DE LA RECHERCHE À L'INDUSTRIE

ROLE OF ELECTRONIC INTERACTIONS ON PROPERTIES OF ACTINIDES

Bernard Amadon, CEA, Bruyères le Châtel

WG3, GDR Resanet, November 13, 2018

www.cea.fr

THE PERIODIC TABLE

	1 H																2 He
	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
$4s/3d/4p$	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
$5s/4d/5p$	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
	55 Cs	56 Ba	57-71 La-Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
	87 Fr	88 Ra	89-103 Ac-Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

Lanthanides $4f$	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides $5f$	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

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	55 Cs	56 Ba	57-71 La-Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
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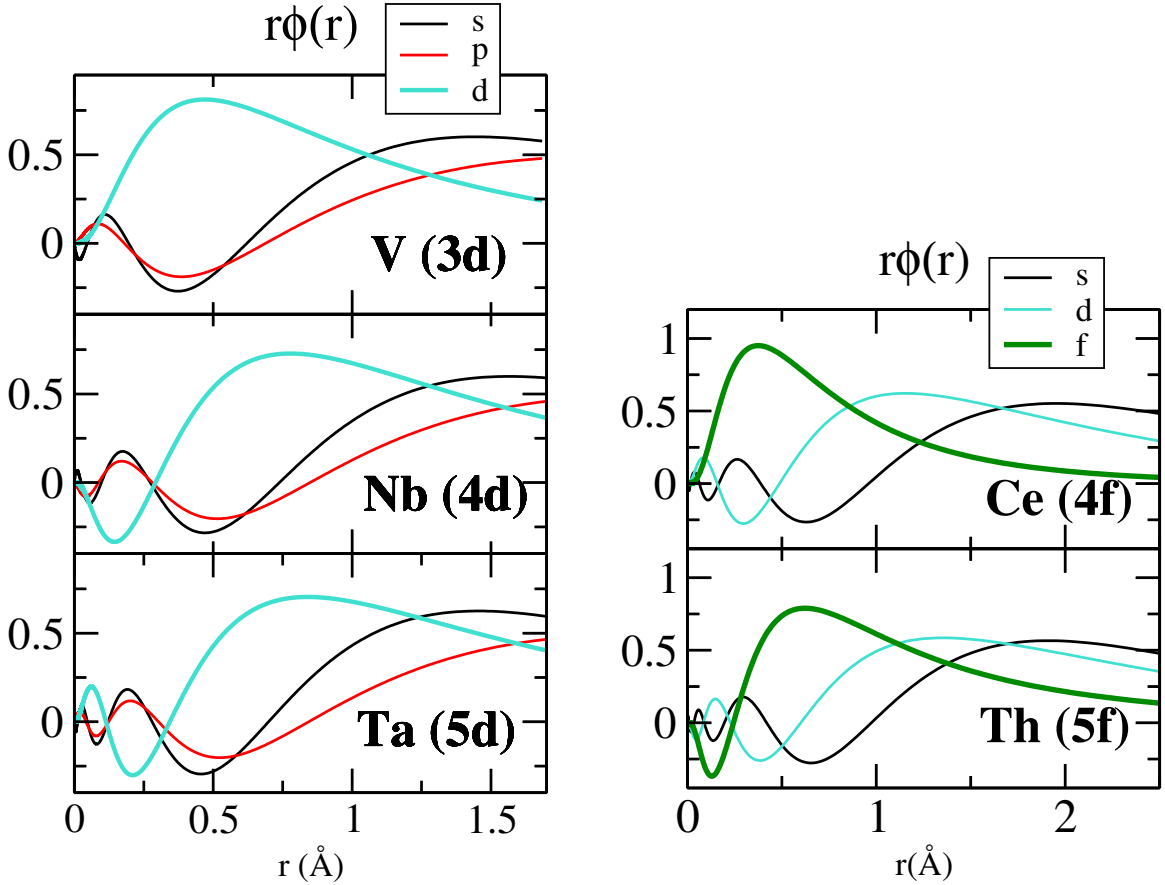
LOCALIZATION OF 3*d*, 4*f* AND 5*f* ORBITALS



3*d* orbitals are more localized than *sp*, 4*d* and 5*d* orbitals.
4*f* and 5*f* orbitals are more localized than *spd* orbitals.

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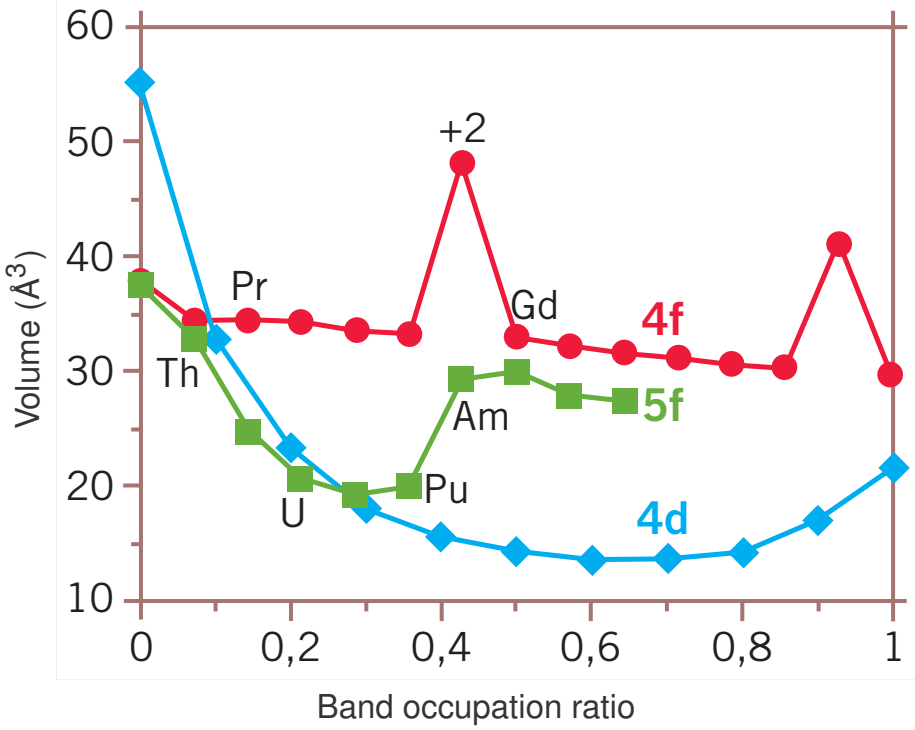
ACTINIDES: INTERMEDIATE CASE OF LOCALIZATION

4*d* element: filling of the 4*d* band (Bonding states and antibonding): 4*d* electrons are **delocalized**.

Lanthanides: 4*f* electrons **localized**, negligible overlap between 4*f* orbitals .

Actinides: intermediate case of localization.

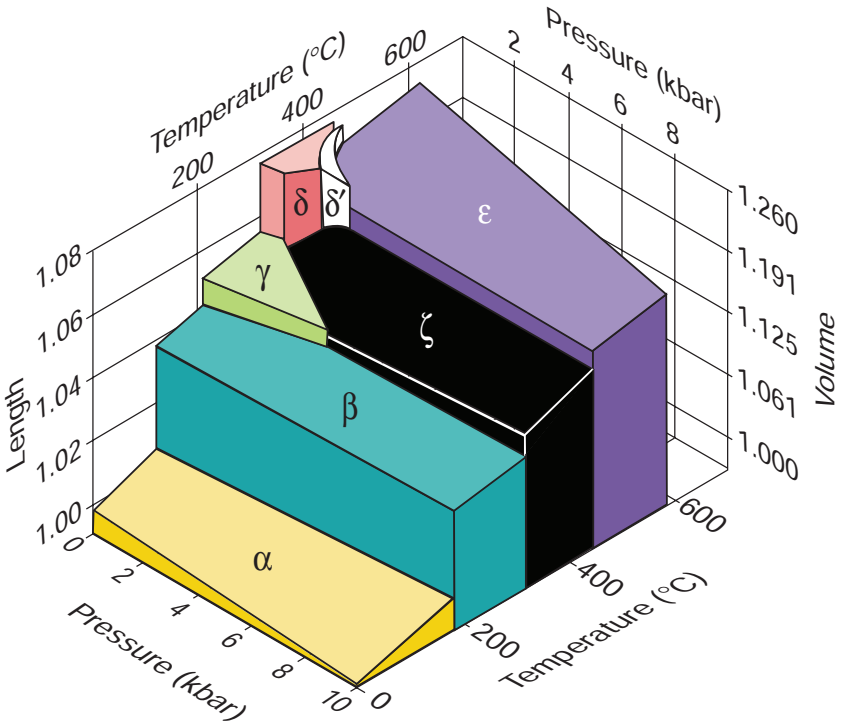
At atmospheric pressure:



[Mac Mahan, et al J. Comp.-Aid. Mater. Des. 5, 131 (1998)]

PLUTONIUM: A LARGE NUMBER OF PHASES.

- Many phases
- Some phases with delocalized electrons (low volume) and phases with localized electrons (large volume).



From Kevin T. Moore and Gerrit van der Laan Rev. Mod. Phys. 81, 235 (2009)

THE EXACT SOLUTION CANNOT BE COMPUTED

The exact hamiltonien is:

$$H = \sum_{i=1}^{N} [-\frac{1}{2}\nabla^2_{\mathbf{r}_i} + V_{\mathrm{ext}}(\mathbf{r}_i)] + \frac{1}{2}\sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

This many body problem can be solved exactly only for small molecules because the number of electronic configurations increase exponentially with the size of the system.

