DE LA RECHERCHE À L'INDUSTRIE

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HYBRID FUNCTIONALS IN ABINIT:

STATE OF THE ART AND PERSPECTIVES

F. Jollet[1], M. Torrent[1], B. Amadon[1],

F. Arnardi[1], X. Gonze[1,2]

[1]CEA, DAM-DIF, Bruyères le Châtel, 91297 Arpajon Cedex
[2]UCL,Louvain la Neuve

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Outlines

Implementation of Fock-exchange with PAW

- **Energy**
- **Forces**
- **Stresses**
- **Range-separated hybrid functionals**

Perspectives: Performance of the calculation- the ACE method

Implementation of Fock-exchange with PAW

Fock exchange term:

$$E^{\prime}_{exch} = -\frac{1}{2}\sum_{\mu}^{val}\sum_{\nu}^{val} f_\mu f_\nu \delta_{\sigma_\mu,\sigma_\nu}\left(\left(\tilde{n}_{\mu\nu}\right) + \hat{n}_{\mu\nu}\right)\right) - \frac{1}{2}\sum_{\sigma}\sum_{ijkl}\rho^{*}_{ij}(\sigma)\rho_{kl}(\sigma)e_{ikjl} - \sum_{ij}\rho_{ij}X_{ij} + E_x^{c-c}$$

with $\left(\left(n_{\mu\nu}\right)\right) = \int d\mathbf{r}d\mathbf{r}' \frac{n^{*}_{\mu\nu}(r)n_{\mu\nu}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$

$n_{\mu\nu}(\mathbf{r}) = \psi^{*}_{\mu}(r)\psi_{\nu}(r)$

$$\hat{n}_{\mu\nu}(\mathbf{r}) = \sum_{LM}\sum_{a}\sum_{i,j} Q_{i,j}^{a,LM}(\mathbf{r})\ \langle\tilde{\psi}_\mu|\tilde{p}^{a}_{i}\rangle\ \langle\tilde{p}^{a}_{j}|\tilde{\psi}_\nu\rangle$$

$$X^{a}_{ij} = \frac{1}{2}\sum_{c}\iint \frac{\phi_i(r)\phi_j(r^{'})\phi_c(r)\phi_c(r^{'})}{|r-r'|}drdr'$$

E_x^{c-c}

given in the JTHv1.0 PAW atomic data files

eikjl is already calculated for the GS

Fock exchange : the new Hamiltonian

- By considering Fock exchange, the Hamiltonian becomes:

$$\widetilde{H}|\tilde{\psi}_\nu\rangle = \left[-\frac{1}{2}\nabla^2 + \widetilde{v}_{\text{eff}}(\mathbf{r})\right]|\tilde{\psi}_\nu\rangle + \sum_a \sum_{i,j} |\tilde{p}_i^a\rangle\, D_{ij}^a\, \langle\tilde{p}_j^a|\tilde{\psi}_\nu\rangle$$

$$+ \sum_{\mu\ \text{occ.}} f_\mu\, [v_x^F(\mathbf{r})]_{\mu\nu}\, |\widetilde{\psi}_\mu\rangle$$

$$+ \sum_a \sum_{i,j} |\tilde{p}_i^a\rangle\, D_{ij}^{Fock\ a}\, \langle\tilde{p}_j^a|\tilde{\psi}_\nu\rangle \quad + \sum_a \sum_{i,j} \sum_{\mu\ \text{occ.}} f_\mu\, |\tilde{p}_i^a\rangle\, \hat{D}_{ij}^{Fock\ a}(\mu,\nu)\, \langle\tilde{p}_j^a|\tilde{\psi}_\mu\rangle$$

The first term is the well-known Fock-exchange potential:

$$[v_x^F(\mathbf{r})]_{\mu\nu} = \int d\mathbf{r}' \frac{\widetilde{n}_{\mu\nu}(\mathbf{r}') + \hat{n}_{\mu\nu}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

The second term is a standard non-local Dij term:

$$D_{ij}^{Fock\,a} = -\sum_{kl} \rho_{kl} e_{ikjl} - X_{ij}^a$$

The last term is a non-standard non-local Dij term:

- A structure similar as the usual

$$\hat{D}_{ij}^{Fock\ a}(\mu,\nu) = -\sum_{LM} \int d\mathbf{r}\, [v_x^F(\mathbf{r})]_{\mu\nu}\, Q_{ij}^{a,LM}(\mathbf{r})$$

- This term can be calculated with the routine paw_dijhat BUT on the fly in fock_getghc.

