Lorde: Te Ao Mārama

"The future of music" – David Bowie

click here for video

Leaving The Group

Backups

Before you leave, you must make two backups of your workstation.

You should already possess one HDD that you have been using for regular backups (see the group's backup policy); ask Edward Linscott for a second HDD for the second backup.

Leave one HDD with Edward and take the other one with you when you leave.

Leaving your office

- Clean and empty your desk, drawer and bookshelf
- Return any equipment you might have borrowed from the lab for remote working
- Leave the drawer key in the keyhole
- Return your office key to the secretaries

Ongoing access

Ask to Irène for an extension of your EPFL account; typically 6 months should suffice (ask Nicola the specific amount of time depending on your future plans and the status of your current projects). The extension needs to be justified, a typical reason is "completion of a publication".

If you require ongoing access to your THEOS workstation after you leave, discuss this with the group's IT managers.

BLOR

a DFT+U-inspired functional that properly linearizes the total energy

Edward Linscott | EPFL | THEOS Group Meeting | 6 June 2023

MARVEL

Swiss National Science Foundation

$$E_{\mathrm{U}} = \sum_{I\sigma} \frac{U^I}{2} \mathrm{Tr}[\hat{n}^{I\sigma}(1 - \hat{n}^{I\sigma})]$$

$$\hat{n}^{I\sigma} = \hat{P}^I \hat{\rho}^\sigma \hat{P}^I = \sum_{i,j} |\varphi_i^I\rangle\langle\varphi_i^I|\hat{\rho}^\sigma|\varphi_j^I\rangle\langle\varphi_j^I|$$

DFT+U

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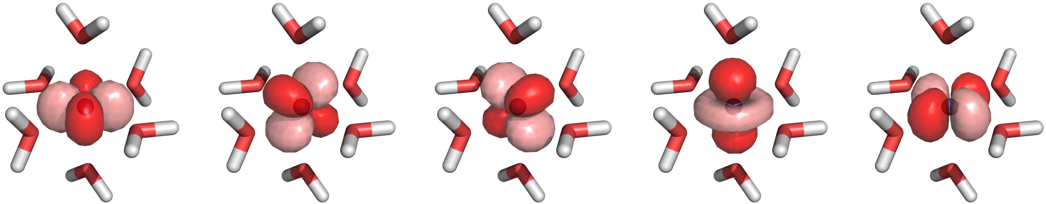

$\langle \mathbf{r}|\varphi_1^I\rangle$ $\langle \mathbf{r}|\varphi_2^I\rangle$ $\langle \mathbf{r}|\varphi_3^I\rangle$ $\langle \mathbf{r}|\varphi_4^I\rangle$ $\langle \mathbf{r}|\varphi_5^I\rangle$

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... but where does this come from?

Time for a history lesson...

Let’s integrate the Hubbard model into the DFT framework!

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$$\hat{U} = \sum_{mnm'n'} \sum_{\sigma\sigma'} U_{mnm'n'} c^{\dagger}_{m\sigma} c^{\dagger}_{n\sigma'} c_{m'\sigma'} c_{n'\sigma},$$

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- ignore all but two-site interaction terms (à la Hubbard model)
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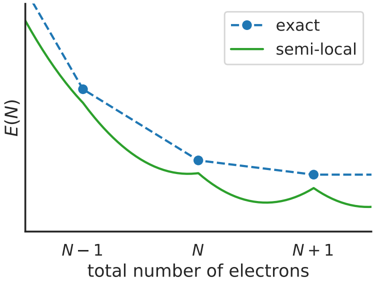
... and finish with a corrective term to DFT

$$E_{DFT+U}[\rho] = E_{\mathrm{DFT}}[\rho] + E_{\mathrm{U}}[\rho] = E_{\mathrm{DFT}}[\rho] + \sum_{I\sigma} \frac{U^I}{2} \mathrm{Tr}[\hat{n}^{I\sigma}(1 - \hat{n}^{I\sigma})]$$



A modern (post hoc) interpretation: in a basis such that $\hat{n}^{I\sigma} = diag(\lambda_1^{I\sigma}, ..., \lambda_n^{I\sigma})$

