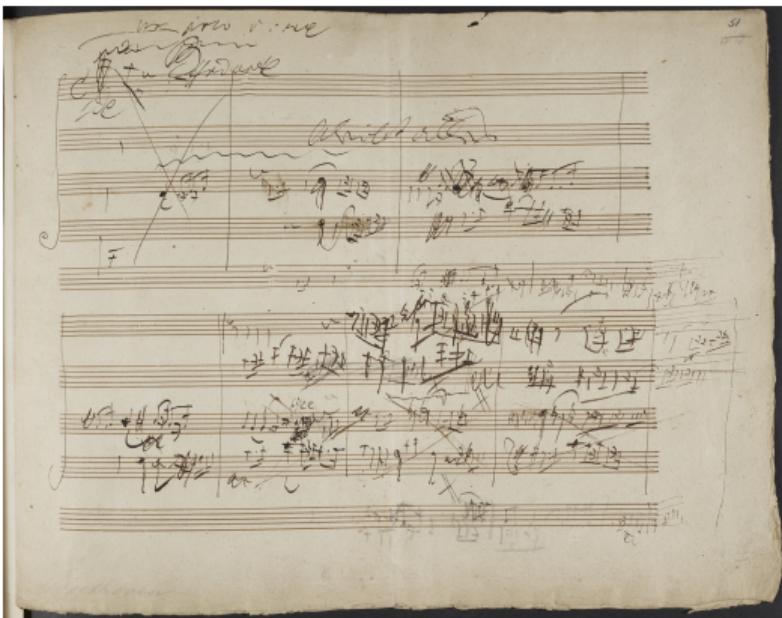


# Beethoven's late string quartets

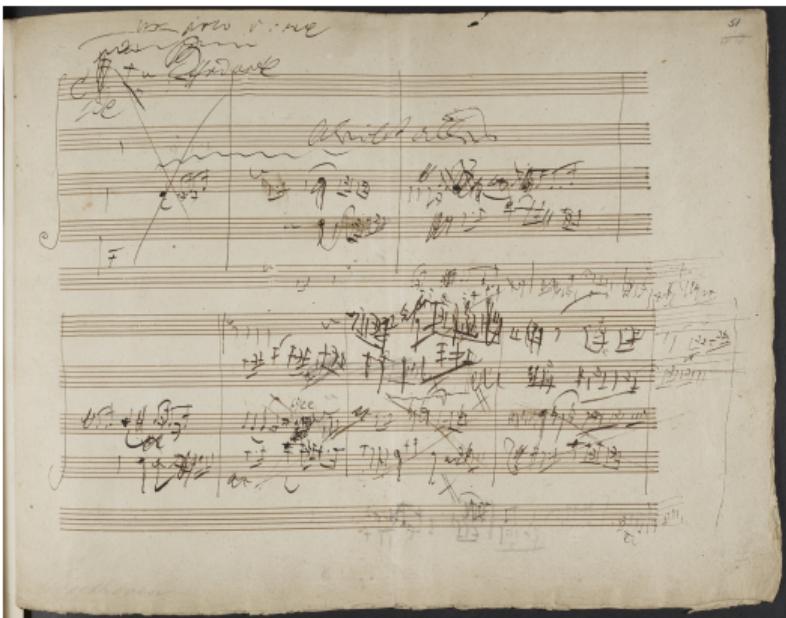
String Quartet No. 14 - Adagio ma non troppo e molto espressivo



[click here for video](#)

# Beethoven's late string quartets

String Quartet No. 14 - Adagio ma non troppo e molto espressivo

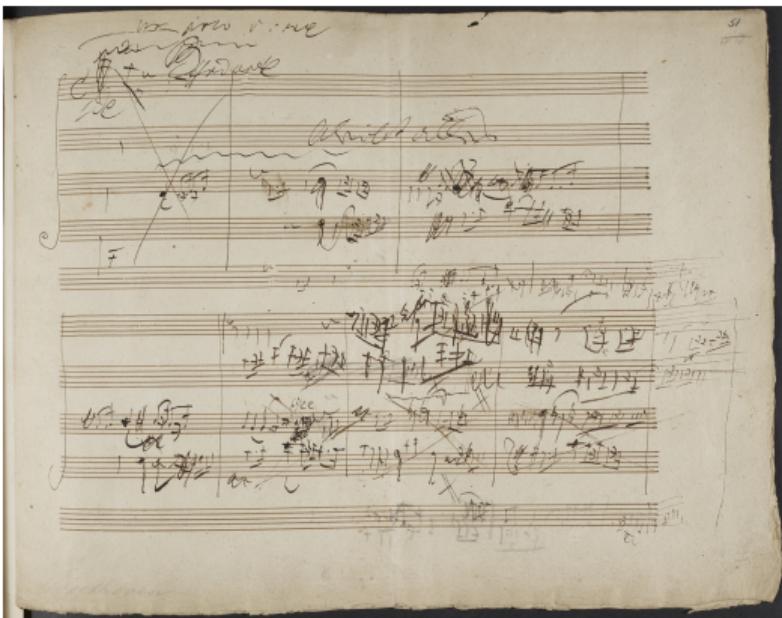


[click here for video](#)

“indecipherable, uncorrected horrors” – Spohr

# Beethoven's late string quartets

String Quartet No. 14 - Adagio ma non troppo e molto espressivo



[click here for video](#)

“indecipherable, uncorrected horrors” – Spohr  
“After this, what is left for us to write?” – Schubert

## THEOS

THEORY AND SIMULATION  
OF MATERIALS

### THEOS

- People
- Research
- Mentoring
- Seminars
- Publications
- Conferences
- Quasimore
- Openings
- Teaching
- Tutorials
- Projects
- Links
- News
  
- Contacts and directions

### MARVEL

- MARVEL Website
- What is MARVEL?
- MARVEL Lectures
- MARVEL Seminars
- Openings

## 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](#).

[view](#) [edit](#) [history](#) [attach](#) [print](#) [logout](#)

