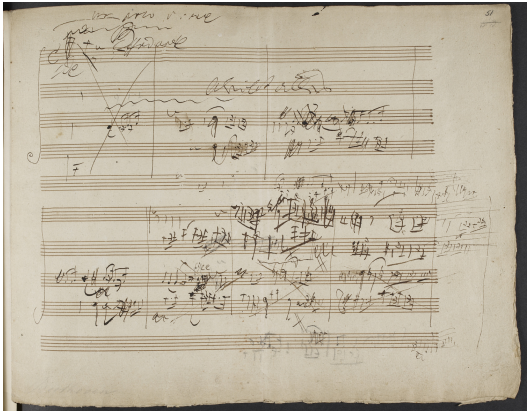
String Quartet No. 14 - Adagio ma non troppo e molto espressivo



click here for video

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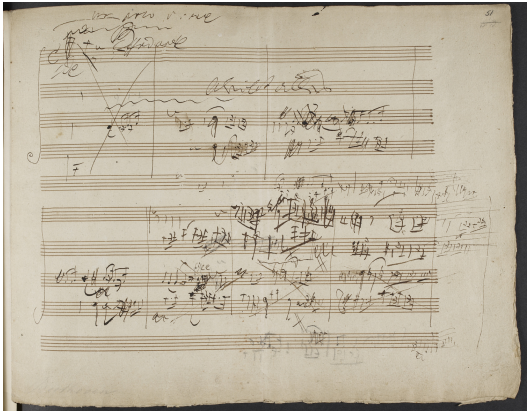

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"indecipherable, uncorrected horrors" – Spohr

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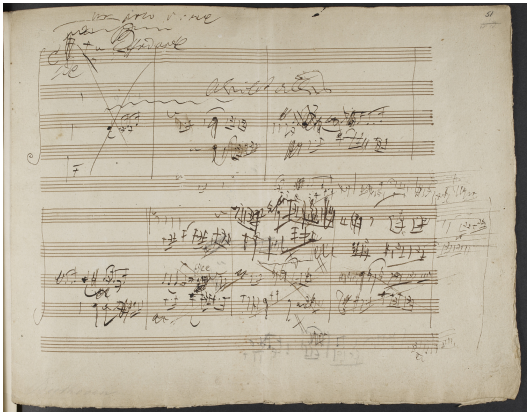

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"indecipherable, uncorrected horrors" – Spohr
"After this, what is left for us to write?" – Schubert

Towards black-box Koopmans band structures

or: getting lost down a pseudopotential-generation rabbit hole

Edward Linscott | PSI | THEOS Group Meeting | 11 April 2024 |

Swiss National Science Foundation
MARVEL

Outline

- a quick recap of Koopmans functionals
- automated Wannierisation and in the context of Koopmans functionals
- generating better PAOs for automated Wannierisation
- how to make this framework systematic and accessible

A quick recap of Koopmans functionals

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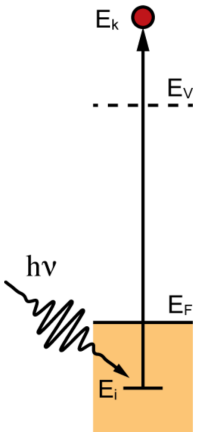
How can we calculate the energies of charged excitations? Why does DFT fail?



R. Costantini et al. “Exciton Dynamics in Molecular Heterojunctions”. PhD thesis. Universita degli Studi di Trieste, 2020

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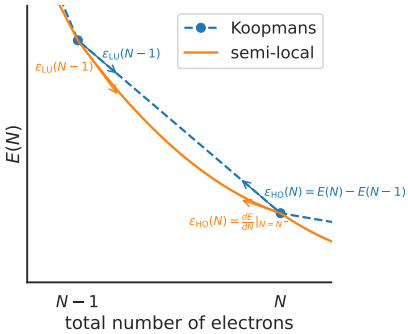
For the exact Green's function, we have poles that correspond to total energy differences

$$\varepsilon_i = \begin{cases} E(N) - E_i(N-1) & i \in \text{occ} \\ E_i(N+1) - E(N) & i \in \text{emp} \end{cases}$$



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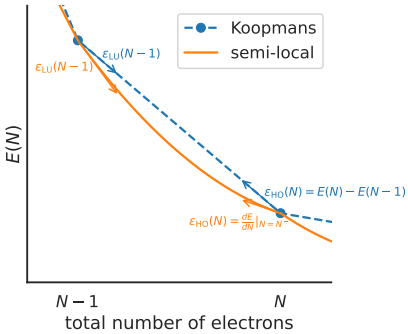
For DFT, this condition is *not* satisfied in general



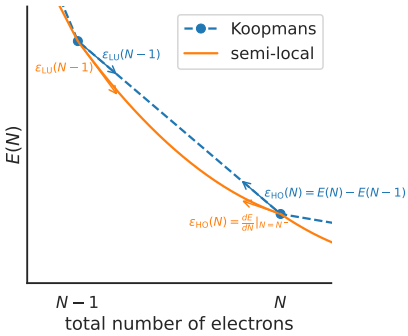
A quick recap of Koopmans functionals

Core idea: for every orbital i their energy

$$\varepsilon_i^{\text{Koopmans}} = \langle \varphi_i | H | \varphi_i \rangle = \partial E_{\text{Koopmans}} / \partial f_i$$

ought to be...

- independent of its own occupation f_i
- equal to the corresponding total energy difference $E_i(N-1) - E(N)$



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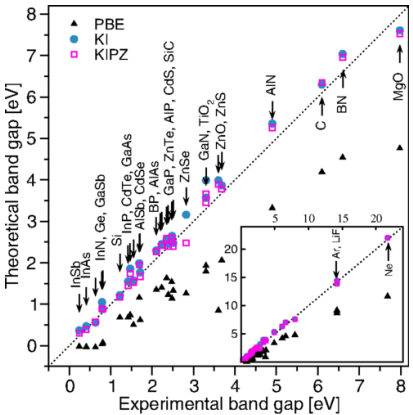
- is orbital-density-dependent $\rightarrow$ localised orbitals

A quick recap of Koopmans functionals



Mean absolute error (eV) across prototypical semiconductors and insulators

	PBE	G_0W_0	KI	KIPZ	QSG$\tilde{W}$
E_{gap}	2.54	0.56	0.27	0.22	0.18
IP	1.09	0.39	0.19	0.21	0.49

A quick recap of Koopmans functionals

	PBE	G_0W_0[1]	scG$\tilde{W}$[2]	KI@[PBE,MLWFs]	KIPZ@PBE	exp[3]
E_g	0.49	1.06	1.14	1.16	1.15	1.17
$\Gamma_{1v} \to \Gamma_{25'v}$	11.97	12.04		11.97	12.09	12.5 $\pm$0.6
$X_{1v} \to \Gamma_{25'v}$	7.82			7.82		7.75
$X_{4v} \to \Gamma_{25'v}$	2.85	2.99		2.85	2.86	2.90
$L_{2'v} \to \Gamma_{25'v}$	9.63	9.79		9.63	9.74	9.3 $\pm$0.4
$L_{1v} \to \Gamma_{25'v}$	6.98	7.18		6.98	7.04	6.8 $\pm$0.2
$L_{3'v} \to \Gamma_{25'v}$	1.19	1.27		1.19		1.2 $\pm$0.2
$\Gamma_{25'v} \to \Gamma_{15c}$	2.48	3.29		3.17	3.20	3.35$\pm$0.01
$\Gamma_{25'v} \to \Gamma_{2'c}$	3.28	4.02		3.95	3.95	4.15$\pm$0.05
$\Gamma_{25'v} \to X_{1c}$	0.62	1.38		1.28	1.31	1.13
$\Gamma_{25'v} \to L_{1c}$	1.45	2.21		2.12	2.13	2.04$\pm$0.06
$\Gamma_{25'v} \to L_{3c}$	3.24	4.18		3.91	3.94	3.9 $\pm$0.1
MSE	0.35	0.02		0.01	0.03	
MAE	0.44	0.21		0.14	0.17	

[1] M. Shishkin et al. *Phys. Rev. Lett.* 99.24 (2007), 246403 for E_g and M. S. Hybertsen et al. *Phys. Rev. B* 34.8 (1986), 5390 for the transitions;

[2] M. Shishkin et al. *Phys. Rev. B* 75.23 (2007), 235102.

[3] O. Madelung. *Semiconductors*. 3rd ed. Berlin: Springer-Verlag, 2004.

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All implemented in Koopmans

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What still stands in our way? Take the example of silicon:

A quick recap of Koopmans functionals

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```

Automated Wannierisation

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One step still very manual: Wannierisation
Can we automate it?