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M. Cococcioni et al. *Phys. Rev. B* 71.3 (2005), 035105

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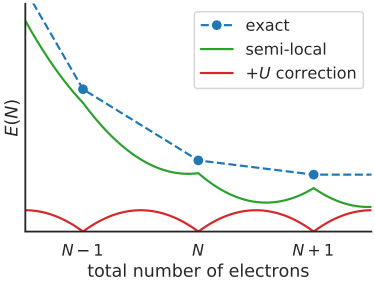

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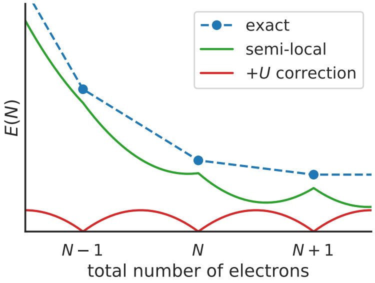

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We can calculate U via linear response → “self-correcting” DFT

M. Cococcioni et al. *Phys. Rev. B* 71.3 (2005), 035105

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$$E_{DFT+U+J}[\rho] = E_{\text{DFT}}[\rho] + \sum_{I\sigma} \frac{U^I - J^I}{2} \text{Tr}[\hat{n}^{I\sigma}(1 - \hat{n}^{I\sigma})] + \sum_{I\sigma} \frac{J^I}{2} \text{Tr}[\hat{n}^{I\sigma}\hat{n}^{I-\sigma} - 2\delta_{\sigma\sigma_{\text{min}}} n^{I\sigma}]$$

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A modern interpretation of $+J$ was never concretely attempted. From Himmetoglu (2011):

> In order to calculate the Hubbard exchange parameter J, we have extended the linear response approach[23] used in the previous section and we have computed the responses of on-site magnetizations $m^I = n^{I\uparrow} - n^{I\downarrow}$ to a magnetic perturbation βm^I. Modeling the total energy of the solid with the double-counting term [either Eq. (6) or (9)], and rewriting it in terms of the on-site occupations n^I and magnetizations m^I, we can calculate the exchange parameter J^I from $\partial^2 E/(\partial m^I)^2 = -J^I/2$. The second derivative of the

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What is the analogue of piecewise linearity?

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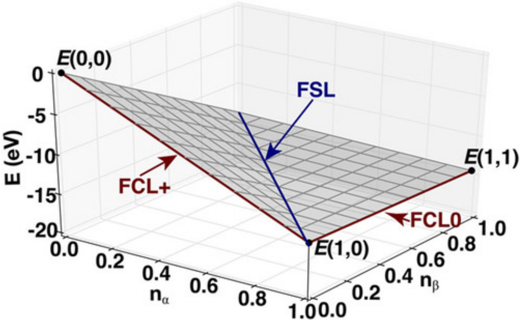
What is the analogue of piecewise linearity?

Static correlation error (SCE)

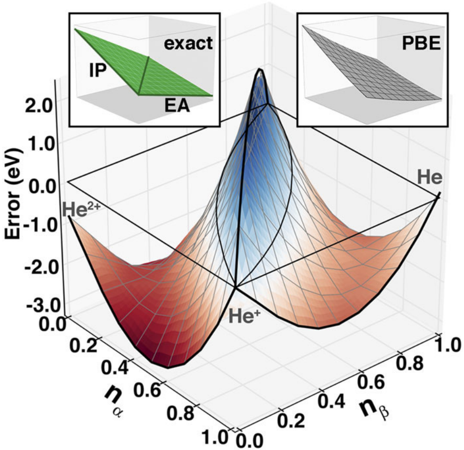
energy should be piecewise linear with respect to magnetisation

B. Himmetoglu et al. *Phys. Rev. B* 84.11 (2011), 115108

SIE and SCE in He^{x+}



the flat plane



PBE error

A. Bajaj et al. *J. Chem. Phys.* 147.19 (2017), 191101

... Does DFT + U + J correct SIE and SCE?