$\Rightarrow$ **Use a more simplified theory**

DENSITY FUNCTIONAL THEORY (DFT)

Density Functional Theory (DFT) is a theory of a simple scalar field: the local electronic density $n(\mathbf{r})$.

- An **exact** theory ...
- ..which can only be used with an **approximation**.
- How to describe electronic interaction ?
  - ”Local Density Approximation”
  - ”Generalized Gradient Approximation”
- DFT gives fast, and fairly accurate structural properties for *sp* systems and semiconductors

ABINIT: AN INTERNATIONAL OPEN SOURCE PROJECT

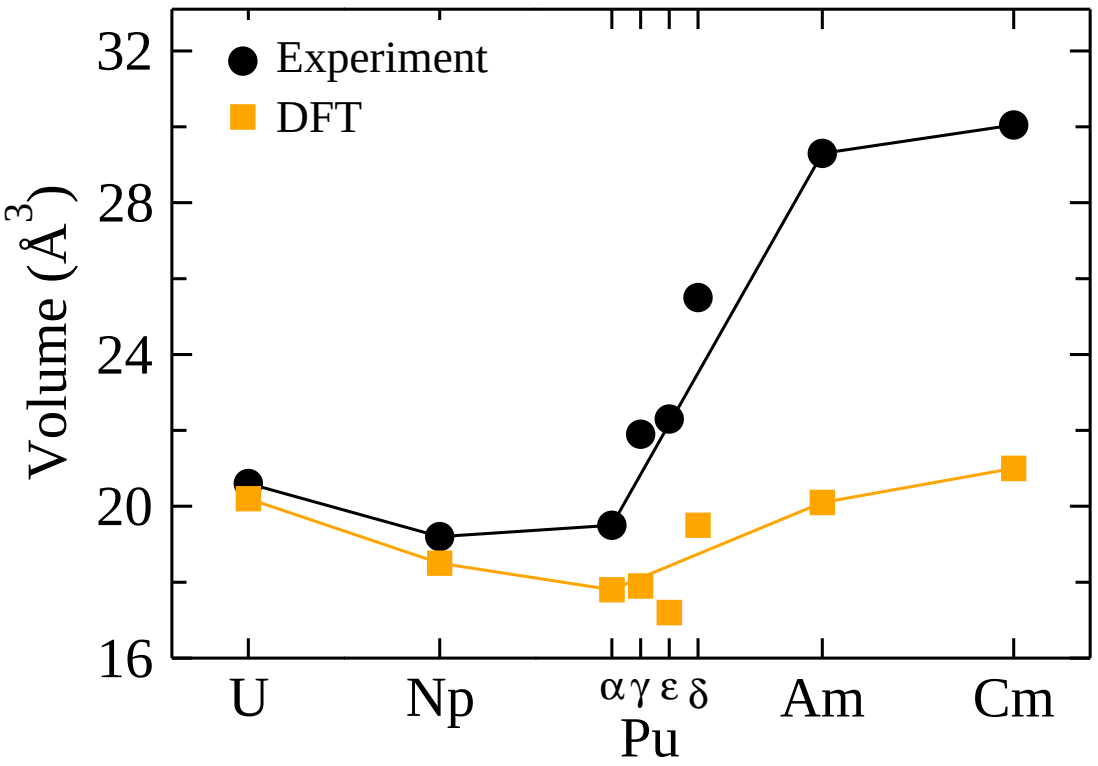
- Open source
- Efficient DFT implementation
- Parallelism
- Many advanced theories and properties available (Optic, GW, BSE, DFPT, DFT+DMFT (see later))

www.abinit.org
(+ tutorials)

An international cooperation, in which CEA (DAM DEN DRF) is one of the main contributor (for the development of the code)

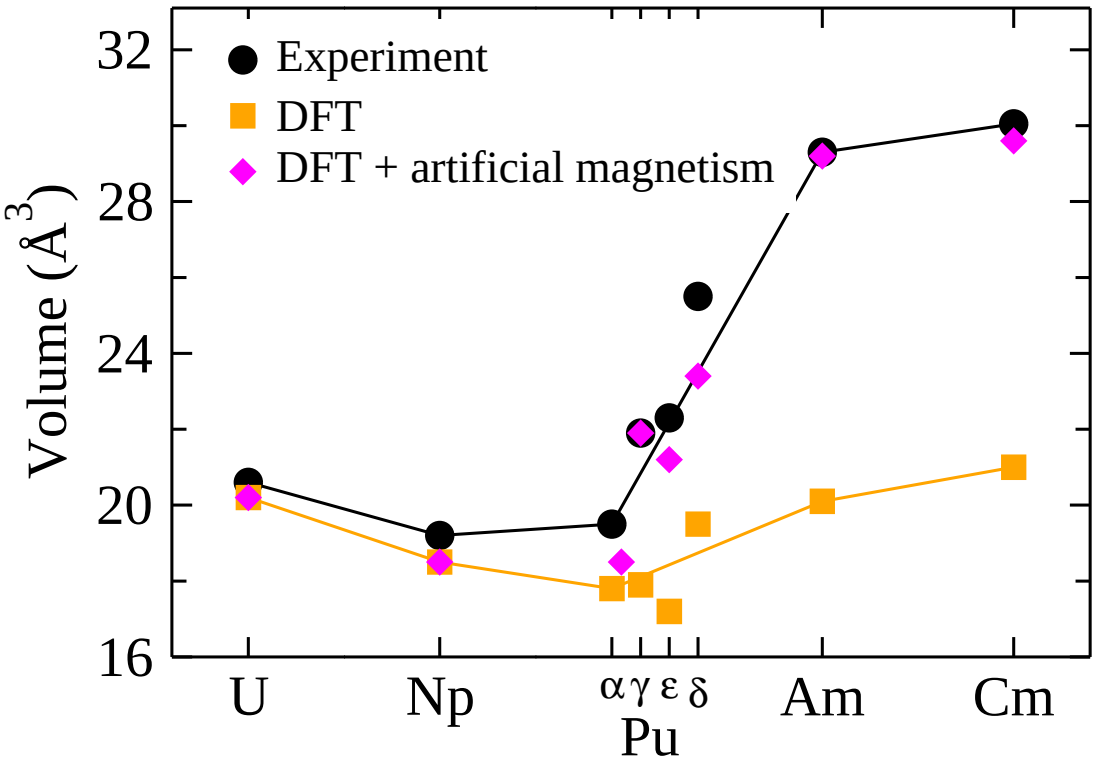
X. Gonze, F. Jollet, F. A. Araujo, D. Adams, B. Amadon, T. Applencourt, C. Audouze, J.-M. Beuken, J. Bieder, A. Bokhanchuk, E. Bousquet, F. Bruneval, D. Caliste, M. Côté , F. Dahm, F. D. Pieve, M. Delaveau, M. Di Gennaro, B. Dorado, C. Espejo, G. Geneste, L. Genovese, A. Gerossier, M. Giantomassi, Y. Gillet, D. Hamann, L. He, G. Jomard, J. L. Janssen, S. L. Roux, A. Levitt, A. Lherbier, F. Liu, I. Lukacevic , A. Martin, C. Martins, M. Oliveira, S. Poncé , Y. Pouillon, T. Rangel, G.-M. Rignanese, A. Romero, B. Rousseau, O. Rubel, A. Shukri, M. Stankovski, M. Torrent, M. V. Setten, B. V. Troeye, M. Verstraete, D. Waroquiers, J. Wiktor, B. Xu, A. Zhou, and J. Zwanziger, Recent developments in the ABINIT software package, Computer Physics Communications **205**, 106 (2016)

DFT UNDERESTIMATES VOLUMES...



DFT: Cohesion is overestimated, not enough interactions

OR DFT WRONGLY DESCRIBES MAGNETISM



DFT+magnetism: good description of volumes but magnetism is wrong

DFT+magnetism (1) G. Robert, A. Pasturel, and B. Siberchicot *et al* Journal of Phys: Cond. Matter 15 8377 (2003), A. Kutepov and S. Kutepova J. Magn. Magn. Mater. 272, E329 (2004)

DFT+magnetism (2) P. Söderlind and B. Sadigh Phys. Rev. Lett. 92, 185702 (2004), P. Söderlind *al* MRS Bull. 35, 883 (2010)

DFT+U J. Bouchet et al 2000 JPCM 12 1723 (2000), S. Savrasov and G. Kotliar PRL 84, 3670 (2000)

MORE EXPLICIT INTERACTIONS

The exact hamiltonien is:

$$H = \sum_{i=1}^{N} [-\frac{1}{2}\nabla^2_{\mathbf{r}_i} + V_{\mathrm{ext}}(\mathbf{r}_i)] + \frac{1}{2}\sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

If interactions are purely local (as in lanthanides), and with only one (localized) orbital per atom, one can write a simplified Hamiltonian as:

LOCALIZATION VERSUS DELOCALIZATION

$$H = \underbrace{\sum_{\mathbf{R},\mathbf{R}'} t_{\mathbf{R},\mathbf{R}'} c^{\dagger}_{\mathbf{R}} c_{\mathbf{R}'}}_{\text{one electron term : delocalization}} + \underbrace{\sum_{\mathbf{R}} U \hat{n}_{\mathbf{R}\uparrow} \hat{n}_{\mathbf{R}\downarrow}}_{\text{interaction term : localization}}$$

Now, we have a parameter to describe the Coulomb interaction which is called U .