L. A. Agapito et al. *Phys. Rev. B* 88.16 (2013), 165127
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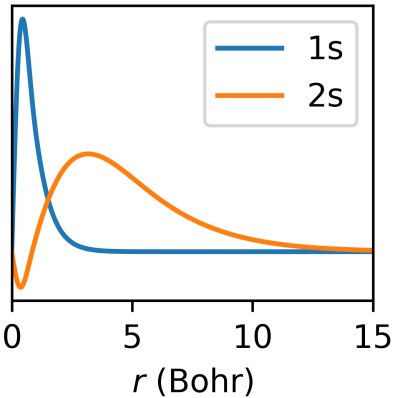

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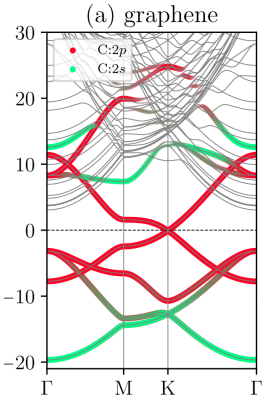

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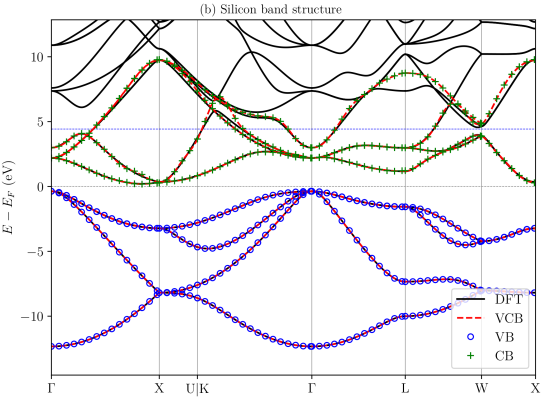
- use a parallel transport algorithm to separate the occupied and empty manifolds



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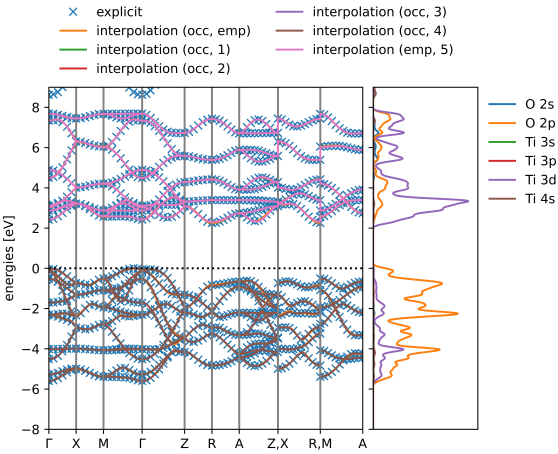

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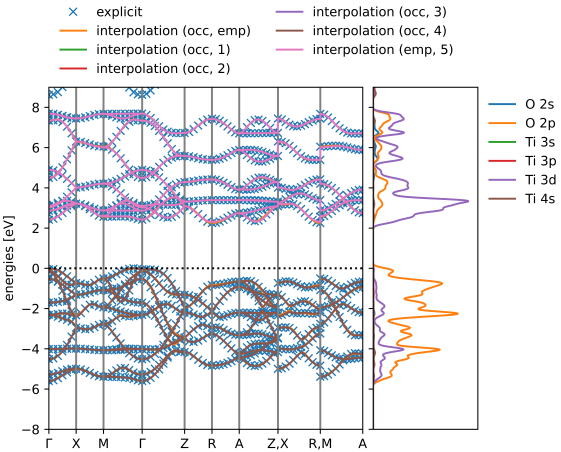


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  "calculator_parameters": {
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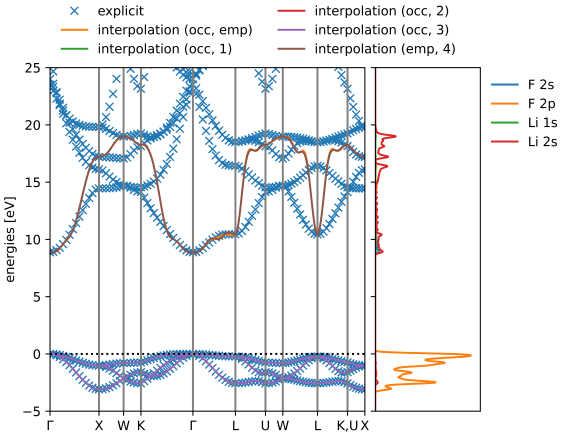

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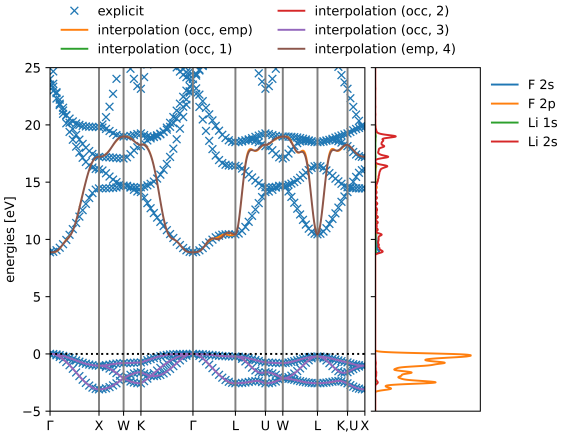
If we want a better representation of the conduction bands, we're gonna need ~~a bigger boat~~ more PAOs...



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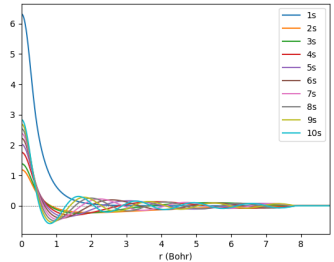

use the PAOs provided by OpenMX

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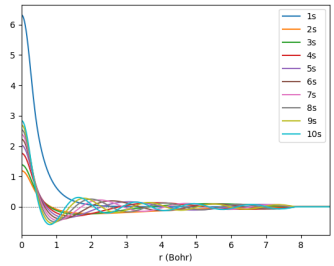

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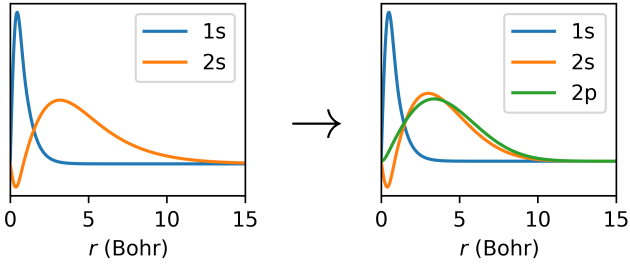

for the pseudopotential in question, resolve the radial Schrödinger equation for the next subshell

Pseudopotential generation

Solving the KS equations for a radial scalar-relativistic potential

Solving the KS equations for a radial scalar-relativistic potential

Solved on a logarithmic grid

$$r_i = r_0 e^{i\Delta x}$$

Solving the KS equations for a radial scalar-relativistic potential
Solved on a logarithmic grid

$$r_i = r_0 e^{i\Delta x}$$

Start with a trial potential $V[n](r)$ and eigenvalue ε. Then the radial wavefunction R_{nl} satisfies

$$\frac{1}{r^2}\frac{d^2R_{nl}(x)}{dx^2} = \frac{1}{r^2}\frac{dR_{nl}(x)}{dx} + \left(\frac{l(l+1)}{r^2} + M(r)(V(r)-\varepsilon)\right)R_{nl}(r) - \frac{\alpha^2}{4M(r)}\frac{dV(r)}{dr}\left(\frac{1}{r}\frac{dR_{nl}(x)}{dx} - \frac{R_{nl}(r)}{r}\right).$$

where $M(r) = 1 - \frac{\alpha^2}{4}(V(r)-\varepsilon)$

Solving scalar-relativisitic radial KS

Extrapolate outwards from the known small-r behaviour

$$R_{nl}(r) \sim r^{\gamma}; \qquad \gamma = \frac{l\sqrt{l^2 - \alpha^2 Z^2} + (l+1)\sqrt{(l+1)^2 - \alpha^2 Z^2}}{2l+1}$$

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- if the wavefunction does not have a discontinuity, we have found a solution! Now cycle for self-consistency over $V[n[(r)$

Pseudopotential generation

Use this procedure to generate extra PAOs for the Wannierisation

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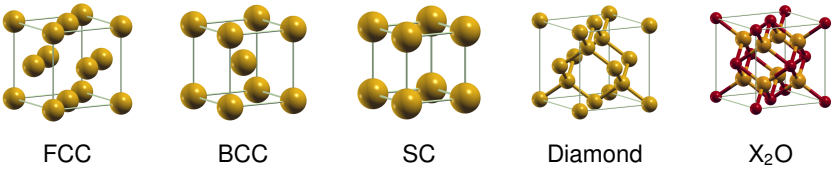
Problem: how to choose the confining potential parameters?
Solution: optimise these criteria across typical structures:



Pseudopotential generation

The projectability is

$$p_{m\mathbf{k}} = \sum_n |\langle \varphi_n \mid \psi_{m\mathbf{k}} \rangle|^2$$

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where $\mathcal{S}_{\mathbf{k}}$ corresponds to the N_w-largest values of $p_{m\mathbf{k}}$.