Fock forces

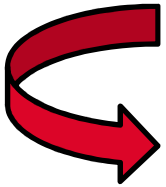
- Norm-conserving case: no contribution to the forces
- PAW case: two new terms

$$\sum_{\nu}\sum_{\mu occ}\sum_{a}\sum_{ij} f_\nu f_\mu \left\langle \tilde{\psi}_\nu \frac{\partial}{\partial \mathbf{R}} \left(|\tilde{p}_i^a\rangle \langle \tilde{p}_j^a| \right) \middle| \tilde{\psi}_\mu \right\rangle \hat{D}_{ij}^{fock\ a}(\mu,\nu)$$

Calculated in nonlop.F90

$$\sum_{\nu}\sum_{\mu occ} f_\mu\, f_\nu \int [v_x^F(\mathbf{r})]_{\mu\nu} \frac{\partial \hat{n}_{\mu\nu}(\mathbf{r})}{\partial(\mathbf{r}-\mathbf{R})} d\mathbf{r}$$

Calculated in pawmknhat_psipsi.F90



Coded and tested in ABINIT

Fock stresses

- Norm-conserving case:

$$strfock(\tilde{n}_{\mu\nu}) = -\frac{\delta_{\alpha\beta}\, E_{\mu\nu}^{Fock}}{\Omega} - \sum_{G\neq 0} 4\pi \frac{G_\alpha G_\beta}{G^4} \tilde{n}_{\mu\nu}(G)\tilde{n}_{\mu\nu}(-G)$$

Equivalent to harstr in ABINIT and calculated in strfock.F90

Coded and tested in ABINIT

- PAW case:

$$\sigma_{\alpha\beta} = \sum_{\mu\nu} f_\mu f_\nu strfock(\tilde{n}_{\mu\nu} + \hat{n}_{\mu\nu}) + \int [v_{xc}^F(r)]_{\mu\nu} \left(\delta_{\alpha\beta}\, \hat{n}_{\mu\nu} + \frac{\partial \hat{n}_{\mu\nu}}{\partial \varepsilon_{\alpha\beta}}\right) d\mathbf{r}$$

$$\sum_{\nu}\sum_{\mu occ}\sum_{a}\sum_{ij} f_\nu f_\mu \left\langle \tilde{\psi}_\nu \frac{\partial}{\partial \varepsilon_{\alpha\beta}} \left(|\tilde{p}_i^a\rangle \langle \tilde{p}_j^a| \right) |\tilde{\psi}_\mu\rangle \widehat{D}_{ij}^{fock\ a}(\mu,\nu) \right.$$

Calculated in nonlop.F90

$$-\sum_{\nu}\sum_{\mu occ} f_\mu\, f_\nu \int [v_x^F(\mathbf{r})]_{\mu\nu} (\mathbf{r}-R)_\beta \frac{\partial \hat{n}_{\mu\nu}(\mathbf{r})}{\partial(\mathbf{r}-\mathbf{R})_\alpha} d\mathbf{r}$$

Coded in ABINIT (but bug…)

Special attention to the norm-conserving case

$$V_x^{hyb}[n_c, n_v] = V_x^{DFT}[n_c + n_v] - \alpha V_x^{DFT}[n_v] + \alpha V_x^{Fock}[n_v]$$

But libxc gives: $V_x^{Libxc}[n] = (1-\alpha) V_x^{DFT}[n]$

Three calls to libxc are therefore necessary:

$V_x^{hyb}[n_v] = (1-\alpha) V_x^{DFT}[n_v]$ (1)

$V_x^{DFT}[n_c + n_v]$ (2)

$V_x^{DFT}[n_v]$ (3)

} (1)+(2)-(3)

done in xchybrid_ncpp_cc.F90 for energy, forces and stresses

Range-separated hybrid functionals

$$V_{XC}^{HSE} = \alpha V_X^{Fock,SR}(\omega) + (1-\alpha)V_X^{PBE,SR}(\omega) + V_X^{PBE,LR}(\omega) + V_C^{PBE}$$

$$\frac{1}{r} = \frac{erfc(\omega r)}{r} + \frac{\mathrm{erf}\,(\omega r)}{r} = SR(\omega) + LR(\omega)$$

- Norm-conserving case: the erfc screening is taken into account in the calculation of $[v_{xc}^F(r)]_{\mu\nu}$
- PAW case: some integrals contributing to the eijkl term must be screened with the erfc function.