# Black-box Koopmans band structures

or: getting lost down a rabbit hole of pseudopotential generation

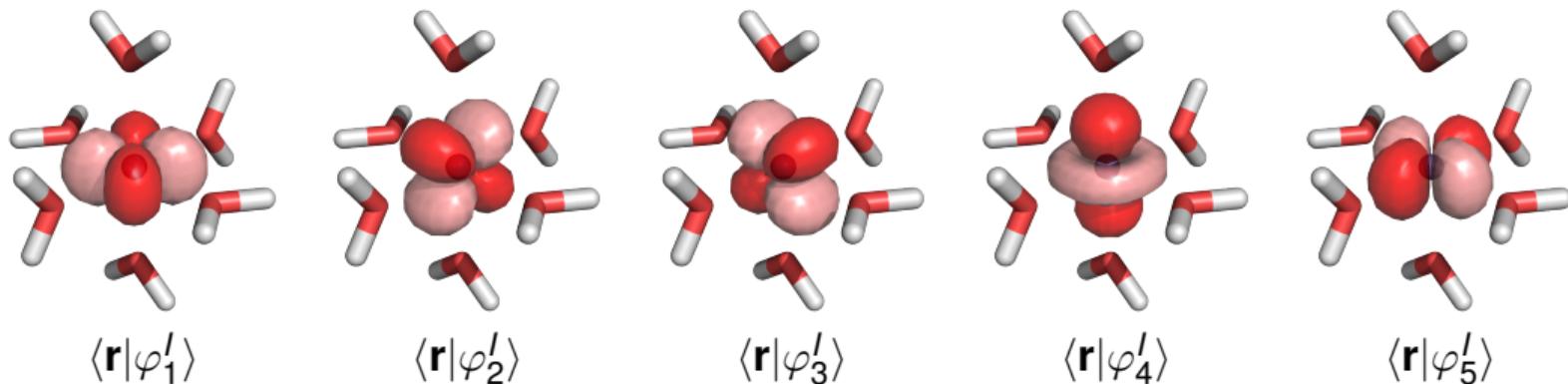


$$E_U = \sum_{l\sigma} \frac{U^l}{2} \text{Tr}[\hat{n}^{l\sigma}(1 - \hat{n}^{l\sigma})]$$

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

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$$\hat{V}_U = \sum_{l\sigma ij} U^l |\varphi_i^l\rangle \left( \frac{1}{2} - n_{ij}^{l\sigma} \right) \langle\varphi_j^l|$$

... 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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Start with an electron-electron interaction term...

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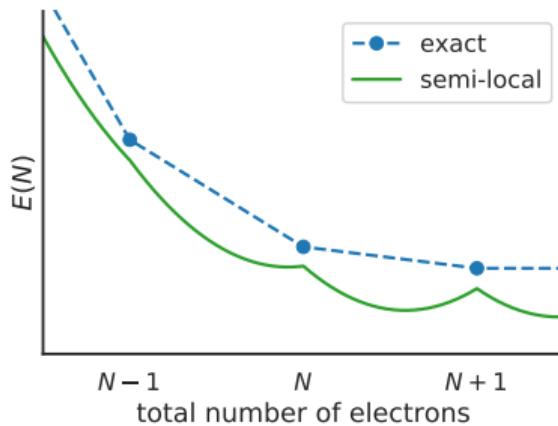
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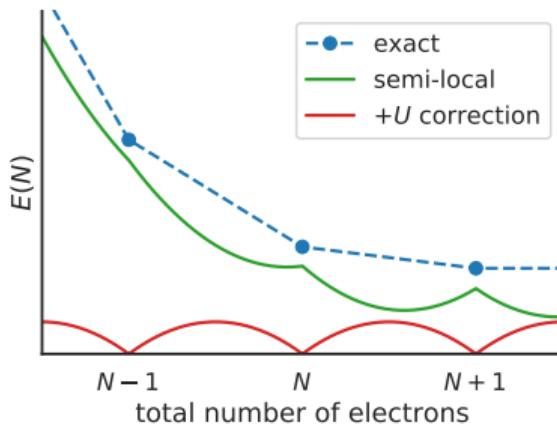
... and finish with a corrective term to DFT

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



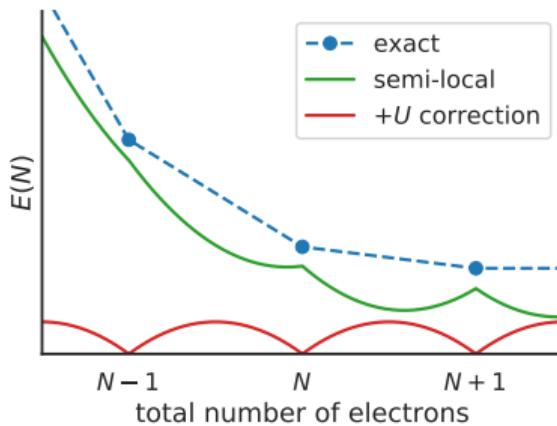
A modern (post hoc) interpretation: in a basis such that  $\hat{n}^{l\sigma} = \text{diag}(\lambda_1^{l\sigma}, \dots, \lambda_n^{l\sigma})$

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We can calculate  $U$  via linear response  $\rightarrow$  “self-correcting” DFT

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What about DFT+ $U$  +  $J$ ?