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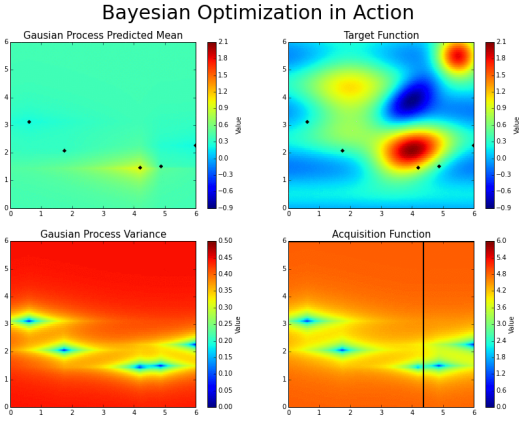
Maximise via *Bayesian optimisation*

Pseudopotential generation



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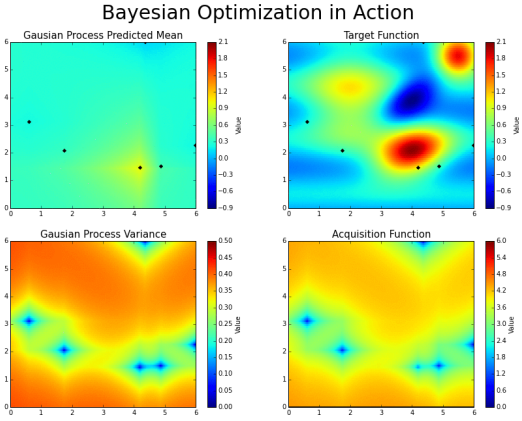

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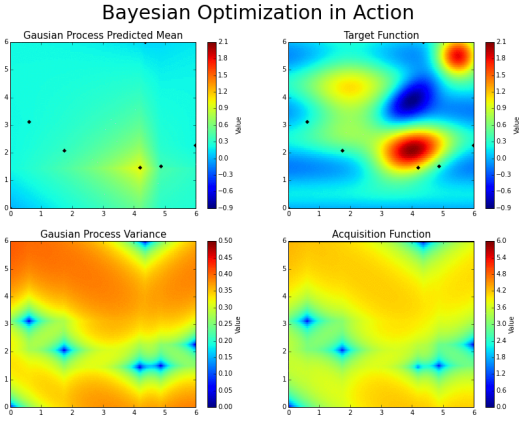

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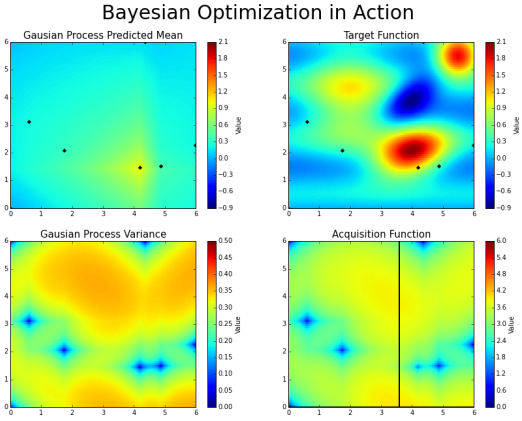
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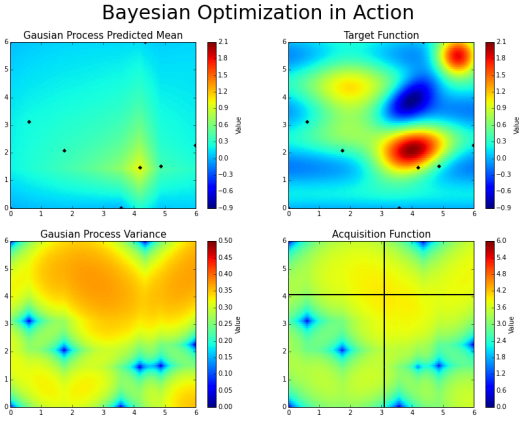
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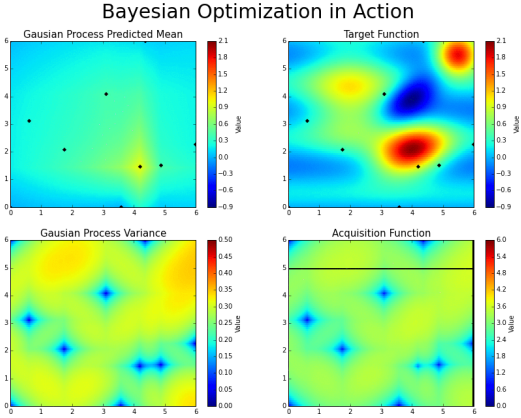

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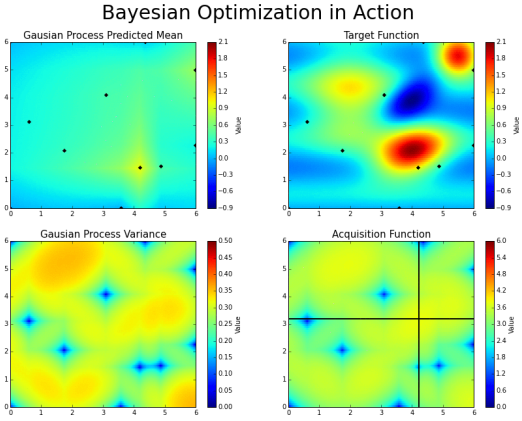

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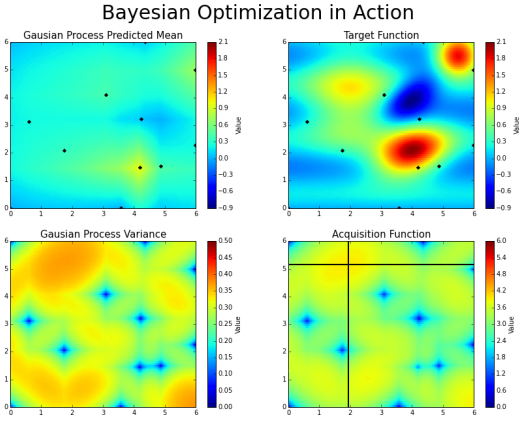

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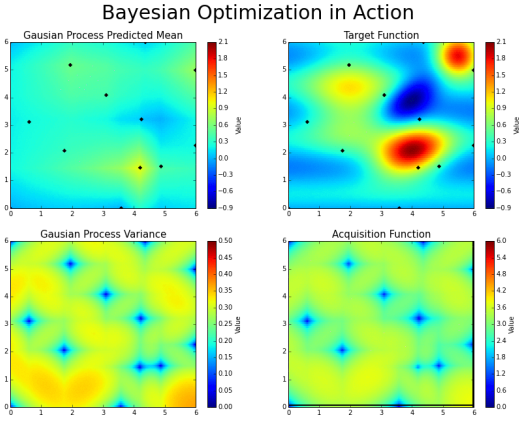

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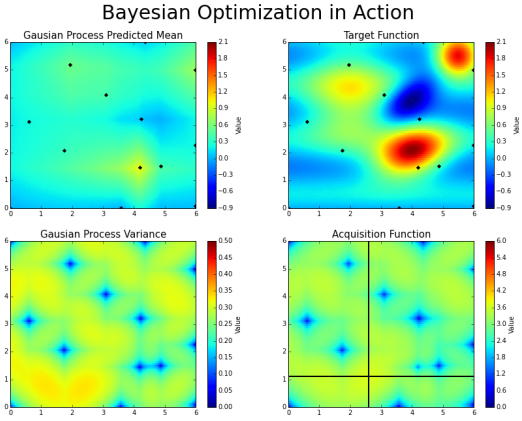
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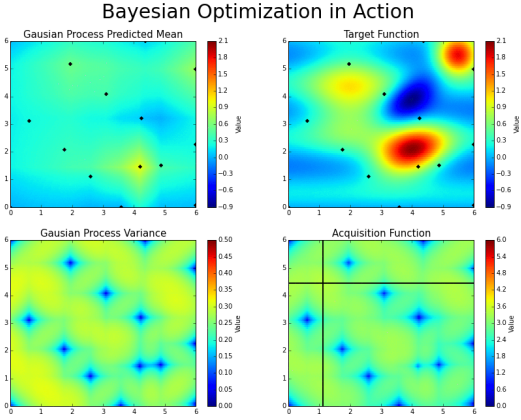

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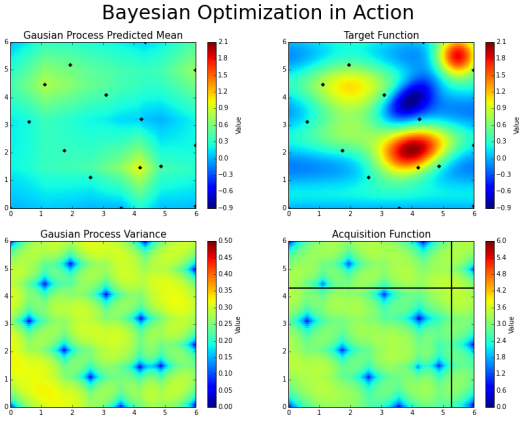

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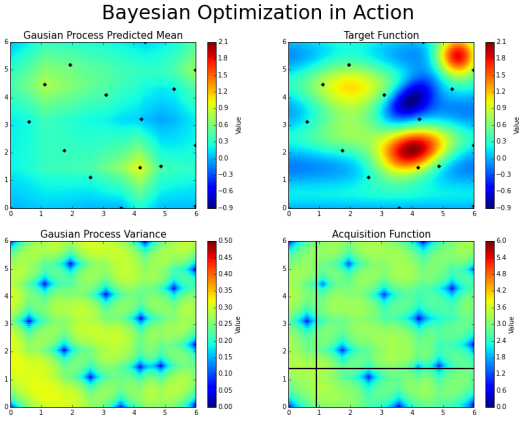

