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.

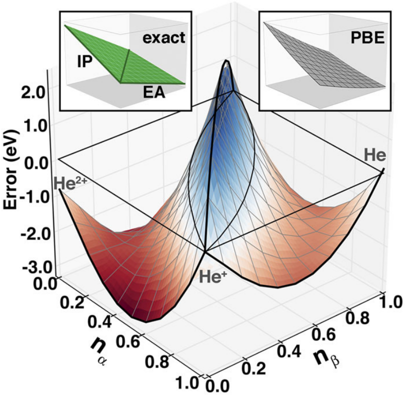
BLOR

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

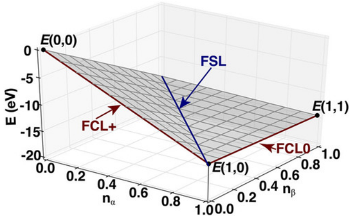
Edward Linscott | EPFL | THEOS Group Meeting | 6 June 2023

$$E_U = \sum_{l\sigma mm'} \frac{U^l}{2} \left(n^{l\sigma}_{mm'} (\delta_{m'm} - n^{l\sigma}_{m'm}) \right) \tag{0.1}$$

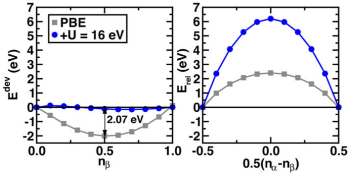
$$E_J = \sum_{l\sigma mm'} \frac{J^l}{2} \left(n^{l\sigma}_{mm'} n^{l-\sigma}_{m'm} - 2\delta_{\sigma\sigma_{\min}} \delta_{mm'} n^{l\sigma}_{m'm} \right) \tag{0.2}$$

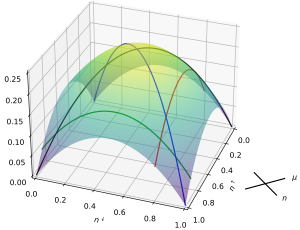


PBE error

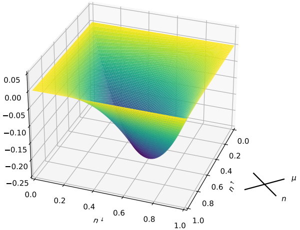


the flat plane





the $+U$ correction



the $+J$ correction

The + U correction

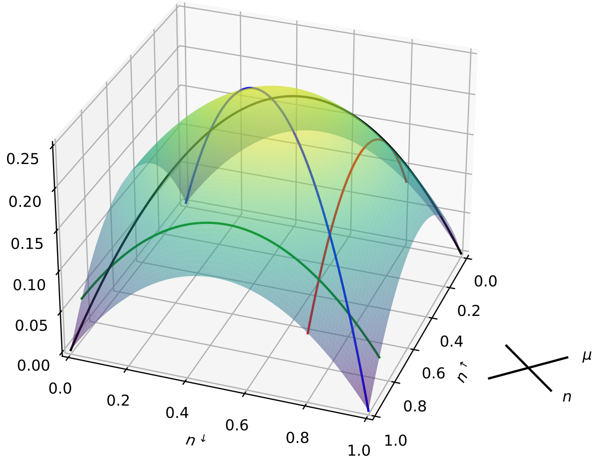


Figure: $E_U(n^\uparrow, n^\downarrow)$

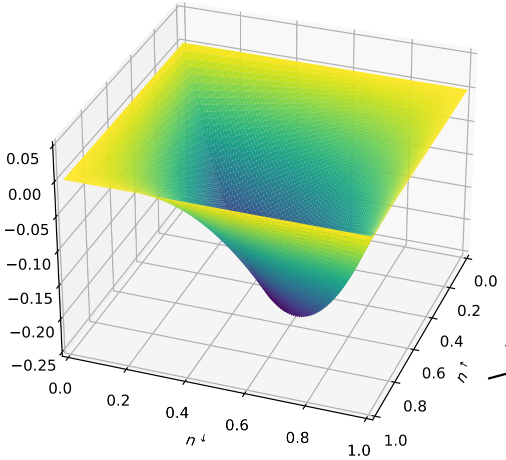
$$\left.\frac{\partial^2 E_U}{\partial n^{\uparrow 2}}\right|_{n^\downarrow} = -U \quad \text{(red)} \tag{0.3a}$$

