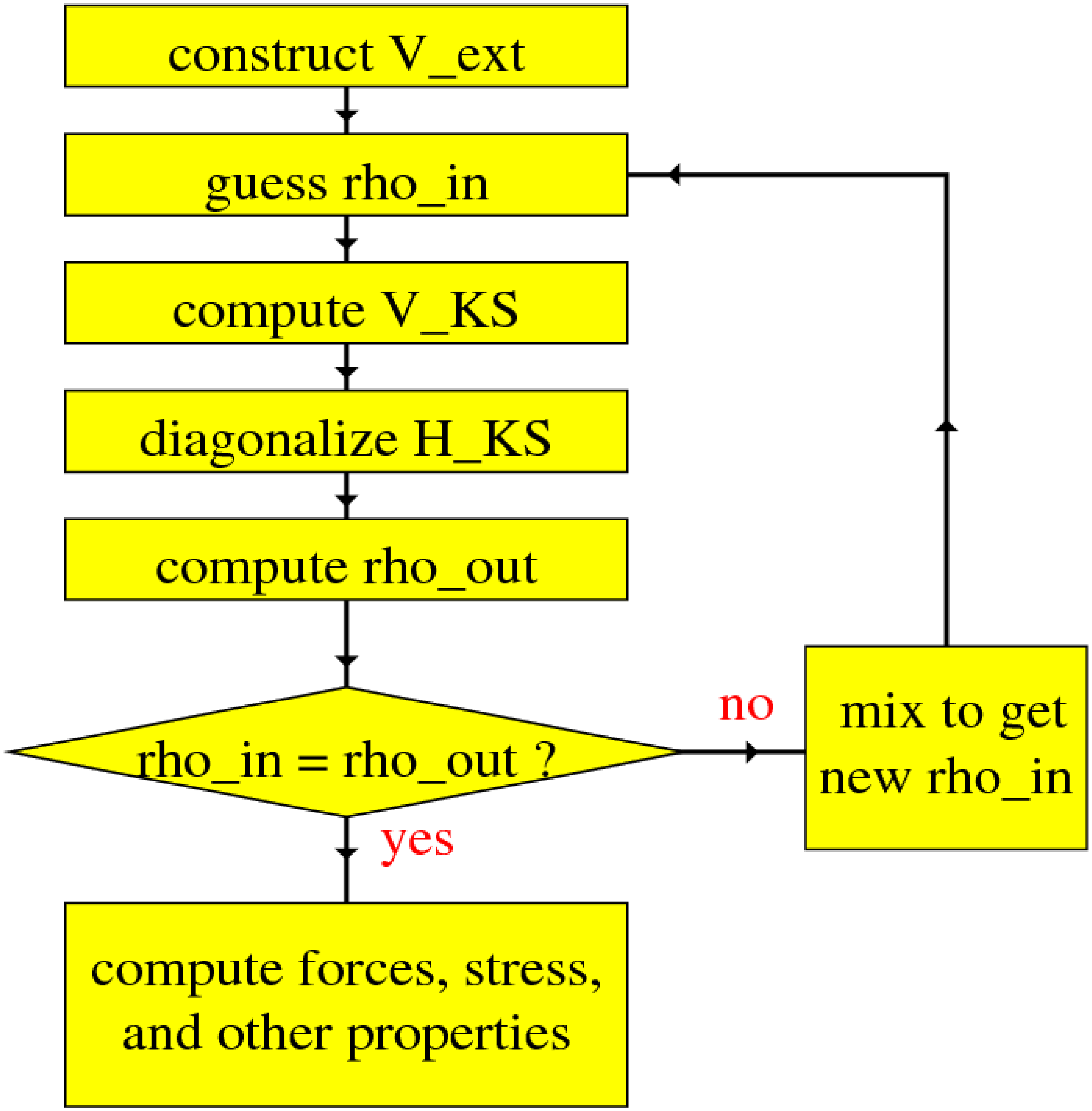
PWSCF

and

new charge density



construct V_ext
guess rho_in
compute V_KS
diagonalize H_KS
compute rho_out
rho_in = rho_out ?
no
mix to get new rho_in
yes
compute forces, stress, and other properties