  This requires the development: $\frac{erfc(\omega|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} = \sum_{l=\grave{a}}^{\infty} \omega\Phi_l(\omega R_>, \omega r_<) P_l(\cos(\widehat{\mathbf{r},\mathbf{r}'}))$

  This is done in poisson.F90 and screened_coul_kernel.F90

HSE03 and HSE06 can be achieved with ixc=-427 and -428

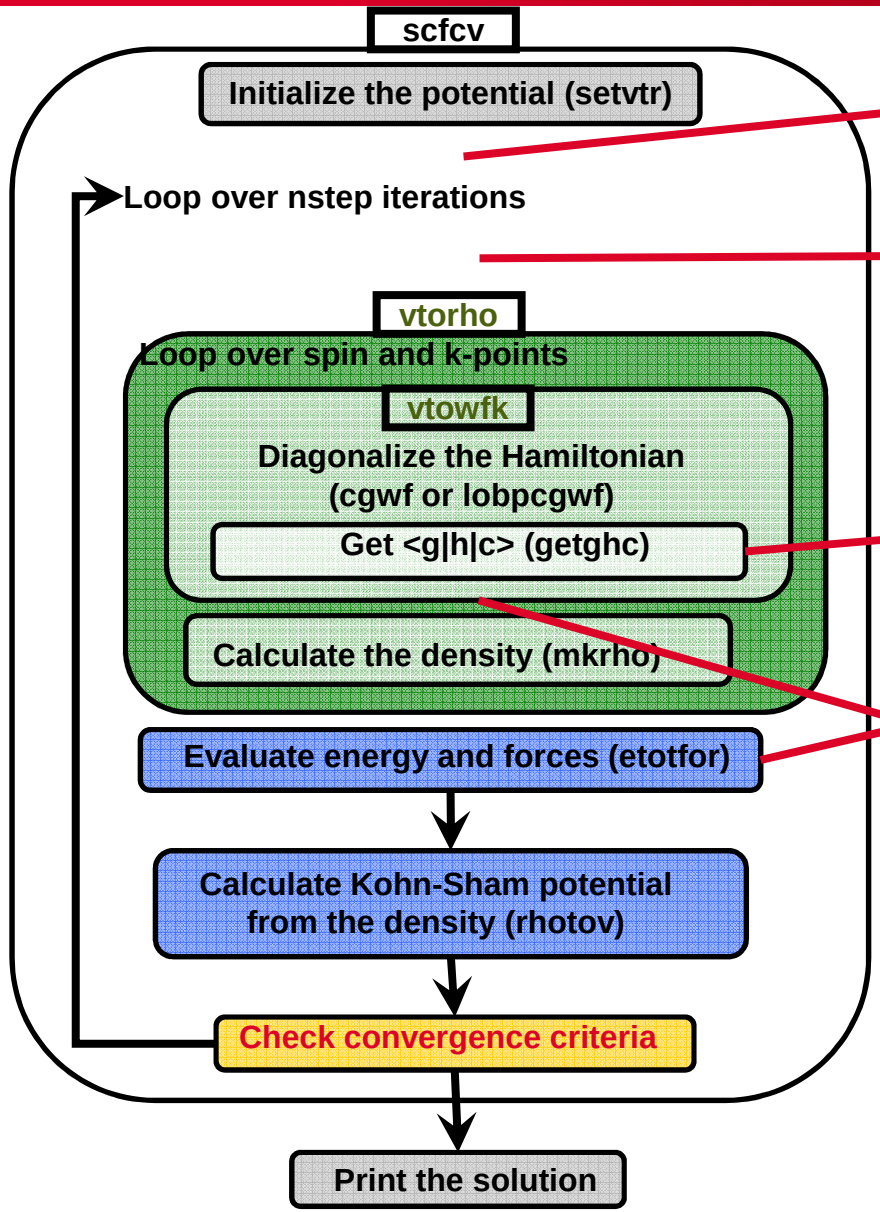
How to calculate the Fock-exchange in practice

- For an ABINIT user, to make a calculation of Fock exchange:
  - Do a first dataset for Ground State
  - Do a second dataset for Fock calculation choosing **ixc=40-42 (HF, PBE0, PBE0-1/3)**
    =-406 (PBE0-Libxc)
    = -456 (PBE0-1/3-Libxc)
    =-427,-428 (HSE03,HSE06)
  - **npkpt** : number of processors for k-point parallelization
  - **nphf**: number of processors for Fock parallelization
  - **nbandhf** : max. number of occupied valence states
  - **nnsclohf** : number of loop without updating the occupied states cwaveocc
    default value: 1 (update at each iteration)
    in practice, 3 seems a good number.