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

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<sup>23</sup> used in the previous section and we have computed the responses of on-site magnetizations  $m^J = n^{J\uparrow} - n^{J\downarrow}$  to a magnetic perturbation  $\beta m^I$ . 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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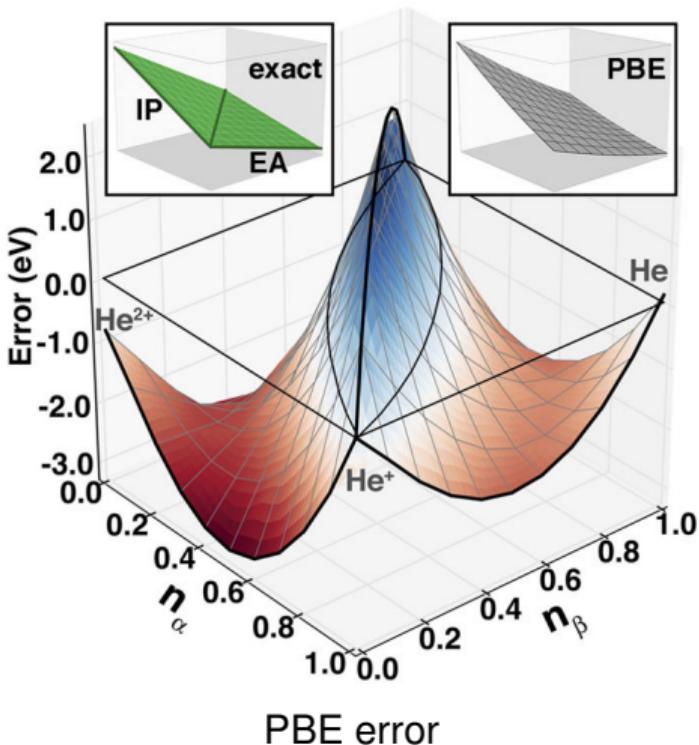
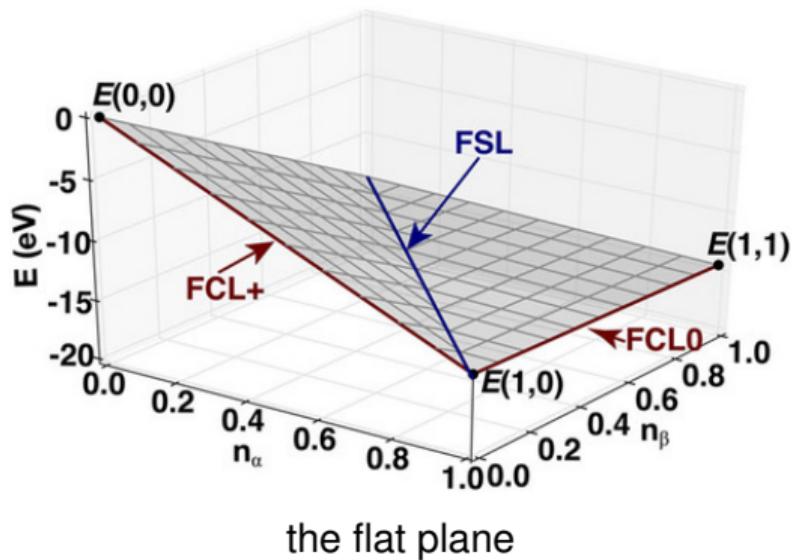
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What is the analogue of piecewise linearity?

### Static correlation error (SCE)

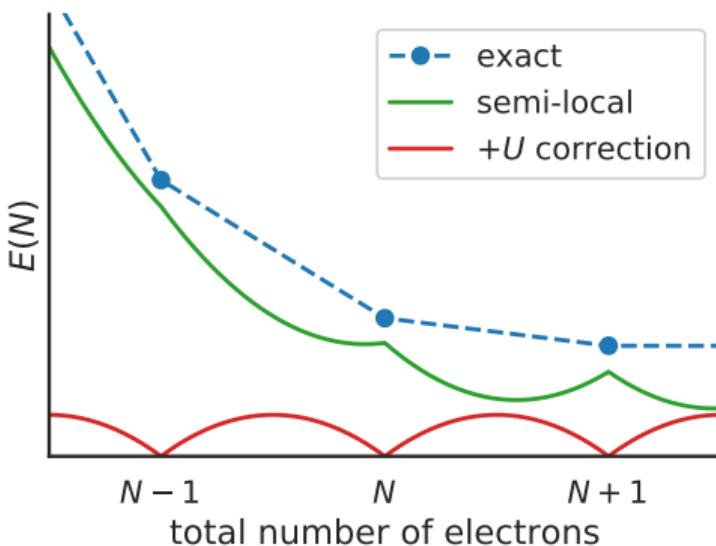
energy should be piecewise linear with respect to magnetisation

# SIE and SCE in $\text{He}^{x+}$



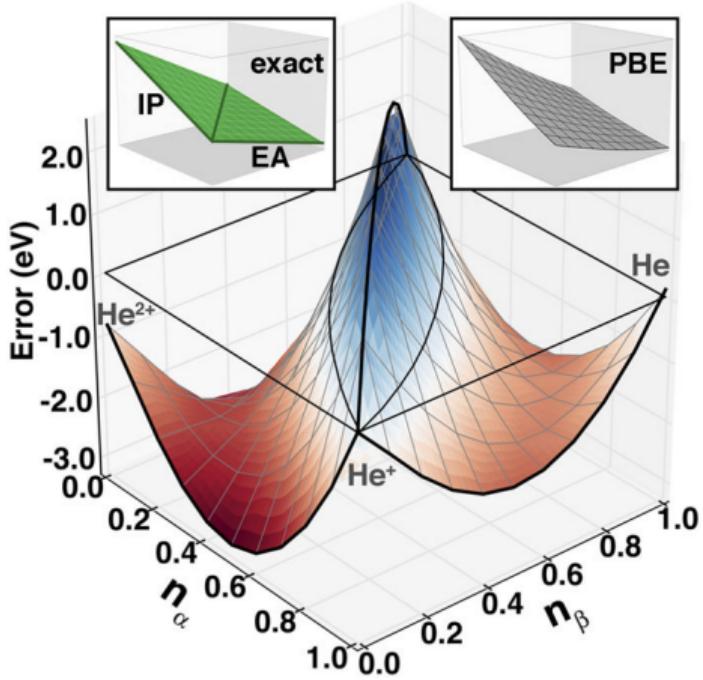
... Does DFT +  $U + J$  correct SIE and SCE?