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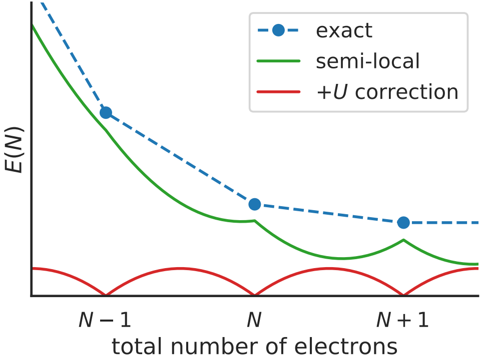
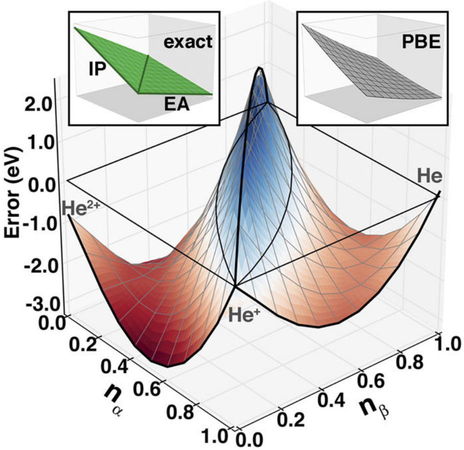


semi-local DFT + U correction = piecewise linear

... Does DFT + U + J correct SIE and SCE?



U + J correction $\overset{?}{=}$ flat plane − semi-local

The + U correction

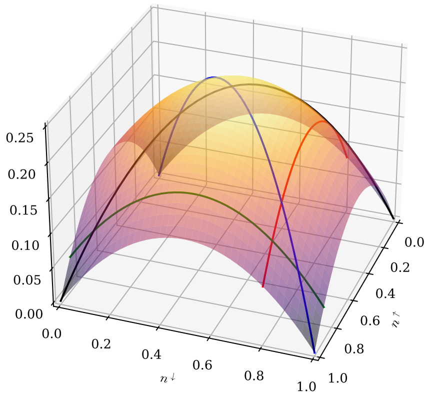


Figure: $E_U(n^\uparrow, n^\downarrow)$

$$\left.\frac{\partial^2 E_U}{\partial n^{\uparrow 2}}\right|_{n^\downarrow} = -U \qquad \text{(red)}$$

$$\left.\frac{\partial^2 E_U}{\partial n^{\downarrow 2}}\right|_{n^\uparrow} = -U \qquad \text{(green)}$$

$$\left.\frac{\partial^2 E_U}{\partial n^2}\right|_{\mu} = -\frac{U}{2} \qquad \text{(blue)}$$

$$\left.\frac{\partial^2 E_U}{\partial \mu^2}\right|_{n} = -\frac{U}{2} \qquad \text{(black)}$$

The + U correction

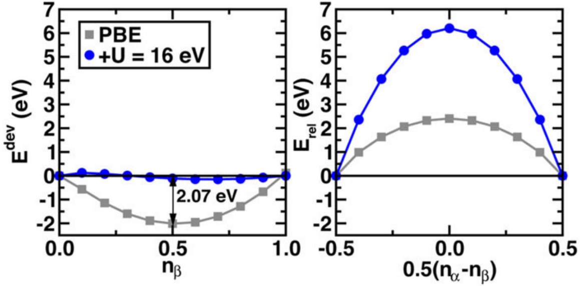


Figure: He^{x+} (He^+ to He on left; He^+ on right)

$$\left.\frac{\partial^2 E_U}{\partial n^{\uparrow 2}}\right|_{n^\downarrow} = -U \qquad \text{(red)}$$

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A. Bajaj et al. *J. Chem. Phys.* 147.19 (2017), 191101