WARNING: the spin polarized case has not been extensively tested
use istwfk=1; iscf=2; paral_kgb=0, paral_atom=0
do not use simultaneously optstress and optforces

Performance of the calculation

Future self consistent cycle



Initialize the structure type fock fock_init

Save a copy of the occupied Kohn Sham eigenstates

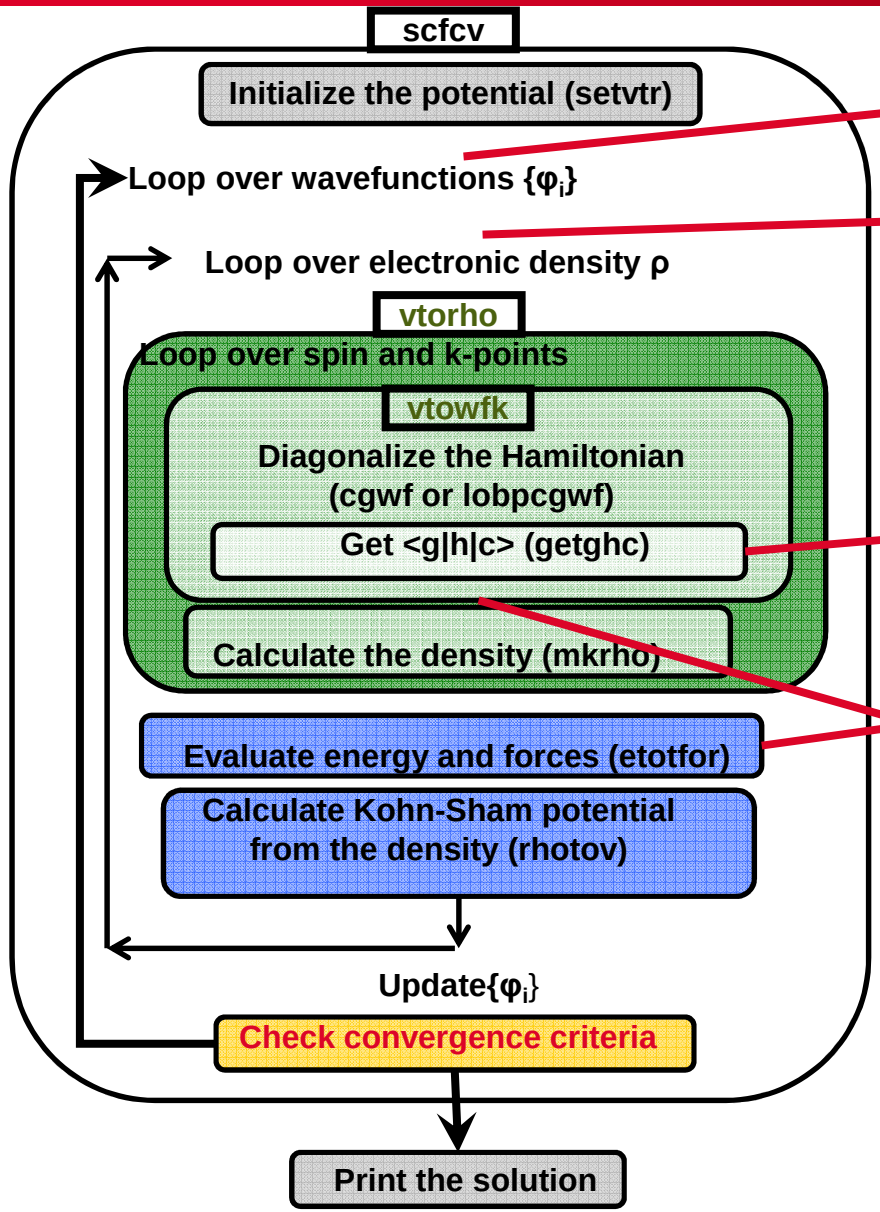
fock_updatecwaveocc

Add Fock exchange potential to the Hamiltonian

fock_getghc

Add Fock exchange contribution to the energy

Future self consistent cycle: the ACE method



Initialize the structure type fock fock_init

fock_update

Add Fock ACE exchange potential to the Hamiltonian

Add Fock exchange contribution to the energy

Adaptively Compressed Exchange (ACE) Operator
Lin Lin, J. Chem. Theory Comput. 2016, 12, 2242-2249

New self consistent cycle: the ACE method

Fock update:

Calculate $[v_{xc}^F(r)]_{\mu\nu}$

Calculate $$W_\nu(r) = \sum_{\mu occ} f_\mu \, [v_{xc}^F(r)]_{\mu\nu} \, |\tilde{\psi}_\nu >$$

Calculate $$M_{kl} = \int \tilde{\psi}_k^*(\mathbf{r}) W_l(\mathbf{r}) d\mathbf{r} = -L_{kl} L_{kl}^T$$

Calculate $$\xi_k(r) = \sum_i W_i(r) (L^{-T})_{ik}$$

Calculate $$V_X^{ACE}(\mathbf{r}, \mathbf{r}') = -\sum_k \xi_k^*(\mathbf{r}) \xi_k(\mathbf{r}')$$ ⇒ Fock operator

Advantage: the full Fock term is calculated only for the loop on the wavefunctions.
The calculation of the ACE Fock term for the loop on the density costs the price of a non-local operator

Thank you for your attention…