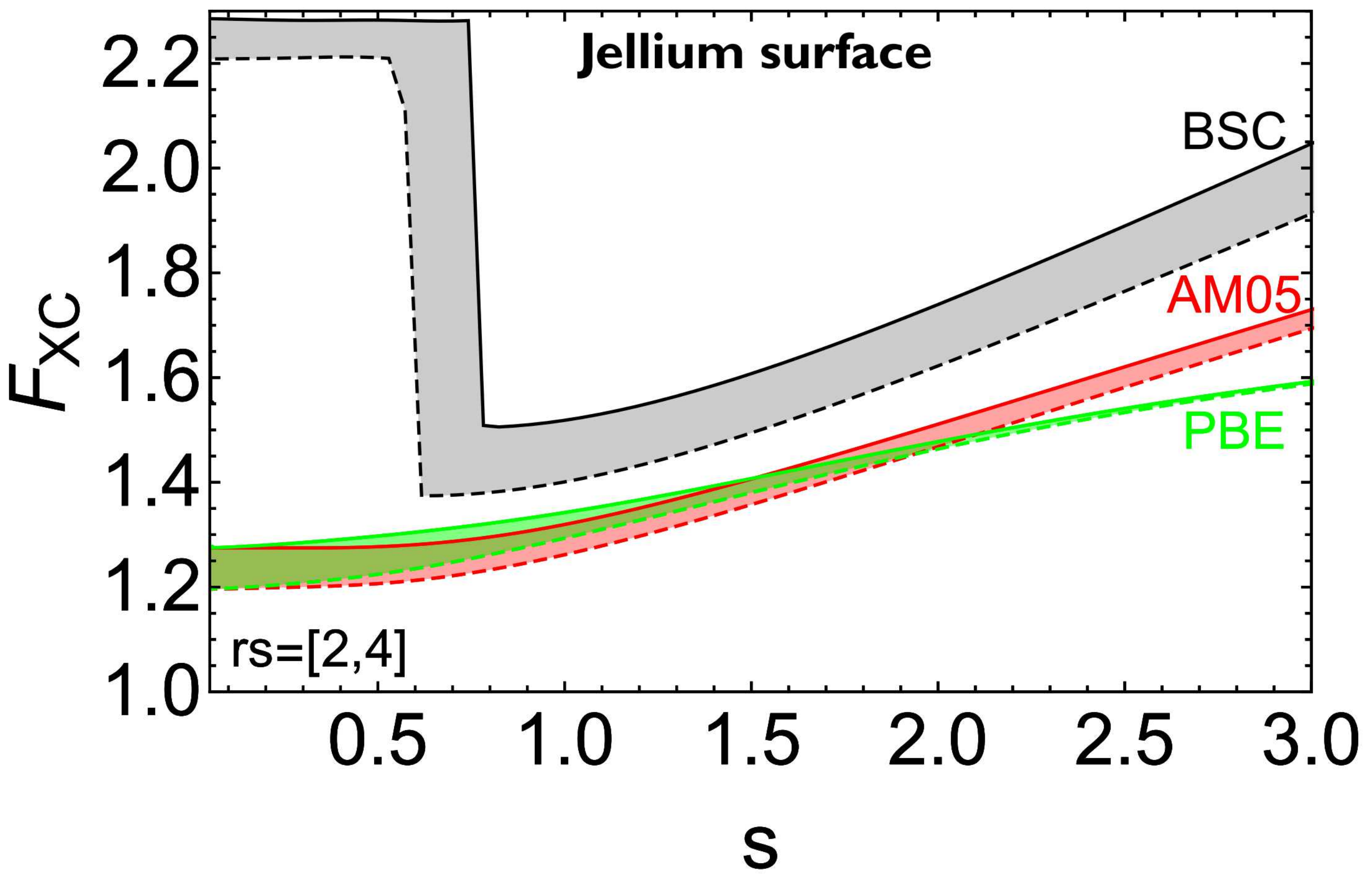
Exchange

- Recovers the correct uniform gas limit
- Satisfies linear response of the UEG (quadratic in the small s limit)
- Partially satisfies LO and tight bound

Correlation

- Recovers the correct uniform gas limit

$$E_{\mathrm{XC}} = \int d\mathbf{r}\; n(\mathbf{r})\, \epsilon_{\mathrm{X}}^{\mathrm{unif}}(n)\, F_{\mathrm{XC}}(n, |\nabla n|, \tau)$$



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Jellium surface

r_S	σ_{XC}^{LDA}	σ_{XC}^{PBE}	σ_{XC}^{AM05}	σ_{XC}^{BSC}	σ_{XC}
2.00	3354				3413
2.07	2961				3015
2.30	2019				2060
2.66	1188				1214
3.00	764				781
3.28	549				563
4.00	261				268
MAPE	2				–

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Assessing the Bulk-Surface-Confinement (BSC) Functional

Jellium surface

r_S	σ_{XC}^{LDA}	σ_{XC}^{PBE}	σ_{XC}^{AM05}	σ_{XC}^{BSC}	σ_{XC}
2.00	3354	3264			3413
2.07	2961	2879			3015
2.30	2019	1960			2060
2.66	1188	1150			1214
3.00	764	738			781
3.28	549	530			563
4.00	261	251			268
MAPE	2	5			–

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Jellium surface

r_S	σ_{XC}^{LDA}	σ_{XC}^{PBE}	σ_{XC}^{AM05}	σ_{XC}^{BSC}	σ_{XC}
2.00	3354	3264	3414.0		3413
2.07	2961	2879	3014.6		3015
2.30	2019	1960	2058.4		2060
2.66	1188	1150	1213.5		1214
3.00	764	738	782.0		781
3.28	549	530	563.4		563
4.00	261	251	269.6		268
MAPE	2	5	0.4		–