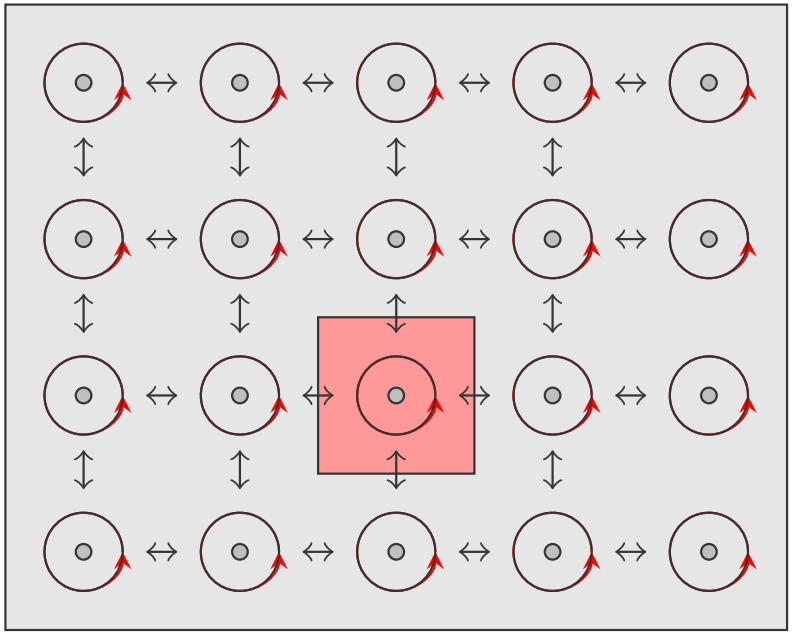
LOCALIZATION VERSUS DELOCALIZATION

$$H = \underbrace{\sum_{\mathbf{R},\mathbf{R}'} t_{\mathbf{R},\mathbf{R}'} c^{\dagger}_{\mathbf{R}} c_{\mathbf{R}'}}_{\text{one electron term : delocalization}} + \underbrace{\sum_{\mathbf{R}} U \hat{n}_{\mathbf{R}\uparrow} \hat{n}_{\mathbf{R}\downarrow}}_{\text{interaction term : localization}}$$

- For large values of the interaction U , electrons are localized
- For low values of the interaction U , electrons are delocalized

DYNAMICAL MEAN FIELD THEORY (DMFT)

DMFT : [Hubbard-like models $\equiv$ Anderson model + Self-consistency]



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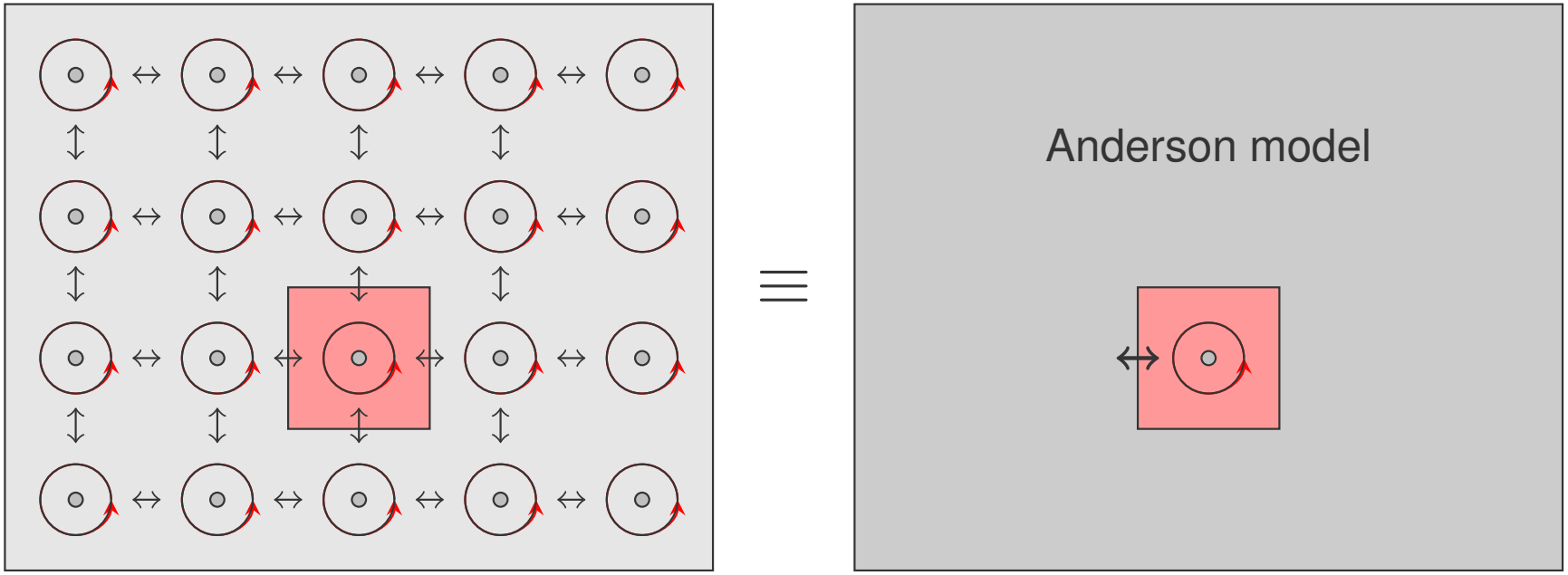

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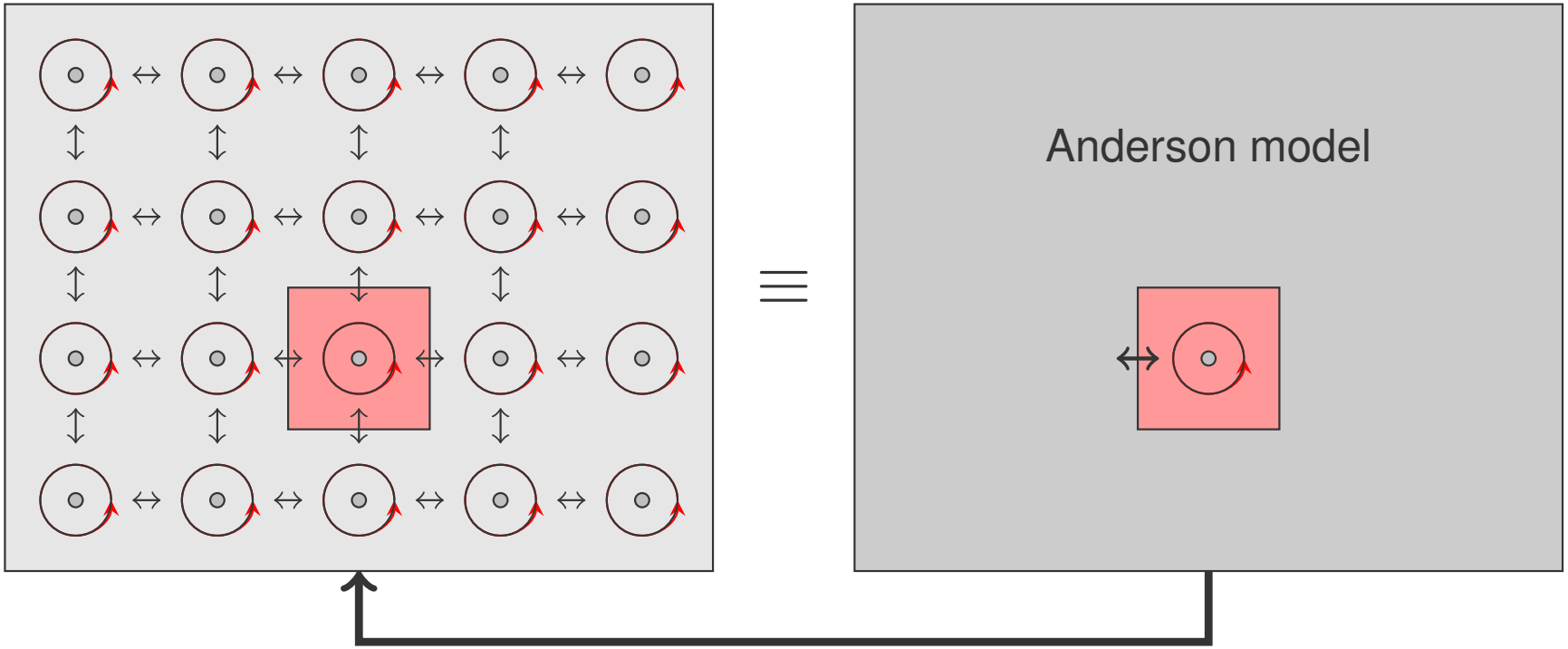

W. Metzner and D. Vollhardt Phys. Rev. Lett. 62 (3) 324 (1989)
A. Georges and G. Kotliar Phys. Rev. B 45 (12) 6479 (1992)
Antoine Georges, Gabriel Kotliar, Werner Krauth, and Marcelo J. Rozenberg Rev. Mod. Phys. 68, 13 (1996)