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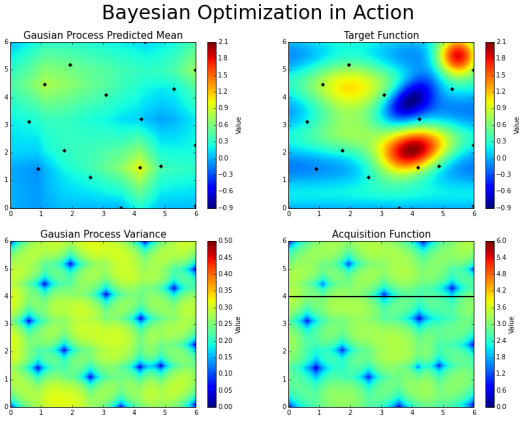

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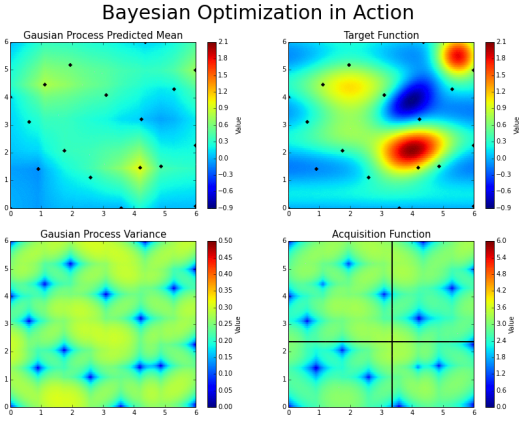

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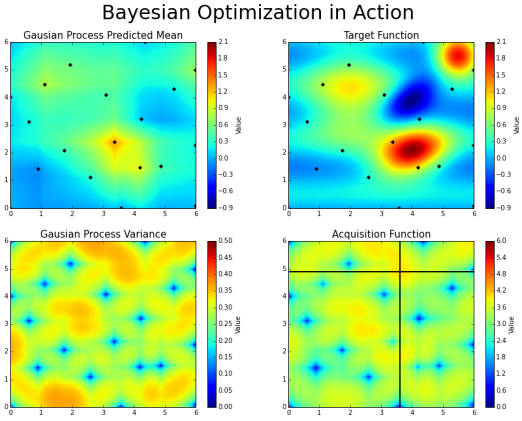

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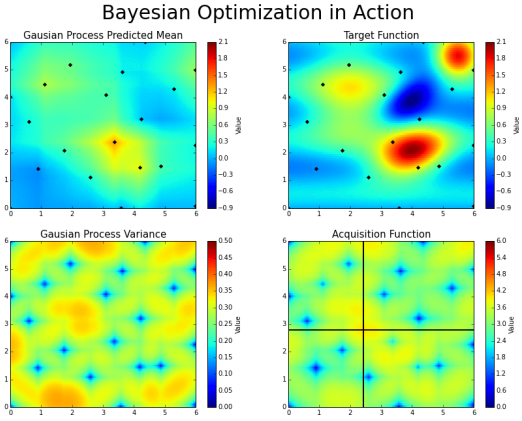

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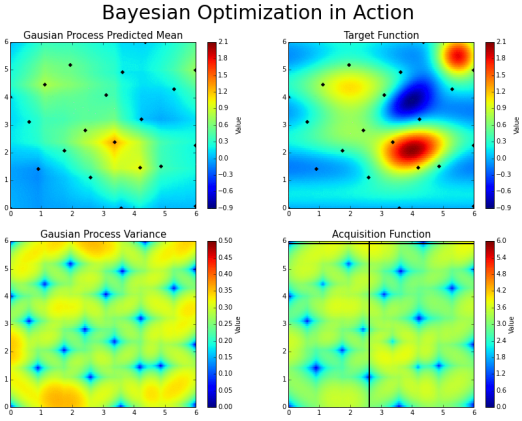

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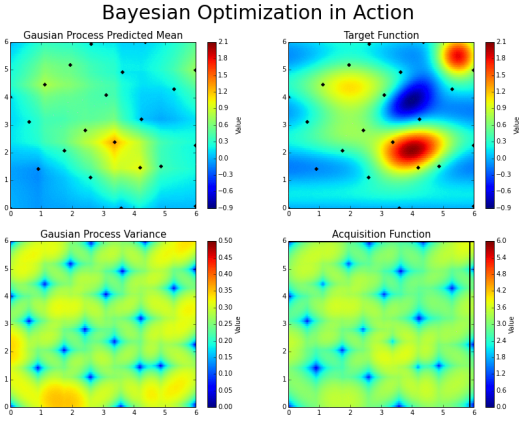

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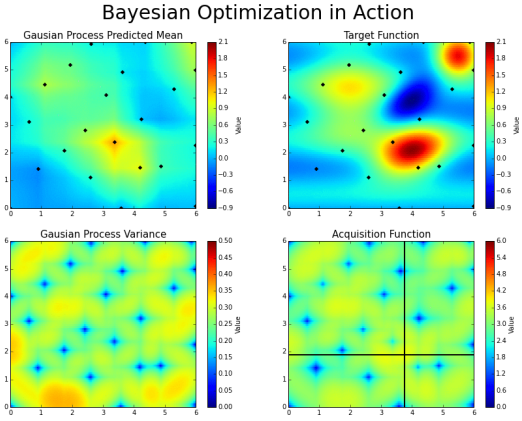

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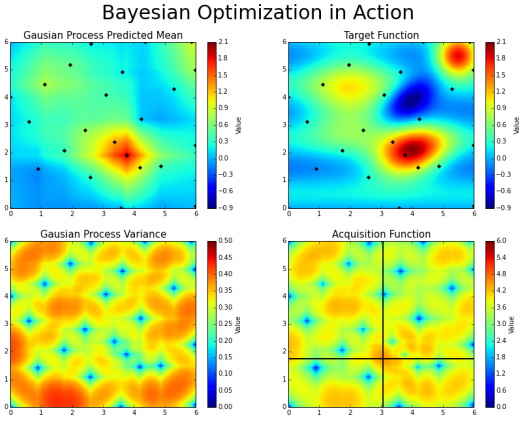

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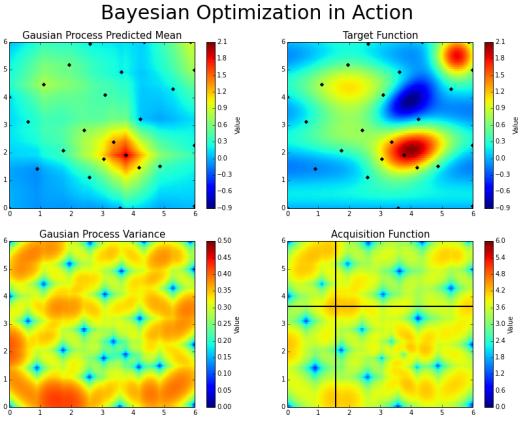
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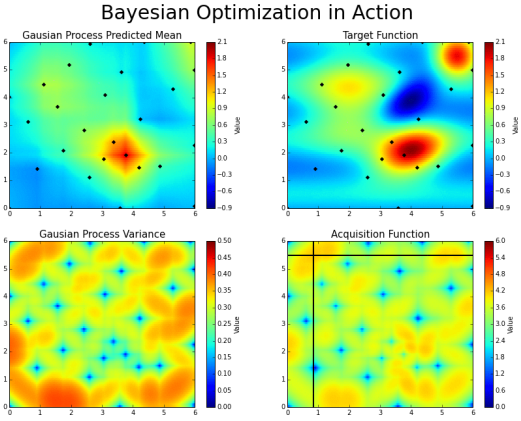

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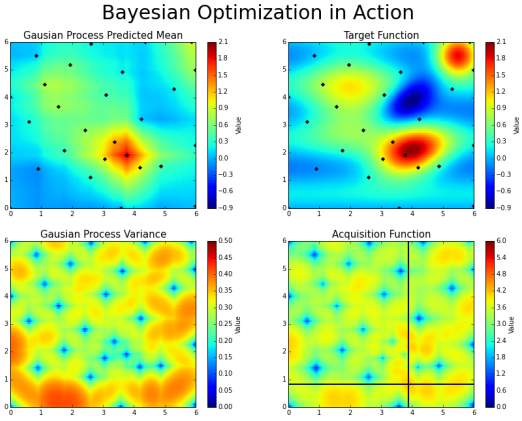

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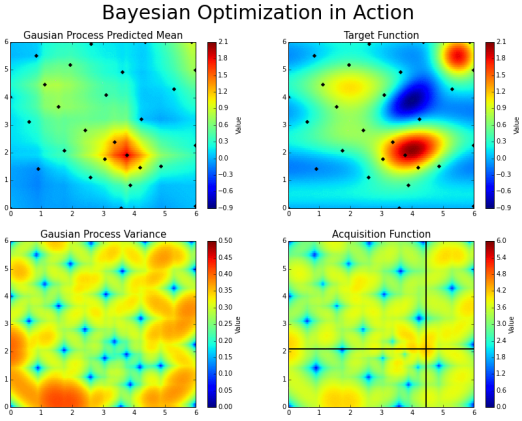