The $+J$ correction

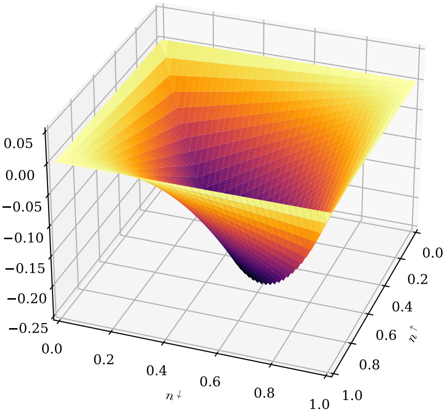

Figure: $E_J(n^\uparrow, n^\downarrow)$

$$\left.\frac{\partial^2 E_J}{\partial n^2}\right|_\mu = \frac{J}{2}$$

$$\left.\frac{\partial^2 E_J}{\partial \mu^2}\right|_n = -\frac{J}{2} \qquad \text{for } \mu \neq 0$$

$$\left.\frac{\partial^2 E_J}{\partial n^{\uparrow 2}}\right|_{n^\downarrow} = 0$$

$$\left.\frac{\partial^2 E_J}{\partial n^{\downarrow 2}}\right|_{n^\uparrow} = 0$$

Not even the right shape!

The combined correction

$U_{\text{eff}} = U - J$:

$$\left.\frac{\partial^2}{\partial n^2}\right|_{\mu} (E_{U_{\text{eff}}} + E_J) = -\frac{U - 2J}{2}$$

$$\left.\frac{\partial^2}{\partial \mu^2}\right|_{n} (E_{U_{\text{eff}}} + E_J) = -\frac{U}{2} \qquad \text{for } \mu \neq 0$$

$$\left.\frac{\partial^2}{\partial n^{\uparrow 2}}\right|_{n^{\downarrow}} (E_{U_{\text{eff}}} + E_J) = -(U - J) \qquad \text{for } \mu \neq 0$$

$$\left.\frac{\partial^2}{\partial n^{\downarrow 2}}\right|_{n^{\uparrow}} (E_{U_{\text{eff}}} + E_J) = -(U - J) \qquad \text{for } \mu \neq 0$$

$U_{\text{eff}} = U$:

$$\left.\frac{\partial^2}{\partial n^2}\right|_{\mu} (E_U + E_J) = -\frac{U - J}{2}$$

$$\left.\frac{\partial^2}{\partial \mu^2}\right|_{n} (E_U + E_J) = -\frac{U + J}{2} \qquad \text{for } \mu \neq 0$$

$$\left.\frac{\partial^2}{\partial n^{\uparrow 2}}\right|_{n^{\downarrow}} (E_U + E_J) = -U \qquad \text{for } \mu \neq 0$$

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Rethinking inter-spin corrections

$$E_U = \sum_{I\sigma mm'} \frac{U^I}{2} \left(n^{I\sigma}_{mm'} (\delta_{m'm} - n^{I\sigma}_{m'm}) \right)$$

$$E_J = \sum_{I\sigma mm'} \frac{J^I}{2} \left(n^{I\sigma}_{mm'} n^{I-\sigma}_{m'm} - 2\delta_{\sigma\sigma_{\min}} \delta_{mm'} n^{I\sigma}_{m'm} \right)$$

Observations on conventional DFT + U and DFT + U + J

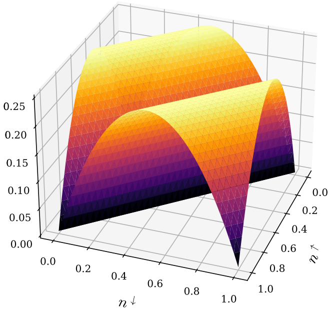
- the correction is not the right shape
- lots of inter-dependence
- (minority J term is important)

Principles for designing a new Hubbard-like correction (i.e. quadratic in $\hat{n}$)

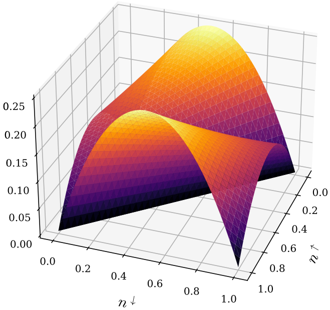
1. decouple our treatment of SIE and SCE
2. vanishing at integer occupancies
3. be continuous

Correction to SIE

$$\sum_\sigma \frac{U^\sigma}{2}\left(n^\uparrow + n^\downarrow - 1\right) \times \begin{cases} -n^\sigma & n < 1 \\ 1 - n^\sigma & n > 1 \end{cases}$$