PWSCF

```
call read_input_file    (input.f90)

call run_pwscf

     call setup              --> SETUP
     call init_run           --> INIT_RUN
     do
        call electrons       --> ELECTRONS
        call forces
        call stress
        call move_ions
        call update_pot
        call hinit1
     end do
```

ELECTRONS

```
call electron_scf
     do iter = 1, niter
        call c_bands       -->    C_BANDS
        call sum_band      -->    SUM_BAND
        call mix_rho
        call v_of_rho
     end do iter
```

SUM_BAND

```
 call weights
 do ik = 1, nks
    call get_buffer      (evc)
    call init_us_2       (vkb)
    do ibnd =1, nbnd
       eband = eband + wg(ibnd,ik) * et(ibnd,ik)
       evc(igk(ig)) → psi(ir)
       call get_rho        -->   GET_RHO
       call sum_bec        -->   SUM_BEC
    end do ibnd
 end do ik
 call addusdens
```

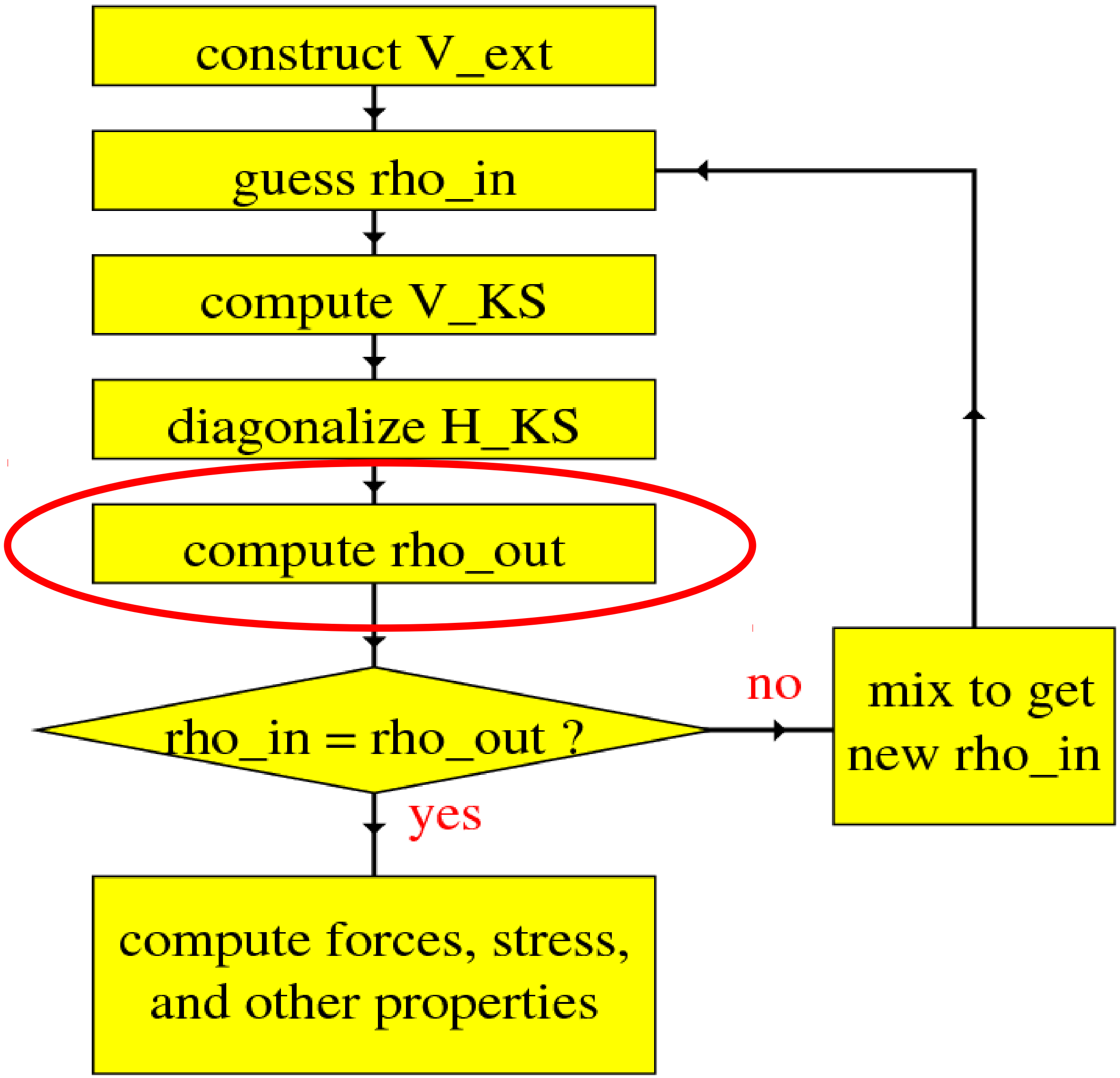
GET_RHO

```
 rho(ir) = rho(ir) + wg * |psi(ir)|**2
```