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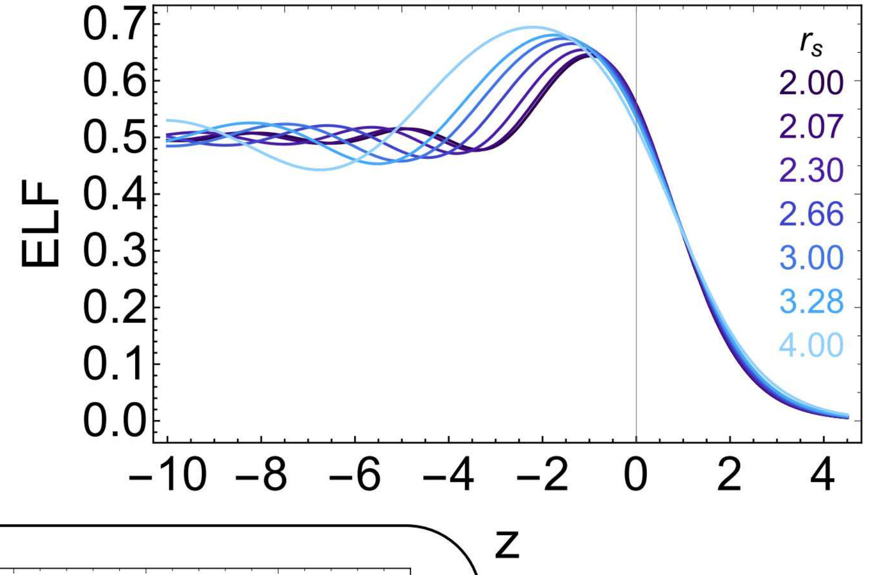
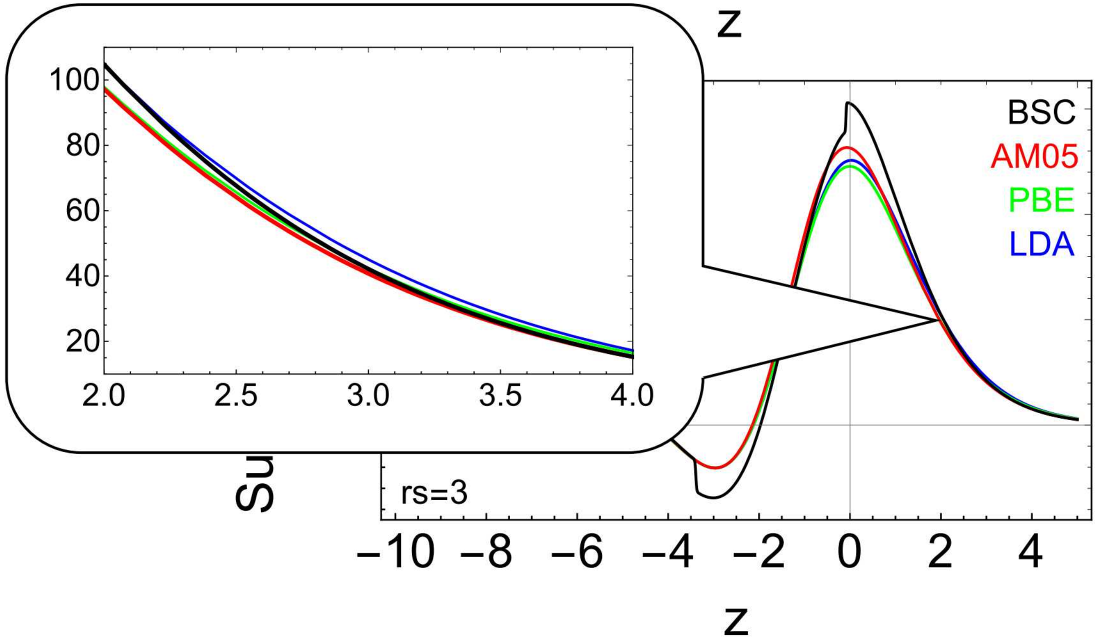
Jellium surface

r_S	σ_{XC}^{LDA}	σ_{XC}^{PBE}	σ_{XC}^{AM05}	σ_{XC}^{BSC}	σ_{XC}
2.00	3354	3264	3414.0	3413.72	3413
2.07	2961	2879	3014.6	3014.64	3015
2.30	2019	1960	2058.4	2058.99	2060
2.66	1188	1150	1213.5	1214.07	1214
3.00	764	738	782.0	782.01	781
3.28	549	530	563.4	562.99	563
4.00	261	251	269.6	267.73	268
MAPE	2	5	0.4	0.05	–