$$\left.\frac{\partial^2 E_U}{\partial n^{\downarrow 2}}\right|_{n^\uparrow} = -U \quad \text{(green)} \tag{0.3b}$$

$$\left.\frac{\partial^2 E_U}{\partial n^2}\right|_{\mu} = -\frac{U}{2} \quad \text{(blue)} \tag{0.3c}$$

$$\left.\frac{\partial^2 E_U}{\partial \mu^2}\right|_{n} = -\frac{U}{2} \quad \text{(black)} \tag{0.3d}$$

The $+J$ correction



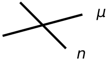


Figure: $E_J(n^{\uparrow}, n^{\downarrow})$

$$\left.\frac{\partial^2 E_J}{\partial n^2}\right|_{\mu} = \frac{J}{2} \tag{0.4a}$$

$$\left.\frac{\partial^2 E_J}{\partial \mu^2}\right|_{n} = -\frac{J}{2} \quad \text{for } \mu \neq 0 \tag{0.4b}$$

$$\left.\frac{\partial^2 E_J}{\partial n^{\uparrow 2}}\right|_{n^{\downarrow}} = 0 \tag{0.4c}$$

$$\left.\frac{\partial^2 E_J}{\partial n^{\downarrow 2}}\right|_{n^{\uparrow}} = 0 \tag{0.4d}$$

The combined correction

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

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

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

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

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

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

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

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

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

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

Rethinking inter-spin corrections

$$E_U = \sum_{l\sigma mm'} \frac{U^l}{2} \left(n^{l\sigma}_{mm'} (\delta_{m'm} - n^{l\sigma}_{m'm}) \right) \tag{0.7}$$

$$E_J = \sum_{l\sigma mm'} \frac{J^l}{2} \left(n^{l\sigma}_{mm'} n^{l-\sigma}_{m'm} - 2\delta_{\sigma\sigma_{\min}} \delta_{mm'} n^{l\sigma}_{m'm} \right) \tag{0.8}$$

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

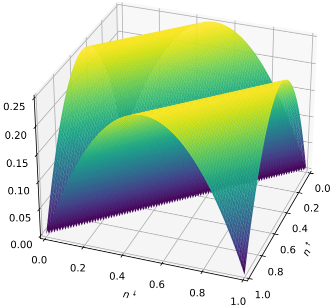
- the correction is not the right shape
- lots of inter-dependence
- U^l not $U^l_{\text{eff}} = U^l - J^l$
- minority J term is important

Principles for designing a new correction

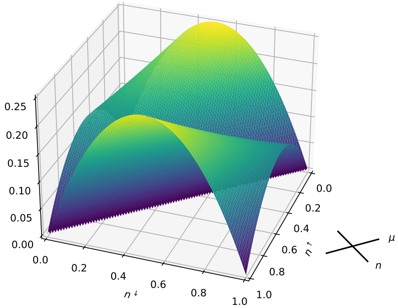
1. vanishing at integer occupancies
2. decouple our treatment of SIE and SCE
3. different U correction for each spin channel

Correction to SIE

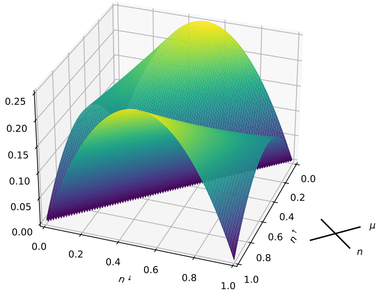
$$E_1(\{U^\sigma\},\{n^\sigma\}) = \sum_\sigma \frac{U^\sigma}{2}\left(n^\uparrow + n^\downarrow - 1\right) \times \begin{cases} -n^\sigma & n < 1 \\ 1 - n^\sigma & n > 1 \end{cases} \tag{0.9}$$