SUM_BEC

```
becsum(m,m') = Sum_ik wg <psi|beta_m><beta_m'|psi>
```

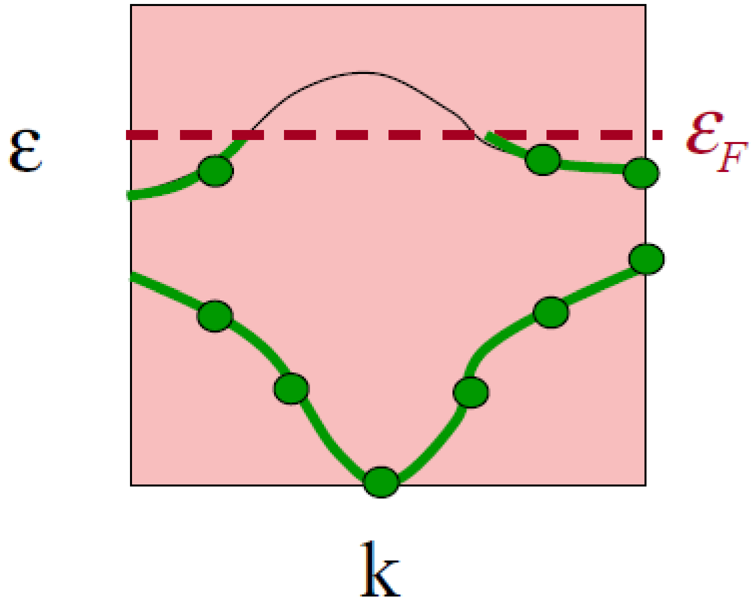
Step 5 : new charge density



Brillouin Zone Sums

Many quantities (e.g., n, Etot) involve sums over k.

- In principle, need infinite number of k's.
- In practice, sum over a finite number: BZ "Sampling".
- Number needed depends on band structure.
- Typically need more k's for metals.
- Need to test convergence wrt k-point sampling.



$$\langle P \rangle = \frac{1}{N_k} \sum_{k \in BZ} P(k) w_k$$

Types of K-points used

Special Points: *[Chadi & Cohen]*

Points designed to give quick convergence for particular crystal structures.

Monkhorst-Pack grids:

Equally spaced mesh in reciprocal space.

