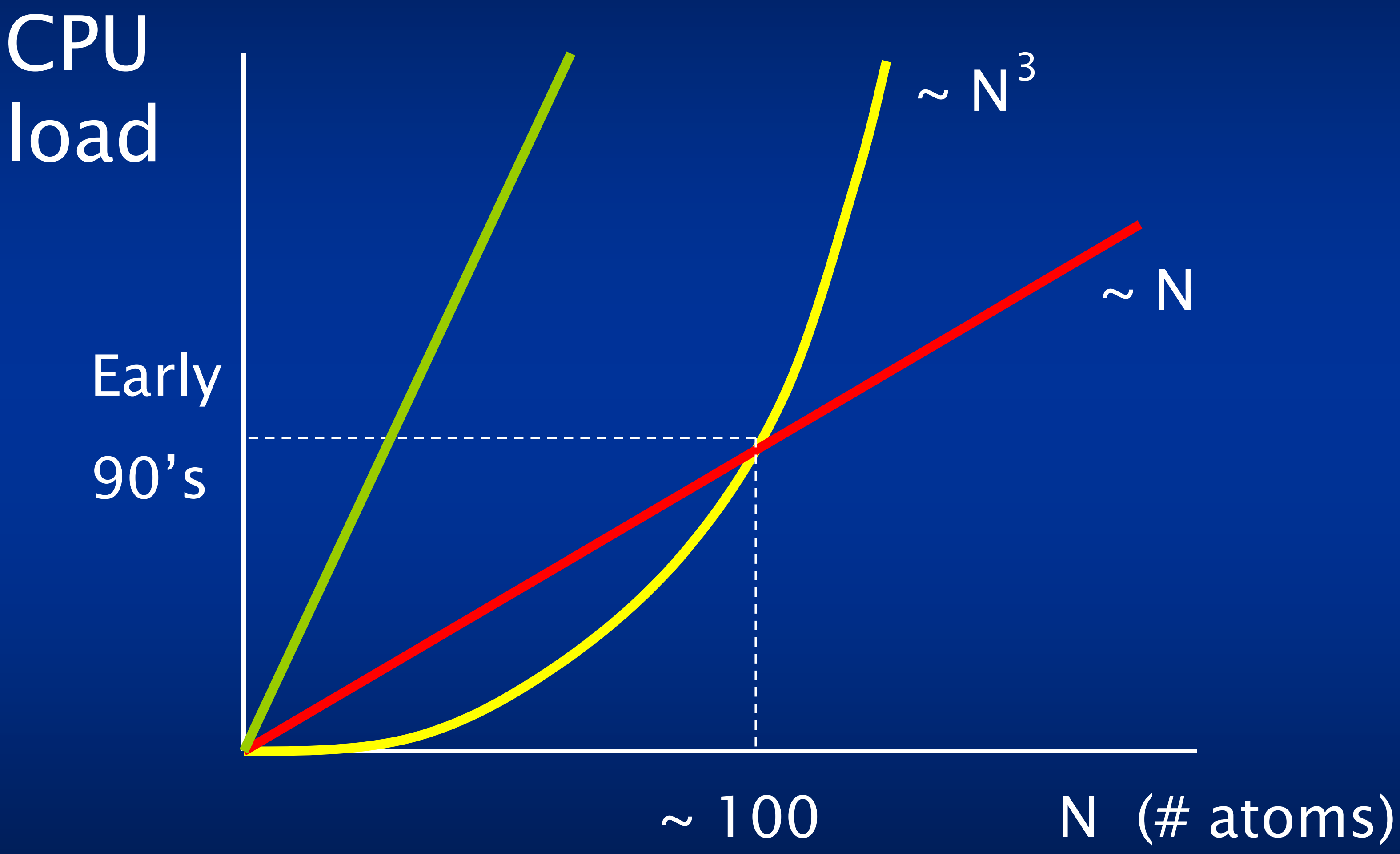
Linear scaling solvers based on Wannier-like functions

P. Ordejón

Institut de Ciència de Materials de Barcelona (CSIC)

Linear scaling = Order(N)