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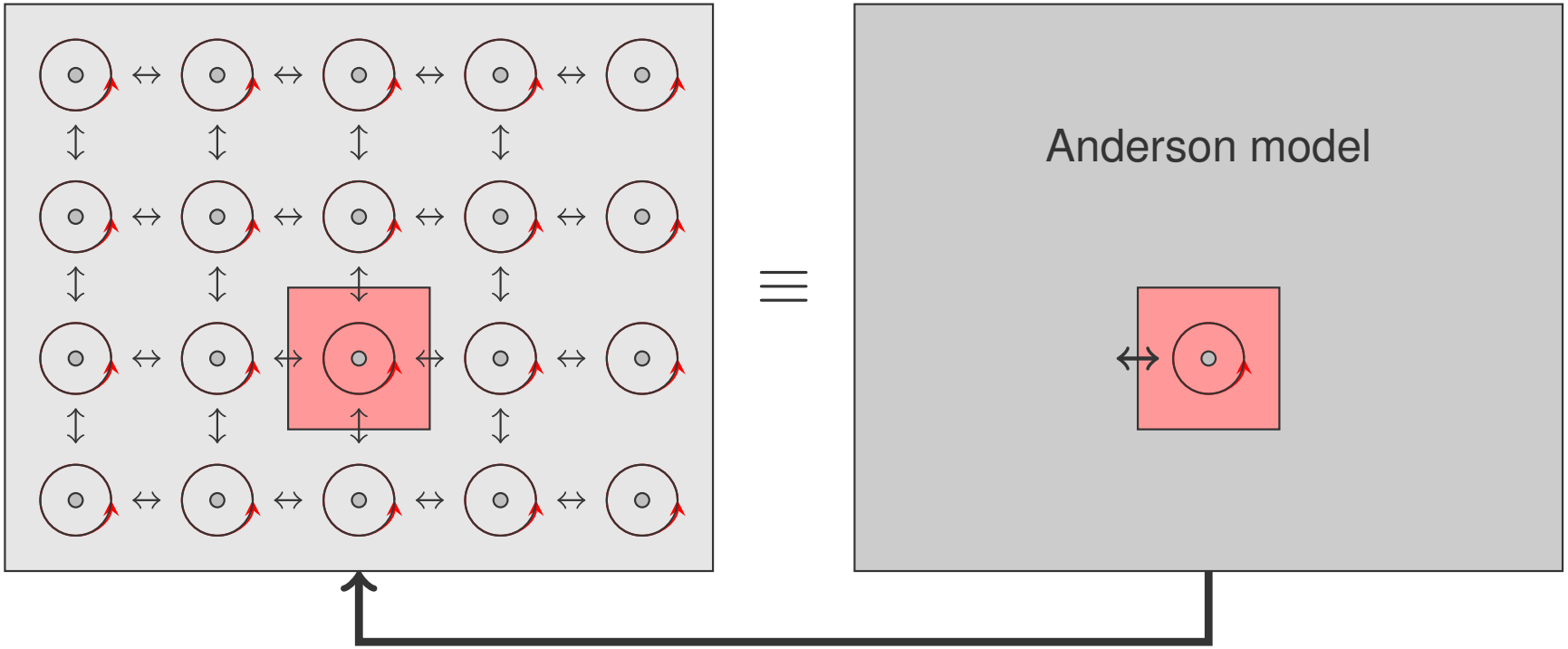
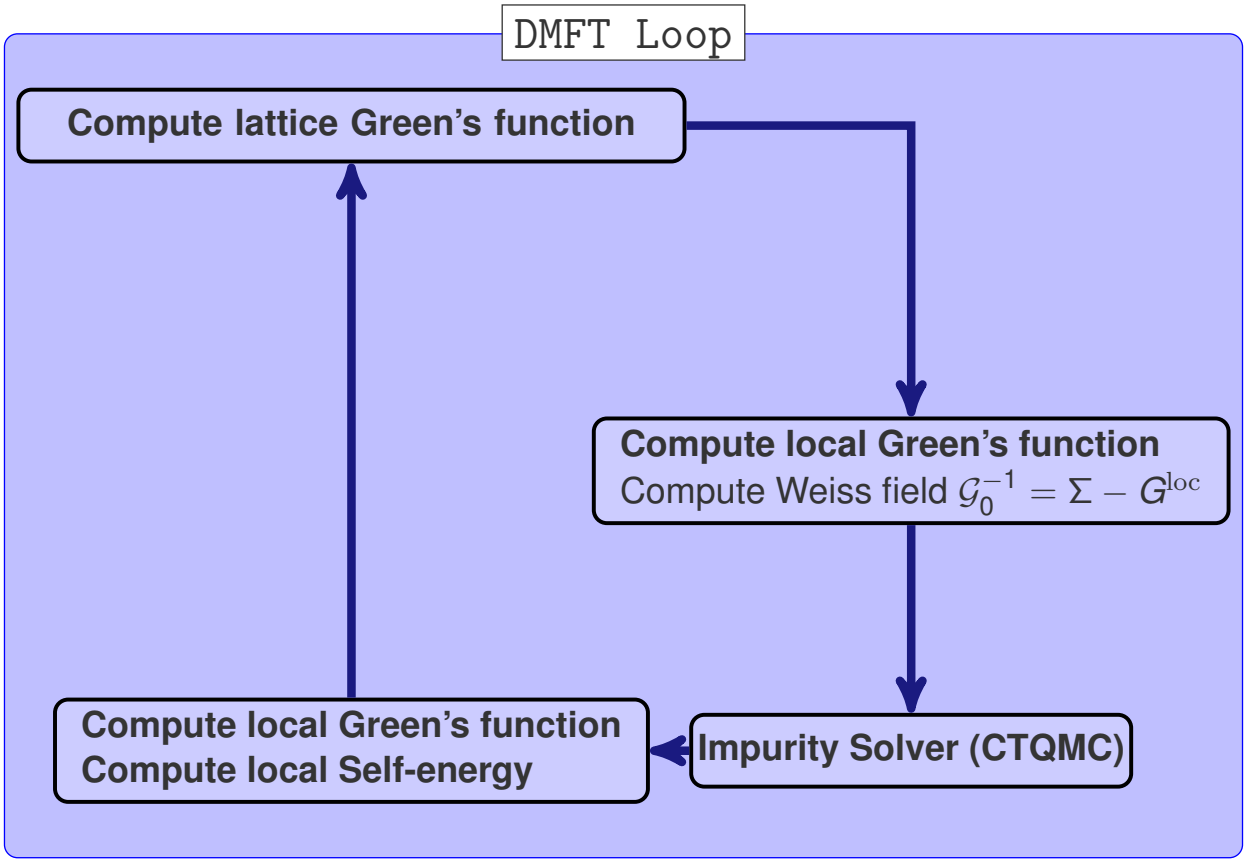


Anderson model solved by Quantum Monte Carlo

- Simplified and efficient implementation in ABINIT [Bieder and Amadon PRB 2014].
- For a general resolution, ABINIT is linked to an external library (TRIQS), developed by **CEA/DRF/IPHT** in Saclay.