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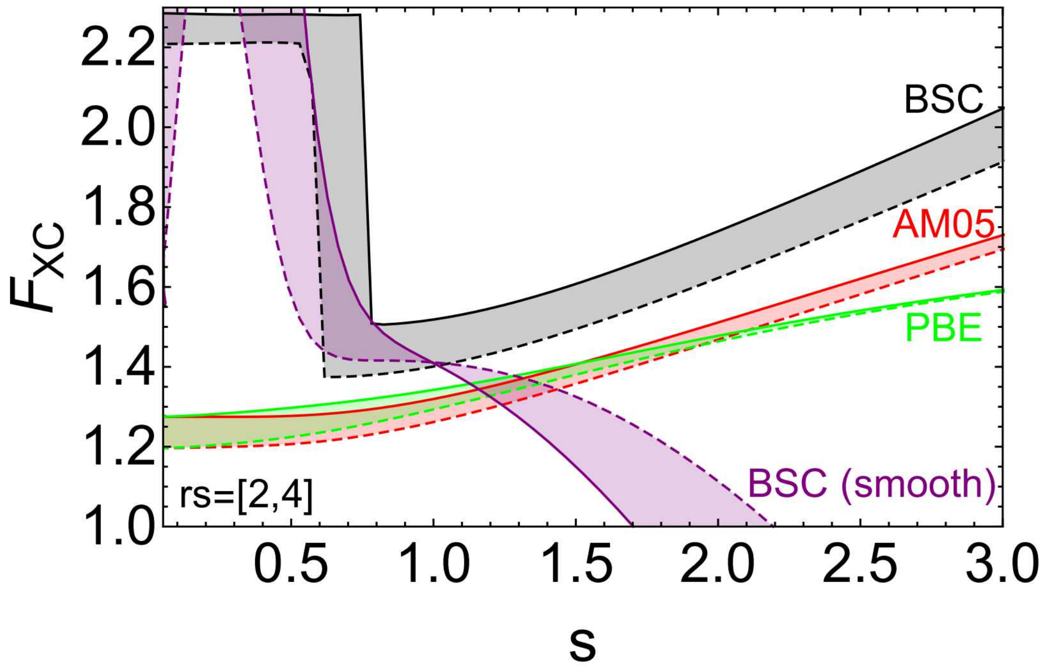
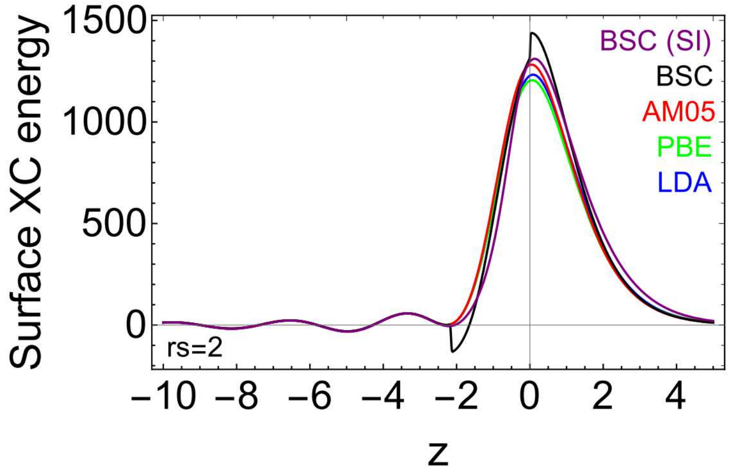
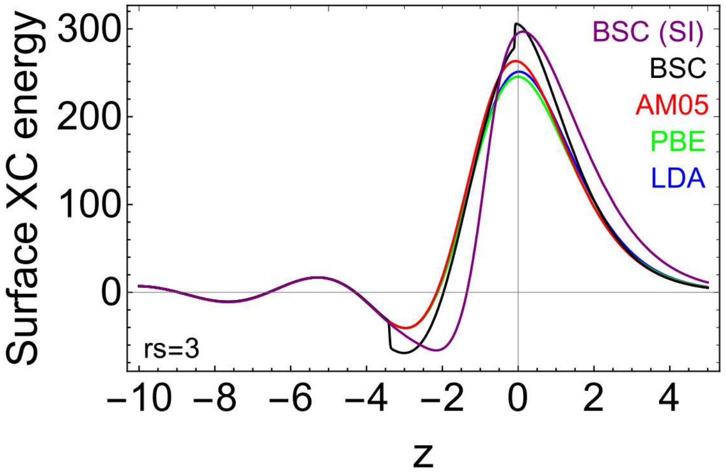
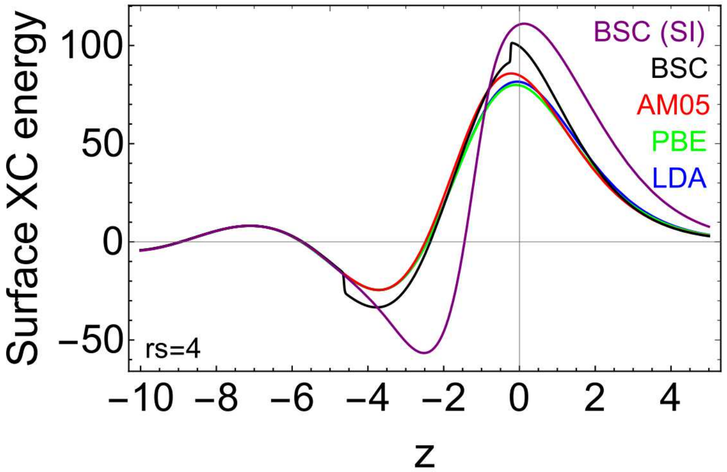
Jellium surface

r_S	σ_{XC}^{LDA}	σ_{XC}^{PBE}	σ_{XC}^{AM05}	σ_{XC}^{BSC}	σ_{XC}^{BSC-SI}	σ_{XC}
2.00	3354	3264	3414.0	3413.72		3413
2.07	2961	2879	3014.6	3014.64		3015
2.30	2019	1960	2058.4	2058.99		2060
2.66	1188	1150	1213.5	1214.07		1214
3.00	764	738	782.0	782.01		781
3.28	549	530	563.4	562.99		563
4.00	261	251	269.6	267.73		268
MAPE	2	5	0.4	0.05		—









