THEOS

THEORY AND SIMULATION OF MATERIALS

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

DFT+U Implementation and Atomic Wavefunctions in PWscf

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QUANTUM ESPRESSO

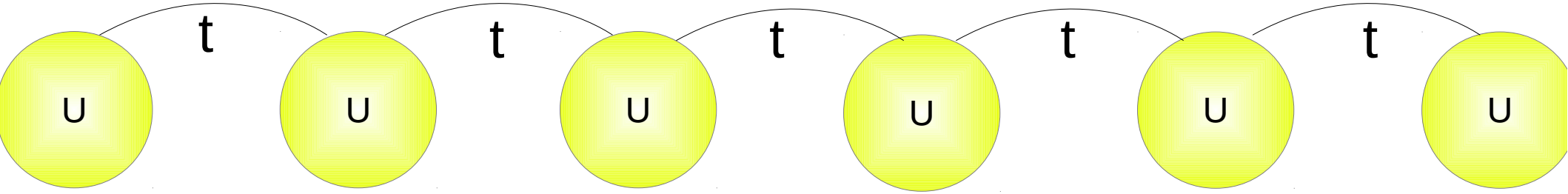
Outline

1. DFT+U Theory
   - Hubbard model and general construction
   - Rotationally invariant form
   - Theoretical understanding
   - Computing the U parameter

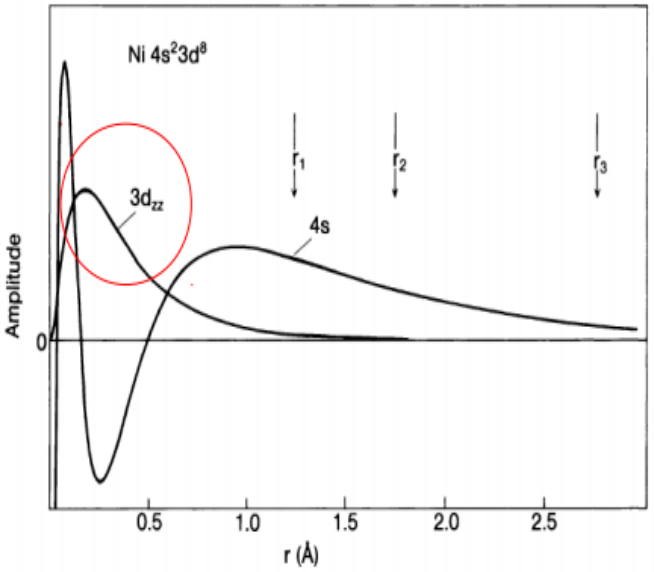
2. DFT+U Implementation
   - Hubbard subspace & Occupations
   - Atomic wavefunctions <
   - Orthonormalized wavefunctions <
   - Potential

Hubbard Model

$$H = -t \sum_{<i,j>,\sigma} (c^{\dagger}_{i,\sigma} c_{j,\sigma} + h.c.) + U \sum_{i} n_{i,\uparrow} n_{i,\downarrow}$$