The DMFT Loop



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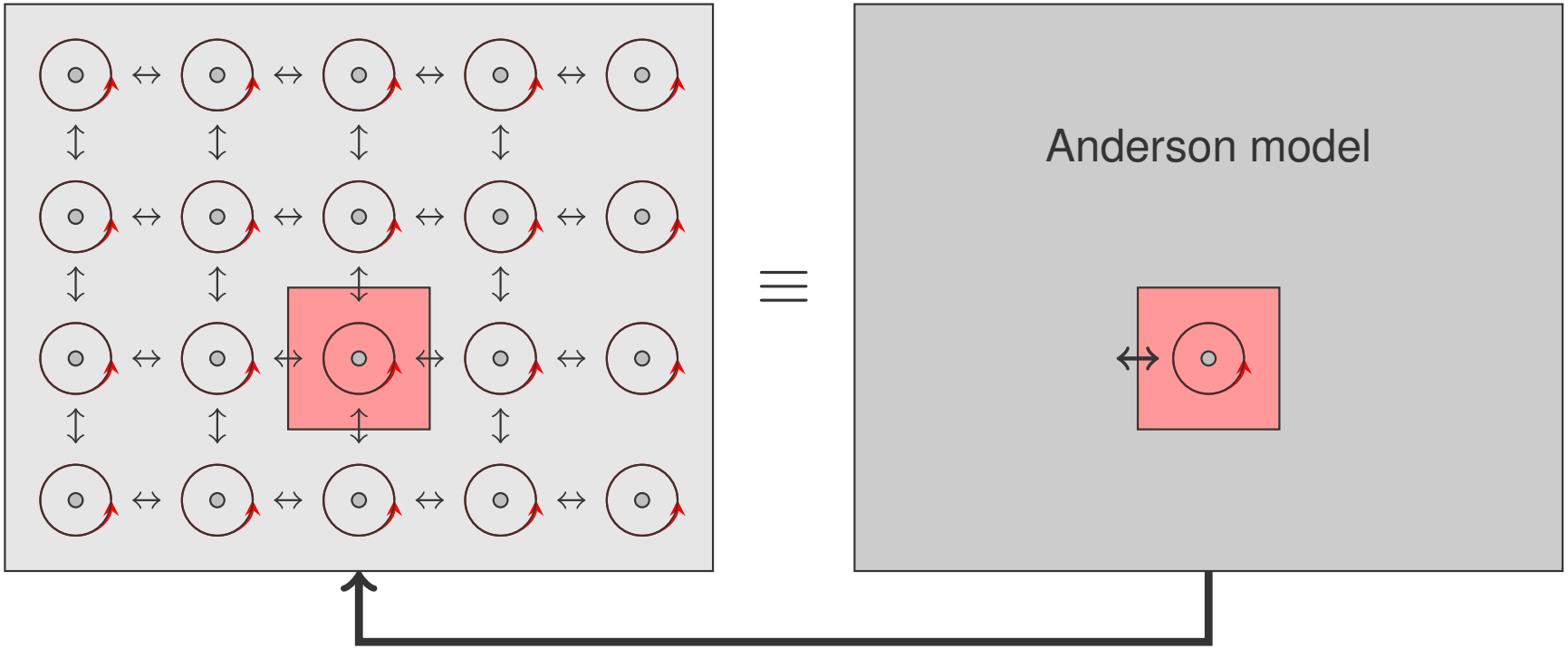
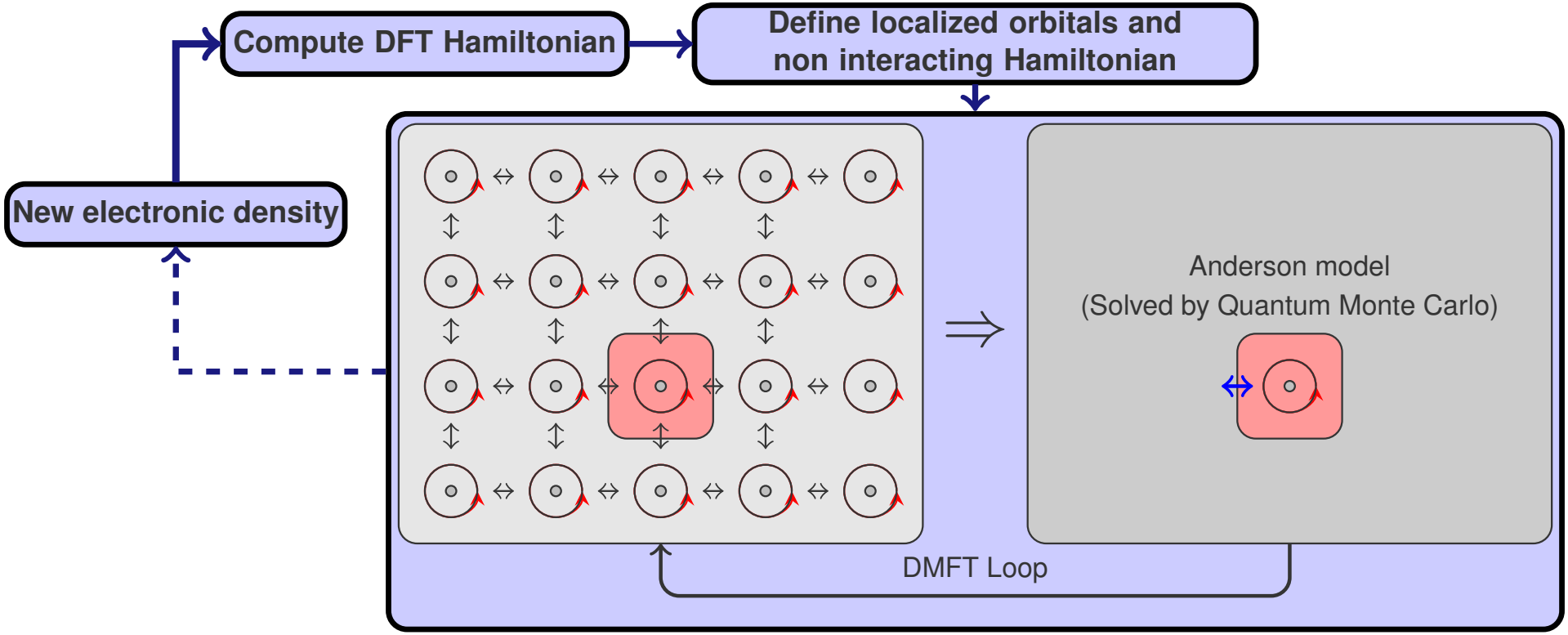


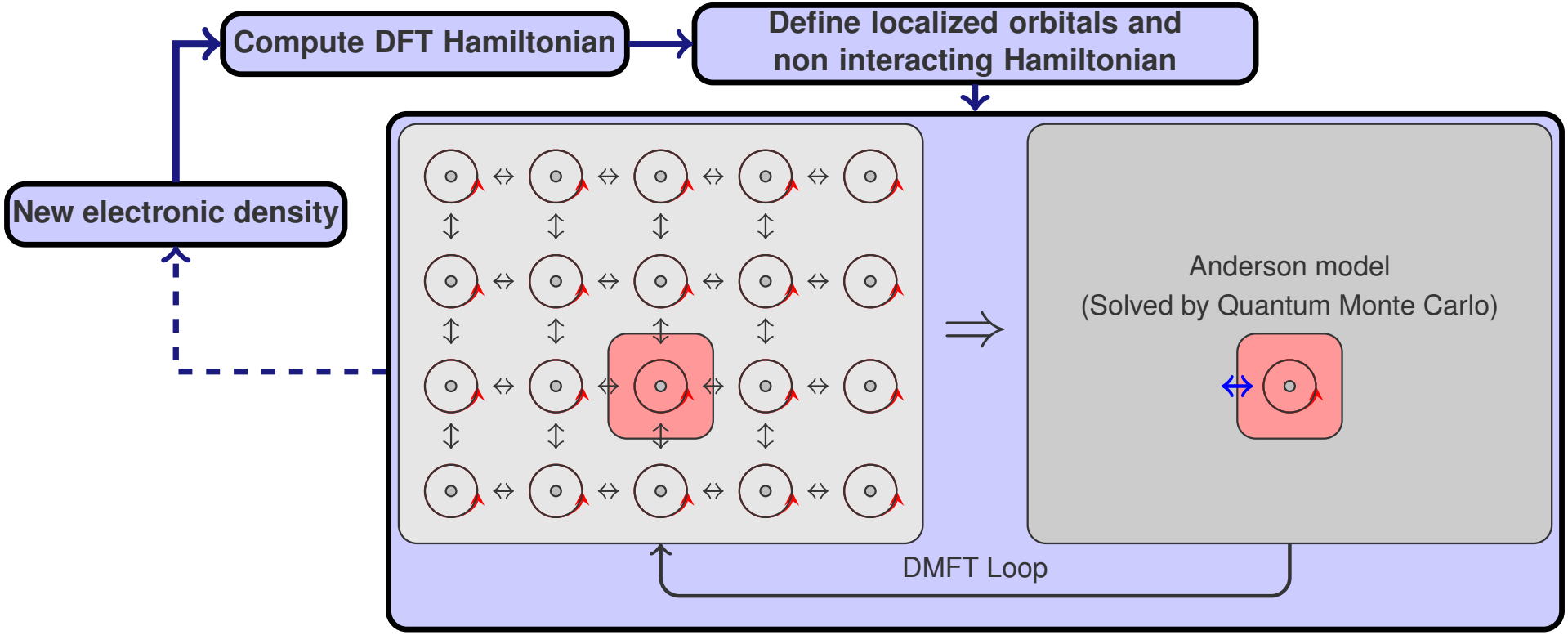
How to apply such idea for a real solid, with both **strongly interacting orbitals**, and **weakly interacting orbitals** ?

DFT+DMFT SCHEME



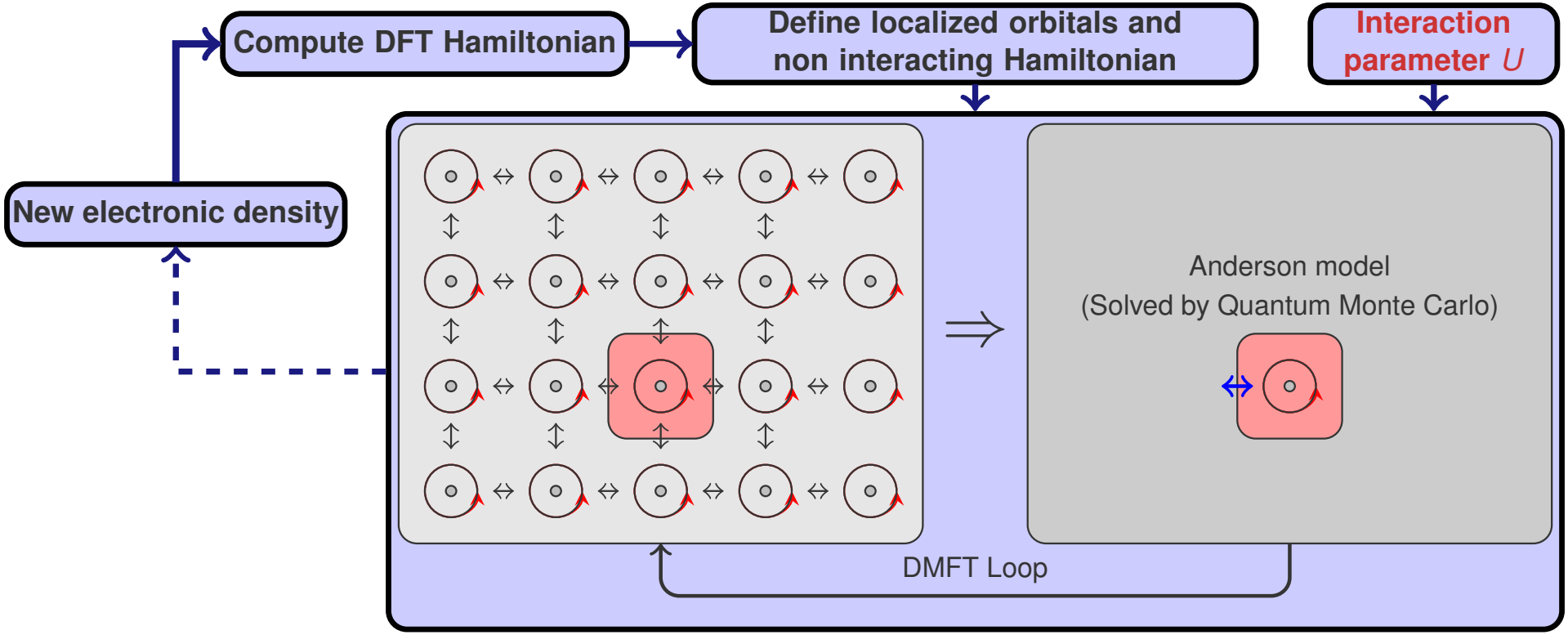
- More generally, DFT+DMFT can be expressed as functional of the local Green's function and the electronic density $\Rightarrow$ Internal and free energies can be computed.