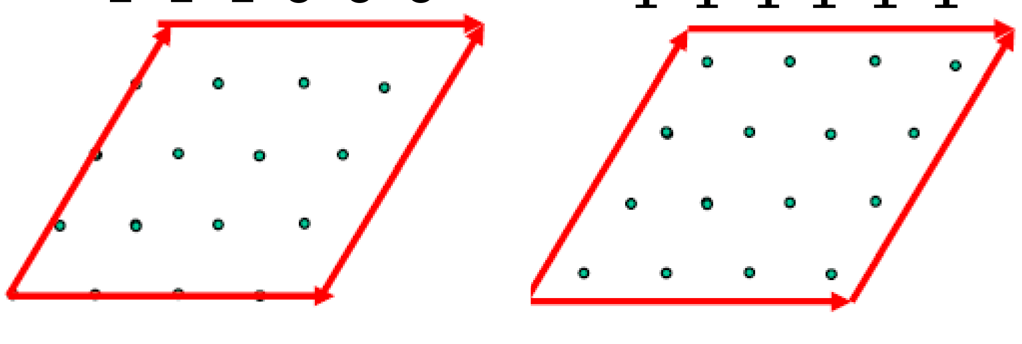
May be centred on origin [‘non-shifted’] or not [‘shifted’]