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



semi-local DFT + U correction = piecewise linear

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



$U + J$  correction  $\stackrel{?}{=}$  flat plane – semi-local

# The $+ U$ correction

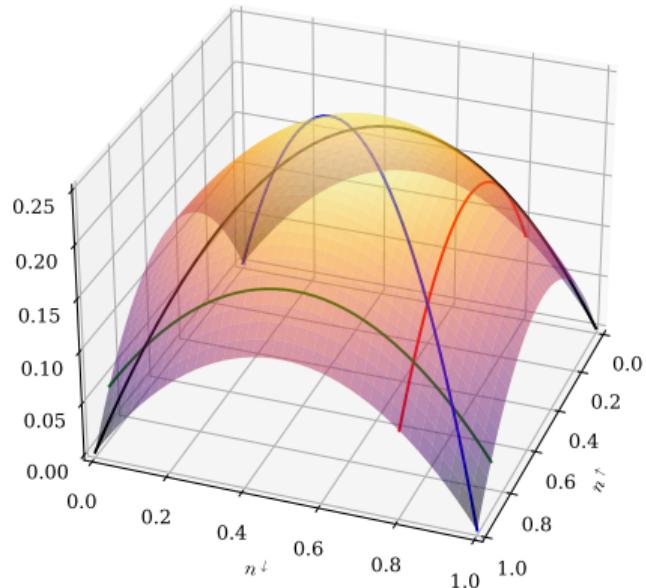


Figure:  $E_U(n^+, n^-)$

$$\frac{\partial^2 E_U}{\partial n^{\downarrow 2}} \Big|_{n^{\downarrow}} = -U \quad (\text{red})$$

$$\frac{\partial^2 E_U}{\partial n^{\uparrow 2}} \Big|_{n^{\uparrow}} = -U \quad (\text{green})$$

$$\frac{\partial^2 E_U}{\partial n^2} \Big|_{\mu} = -\frac{U}{2} \quad (\text{blue})$$

$$\frac{\partial^2 E_U}{\partial \mu^2} \Big|_n = -\frac{U}{2} \quad (\text{black})$$

# The $+U$ correction

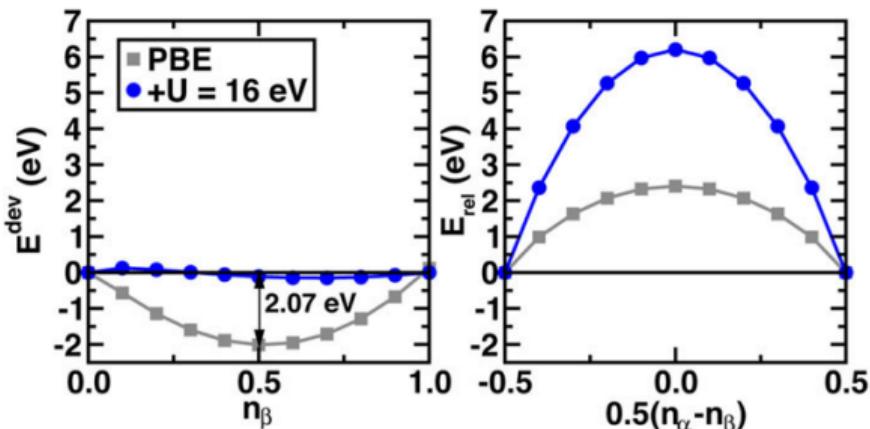


Figure:  $\text{He}^{x+}$  ( $\text{He}^+$  to  $\text{He}$  on left;  $\text{He}^+$  on right)

$$\begin{aligned}\frac{\partial^2 E_U}{\partial n_{\beta}^2} \Big|_{n_{\beta}} &= -U && \text{(red)} \\ \frac{\partial^2 E_U}{\partial n_{\alpha}^2} \Big|_{n_{\alpha}} &= -U && \text{(green)} \\ \frac{\partial^2 E_U}{\partial n^2} \Big|_{\mu} &= -\frac{U}{2} && \text{(blue)} \\ \frac{\partial^2 E_U}{\partial \mu^2} \Big|_n &= -\frac{U}{2} && \text{(black)}\end{aligned}$$

# The $+ J$ correction

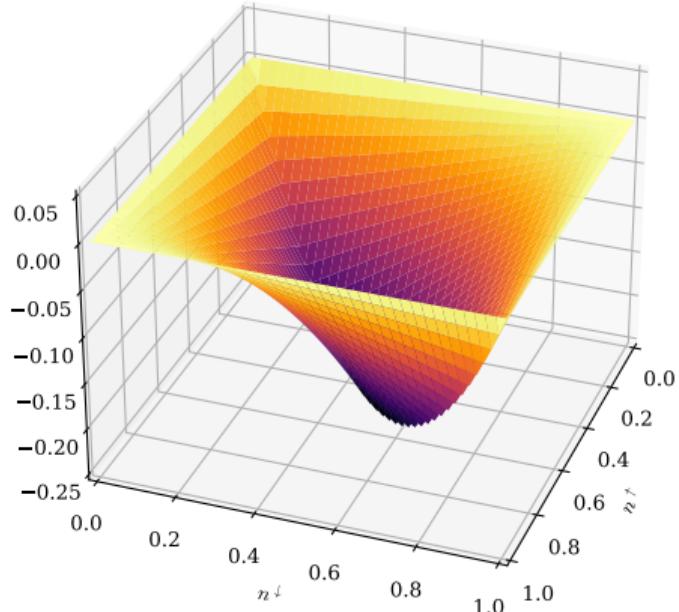


Figure:  $E_J(n^{\uparrow}, n^{\downarrow})$

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

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

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

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

Not even the right shape!