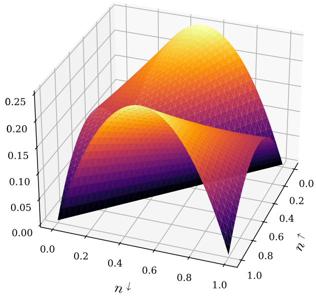


(a) $U^\uparrow = U^\downarrow$



(b) $U^\uparrow = U^\downarrow/2$

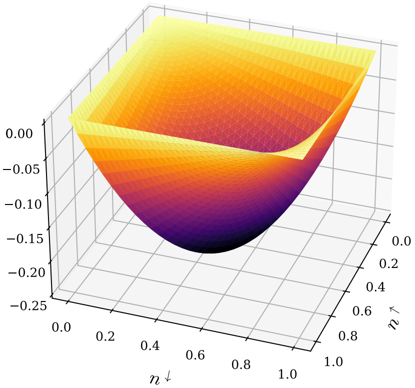
Correction to SIE

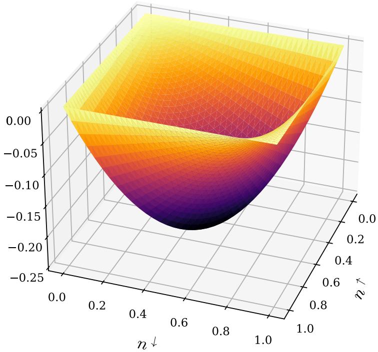


1. it is zero for integer numbers of electrons
2. the curvature with respect to n^σ is entirely controlled by U^σ, i.e.
$$\left.\frac{\partial^2 E_1}{\partial n^{\sigma 2}}\right|_{n^{-\sigma}} = -U^\sigma$$
3. the curvature with respect to μ is *untouched* by this correction
$$\left.\frac{\partial^2 E_1}{\partial \mu^2}\right|_{n} = 0$$
which would imply that this correction will selectively address SIE and not SCE
4. the curvature with respect to the total occupancy $n = n^\uparrow + n^\downarrow$ is given by the average
$$\left.\frac{\partial^2 E_1}{\partial n^2}\right|_{\mu} = -\frac{U^\uparrow + U^\downarrow}{2}$$

Correction to SCE

$$\begin{cases} -Jn^{\uparrow}n^{\downarrow} & n < 1 \\ -J(1-n^{\uparrow})(1-n^{\downarrow}) & n > 1 \end{cases}$$

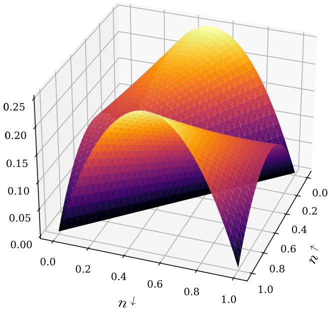




This second energy correction term possesses the following important properties:

1. it is zero for integer numbers of electrons
2. the curvature with respect to μ is controlled by the parameter J
$$\left.\frac{\partial^2 E_2}{\partial \mu^2}\right|_n = \frac{J}{2}$$
3. the curvature with respect to n^σ is zero
$$\left.\frac{\partial^2 E_2}{\partial n^{\sigma 2}}\right|_{n^{-\sigma}} = 0$$

The combined correction



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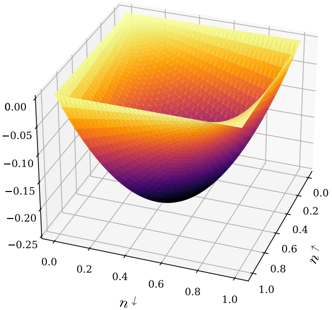