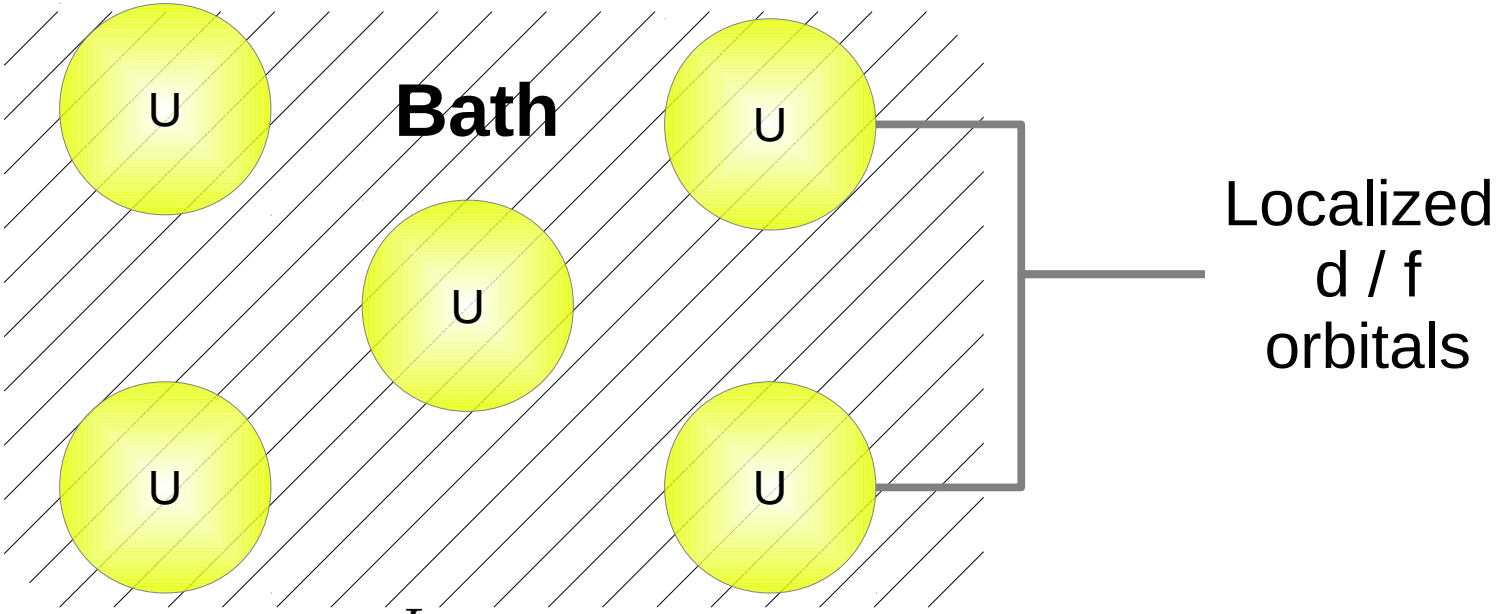
Competition between hopping
vs on-site Coulomb repulsion
Metal to insulator transitions
(ex: Mott Insulators)
Improvement over *tight binding* but also *DFT* ?
Unknown functional issue
→ Accessible solutions favored metals



When correlation is dominant

DFT+U Theory I

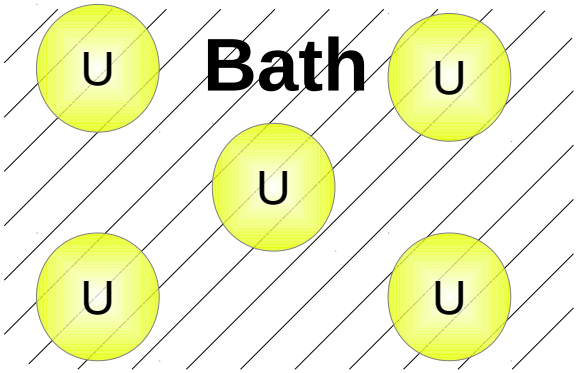
$$H = -t \sum_{<i,j>,\sigma} (c^{\dagger}_{i,\sigma} c_{j,\sigma} + h.c.) + U \sum_{i} n_{i,\uparrow} n_{i,\downarrow}$$



$$E_{Hub} = \sum_{I} \frac{U^I}{2} \sum_{m,\sigma \neq m',\sigma'} n^I_{m,\sigma} n^I_{m',\sigma'}$$

$$\mathrm{n}^{I,\sigma}_{m,m'} = \sum_{k,v} f^{\sigma}_{k,v} \left\langle \psi^{\sigma}_{k,v} | \phi^{I}_{m'} \right\rangle \left\langle \phi^{I}_{m} | \psi^{\sigma}_{k,v} \right\rangle$$

DFT+U Theory II



$$H = -t \sum_{<i,j>,\sigma} (c^{\dagger}_{i,\sigma} c_{j,\sigma} + h.c.) + U \sum_{i} n_{i,\uparrow} n_{i,\downarrow}$$

$$E_{Hub} = \sum_{I} \frac{U^I}{2} \sum_{m,\sigma \neq m',\sigma'} n^I_{m,\sigma} n^I_{m',\sigma'}$$

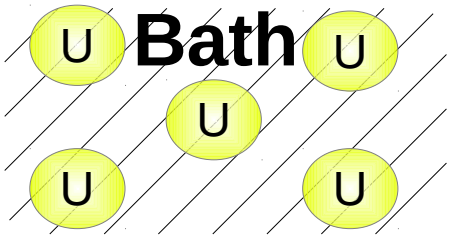
$$n^I = \sum_{m,\sigma} n^I_{m,\sigma}$$

$$E_{dc} = < E_{Hub} > = \sum_{I} \frac{U^I}{2} n^I (n^I - 1)$$

$$E_{Hub} = \sum_{I} \frac{U^I}{2} \left[n^I n^I - \sum_{\sigma} Tr[\mathbf{n}^{I\,2}_{\sigma}] \right]$$

Rotationally invariant in Hilbert space

$$E_{DFT+U} = E_{Hub} - E_{dc} = \sum_{I,\sigma} \frac{U^I}{2} Tr[\mathbf{n}^I_{\sigma}(1 - \mathbf{n}^I_{\sigma})]$$