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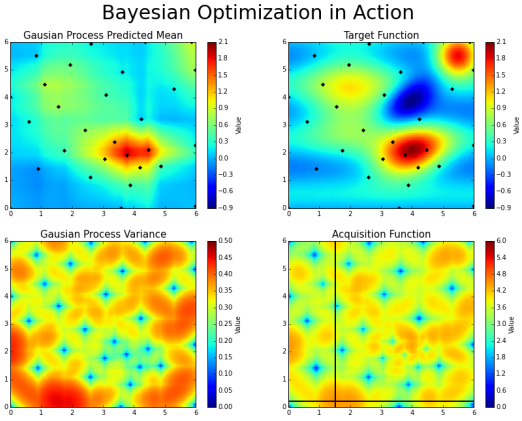
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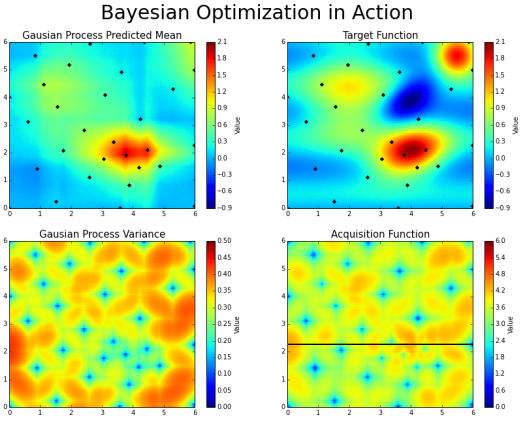

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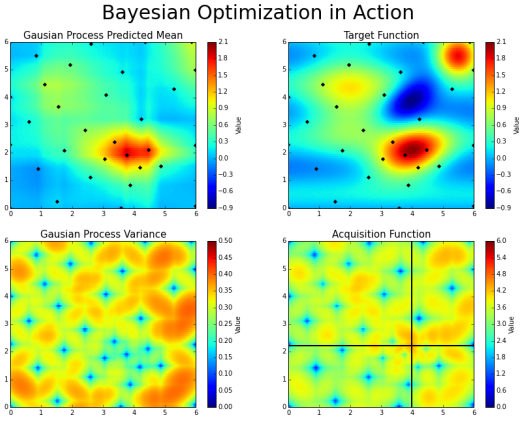

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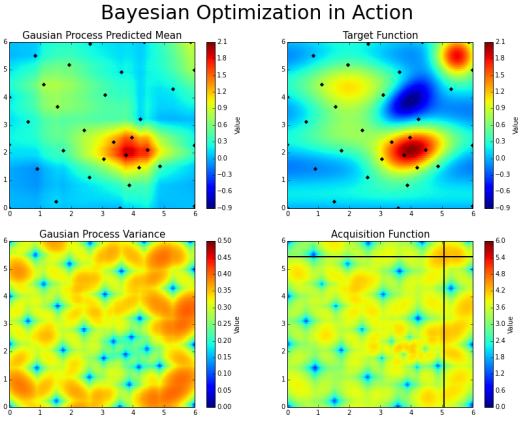

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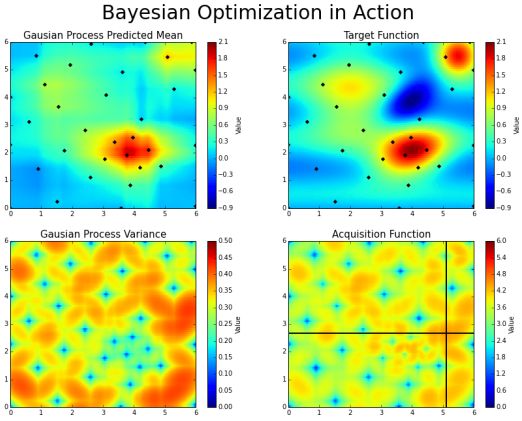

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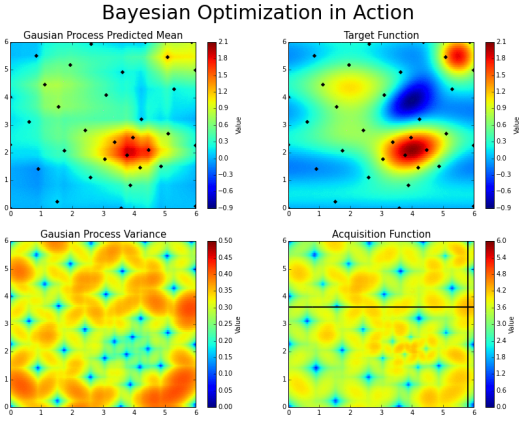

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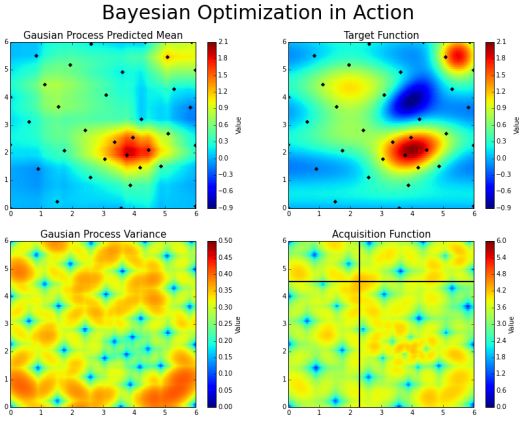
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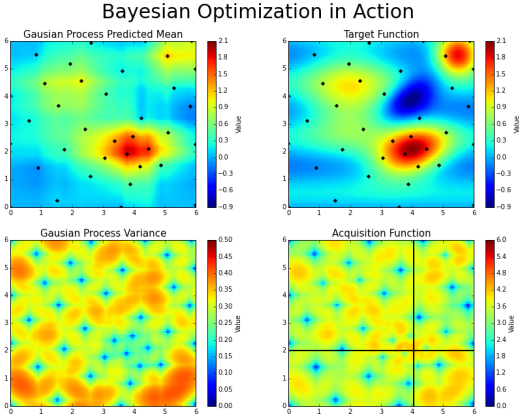

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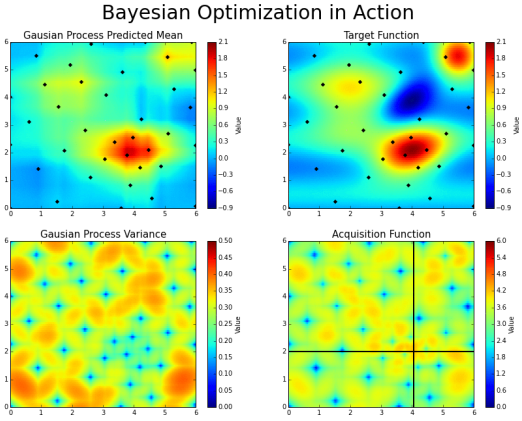

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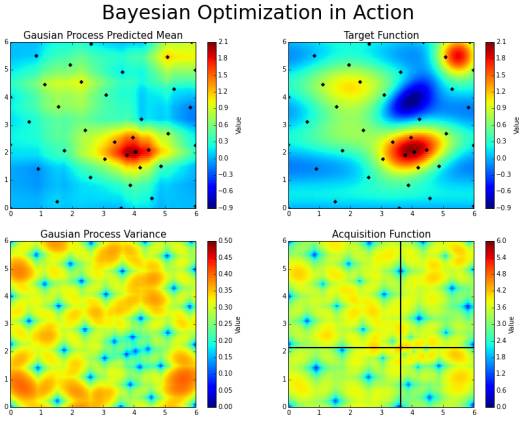
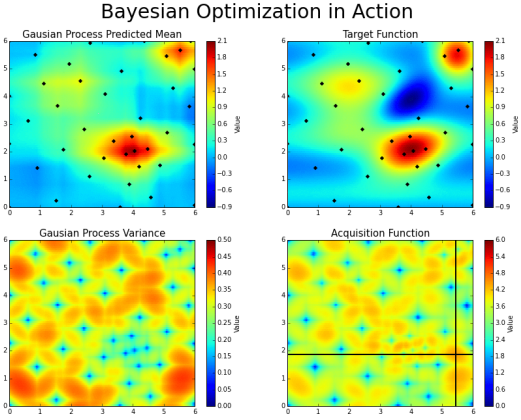


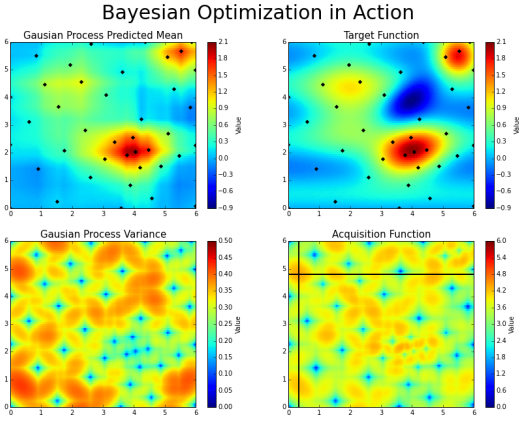
https://github.com/bayesian-optimization/BayesianOptimization

Pseudopotential generation



https://github.com/bayesian-optimization/BayesianOptimization

Pseudopotential generation



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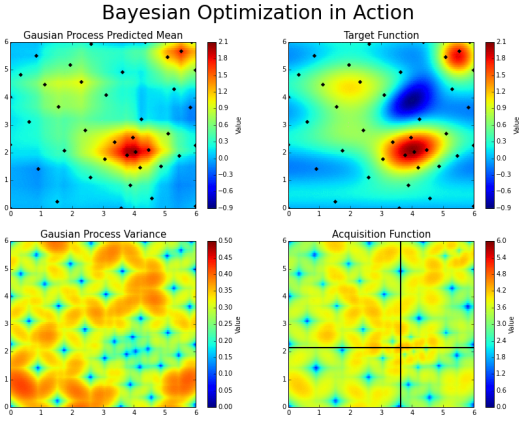
Pseudopotential generation