# The combined correction

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

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

$$\frac{\partial^2}{\partial \mu^2} \Big|_n (E_{U_{\text{eff}}} + E_J) = -\frac{U}{2} \quad \text{for } \mu \neq 0$$

$$\frac{\partial^2}{\partial n_{\uparrow}^2} \Big|_{n_{\downarrow}} (E_{U_{\text{eff}}} + E_J) = -(U - J) \quad \text{for } \mu \neq 0$$

$$\frac{\partial^2}{\partial n_{\downarrow}^2} \Big|_{n_{\uparrow}} (E_{U_{\text{eff}}} + E_J) = -(U - J) \quad \text{for } \mu \neq 0$$

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

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

$$\frac{\partial^2}{\partial \mu^2} \Big|_n (E_U + E_J) = -\frac{U + J}{2} \quad \text{for } \mu \neq 0$$

$$\frac{\partial^2}{\partial n_{\uparrow}^2} \Big|_{n_{\downarrow}} (E_U + E_J) = -U \quad \text{for } \mu \neq 0$$

$$\frac{\partial^2}{\partial n_{\downarrow}^2} \Big|_{n_{\uparrow}} (E_U + E_J) = -U \quad \text{for } \mu \neq 0$$

$$E_U = \sum_{l\sigma mm'} \frac{U^l}{2} \left( n_{mm'}^{l\sigma} (\delta_{m'm} - n_{m'm}^{l\sigma}) \right)$$
$$E_J = \sum_{l\sigma mm'} \frac{J^l}{2} \left( n_{mm'}^{l\sigma} n_{m'm}^{l-\sigma} - 2\delta_{\sigma\sigma_{\min}} \delta_{mm'} n_{m'm}^{l\sigma} \right)$$

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

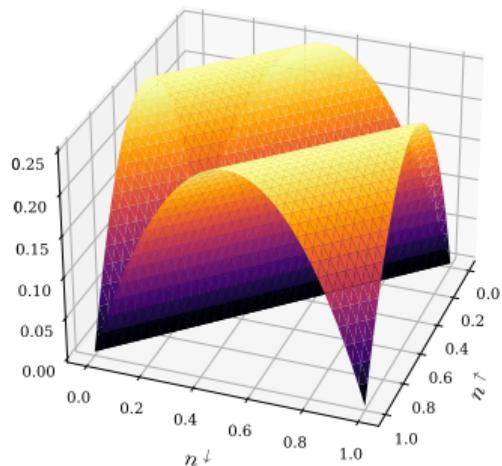
- the correction is not the right shape
- lots of inter-dependence
- (minority  $J$  term is important)

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

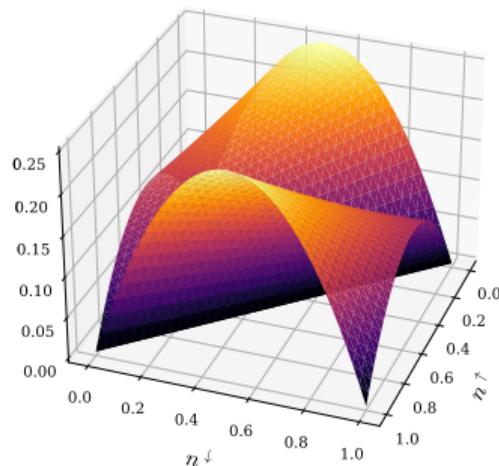
1. decouple our treatment of SIE and SCE
2. vanishing at integer occupancies
3. be continuous

# Correction to SIE

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

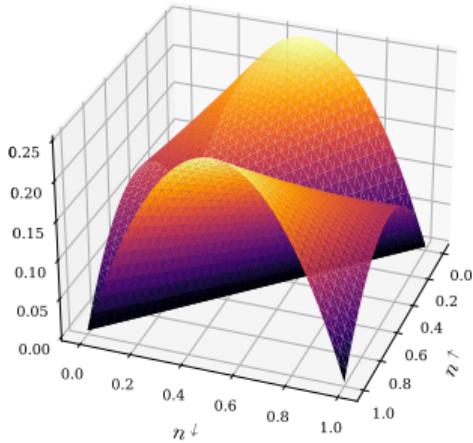


(a)  $U^{\uparrow} = U^{\downarrow}$



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

# Correction to SIE



1. it is zero for integer numbers of electrons
2. the curvature with respect to  $n^\sigma$  is entirely controlled by  $U^\sigma$ , i.e.

$$\frac{\partial^2 E_1}{\partial n^{\sigma 2}} \Big|_{n=\sigma} = -U^\sigma$$

3. the curvature with respect to  $\mu$  is *untouched* by this correction

$$\frac{\partial^2 E_1}{\partial \mu^2} \Big|_n = 0$$

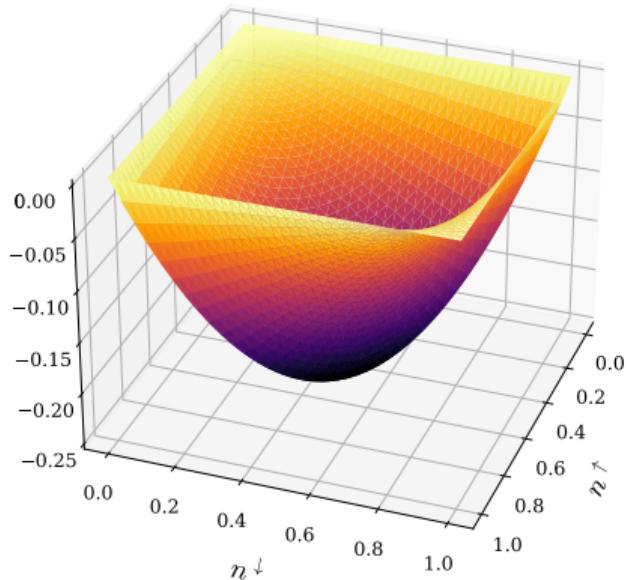
which would imply that this correction will selectively address SIE and not SCE

4. the curvature with respect to the total occupancy  $n = n^{\uparrow} + n^{\downarrow}$  is given by the average

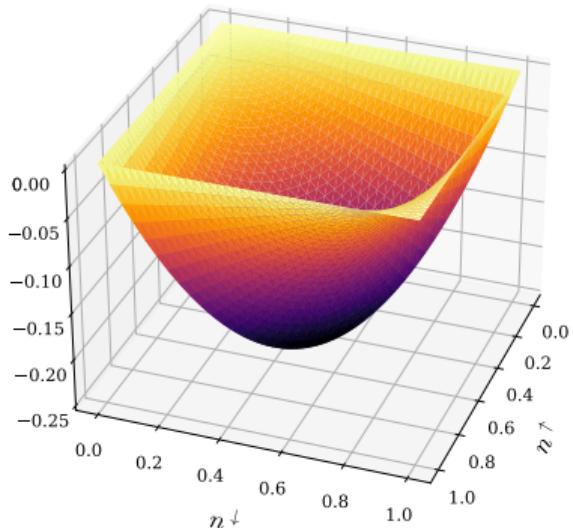
$$\frac{\partial^2 E_1}{\partial n^2} \Big|_\mu = -\frac{U^\uparrow + U^\downarrow}{2}$$