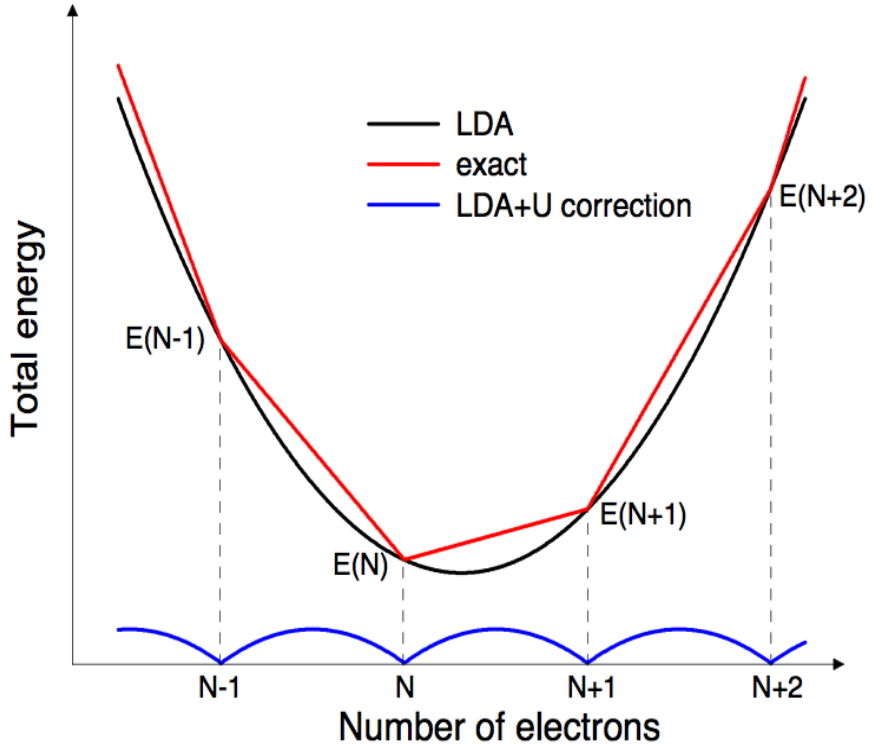


DFT+U Theory III

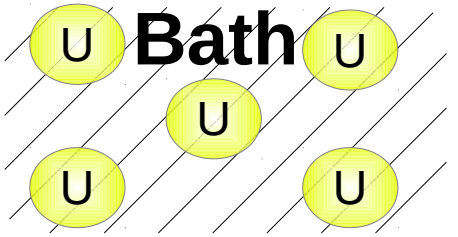
$$E_{DFT+U} = E_{Hub} - E_{dc} = \sum_{I,\sigma} \frac{U^I}{2} Tr[\mathbf{n}^I_\sigma (1 - \mathbf{n}^I_\sigma)]$$

But
U = ??

$$\mathrm{V}\left|\psi^\sigma_{k,v}\right\rangle = V_{LDA}\left|\psi^\sigma_{k,v}\right\rangle + \sum_{I,mm'} U^I \left(\tfrac{1}{2}\delta_{mm'} - n^I_{mm'}\right)\left|\phi^I_m\right\rangle\left\langle\phi^I_{m'}|\psi^\sigma_{k,v}\right\rangle$$