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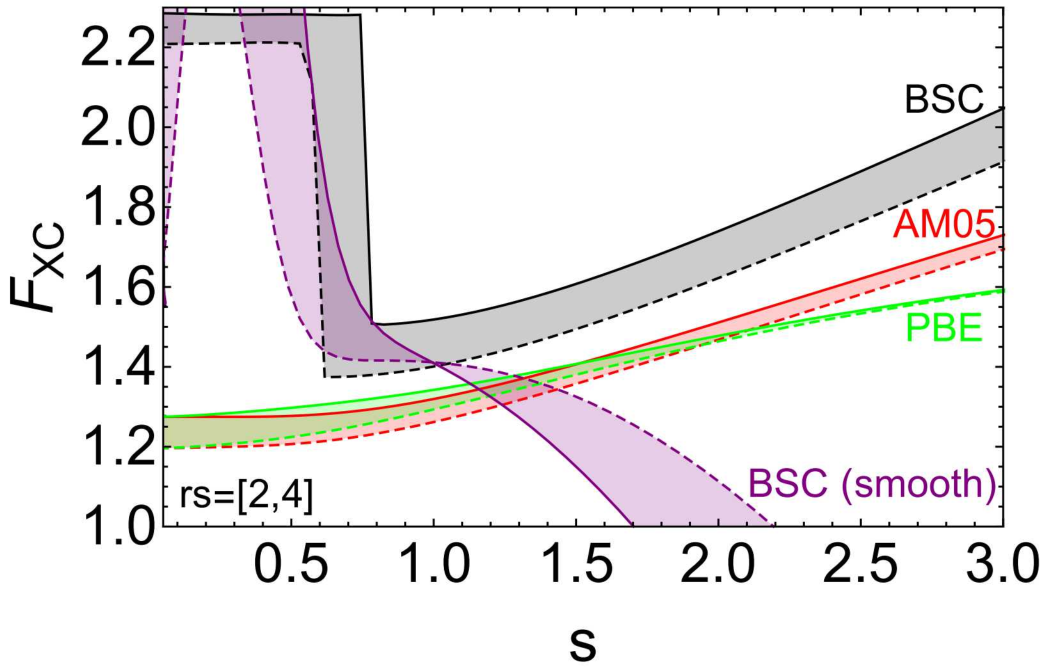
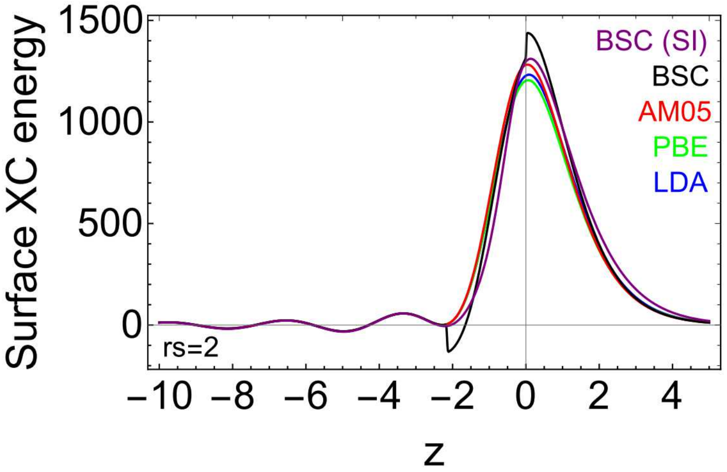
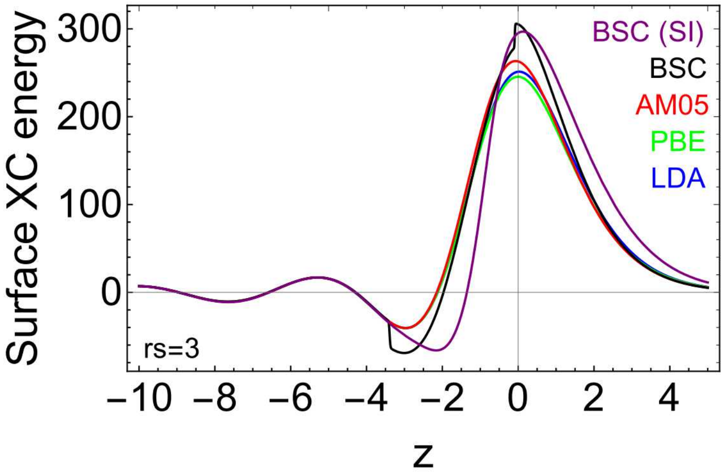
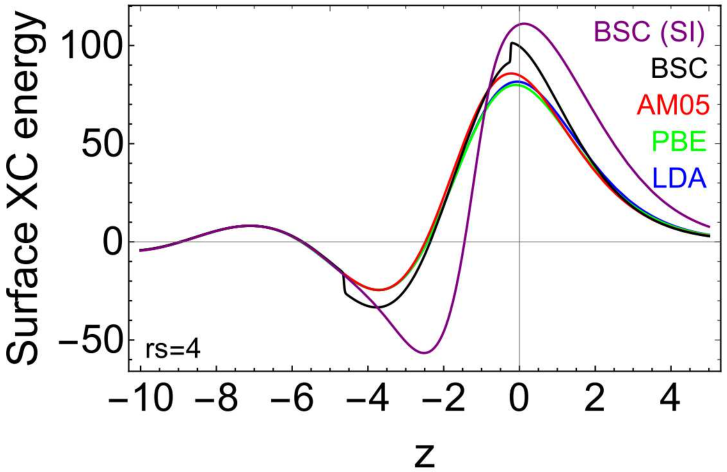
Jellium surface

r_S	σ_{XC}^{LDA}	σ_{XC}^{PBE}	σ_{XC}^{AM05}	σ_{XC}^{BSC}	σ_{XC}^{BSC-SI}	σ_{XC}
2.00	3354	3264	3414.0	3413.72	3412.84	3413
2.07	2961	2879	3014.6	3014.64	3014.64	3015
2.30	2019	1960	2058.4	2058.99	2059.64	2060
2.66	1188	1150	1213.5	1214.07	1213.99	1214
3.00	764	738	782.0	782.01	781.43	781
3.28	549	530	563.4	562.99	562.27	563
4.00	261	251	269.6	267.73	268.13	268
MAPE	2	5	0.4	0.05	0.04	–