DFT+DMFT SCHEME



- Scheme well adapted to supercomputers, implemented in ABINIT.
  L.V. Pourovskii, B. Amadon, S. Biermann, A. Georges Phys. Rev. B **76**, 235101 (2007)
  B. Amadon, F. Lechermann, A. Georges, F. Jollet, T. Wehling and A. I. Lichtenstein Phys. Rev. B **77**, 205112 (2008)
  B. Amadon, Journal of Physics: Condensed Matter **24**, 075604 (2012).

DFT+DMFT SCHEME



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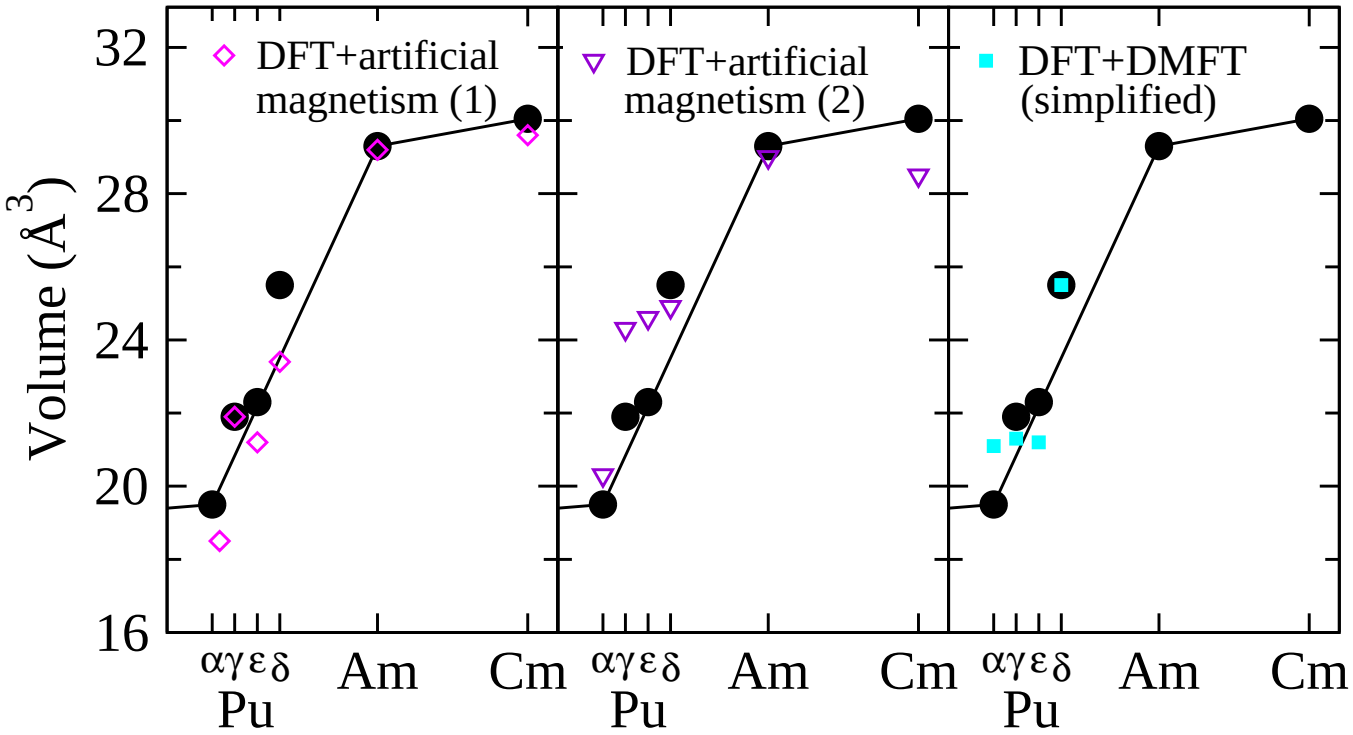
A SIMPLIFIED DFT+DMFT + PARAMETERS *U*



Simplified DFT+DMFT by Lanata and coworkers:

Interaction parameter are ajusted for a better agreement with experiment

DFT+magnetism (1): G. Robert, A. Pasturel, and B. Siberchicot *et al* Journal of Phys: Cond. Matter 15 8377 (2003), A. Kutepov and S. Kutepova J. Magn. Magn. Mater. 272, E329 (2004)

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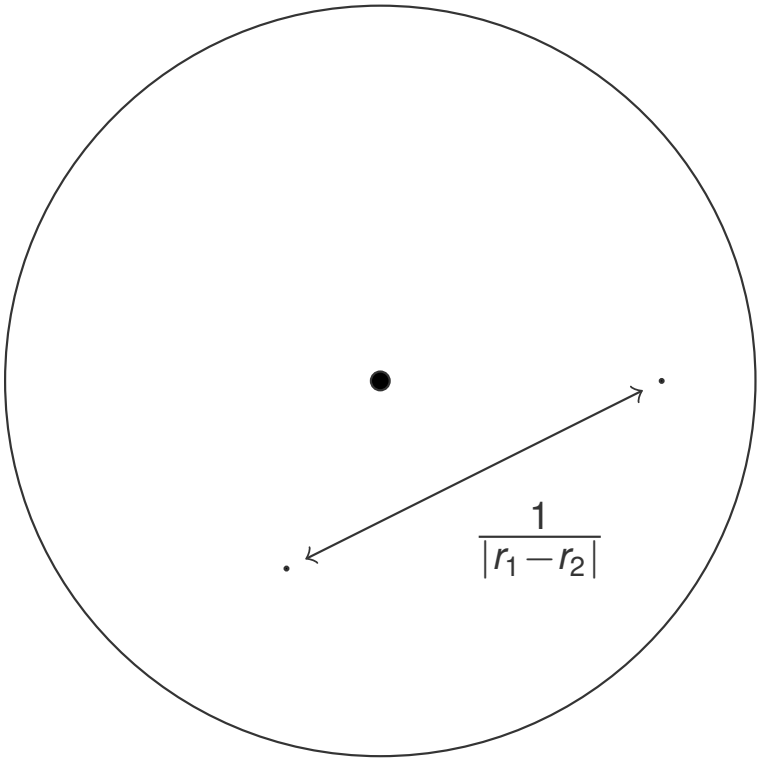
DFT+DMFT (simplified): N. Lanatà, Y. Yao, C.-Z. Wang, K.-M. Ho, and G. Kotliar Phys. Rev. X 5, 011008 (2015)

CALCULATION OF U AND SCREENING



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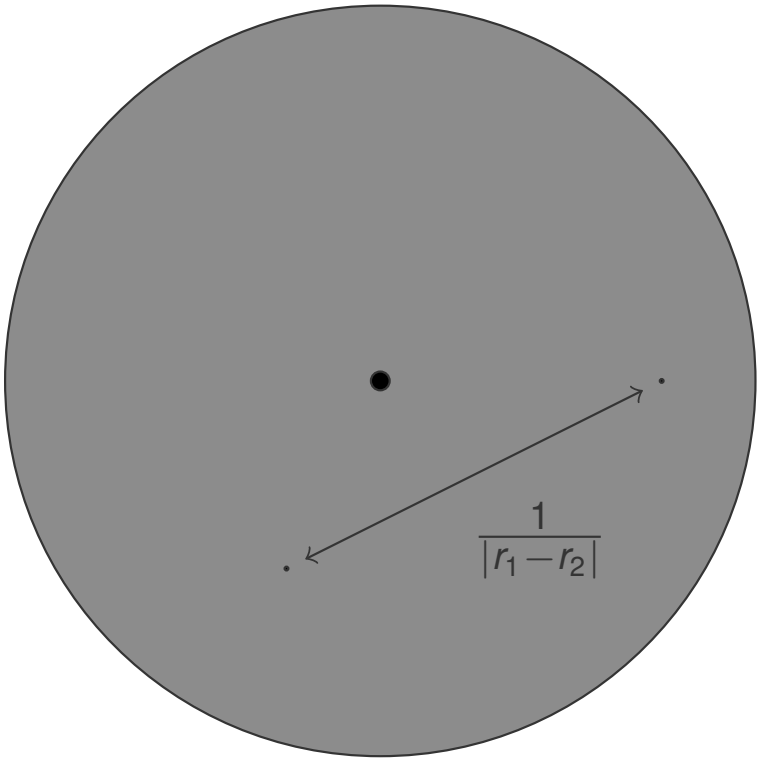