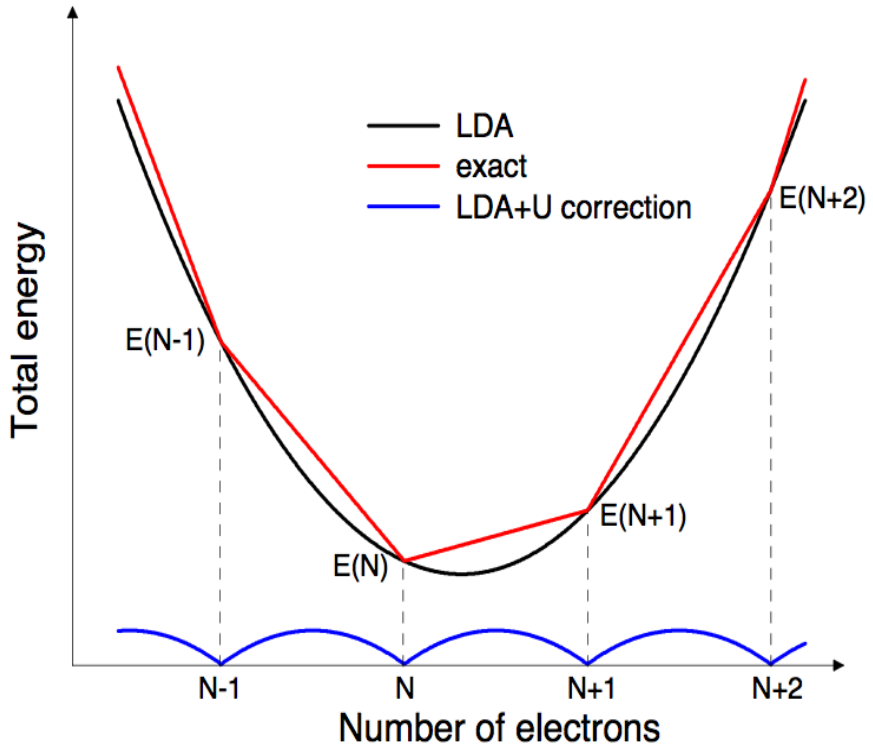


The contribution of U to restore the derivative discontinuity (piece-wise linearity) or introduce self-interaction correction



DFT+U Theory IV

$$E_{DFT+U} = E_{Hub} - E_{dc} = \sum_{I,\sigma} \frac{U^I}{2} Tr[\mathbf{n}^I_\sigma (1 - \mathbf{n}^I_\sigma)]$$



Screened Unscreened

$$U = \frac{\partial^2 E}{\partial n^2} - \frac{\partial^2 E_0}{\partial n^2}$$

$$E[\alpha] = min_n \left(E[n] + \alpha n\right)$$

$$E[n] = min_a \left(E[\alpha] - \alpha n\right)$$

$$\frac{\partial E[n]}{\partial n} = -\alpha \longrightarrow \frac{\partial^2 E[n]}{\partial n^2} = -\frac{\partial \alpha}{\partial n}$$

$$\chi = \frac{\partial n}{\partial \alpha}$$

$$U = \chi_0^{-1} - \chi^{-1}$$

Occupations: How to I

$$\mathrm{n}^{I,\sigma}_{m,m'} = \sum_{k,v} f^{\sigma}_{k,v} \left\langle \psi^{\sigma}_{k,v} | \phi^{I}_{m'} \right\rangle \left\langle \phi^{I}_{m} | \psi^{\sigma}_{k,v} \right\rangle$$

ns(m1, m2, s, I)

Defined & allocated in **scf_mod.f90**, module scf, **rho%ns(:,:,:,:)**

```
REAL(DP),   ALLOCATABLE :: ns(:,:,:,:)
if (lda_plus_u) then
   allocate (rho%ns(2*Hubbard_lmax+1, &&
                    2*Hubbard_lmax+1, &&
                    nspin,nat))
endif
```

Initialized in **init_ns.f90** following Hund's rule, and using tables **flib/set_Hubbard_l.f90** **tabd.f90**

Calculated in **new_ns.f90** each time the density is updated

Mixed in **mix_rho.f90** at the end of each scf step

Occupations: How to II

$$n^{I,\sigma}_{m,m'} = \sum_{k,v} f^{\sigma}_{k,v} \left\langle \psi^{\sigma}_{k,v} | \phi^{I}_{m'} \right\rangle \left\langle \phi^{I}_{m} | \psi^{\sigma}_{k,v} \right\rangle$$

new_ns.f90

```
! make the projection
      CALL calbec ( npw, swfcatom, evc, proj )
```

atomic wavefunctions

```
DO is = 1, nspin
   DO na = 1, nat
      nt = ityp (na)
      IF (Hubbard_U(nt).NE.0.d0) THEN
         DO m1 = 1, 2 * Hubbard_l(nt) + 1
            DO m2 = m1, 2 * Hubbard_l(nt) + 1
               DO ik = 1, nks
                  DO ibnd = 1, nbnd
                     nr(m1,m2,is,na) = nr(m1,m2,is,na) +    &&
                        DBLE( proj%k(oatwfc(na)+m2,ibnd) * &&
                        CONJG(proj%k(oatwfc(na+m1,ibnd)))* &&
                        wg(ibnd,ik)
                  ENDDO
               ...
```

Occupations: How to III

$$n^{I,\sigma}_{m,m'} = \sum_{k,v} f^{\sigma}_{k,v} \left\langle \psi^{\sigma}_{k,v} | \phi^{I}_{m'} \right\rangle \left\langle \phi^{I}_{m} | \psi^{\sigma}_{k,v} \right\rangle$$

```
! make the projection
     CALL calbec ( npw, swfcatom, evc, proj )
```