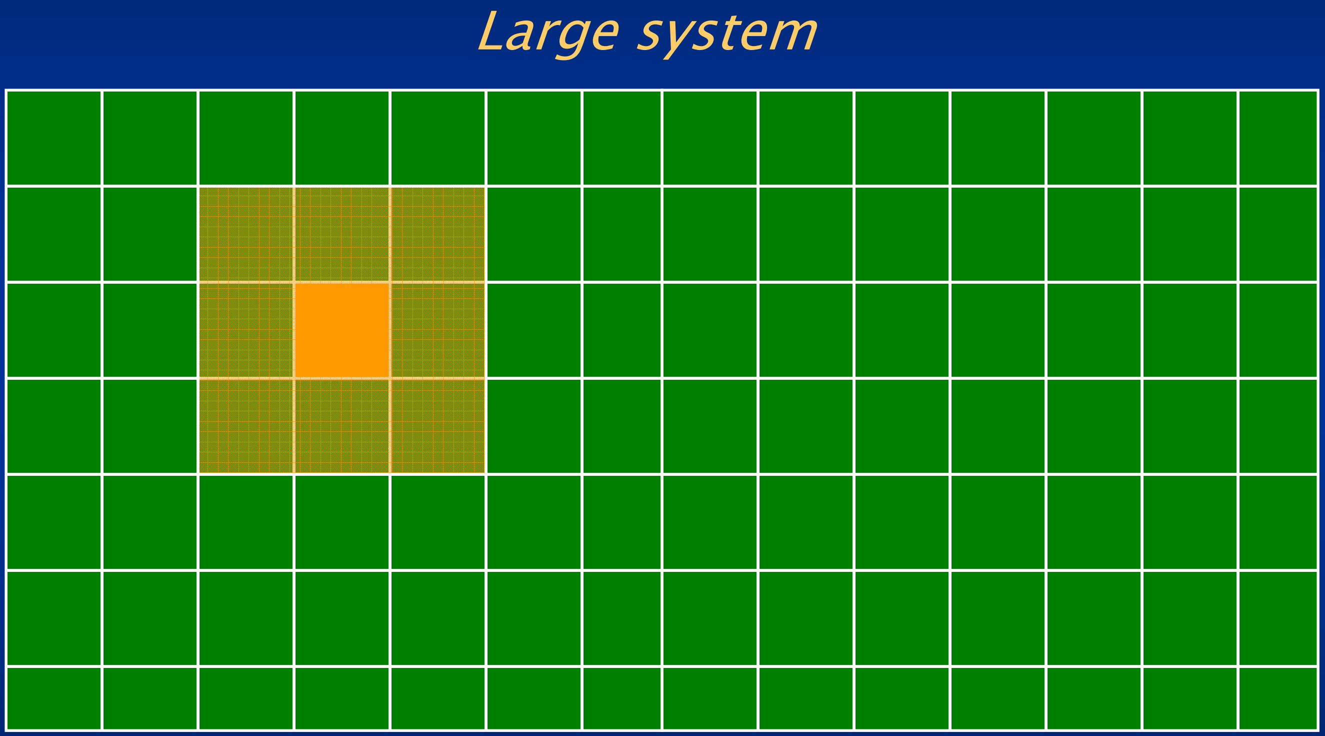


Order-N DFT

1. Find density and hamiltonian (80% of code)
2. Find “eigenvectors” and energy (20% of code)
3. Iterate SCF loop

Steps 1 and 3 spared in tight-binding schemes

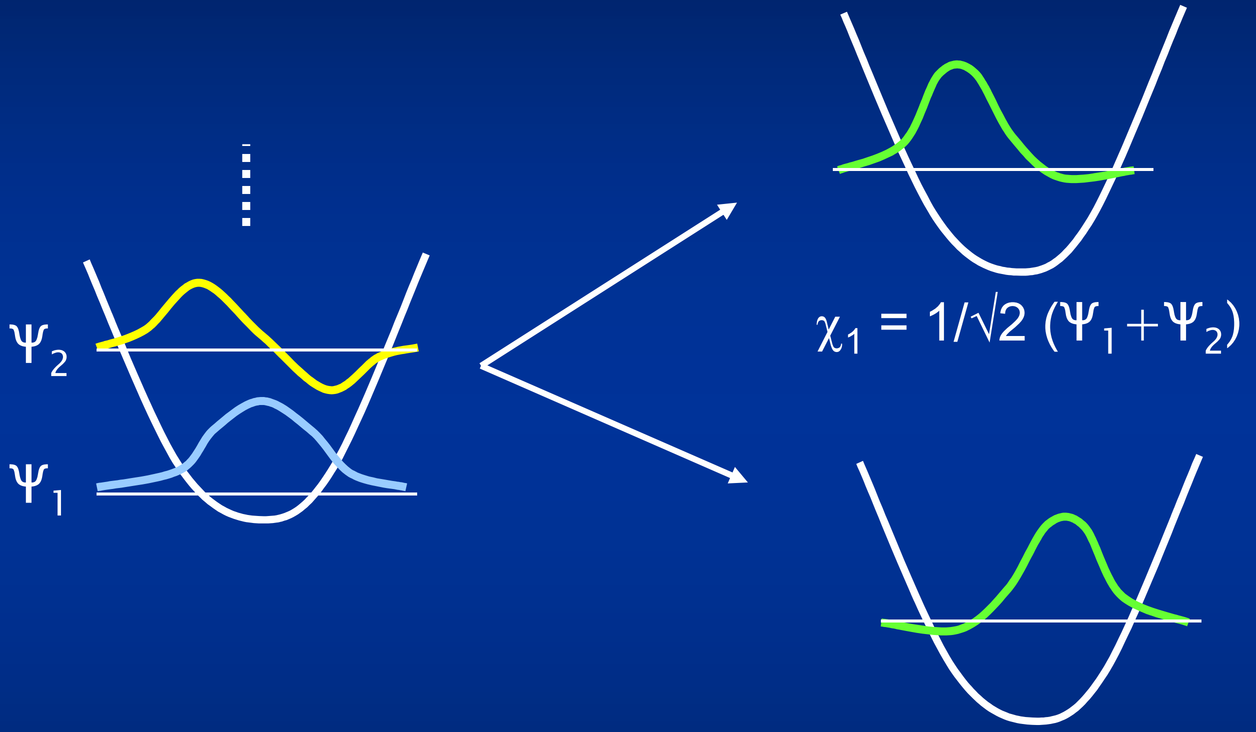
Key to O(N): locality



``Divide and conquer'' *W. Yang, Phys. Rev. Lett. 66, 1438 (1992)*

``Nearsightedness'' *W. Kohn, Phys. Rev. Lett. 76, 3168 (1996)*

Locality of Wave Functions



$\chi_1 = 1/\sqrt{2}\,(\Psi_1 + \Psi_2)$

$\chi_2 = 1/\sqrt{2}\,(\Psi_1 - \Psi_2)$

$$\left|\chi^{occ}\right\rangle = \mathbf{U}\left|\psi^{occ}\right\rangle$$

Wannier functions (crystals)

Localized Molecular Orbitals (molecules)

Locality of Wave Functions

Energy:

$$E = \langle \psi_1 | H | \psi_1 \rangle + \langle \psi_2 | H | \psi_2 \rangle = Tr_{occ}(H)$$

Unitary Transformation: $\{ | \psi_i \rangle \} \rightarrow \{ | \chi_i \rangle \}$