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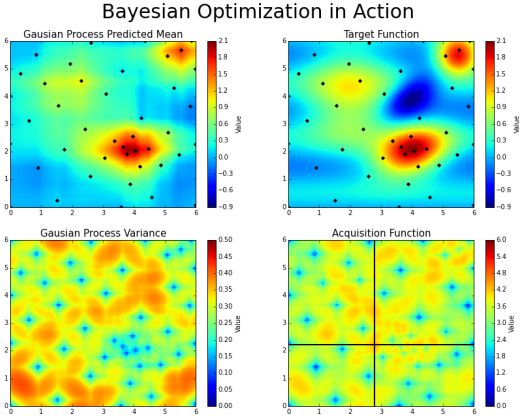
Pseudopotential generation



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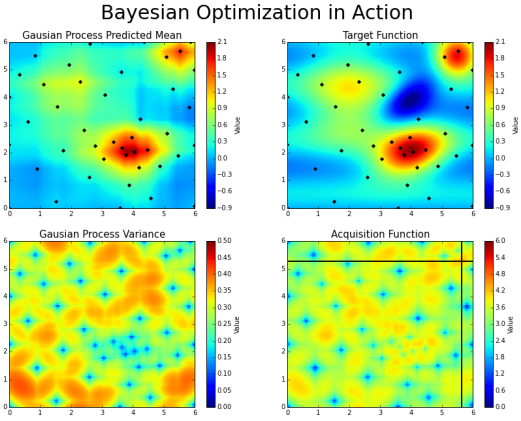
Pseudopotential generation



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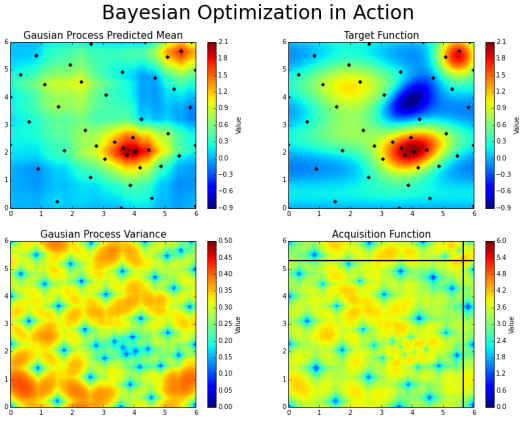

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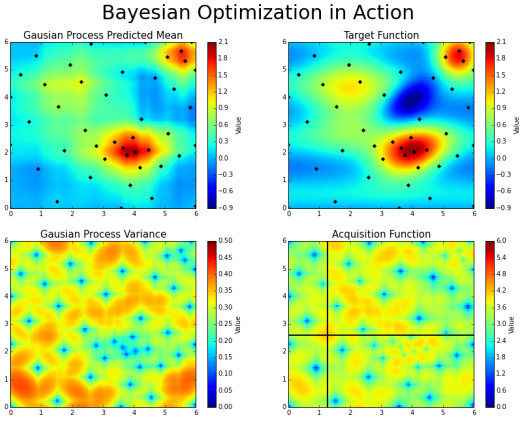

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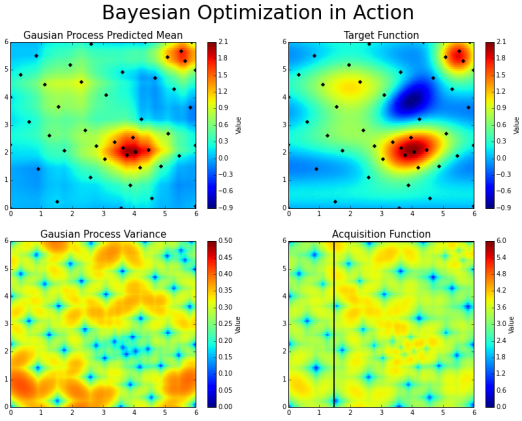
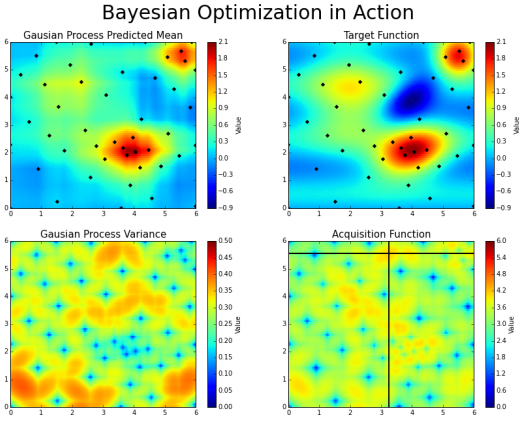
Pseudopotential generation



Pseudopotential generation



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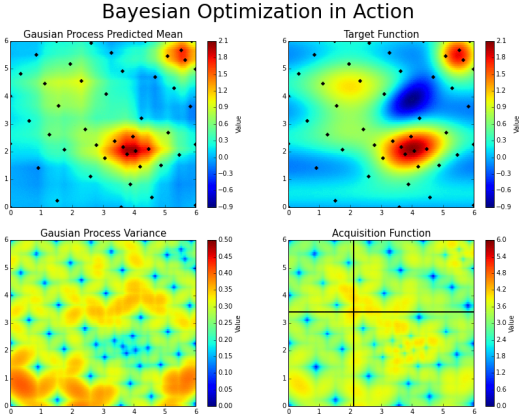
Pseudopotential generation



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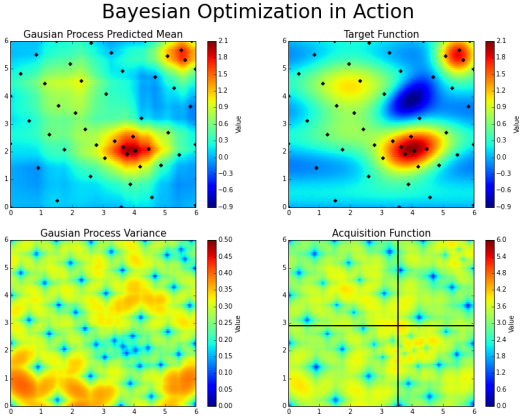

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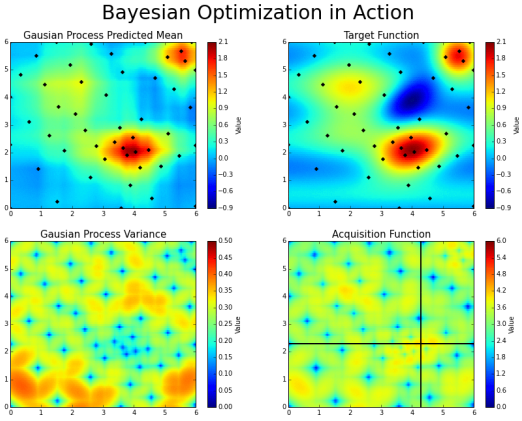
Pseudopotential generation



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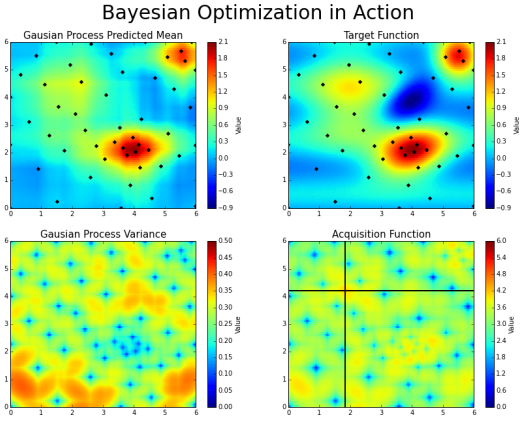

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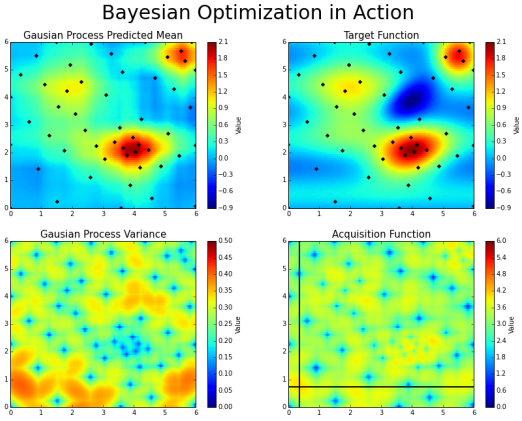