S atomic wavefunctions

m=
1 dz2
2 dzx
3 dzy
4 d(x2-y2)
5 dxy

Atomic wfc are

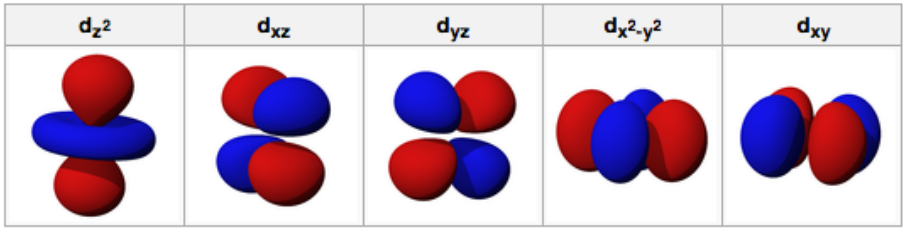
-read from pseudo: **upf(nt)%nwfc**
upf(nt)%chi(ir,nb)

-init_at_1.f90 prepares the **tab_at**

-atomic_wfc.f90 uses tab_at to prepare
wfcatom(npwx,npol,natomwfc)

-**orthoatwfc.f90** multiplies wfcatom with S
And saves in unit **iunsat**
(orthonormalization is available)

flib/ylmr2.f90
PP/src/projwfc.f90



Potential I

$$V\left|\psi^{\sigma}_{k,v}\right\rangle = V_{LDA}\left|\psi^{\sigma}_{k,v}\right\rangle + \sum_{I,mm'} U^{I}\left(\frac{1}{2}\delta_{mm'} - n^{I}_{mm'}\right)\left|\phi^{I}_{m}\right\rangle\left\langle\phi^{I}_{m'}|\psi^{\sigma}_{k,v}\right\rangle$$

$$E_{DFT+U} = E_{Hub} - E_{dc} = \sum_{I,\sigma}\frac{U^{I}}{2}Tr[\mathbf{n}^{I}_{\sigma}(1-\mathbf{n}^{I}_{\sigma})]$$

Hubbard potential is

-calculated in **v_hubbard** in **v_of_rho.f90**

```
DO na = 1, nat
   nt = ityp (na)
   IF (Hubbard_U(nt).NE.0.d0 .OR. Hubbard_alpha(nt).NE.0.d0) THEN
      DO is = 1, nspin
         DO m1 = 1, 2 * Hubbard_l(nt) + 1
            eth = eth + ( Hubbard_alpha(nt) + 0.5D0 * effU ) * ns(m1,m1,is,na)
            v_hub(m1,m1,is,na) = v_hub(m1,m1,is,na) + ( Hubbard_alpha(nt) + 0.5D0 * effU )
            DO m2 = 1, 2 * Hubbard_l(nt) + 1
               eth = eth - 0.5D0 * effU * ns(m2,m1,is,na)* ns(m1,m2,is,na)
               v_hub(m1,m2,is,na) = v_hub(m1,m2,is,na) - effU * ns(m2,m1,is,na)
            ENDDO
         ENDDO
      ENDDO
   ENDIF
ENDDO
```

Potential II

$$V\left|\psi^{\sigma}_{k,v}\right\rangle = V_{LDA}\left|\psi^{\sigma}_{k,v}\right\rangle + \sum_{I,mm'} U^I\left(\tfrac{1}{2}\delta_{mm'} - n^I_{mm'}\right)\left|\phi^I_m\right\rangle\left\langle\phi^I_{m'}|\psi^{\sigma}_{k,v}\right\rangle$$

$$E_{DFT+U} = E_{Hub} - E_{dc} = \sum_{I,\sigma}\frac{U^I}{2}Tr[\mathbf{n}^I_{\sigma}(1-\mathbf{n}^I_{\sigma})]$$

The action of the potential

-calculated in **vhpsi.f90 vhpsi (ldap, np, mps , psip , hpsi)**

```
CALL calbec (np , swfcatom , psip , proj)
DO ibnd=1,mps
  DO na = 1, nat
    nt = ityp (na)
    IF (Hubbard_U(nt).NE.0.d0 .OR. Hubbard_alpha(nt).NE.0.d0) THEN
       DO m1 = 1, 2 * Hubbard_l(nt) + 1
          temp= 0.d0
          DO m2 = 1, 2 * Hubbard_l(nt) + 1
             temp=temp+v%ns(m1,m2,current_spin,na ) * proj%k(oatwfc(na)+m2, ibnd)
          ENDDO
          CALL zaxpy( np, temp,swfcatom(1,oatwfc(na)+m1), 1, hpsi(1,ibnd) )
       ENDDO
    ENDIF
  ENDDO
ENDDO
```