# Correction to SCE

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



# Correction to SCE



This second energy correction term possesses the following important properties:

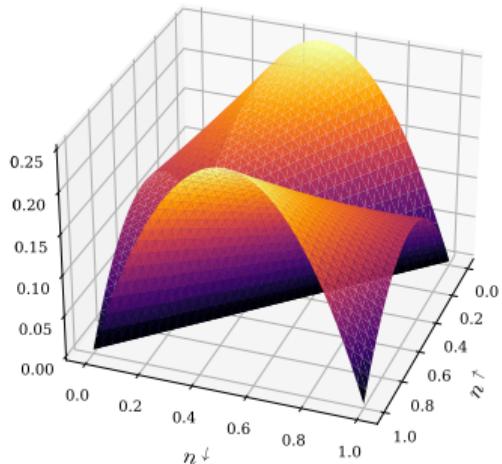
1. it is zero for integer numbers of electrons
2. the curvature with respect to  $\mu$  is controlled by the parameter  $J$

$$\left. \frac{\partial^2 E_2}{\partial \mu^2} \right|_n = \frac{J}{2}$$

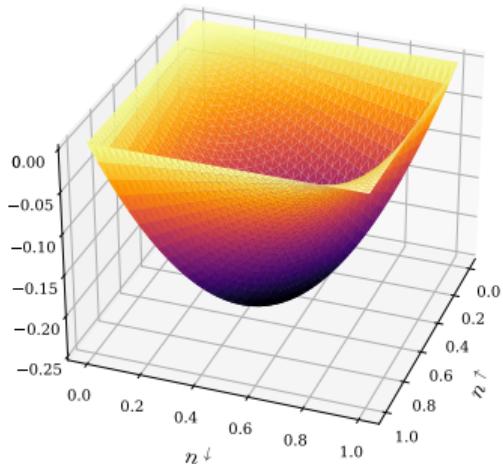
3. the curvature with respect to  $n^\sigma$  is zero

$$\left. \frac{\partial^2 E_2}{\partial n^\sigma{}^2} \right|_{n^{-\sigma}} = 0$$

# The combined correction



+



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

## BLOR



Andrew Burgess



Edward Linscott



David O'Regan

## BLOR



Andrew **Burgess**



Edward **Linscott**



David **O'Regan**

## BLOR



Andrew **Burgess**



Edward **Linscott**



David **O'Regan**

Initially was going to be “BLR22” but...

# What's in a name?

Google BLR22

browning bl22 grade 2 horamavu tide broke model 81 the tide crockett club grade ii boone browning blr22

Fishing World Browning BLR22 Lever Grade 1

Browning BL-22 - Lever-Action Rimfire Rifles ...

Browning.eu BL Grade 2 - Browning .22 rifles

Smith Auctions Browning BLR22 70B19817 Rifle .22 S-L ...

Guns and Ammo The Browning BL22 Lever Action Rifle ...

Guns International Browning - BLR - .22 Cal caliber

Guns International 1999 Browning BLR-22 Grade 2 Lever ...

Collectors Firearms Browning BLR .22-250 Rem (NGZ903) New

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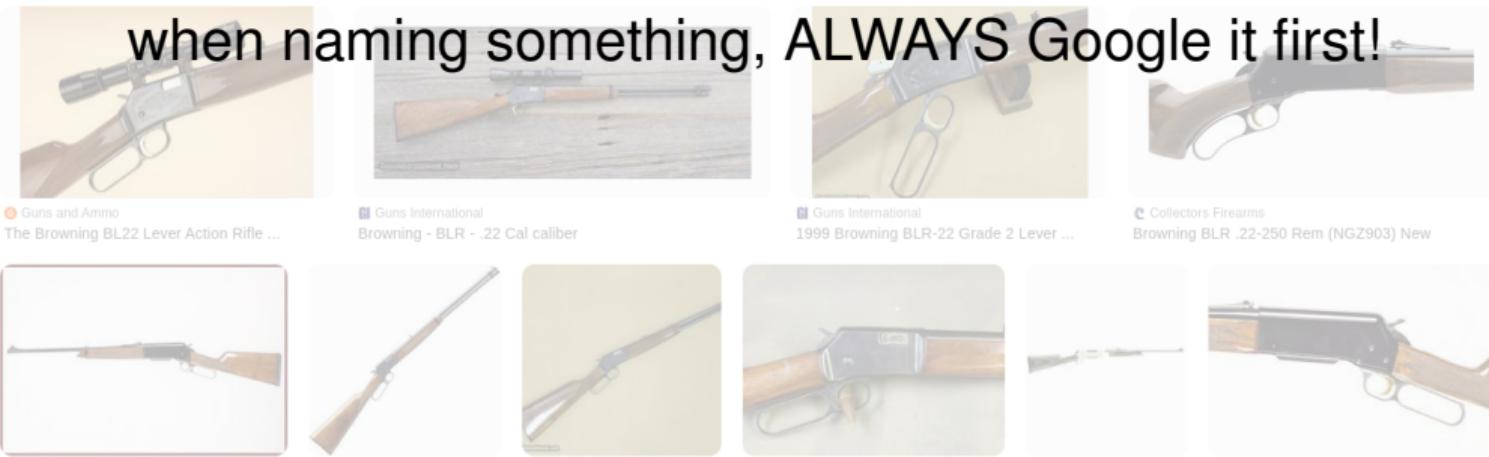
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Smith Auctions Browning BLR22 70B19817 Rifle .22 S-L ...

when naming something, ALWAYS Google it first!