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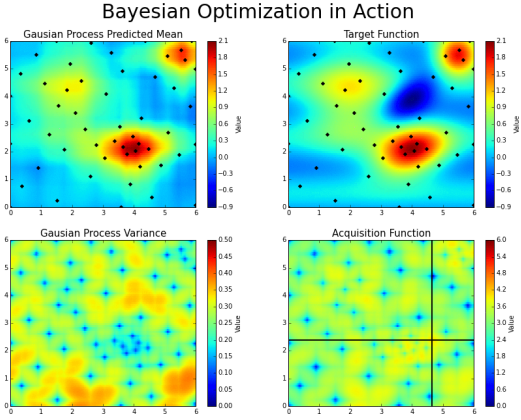
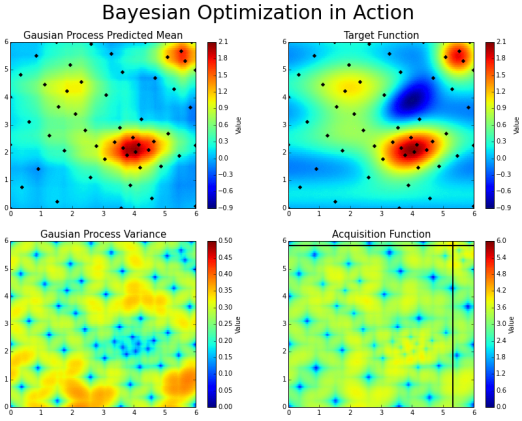

Bayesian Optimization in Action
Gausian Process Predicted Mean
Target Function
Gausian Process Variance
Acquisition Function
Value

Pseudopotential generation



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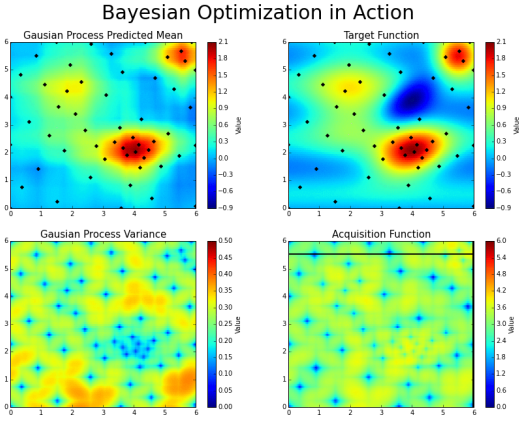
Pseudopotential generation



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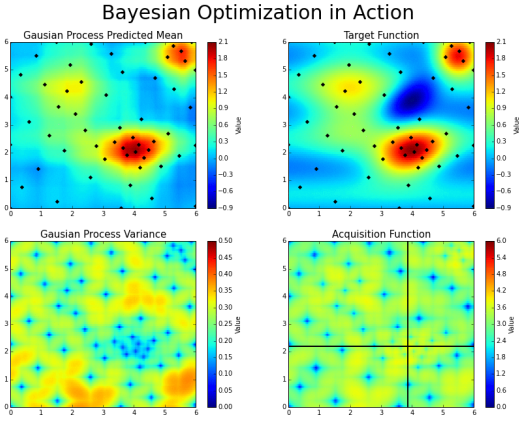
Pseudopotential generation



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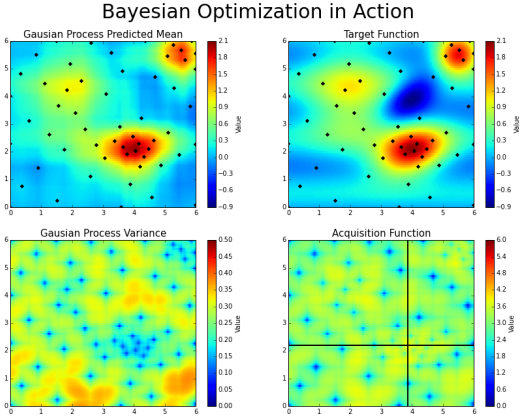
Pseudopotential generation



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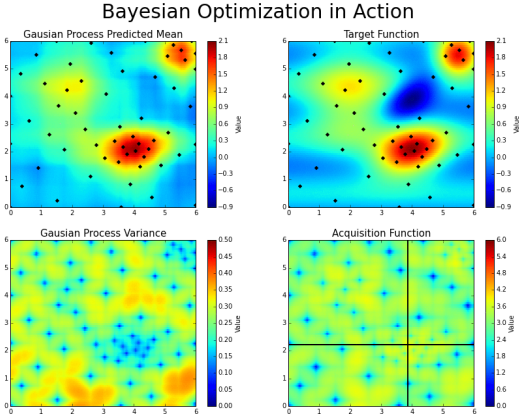

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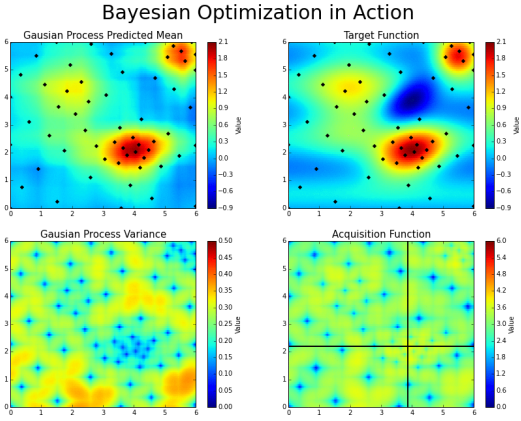
Pseudopotential generation



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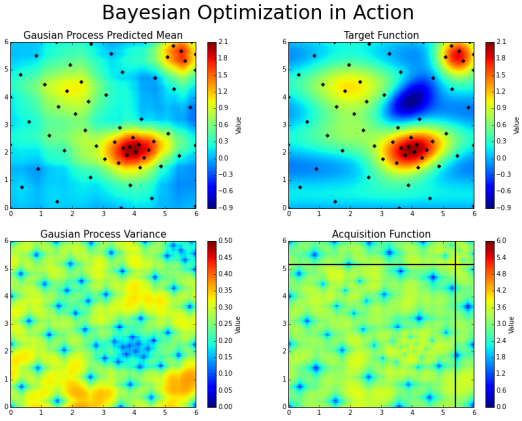
Pseudopotential generation



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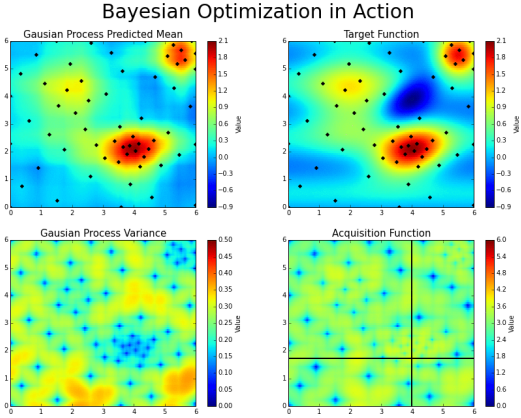

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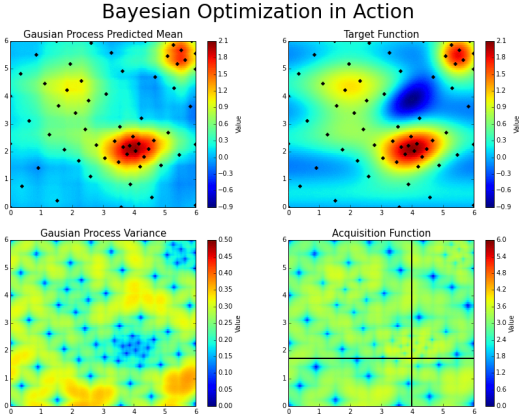
Pseudopotential generation



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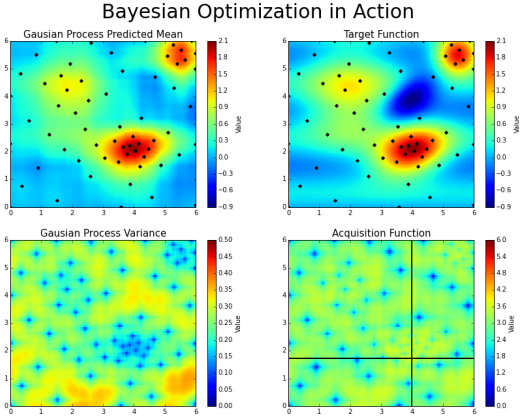
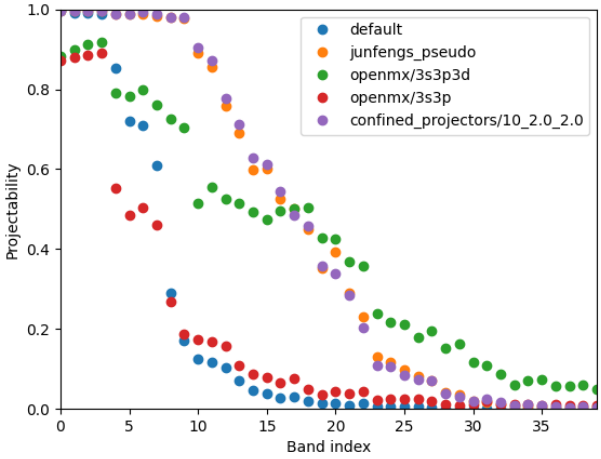
Pseudopotential generation



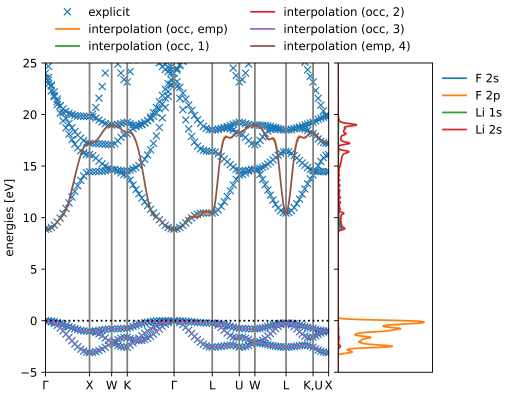
https://github.com/bayesian-optimization/BayesianOptimization