$$E_{\mathrm{BLOR}} = \begin{cases} \sum_{\sigma mm'} \frac{U^\sigma}{2} n^\sigma_{mm\sigma}\delta_{mm'} - \frac{U^\sigma}{2} n^\sigma_{mm'} n^\sigma_{m'm} - \frac{U^\sigma+2J}{2} n^\sigma_{mm'} n^{\bar\sigma}_{m'm}, & N \leqslant 2l+1 \\ \sum_{\sigma mm'} \left(U^\sigma + \frac{U^{\bar\sigma}}{2} + 2J\right) n^\sigma_{mm'}\delta_{mm'} - \frac{U^\sigma}{2} n^\sigma_{mm'} n^\sigma_{m'm} - \frac{U^\sigma+2J}{2} n^\sigma_{mm'} n^{\bar\sigma}_{m'm} - \frac{U^\sigma+2J}{2(2l+1)}, & N > 2l+1 \end{cases}$$

BLOR

Andrew Burgess

Edward Linscott

David O’Regan

What's in a name?

BLOR

Andrew **B**urgess

Edward **L**inscott

David **O**'**R**egan

BLOR

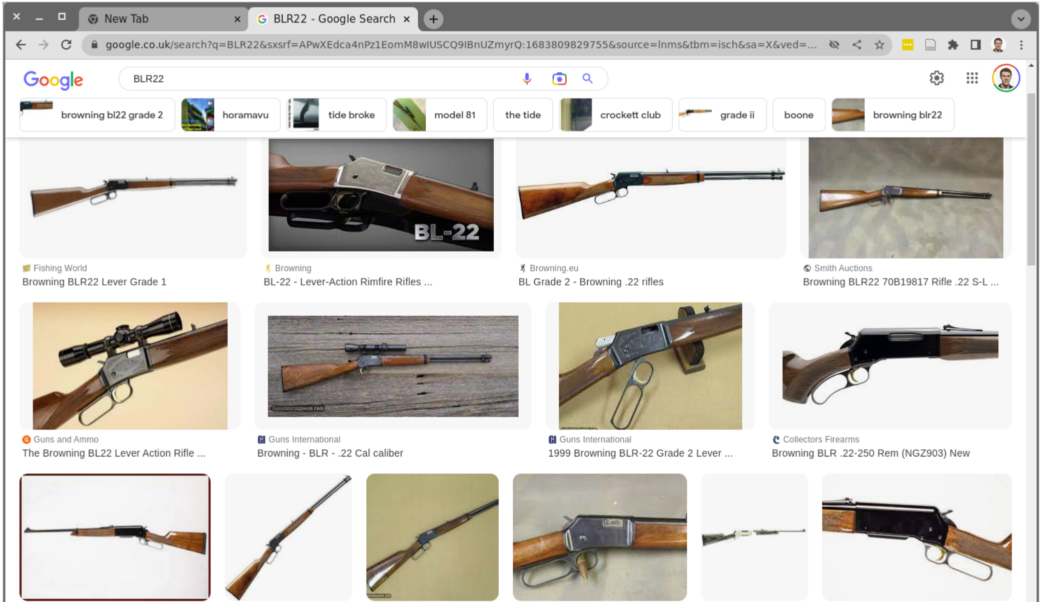
Andrew **B**urgess

Edward **L**inscott

David **O'R**egan

Initially was going to be "BLR22" but...

What's in a name?