Scalar (conventional) approach:

$$\chi_{IJ} = \frac{dn^I}{dv_{\text{ext}}^J} \quad \hat{v}_{\text{ext}}^J = v_{\text{ext}} \hat{P}^J$$

Spin-resolved approach<sup>1</sup>:

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

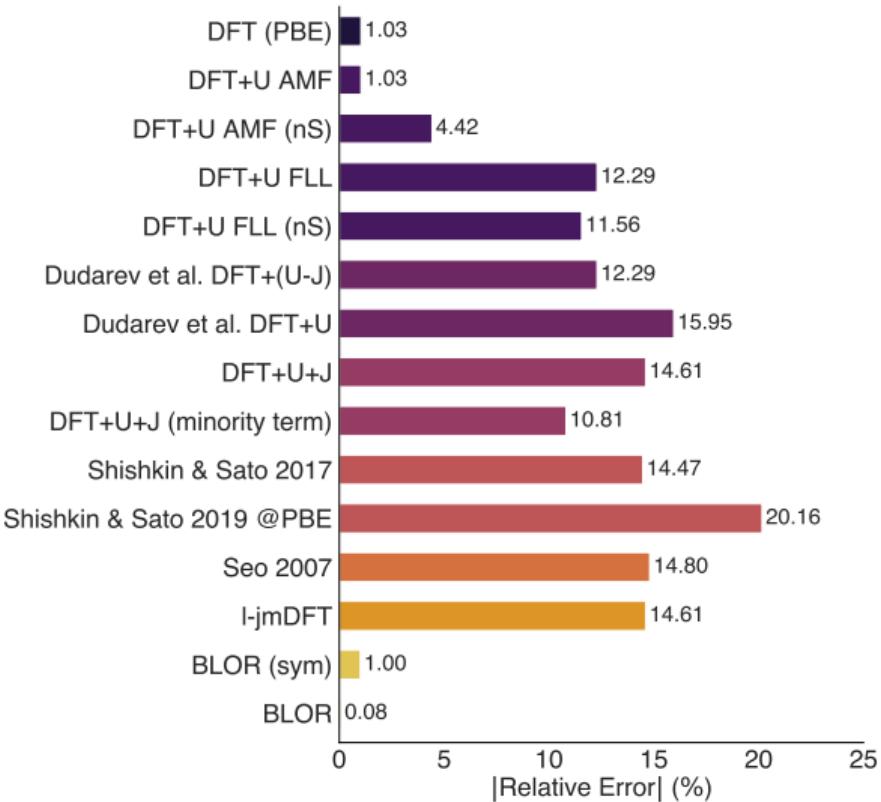
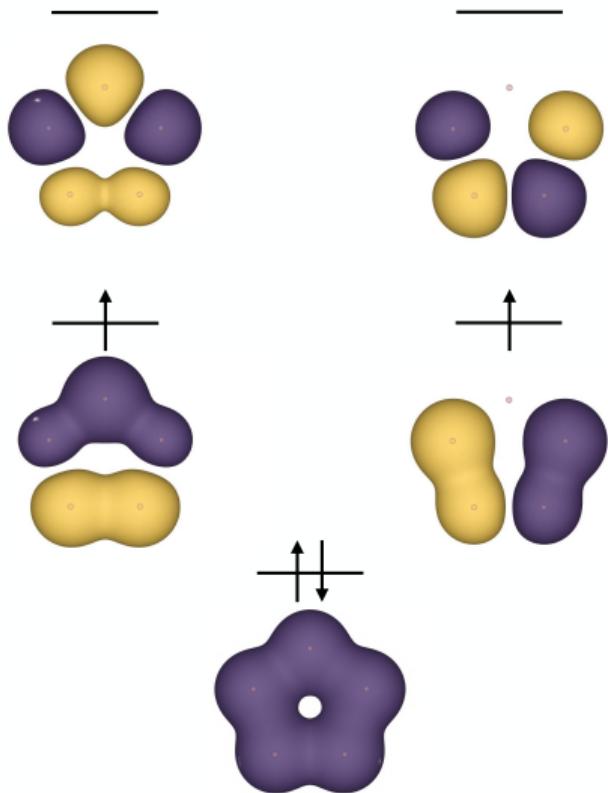
Allows us to construct perturbations while holding variables constant without a headache

e.g.  $\frac{d}{dn^\uparrow} \Big|_{n^\downarrow}$

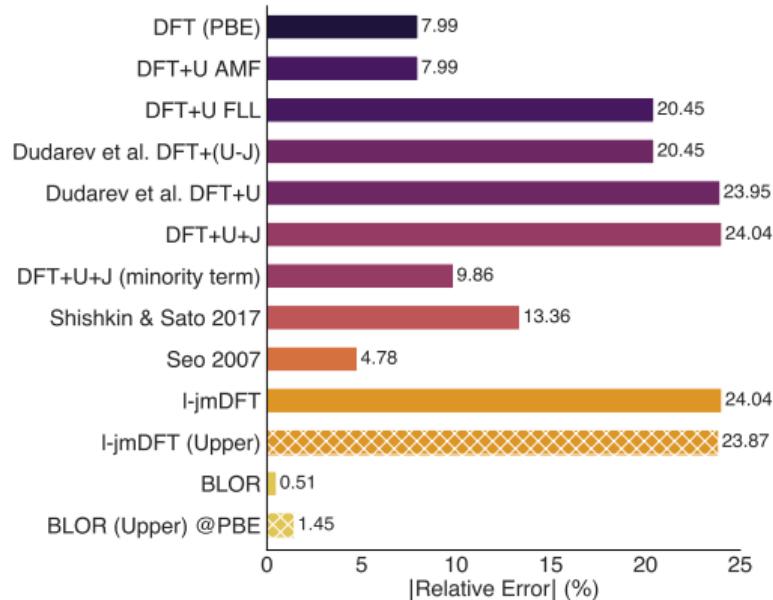
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<sup>1</sup> E. B. Linscott et al. *Phys. Rev. B* 98.23 (2018), 235157.