K_POINTS {tpiba|crystal|automatic|gamma}

If 'automatic' use M-P grids

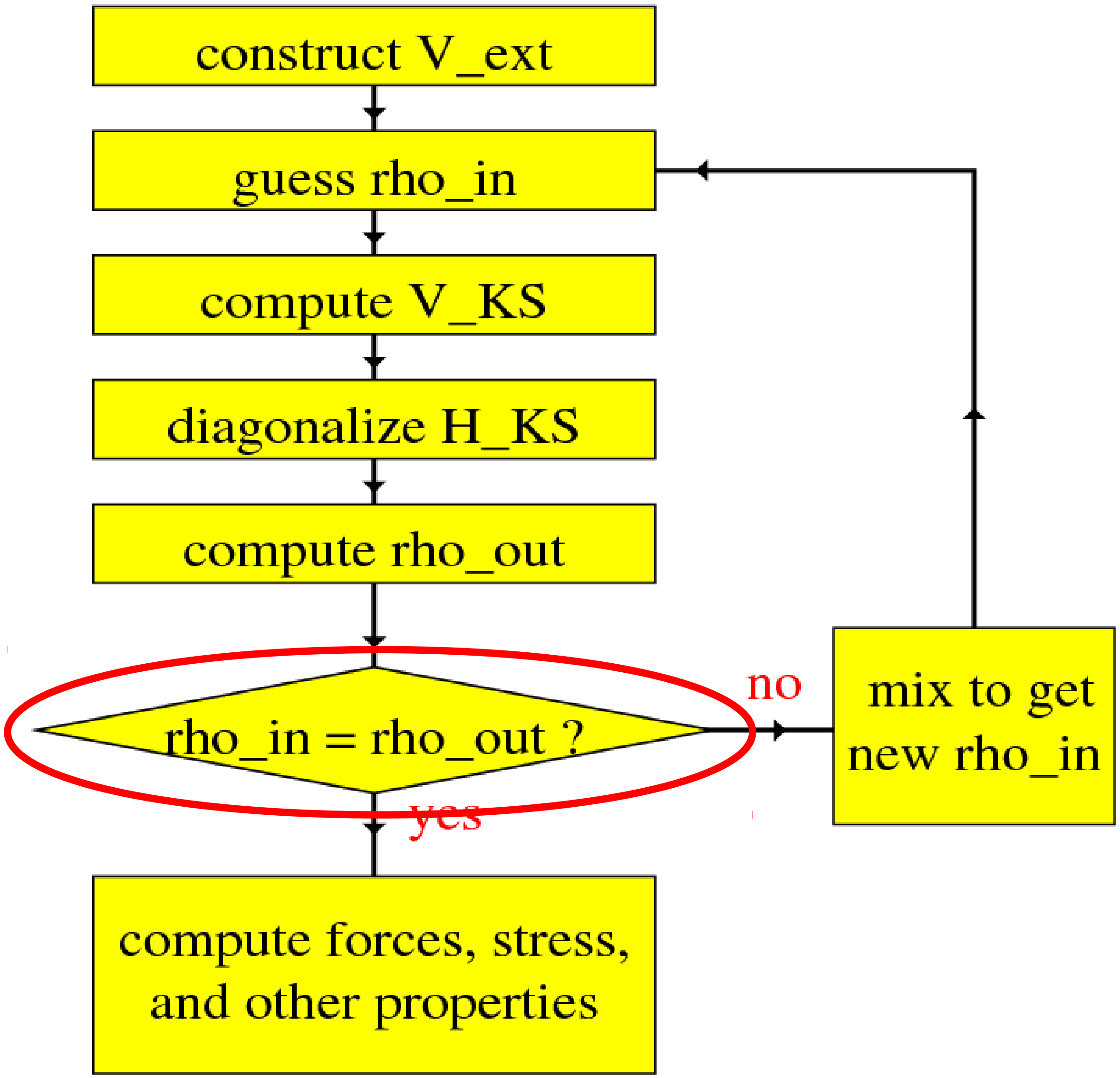
nk1, nk2, nk3, ik1, ik2, ik3

4 4 4 0 0 0   4 4 4 1 1 1



shift

Step 6 : test for convergence



How to decide if converged ?

Check for self-consistency. Could compare:

- New and old wavefunctions / charge densities.
- New and old total energies.
- Compare with energy estimated using Harris-Foulkes