Pseudopotential generation

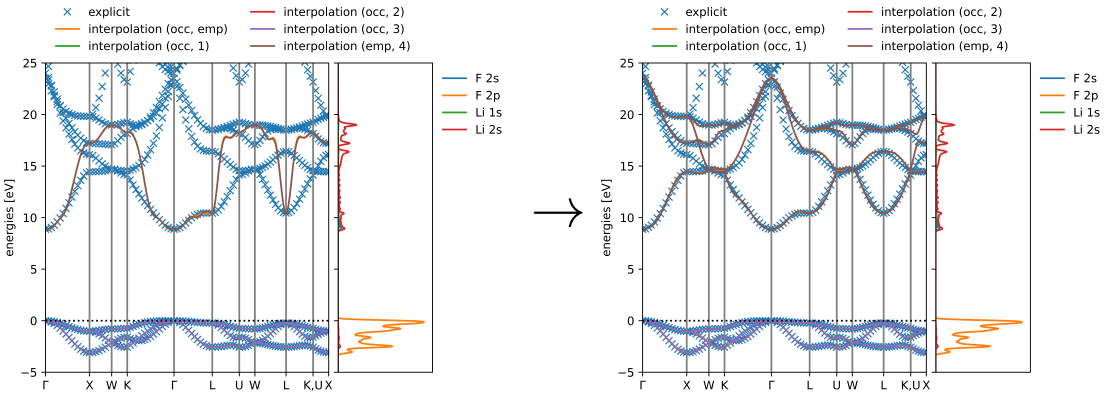
It works!



Pseudopotential generation

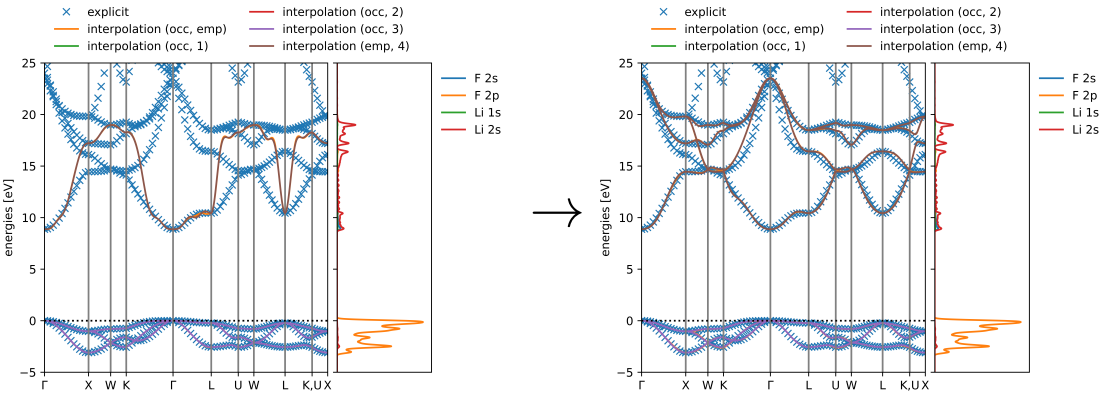


Pseudopotential generation



N. Colonna et al. *J. Chem. Theory Comput.* 18.9 (2022), 5435

Pseudopotential generation



	LDA	HSE	GW_0	scG$\tilde{W}$	KI	exp
E_{gap} (eV)	8.87	11.61	13.96	14.5	15.28	15.35

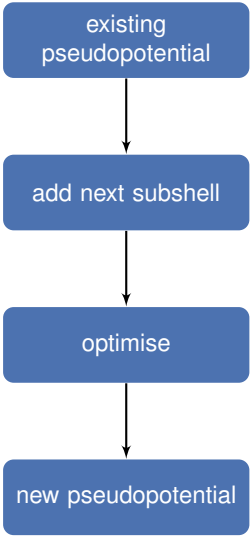
Systematic and accessible infrastructure?

Systematic and accessible infrastructure?

Currently implemented within a modified version of `oncvpsp.x`
In `oncvpsp.x...`

- the bracketing of ε is not robust (especially bad with the external potential)
- the code is not modular
- the code repository is not actively maintained

Systematic and accessible infrastructure?



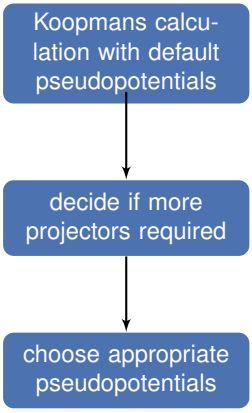
must be generated via `oncvpsp.x`

performed with a modified version of `oncvpsp.x`; would be nice to replace with a general solver

use Bayesian optimisation to select a confining potential that maximises projectability across the SSSP dataset

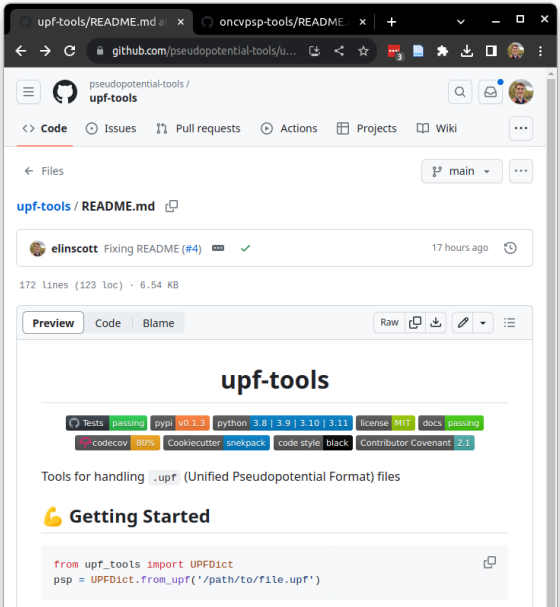
how to distribute?

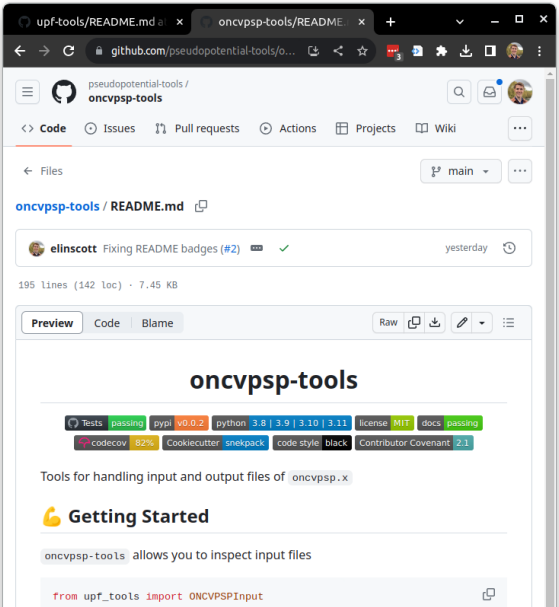
Systematic and accessible infrastructure?



band interpolation criteria? (But there are many reasons why bands don't match...)

we don't need/want extra subshells for all elements


upf-tools/README.md
github.com/pseudopotential-tools/u...
pseudopotential-tools /
upf-tools
Code
Issues
Pull requests
Actions
Projects
Wiki
Files
main
upf-tools / README.md
elinscott Fixing README (#4)
17 hours ago
172 lines (123 loc) · 6.54 KB
Preview
Code
Blame
Raw
upf-tools
Tests passing
pypi v0.1.3
python 3.8 | 3.9 | 3.10 | 3.11
license MIT
docs passing
codecov 80%
Cookiecutter snekpack
code style black
Contributor Covenant 2.1
Tools for handling .upf (Unified Pseudopotential Format) files
Getting Started
from upf_tools import UPFDict
psp = UPFDict.from_upf('/path/to/file.upf')


upf-tools/README.md
oncvpsp-tools/README
github.com/pseudopotential-tools/o...
pseudopotential-tools /
oncvpsp-tools
Code
Issues
Pull requests
Actions
Projects
Wiki
Files
main
oncvpsp-tools / README.md
elinscott Fixing README badges (#2)
yesterday
195 lines (142 loc) · 7.45 KB
Preview
Code
Blame
Raw
oncvpsp-tools
Tests passing
pypi v0.0.2
python 3.8 | 3.9 | 3.10 | 3.11
license MIT
docs passing
codecov 82%
Cookiecutter snekpack
code style black
Contributor Covenant 2.1
Tools for handling input and output files of oncvpsp.x
Getting Started
oncvpsp-tools allows you to inspect input files
from upf_tools import ONCVPSPInput

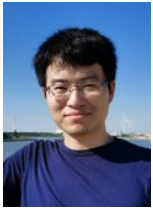
Publish your code!

- It's easy: most of the infrastructure was from the `cookiecutter` I used (see my July 2022 GM)
- It avoids duplication: `upf-tools` was discovered by Marnik and is now used in `AiiDA`

Acknowledgements


Nicola Marzari


Nicola Colonna


Junfeng Qiao

Swiss National Science Foundation

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NATIONAL CENTRE OF COMPETENCE IN RESEARCH

slides available at github/elinscott-talks and on the THEOS wiki