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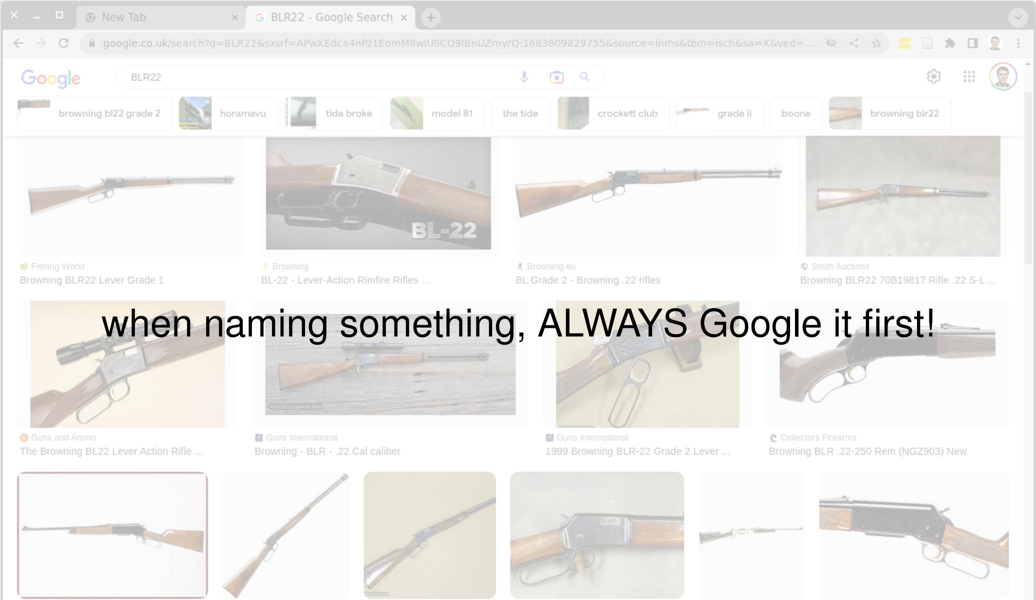


when naming something, ALWAYS Google it first!

Determining U^σ and J via spin-resolved LR

Scalar (conventional) approach:

$$\chi_{IJ} = \frac{dn^I}{dv^J_{\text{ext}}} \qquad \hat{v}^J_{\text{ext}} = v_{\text{ext}} \hat{P}^J$$

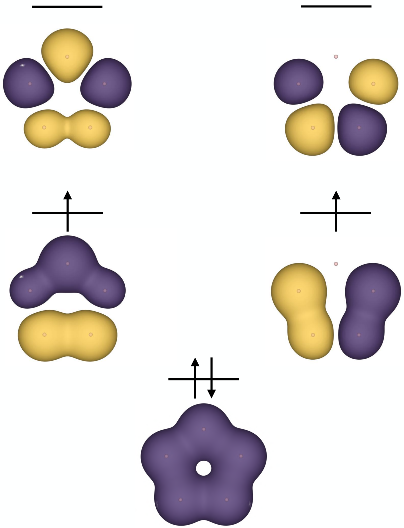
Spin-resolved approach[1]:

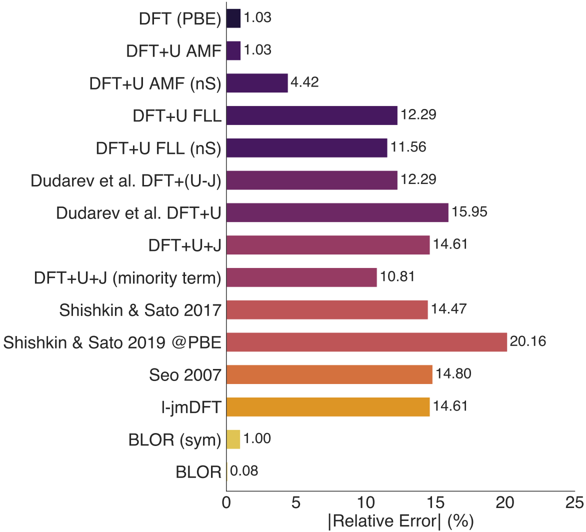
$$\chi_{IJ\sigma\sigma'} = \frac{dn^{I\sigma}}{dv^{J\sigma'}_{\text{ext}}} \qquad \hat{v}^{J\sigma}_{\text{ext}} = \delta_{\sigma\sigma'} v^{\sigma'}_{\text{ext}} \hat{P}^J$$

Allows us to construct perturbations while holding variables constant without a headache e.g. $\frac{d}{dn^\uparrow}\Big|_{n^\downarrow}$

[1] E. B. Linscott et al. *Phys. Rev. B* 98.23 (2018), 235157.