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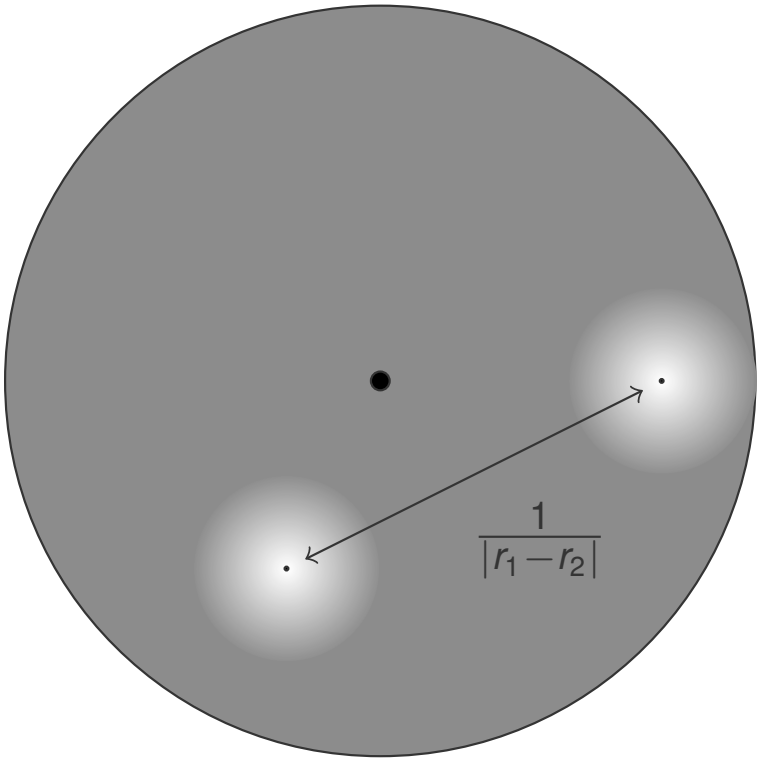

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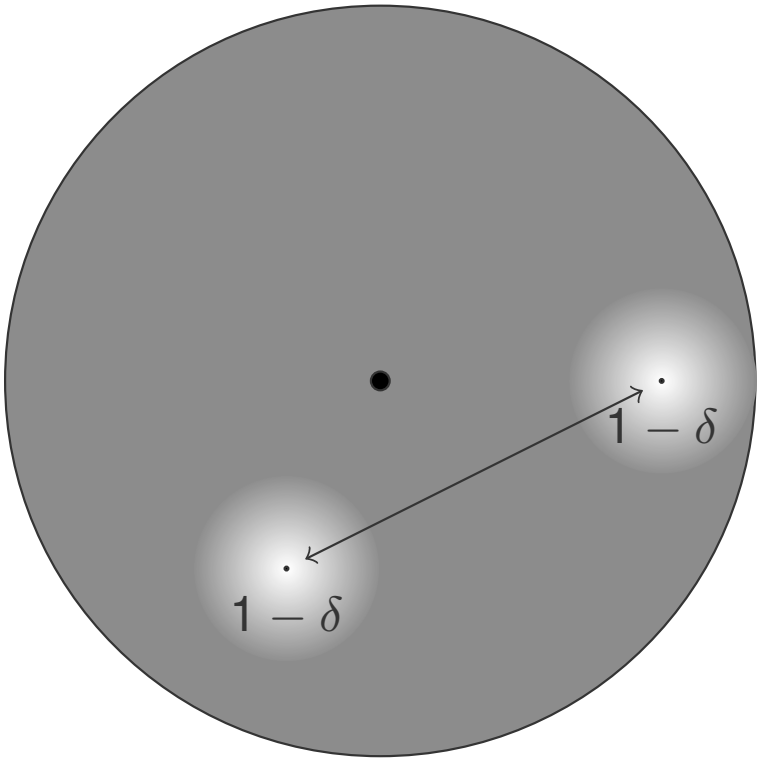

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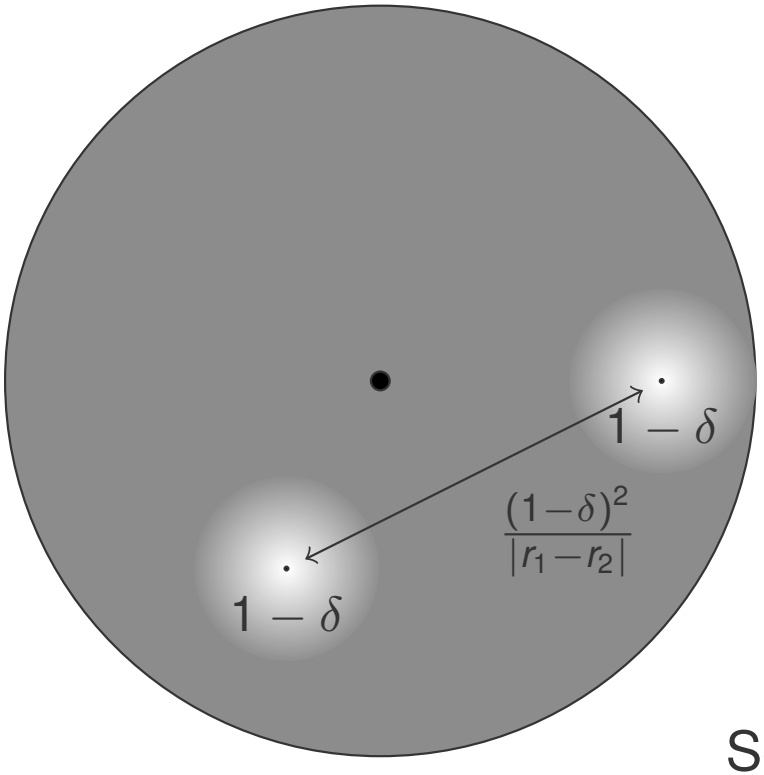


Screening

THE CALCULATION OF THE PARAMETER U

In quantum mechanics, such description can be formulated in terms of electronic transitions.

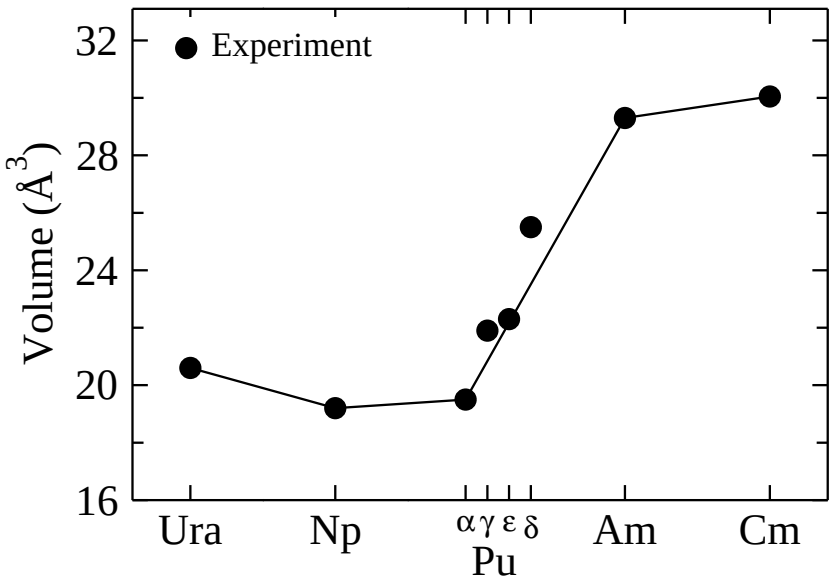
$\Rightarrow$ constrained Random Phase Approximation method

F. Aryasetiawan, M. Imada, A. Georges, G. Kotliar, S. Biermann, and A. I. Lichtenstein PRB 70, 195104 (2004)

$\Rightarrow$ Developed in `ABINIT` in collaboration with **CEA/DEN**

B. Amadon, T. Applencourt and F. Bruneval Phys. Rev. B **89**, 125110 (2014)

CALCULATION OF U IN ACTINIDES



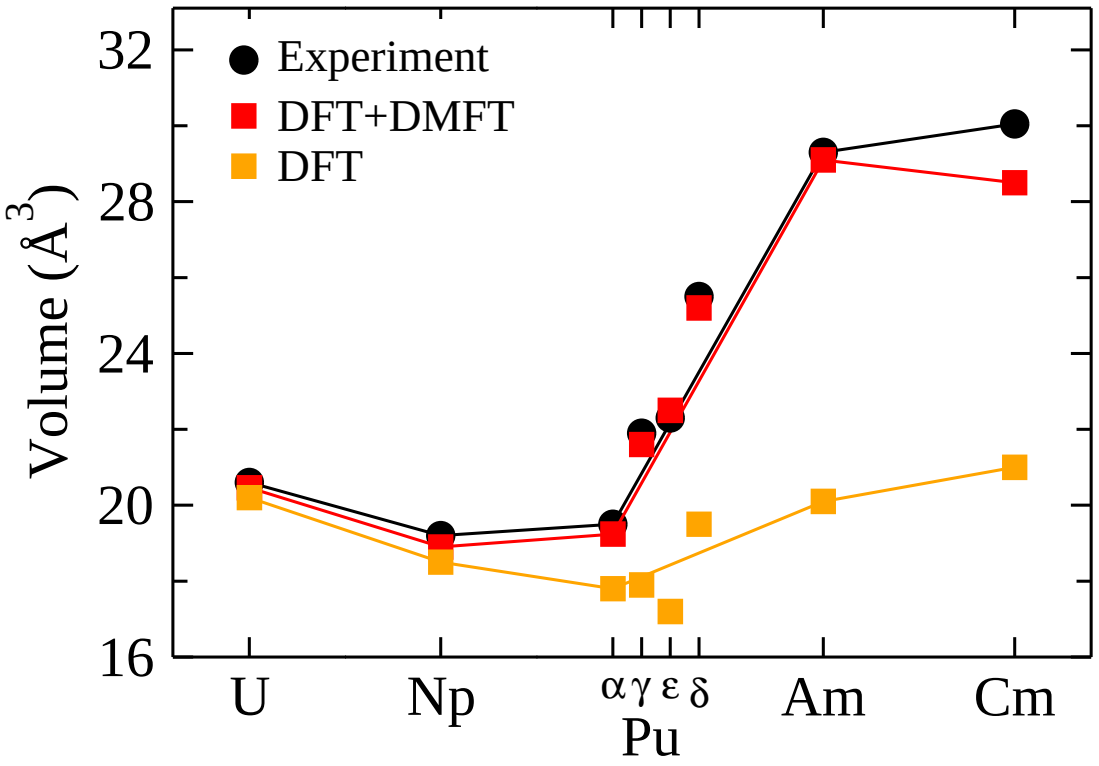
[eV]	Ura	Np	Pu	Am	Cm
U (literature)	1	1	4.5	4.5	4.5
U (this work)	0.8	1.0	0.9	1.5	3.4

- We find weak values of U !