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



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

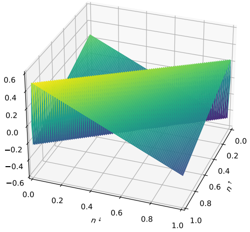


1. it is zero for integer numbers of electrons
2. the curvature with respect to n^σ is entirely controlled by U^σ, i.e.
$$\left.\frac{\partial^2 E_1}{\partial n^{\sigma 2}}\right|_{n^{-\sigma}} = -U^\sigma \tag{0.10}$$
3. the curvature with respect to μ is *untouched* by this correction
$$\left.\frac{\partial^2 E_1}{\partial \mu^2}\right|_{n} = 0 \tag{0.11}$$
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
$$\left.\frac{\partial^2 E_1}{\partial n^2}\right|_{\mu} = -\frac{U^\uparrow + U^\downarrow}{2} \tag{0.12}$$

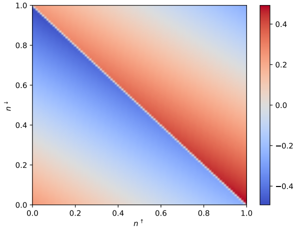
Correction to SIE

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

$$v_1^\sigma(n^\uparrow, n^\downarrow) = \begin{cases} U^\sigma\left(\frac{1}{2} - n^\sigma\right) + \left(1 - n^{-\sigma}\right)\frac{U^\uparrow + U^\downarrow}{2} & n > 1 \\ U^\sigma\left(\frac{1}{2} - n^\sigma\right) - n^{-\sigma}\frac{U^\uparrow + U^\downarrow}{2} & n < 1 \end{cases} \tag{0.13}$$



(a)



(b)

Figure: my proposed potential correction $v_1^\uparrow(\{U^\sigma\}, \{n^\sigma\})$ for addressing SIE, with $U^\downarrow = 2U^\uparrow$

Correction to SCE

$$E_2(K, \{n^\sigma\}) = \begin{cases} -Kn^\uparrow n^\downarrow & n < 1 \\ -K(1 - n^\uparrow)(1 - n^\downarrow) & n > 1 \end{cases} \tag{0.14}$$

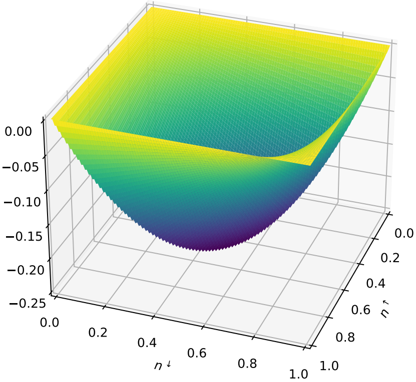
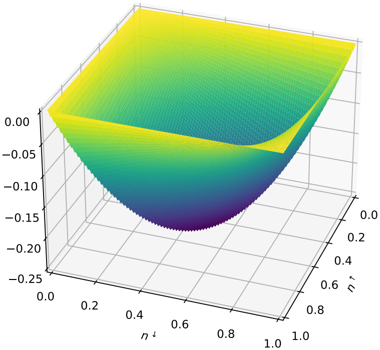


Figure: My proposed second correction, $E_2(K, \{n^\sigma\})$ for addressing SCE, with $K = 1$



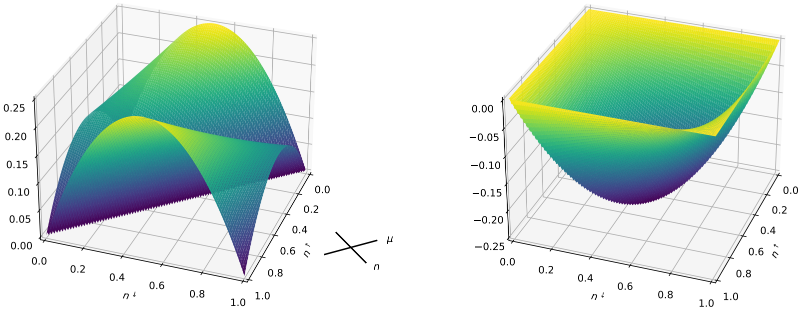
This second energy correction term possesses the following important properties:

1. it is zero for integer numbers of electrons (the four corners of fig. 10)
2. the curvature with respect to μ is controlled by the parameter K
$$\left.\frac{\partial^2 E_2}{\partial \mu^2}\right|_n = \frac{K}{2} \tag{0.15}$$
3. the curvature with respect to n^σ is zero
$$\left.\frac{\partial^2 E_2}{\partial n^{\sigma 2}}\right|_{n^{-\sigma}} = 0 \tag{0.16}$$

However, by fulfilling these three properties it necessarily possesses one undesirable property: namely, the curvature with respect to the total occupancy $n = n^\uparrow + n^\downarrow$ is given by

$$\left.\frac{\partial^2 E_2}{\partial n^2}\right|_\mu = -\frac{K}{2} \tag{0.17}$$

The combined correction



(a) E_1 with $U^{\uparrow} = U^{\downarrow}/2$

(b) E_2

$$v^{\sigma}(n^{\uparrow}, n^{\downarrow}) = \begin{cases} U^{\sigma}\left(\frac{1}{2} - n^{\sigma}\right) + (1 - n^{-\sigma})\left(\frac{U^{\uparrow}+U^{\downarrow}}{2} + K\right) & n > 1 \\ U^{\sigma}\left(\frac{1}{2} - n^{\sigma}\right) - n^{-\sigma}\left(\frac{U^{\uparrow}+U^{\downarrow}}{2} + K\right) & n < 1 \end{cases} \tag{0.18}$$

Determining U^σ and K via spin-resolved LR

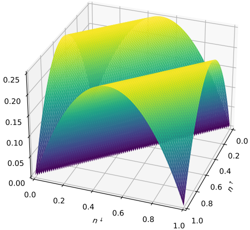
$$\frac{\partial^2}{\partial n^{\sigma 2}} (E_1 + E_2)\bigg|_{n^{-\sigma}} = -U^\sigma \tag{0.19}$$

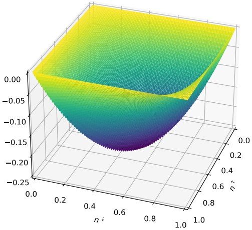
and thus it follows that we should set $U^\sigma = U^{\sigma\sigma}$. Meanwhile, the mixed derivatives

$$\frac{\partial}{\partial n^\sigma}\left[\frac{\partial}{\partial n^{-\sigma}} (E_1 + E_2)\bigg|_{n^\sigma}\right]\bigg|_{n^{-\sigma}} = -\frac{U^\uparrow + U^\downarrow + K}{2} \tag{0.20}$$

and thus by equating the LHS with $-\frac{1}{2}(U^{\uparrow\downarrow} + U^{\downarrow\uparrow})$ it follows that
$K = -U^{\uparrow\uparrow} + U^{\uparrow\downarrow} + U^{\downarrow\uparrow} - U^{\downarrow\downarrow}$

My new functional





$$E_1(\{U^\sigma\},\{n^\sigma\}) = \sum_\sigma \frac{U^\sigma}{2}\left(n^\uparrow + n^\downarrow - 1\right) \times \begin{cases} -n^\sigma & n < 1 \\ 1 - n^\sigma & n > 1 \end{cases} \tag{0.21}$$

$$E_2(K,\{n^\sigma\}) = \begin{cases} -Kn^\uparrow n^\downarrow & n < 1 \\ -K(1-n^\uparrow)(1-n^\downarrow) & n > 1 \end{cases} \tag{0.22}$$

$$v^\sigma(n^\uparrow, n^\downarrow) = \begin{cases} U^\sigma\left(\frac{1}{2} - n^\sigma\right) + (1 - n^{-\sigma})\left(\frac{U^\uparrow + U^\downarrow}{2} + K\right) & n > 1 \\ U^\sigma\left(\frac{1}{2} - n^\sigma\right) - n^{-\sigma}\left(\frac{U^\uparrow + U^\downarrow}{2} + K\right) & n < 1 \end{cases} \tag{0.23}$$

Open questions:

- does this fix total energies?
- is the discontinuity at $n = 1$ a problem?
- how best to generalise to multiple orbitals?
- what is the effect of orbital relaxation?

Acknowledgements

Andrew Burgess

David O'Regan

paper available at PRB 107, L121115 (2023) | slides available at github/elinscott

SPARE SLIDES

Spare slide

Edward Linscott
EPFL