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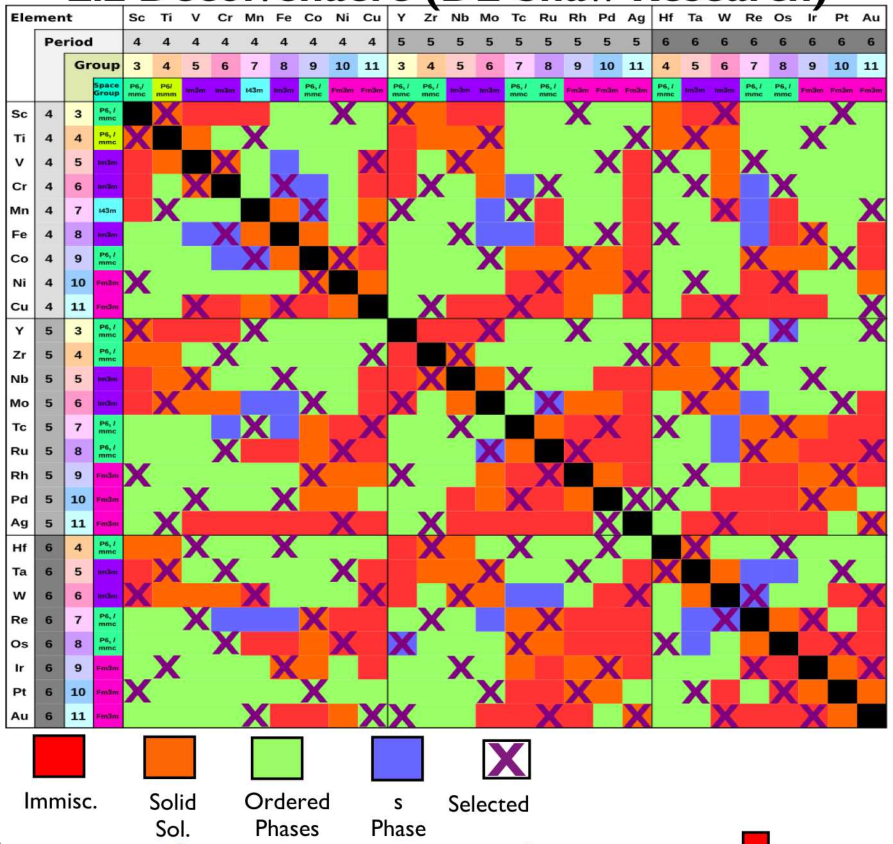
Generating a Test Set of Binary Transition Metal Compounds

Liz Decolvenaere (DE Shaw Research)



Selection of binary transition metal compounds

- 26 transition metals
- 80 binary compounds
- Experimentally known configurations
- Several functionals (LDA, PW91, PBE, AM05, PBEsol, RTPSS, SCAN)

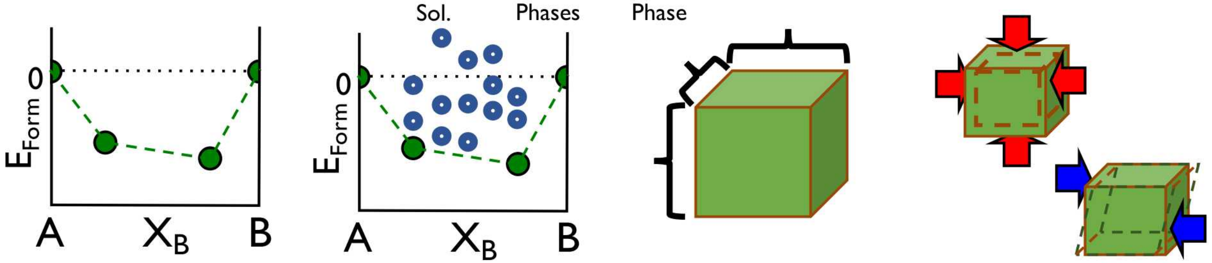
Data analysis

- **Standard test set**
  All experimental and DFT ground states and "almost" ground states
- **Micro test set**
  < 300 structures capturing the most astounding failures and important experimental results
- **Macro test set**
  All ~12,000 structures

Data management

NIST Materials Data Repository

The National Institute of Standards and Technology has created a materials science data repository as part of an effort in coordination with the Materials Genome Initiative (MGI) to establish data exchange protocols and mechanisms that will foster data sharing and reuse across a wide community of researchers, with the goal of enhancing the quality of materials data and models. Data present on this system are varied and may originate from within NIST



1 Formation energies

2 Ground-state energies

3 Lattice constants

4 Elastic constants

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Summary

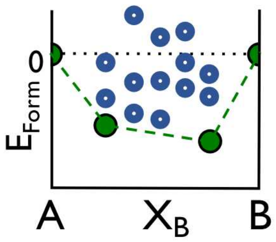
- Implementation in electronic structure codes

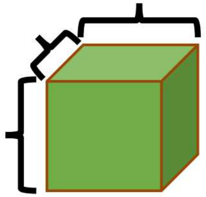
Elk code (http://elk.sourceforge.net)

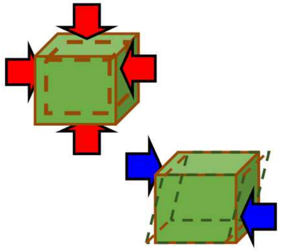
Libxc - a library of exchange-correlation functionals for density-functional theory

(https://gitlab.com/libxc/libxc)

- Assessment for materials (energetics, lattice constants, and elastic properties)







Collaborators

- Liz Decolvenaere (DE Shaw Research)
- Francisca Sagredo (UC, Irvine)
- Ann E. Mattsson (Los Alamos National Laboratory)

References

- F. Hao, R. Armiento and A. E. Mattsson, Phys. Rev. B 82, 115103 (2010).
- F. Hao, R. Armiento and A. E. Mattsson, J. Chem. Phys. 140 18A536 (2014).
- Ann E. Mattsson and John M. Wills, Int. J. Quantum Chem. 116 834 (2016).