Does BLOR work? Stretched H^{5+}





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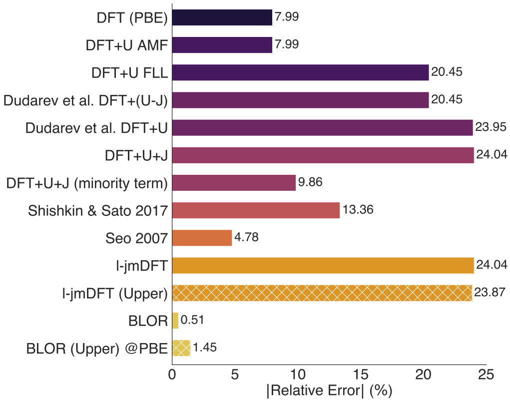
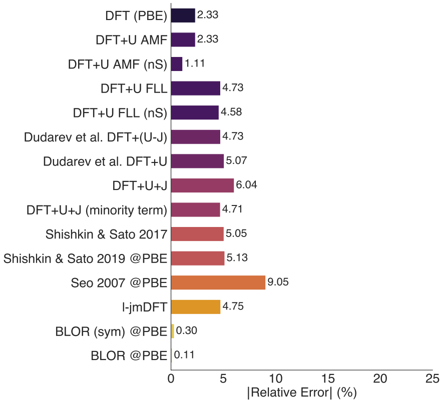
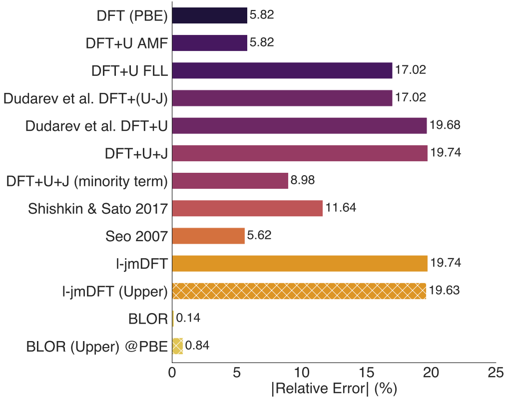


stretched H_2

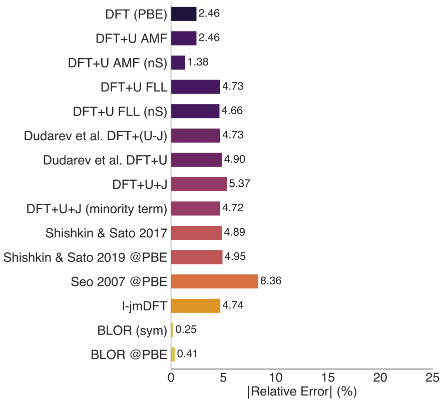


stretched He_2^+

Does BLOR work?



stretched Li_2



stretched Be_2^+

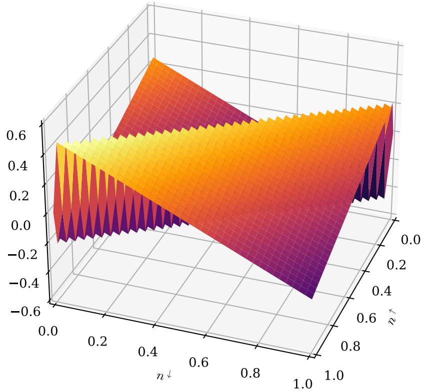
Conclusions

- we can get excellent total energies when we take the mandate of the flat plane seriously
- BUT still many important details to be worked out...

"Potential" issues...

The resulting potential from the SIE energy correction is given by $\hat{v}_1^\sigma = v_1^\sigma(n_i^\uparrow, n_i^\downarrow)|i\rangle\langle i|$ where

$$v_1^\sigma(n^\uparrow, n^\downarrow) = \begin{cases} U^\sigma\left(\frac{1}{2} - n^\sigma\right) + (1 - n^{-\sigma})\frac{U^\uparrow + U^\downarrow}{2} & n > 1 \\ U^\sigma\left(\frac{1}{2} - n^\sigma\right) - n^{-\sigma}\frac{U^\uparrow + U^\downarrow}{2} & n < 1 \end{cases}$$



→ issues for single-particle energies?

Numerically, can either adopt some smoothing OR Hund's rule comes to the rescue

Other issues include local vs global curvature

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paper available at PRB 107, L121115 (2023) | slides available at elinscott (and the wiki!)