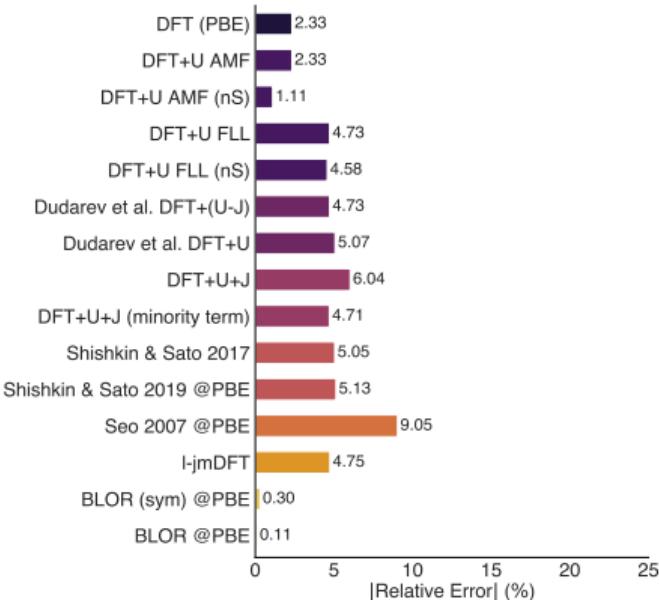
# Does BLOR work? Stretched H<sup>5+</sup>



# Does BLOR work?

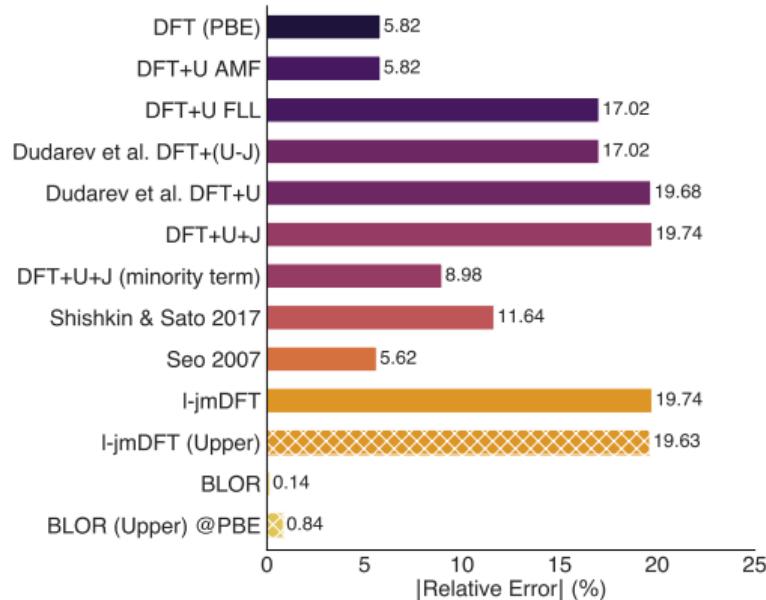


stretched  $\text{H}_2$

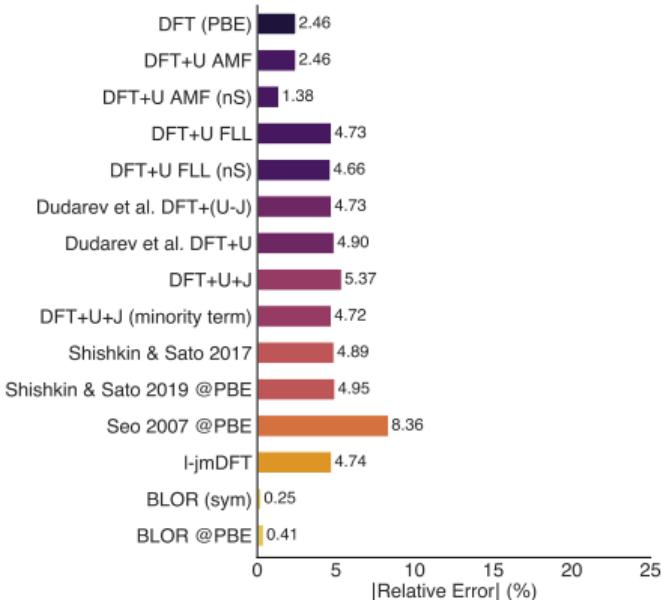


stretched  $\text{He}_2^+$

# Does BLOR work?



stretched  $\text{Li}_2$



stretched  $\text{Be}_2^+$

# 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...

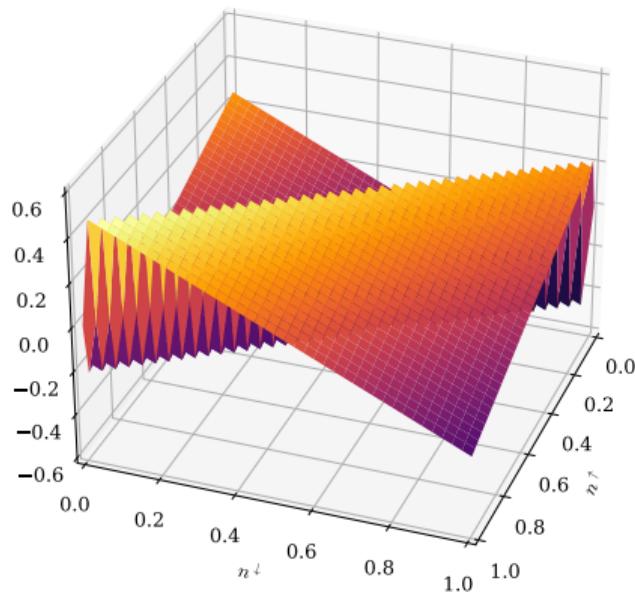
The resulting potential from the SIE energy correction is given by  $\hat{v}_1^\sigma = v_1^\sigma(n_i^\uparrow, n_i^\downarrow)|i\rangle\langle i|$  where

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

→ 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



# Acknowledgements



Andrew Burgess



David O'Regan

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