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Supplemental Material

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$$\text{Hamiltonian}: \quad \hat{H} = \hat{T} + \hat{V} + \hat{W}^{\text{ee}}$$

$$\text{Universal functional}: \quad F[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{W}^{\text{ee}} | \Psi \rangle$$

$$\text{Ground-state energy}: \quad E_v = \min_n \left\{ F[n] + \int d^3r \; n(\mathbf{r})\, v(\mathbf{r}) \right\}$$

$$\text{Kohn-Sham equations}: \quad \epsilon_i \, \phi_i(\mathbf{r}) = \left\{ -\frac{\nabla^2}{2} + v_{\text{S}}(\mathbf{r}) \right\} \phi_i(\mathbf{r})$$

$$\text{Electronic density}: \quad n(\mathbf{r}) = \sum_i^N \phi_i^*(\mathbf{r}) \phi(\mathbf{r})$$

$$\text{Exchange-correlation energy}: \quad F[n] = T_{\text{S}}[n] + U[n] + E_{\text{XC}}[n]$$

$$\text{Kohn-Sham potential}: \quad v_{\text{S}}(\mathbf{r}) = v(\mathbf{r}) + \frac{\delta U[n]}{\delta n(\mathbf{r})} + \frac{\delta E_{\text{XC}}[n]}{\delta n(\mathbf{r})}$$

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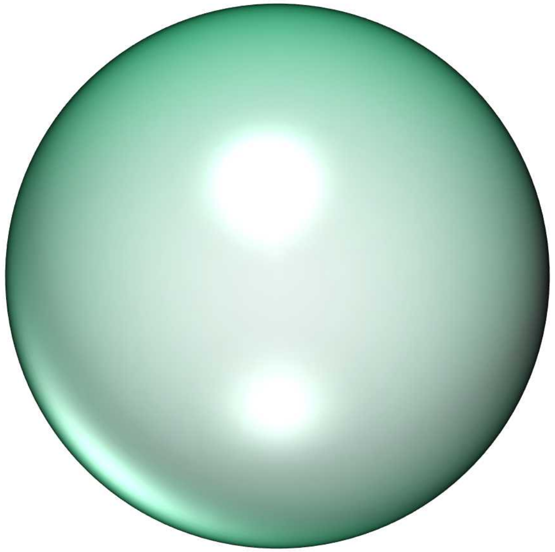
Wigner-Seitz Radius

$$r_{\mathrm{S}} = \left(\frac{3}{4\pi n}\right)^{1/3}$$



The Wigner-Seitz is a dimensionless radius of a sphere that contains the charge of one electron and is commonly used as a measure to characterize the density of a system.

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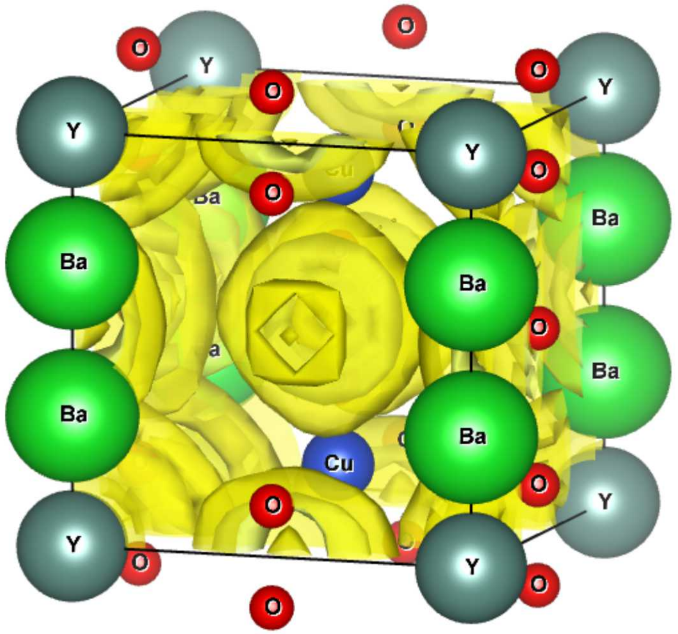
Electron Localization Function

$$ELF = \frac{1}{1 + [D/D_h]^2}$$

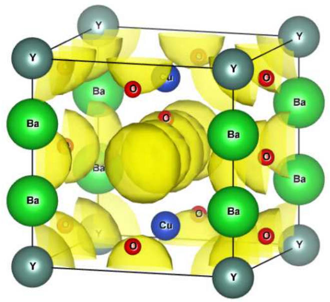
$$D = \tau_S - \frac{1}{8}\frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})}$$

$$D_h = \frac{3}{10}(3\pi^2)^{2/3}\, n(\mathbf{r})^{5/3}$$

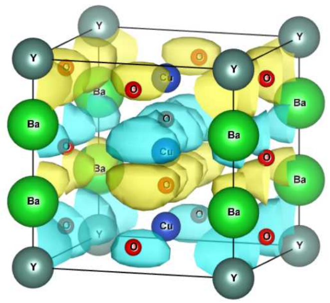
A measure of the likelihood of finding an electron in the neighborhood space of a reference electron located at a given point and with the same spin.