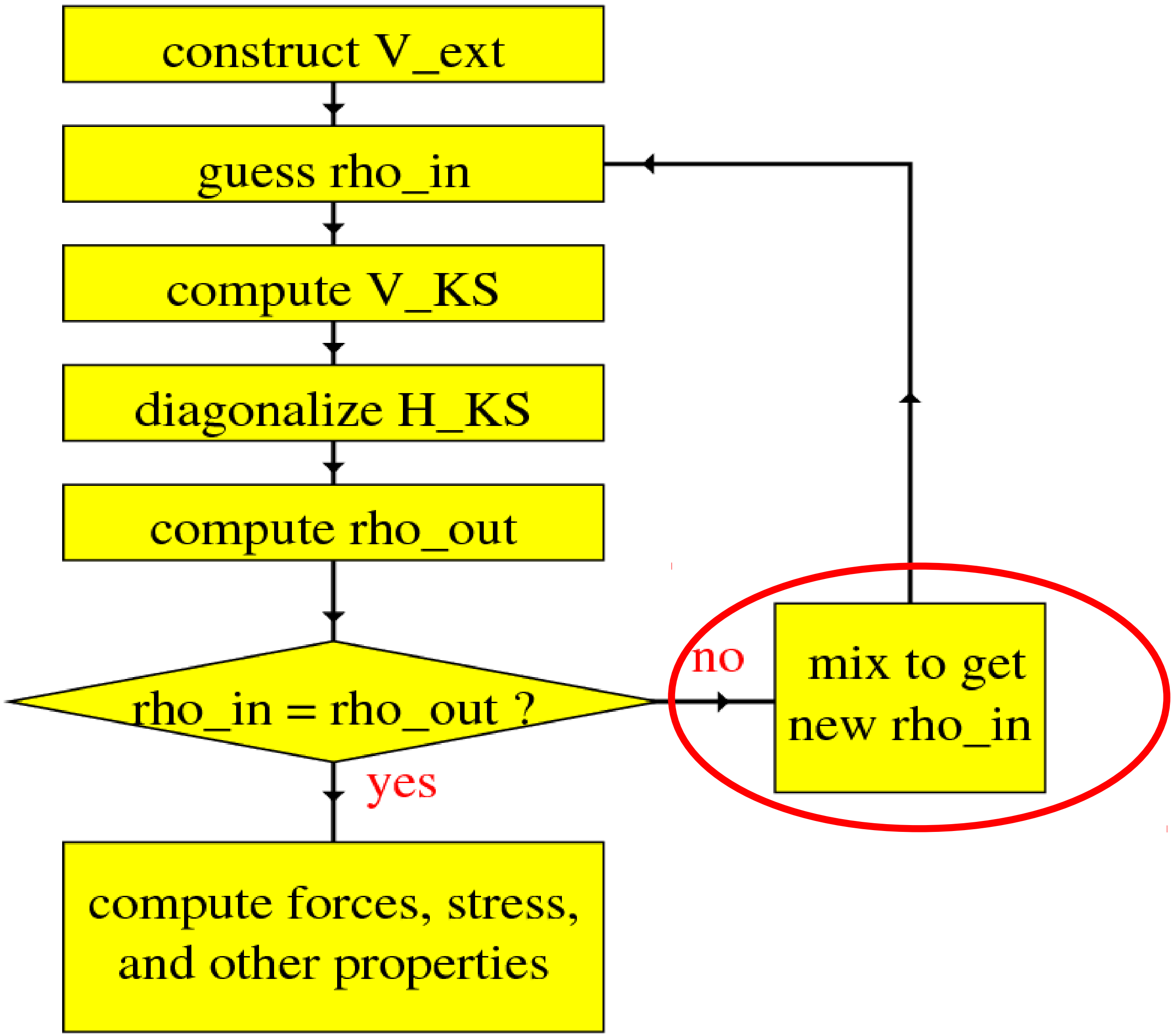
Input parameter conv_thr

typically ok to use 1.d-8

Input parameter electron_maxstep

maximum number of scf steps performed

Step 7 : mixing



Mixing

Once iteration n of the self-consistent cycle has completed … how to get next guess for rho ?

direct iteration in which rho_out is fed directly in rho_in

rho_in(n) → rho_out$_t$(n) → rho_in(n+1)

usually doesn't converge.

One needs to mix, take some combination of input and output densities (may include information from several previous iterations).

Goal is to achieve self consistency (rho_out=rho_in) in as few iterations as possible.

Mixing

Simplest prescription: linear mixing

rho_in(n+1) = beta * rho_out(n) + (1-beta) rho_in(n).

Usually slow but should converge for small enough values of beta

There exist more sophisticated prescriptions (Broyden mixing, modified Broyden mixing of various kinds…) based on Quasi Newton Raphson methods.

Input parameter mixing_mode

plain | TF| local-TF

Input parameter mixing_beta

-Typical values between 0.1 & 0.7 (depend on type of system)

Broyden Mixing

$$\rho_{in}^{i} = \overline{\rho} + \delta\rho_{in}^{i} \longrightarrow \rho_{out}^{i} = \overline{\rho} + \delta\rho_{out}^{i}$$

In the linear regime if M iterations have been accumulated

$$\rho_{in} = \rho_{in}^{M} + \sum_{i=1}^{M-1} \alpha_i(\rho_{in}^{i} - \rho_{in}^{i+1}) \longrightarrow \rho_{out} = \rho_{out}^{M} + \sum_{i=1}^{M-1} \alpha_i(\rho_{out}^{i} - \rho_{out}^{i+1})$$

BM determines ρ_{in}^{best} and ρ_{out}^{best} in the already explored manifold by minimizing the norm of $\Delta\rho_{I/O}$ w.r.t. the α_i coefficients and then applies SM to them.

$$\rho_{in}^{new} = \rho_{in}^{best} + \beta\Delta\rho_{I/O}^{best} = (1-\beta)\rho_{in}^{best} + \beta\rho_{out}^{best}$$

Simple Mixing Revisited

Ideally one would like

$$\rho_{in}^{new} = \rho_{in} - \delta\rho_{in} = \overline{\rho}$$

but we only have access to

$$\Delta\rho_{I/O} = -\chi_0\chi^{-1}\delta\rho_{in}$$

If some simple approximation A to $\chi\chi_0^{-1}$ is available one can then use it to improve the new trial density

$$\delta\rho_{in} \approx A\Delta\rho_{I/O}$$

$$\rho_{in}^{new} = \rho_{in} + \beta A\Delta\rho_{I/O} \approx \rho_{in} - \beta\delta\rho_{in}$$

Thomas-Fermi screening can provide a useful approximate inverse; for very inhomogeneous systems a local TF scheme may be required.

The end : convergence achieved