⇒ The jump in volume is not directly related to the change of U .

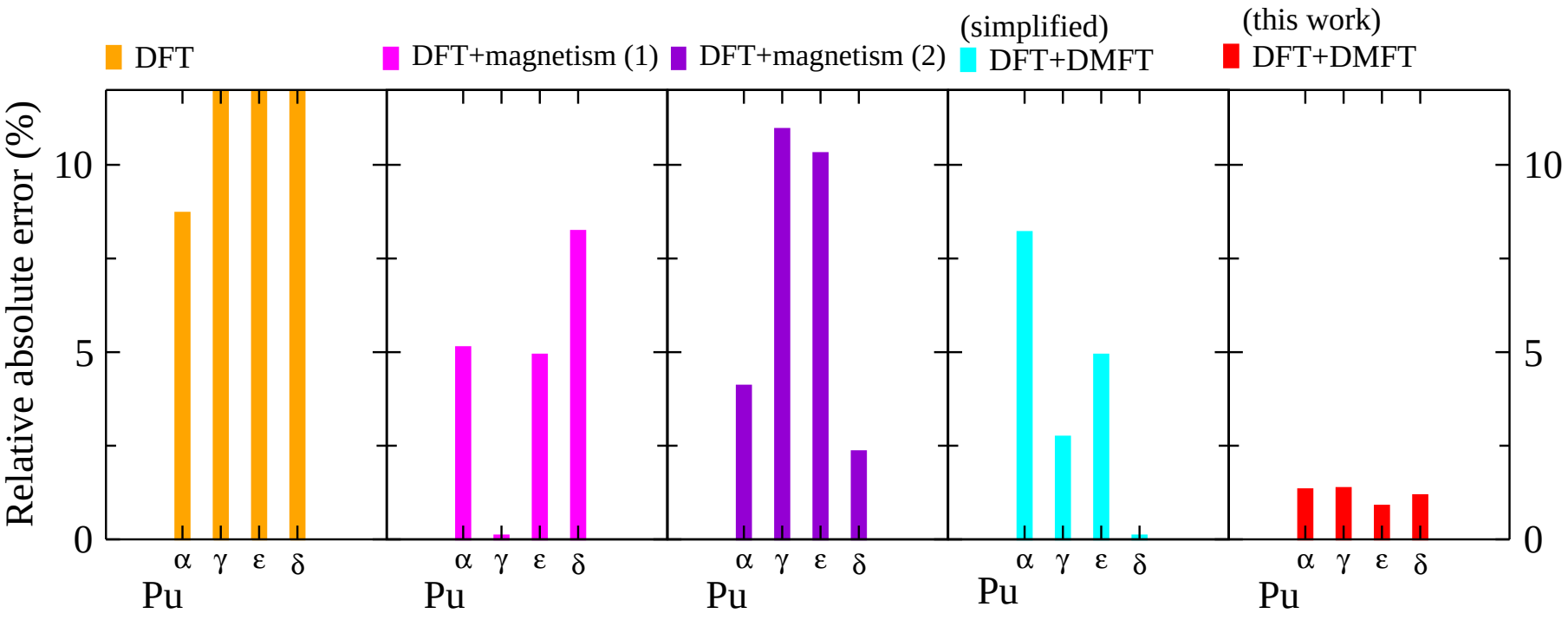
[B. Amadon, Phys. Rev. B **94**, 115148 (2016)]

DFT+DMFT RESULTS



A good description of structural and magnetic properties **without parameters**
B. Amadon, Phys. Rev. B **94**, 115148 (2016)

PHASES OF PU: COMPARISON TO OTHER METHODS



A good description of structural and magnetic properties

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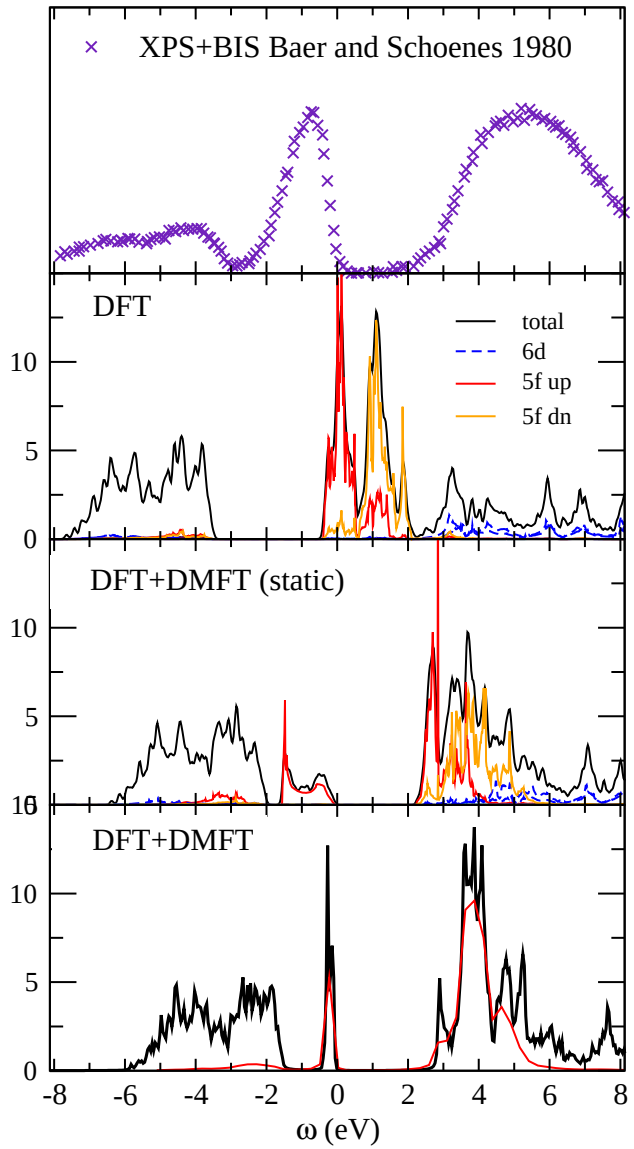
DFT+DMFT B. Amadon, Phys. Rev. B **94**, 115148 (2016)

URANIUM DIOXIDE UO_2



Experiment: Paramagnetic insulator

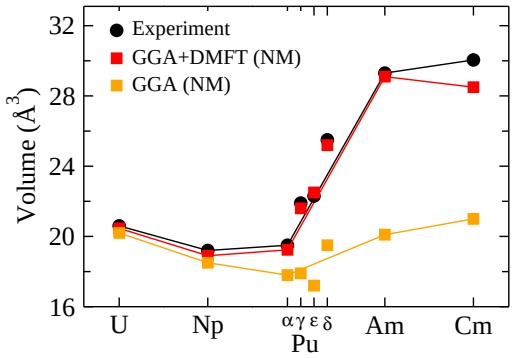
DFT : metallic

DFT+DMFT (static, simplified): antiferromagnetic insulator

DFT+DMFT : Paramagnetic insulator
$\Rightarrow$ Good electronic and magnetic properties.

CONCLUSION

- Development of methods:
  - A state of the art implementation of DFT+DMFT and of the calculation of U in `ABINIT`
- The combination of the calculation of U and DFT+DMFT offers:
  - A much better and consistent description of the structure of actinides metals.
  - A consistent description of magnetism, optics, and structure of oxydes.
- Defects and dislocations properties are impacted by interaction effects $\Rightarrow$ Macroscopic physics is impacted.



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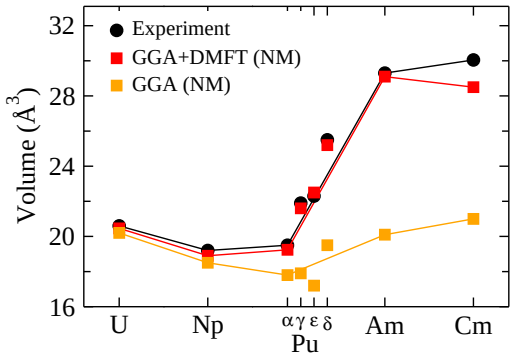

Thanks to

- T. Applencourt, J. Bieder, C. Denoual, B. Dorado, G. Geneste, A. Gerossier, F. Jollet, M. Torrent, F. Bruneval, T. Ayral, P. Seth