Yttrium barium copper oxide



Charge density



Charge density gradient

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Enhancement Factor of HOG Exchange: Further Details

$$\alpha\left(n(\mathbf{r}), |\nabla n(\mathbf{r})|, \mathrm{ELF}(\mathbf{r})\right) = \left\{ e^{-\alpha_1\, s^2(\mathbf{r})} \left[\frac{\beta_1 \frac{D(\mathbf{r})}{D^{\mathrm{LDA}}(\mathbf{r})}}{1 + e^{\alpha_2\left(\beta_1 \frac{D(\mathbf{r})}{D^{\mathrm{LDA}}(\mathbf{r})} - \beta_2\right)}} + \frac{\beta_2^2 \left(\beta_1 \frac{D(\mathbf{r})}{D^{\mathrm{LDA}}(\mathbf{r})}\right)^{-1}}{1 + e^{\alpha_2\left(-\beta_1 \frac{D(\mathbf{r})}{D^{\mathrm{LDA}}(\mathbf{r})} + \beta_2\right)}} \right] \right.$$

$$\left. + \left(1 - e^{-\alpha_1\, s^2(\mathbf{r})}\right) \beta_1 \frac{D(\mathbf{r})}{D^{\mathrm{LDA}}(\mathbf{r})} \right\} \frac{\bar{z}^2(|\nabla n(\mathbf{r})|, ELF(\mathbf{r}))}{s^2(\mathbf{r})}$$

$$\bar{z}^2(|\nabla n(\mathbf{r})|, ELF(\mathbf{r})) = \frac{1}{2} W \left[18\pi \left(\beta_1 \frac{D(\mathbf{r})}{D^{\mathrm{LDA}}(\mathbf{r})}\right)^2 s^2(\mathbf{r}) \right]$$

BSC Exchange-Correlation Functional

$$E_{\mathrm{XC}}[n] = \int_\Omega d^3r \; n(\mathbf{r})\, \epsilon_{\mathrm{XC}}[n, \nabla n, \tau; \{\gamma_i\}, \{\eta_i\}](\mathbf{r})$$

$$\begin{aligned}
\epsilon_{\mathrm{XC}}^{\mathrm{BSC}}[n, |\nabla n|, \mathrm{ELF}](\mathbf{r}) &= \epsilon_{\mathrm{X}}^{\mathrm{BSC}}[n, |\nabla n|, \mathrm{ELF}](\mathbf{r}) + \epsilon_{\mathrm{C}}^{\mathrm{HOG}}[n, |\nabla n|](\mathbf{r}) \\
\epsilon_{\mathrm{X}}^{\mathrm{BSC}} &= \epsilon_{\mathrm{X}}^{\mathrm{surf}} \left\{1 + [X_{\mathrm{ELF}} - 1][1 + X_{\mathrm{ELF}}\,(X_{\mathrm{surf},2} - 1)] X_{\mathrm{surf},2}\right\} \\
&\quad + \epsilon_{\mathrm{X}}^{\mathrm{conf}} \left\{1 + X_{\mathrm{ELF}}[X_{\mathrm{surf},2} - 1]\right\} [1 - X_{\mathrm{ELF}} X_{\mathrm{surf},2}] \\
X_{\mathrm{ELF}}(\mathbf{r}; \eta_2) &= 1 - \frac{\eta_2\; [\mathrm{ELF}(\mathbf{r}) - 1/2]^4}{1 + \eta_2\; [\mathrm{ELF}(\mathbf{r}) - 1/2]^4} \\
X_{\mathrm{surf},2}(\mathbf{r}; \eta_3) &= \frac{2}{1 + e^{2\,\eta_3\, s^2(\mathbf{r})}} \\
\epsilon_{\mathrm{XC}}^{bulk}[n](\mathbf{r}) &= \epsilon_{\mathrm{XC}}^{\mathrm{LDA}}[n](\mathbf{r}) \\
\epsilon_{\mathrm{XC}}^{surf}[n](\mathbf{r}) &= \epsilon_{\mathrm{XC}}^{\mathrm{AM05}}[n, |\nabla n|](\mathbf{r}) \\
\epsilon_{\mathrm{XC}}^{conf}[n](\mathbf{r}) &= \epsilon_{\mathrm{XC}}^{\mathrm{HOG}}[n, |\nabla n|, \mathrm{ELF}](\mathbf{r}) \\
\epsilon_{\mathrm{C}}^{\mathrm{HOG}}[n, |\nabla n|](\mathbf{r}) &= \epsilon_{\mathrm{C}}^{\mathrm{LDA}}[n](\mathbf{r}) \left\{X_{\mathrm{surf},1}(\mathbf{r}; \eta_1) + [1 - X_{\mathrm{surf},1}(\mathbf{r}; \eta_1)](\gamma_1 + \gamma_2\, r_{\mathrm{S}})\right\} \\
X_{\mathrm{surf},1}(\mathbf{r}; \eta_1) &= 1 - \frac{\eta_1\, s^2(\mathbf{r})}{1 + \eta_1\, s^2(\mathbf{r})} \\
\epsilon_{\mathrm{X}}^{\mathrm{conf}}[n](\mathbf{r}) = \epsilon_{\mathrm{X}}^{\mathrm{HOG}}[n](\mathbf{r}) &= \epsilon_{\mathrm{X}}^{\mathrm{LDA}}[n, |\nabla n|, \mathrm{ELF}](\mathbf{r})\, F_{\mathrm{X}}^{\mathrm{HOG}}[n, |\nabla n|, \mathrm{ELF}](\mathbf{r}) \\
F_{\mathrm{X}}^{\mathrm{HOG}}[n, |\nabla n|, \mathrm{ELF}](\mathbf{r}) &= \frac{[l\, \epsilon_{\mathrm{X}}[n, |\nabla n|, \mathrm{ELF}](\mathbf{r})]^{\mathrm{HOG}}}{[l\, \epsilon_{\mathrm{X}}[n, |\nabla n|, \mathrm{ELF}](\mathbf{r})]^{\mathrm{LDA}}} \\
[l\, \epsilon_{\mathrm{X}}\,(n(\mathbf{r}), |\nabla n(\mathbf{r})|, ELF(\mathbf{r}))]^{\mathrm{LDA}} &= -\frac{3}{4\pi} \left(3\sqrt{\pi} \exp[-\bar{z}^2]\alpha\,(n(\mathbf{r}), |\nabla n(\mathbf{r})|, \mathrm{ELF}(\mathbf{r}))\right)^{1/3} \\
[l\, \epsilon_{\mathrm{X}}\,(n(\mathbf{r}), |\nabla n(\mathbf{r})|, \mathrm{ELF}(\mathbf{r}))]^{\mathrm{conf}} &= \frac{a_0(\alpha) + a_2(\alpha)\bar{z}^2 + a_4(\alpha)\bar{z}^4 + a_6(\alpha)\bar{z}^6 - \bar{z}^8}{-\bar{z}^8/[2\sqrt{2\alpha}\, l\, \epsilon_{\mathrm{X}}^{>}(2\sqrt{2\alpha}\,\bar{z})] + 1}
\end{aligned}$$

$$\begin{aligned}
\epsilon_{\mathrm{X}}^{>}(t) &= \frac{1}{t}\left[\frac{1}{2} - \frac{I_1(t)}{t} + \frac{L_1(t)}{t}\right] \\
a_0(\alpha) &= 2\,A(\alpha)\,, \\
a_2(\alpha) &= \frac{B(\alpha)}{2(\alpha)} - 2\,A(\alpha)\,, \\
a_4(\alpha) &= \frac{C(\alpha)}{48\alpha^2} - \frac{B(\alpha)}{2\alpha} + A(\alpha)\,, \\
a_6(\alpha) &= \frac{D(\alpha)}{2880\alpha^3} - \frac{C(\alpha)}{48\alpha^2} + \frac{B(\alpha)}{4\alpha} - \frac{A(\alpha)}{3} \\
A(\alpha) &= \frac{1 - \gamma - \ln(-2\alpha) - \Gamma(0, -2\alpha)}{4\sqrt{\pi}} - \frac{2\sqrt{2\alpha}}{3\pi} + \frac{1 - e^{2\alpha}}{8\sqrt{\pi}\alpha} - \frac{4(2\alpha)^{3/2}}{45\pi}\, {}_2F_2\left(1, \frac{3}{2}; \frac{5}{2}, \frac{7}{2}; 2\alpha\right. \\
B(\alpha) &= \frac{e^{2\alpha}\,\mathrm{erfc}(\sqrt{2\alpha}) - 2\alpha - 1}{\sqrt{\pi}} + \frac{2\sqrt{2\alpha}}{\pi} \\
C(\alpha) &= \frac{16\alpha^2}{\sqrt{\pi}} \left[e^{2\alpha}\,\mathrm{erfc}(\sqrt{2\alpha}) - 1\right] \\
D(\alpha) &= \frac{128\alpha^3}{\sqrt{\pi}} \left[2(1 + \alpha)\, e^{2\alpha}\,\mathrm{erfc}(\sqrt{2\alpha}) - \sqrt{2\alpha/\pi} - 2\right] \\
\alpha\,(n(\mathbf{r}), |\nabla n(\mathbf{r})|, \mathrm{ELF}(\mathbf{r})) &= \Bigg\{ e^{-\alpha_1\, s^2(\mathbf{r})} \left[\frac{\beta_1 \frac{D(\mathbf{r})}{D^{\mathrm{LDA}}(\mathbf{r})}}{1 + e^{\alpha_2\left(\beta_1 \frac{D(\mathbf{r})}{D^{\mathrm{LDA}}(\mathbf{r})} - \beta_2\right)}} + \frac{\beta_2^2 \left(\beta_1 \frac{D(\mathbf{r})}{D^{\mathrm{LDA}}(\mathbf{r})}\right)^{-1}}{1 + e^{\alpha_2\left(-\beta_1 \frac{D(\mathbf{r})}{D^{\mathrm{LDA}}(\mathbf{r})} + \beta_2\right)}}\right] \\
&\quad + \left(1 - e^{-\alpha_1\, s^2(\mathbf{r})}\right) \beta_1 \frac{D(\mathbf{r})}{D^{\mathrm{LDA}}(\mathbf{r})} \Bigg\} \frac{\bar{z}^2(|\nabla n(\mathbf{r})|, ELF(\mathbf{r}))}{s^2(\mathbf{r})} \\
\bar{z}^2(|\nabla n(\mathbf{r})|, ELF(\mathbf{r})) &= \frac{1}{2} W \left[18\pi \left(\beta_1 \frac{D(\mathbf{r})}{D^{\mathrm{LDA}}(\mathbf{r})}\right)^2 s^2(\mathbf{r})\right]
\end{aligned}$$

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Assessing the Bulk-Surface-Confinement (BSC) Functional

Jellium surface

r_S	σ_{XC}^{LDA}	σ_{XC}^{PBE}	σ_{XC}^{AM05}	σ_{XC}^{BSC}	σ_{XC}
2.00	3354	3264	3414.0	3413.72	3413
2.07	2961	2879	3014.6	3014.64	3015
2.30	2019	1960	2058.4	2058.99	2060
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MAPE	2	5	0.4	0.05	–