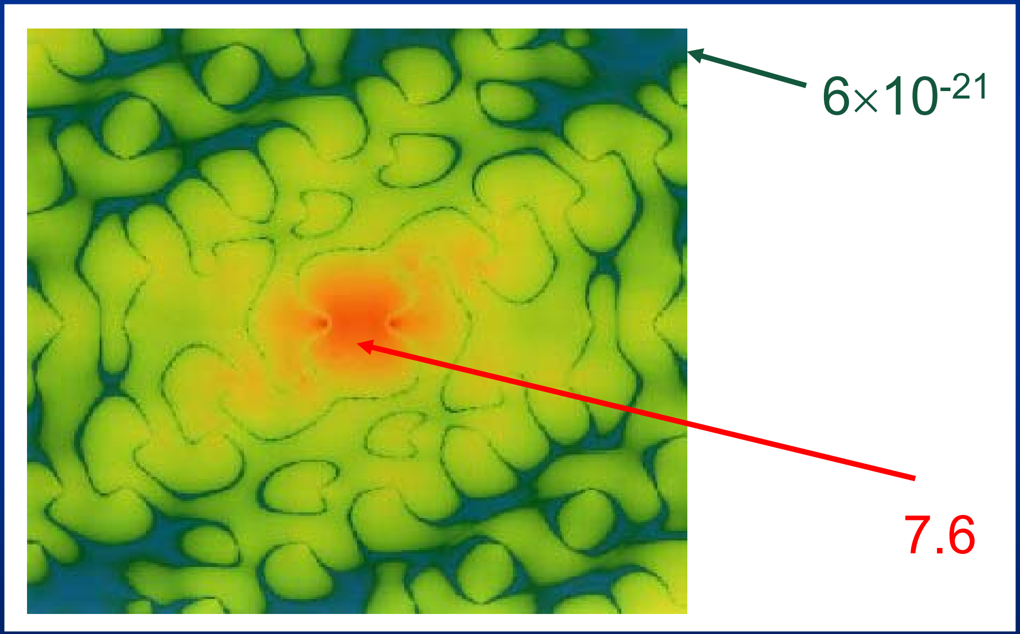
$$E = Tr_{occ}(H) = \langle \chi_1 | H | \chi_1 \rangle + \langle \chi_2 | H | \chi_2 \rangle$$

We do NOT need eigenstates!

We can compute energy with Loc. Wavefuncs.

Locality of Wave Functions

Exponential localization (insulators):

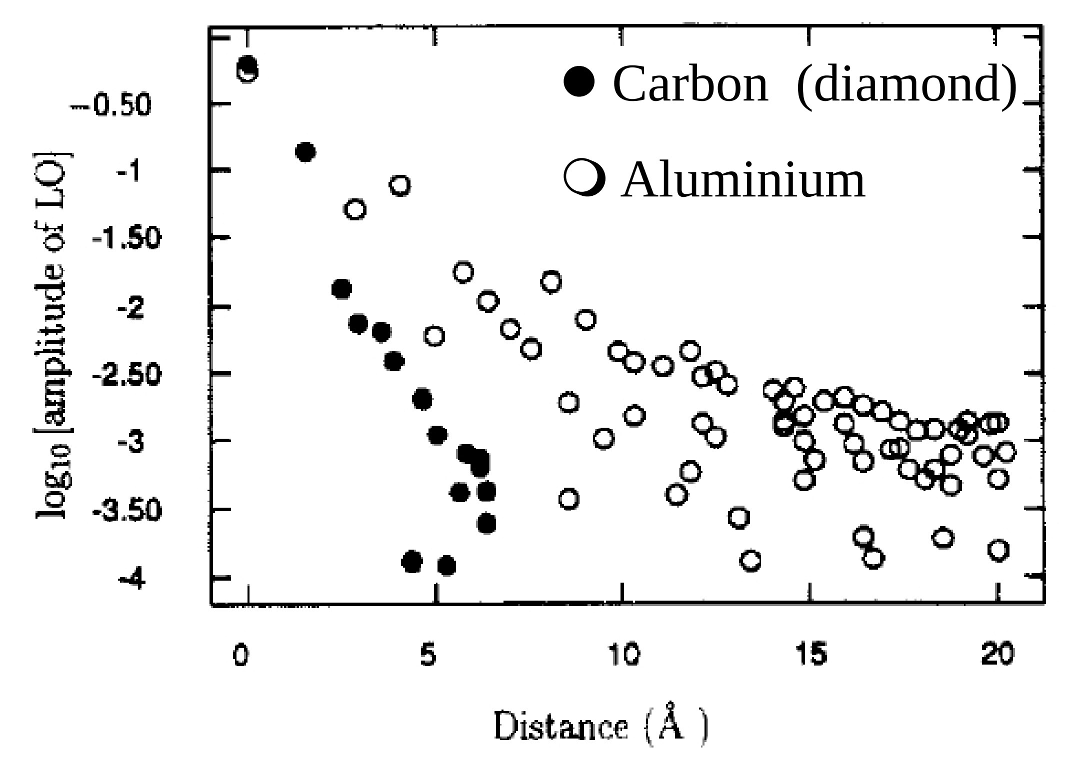


Wannier function in Carbon (diamond)

Drabold et al.

Locality of Wave Functions

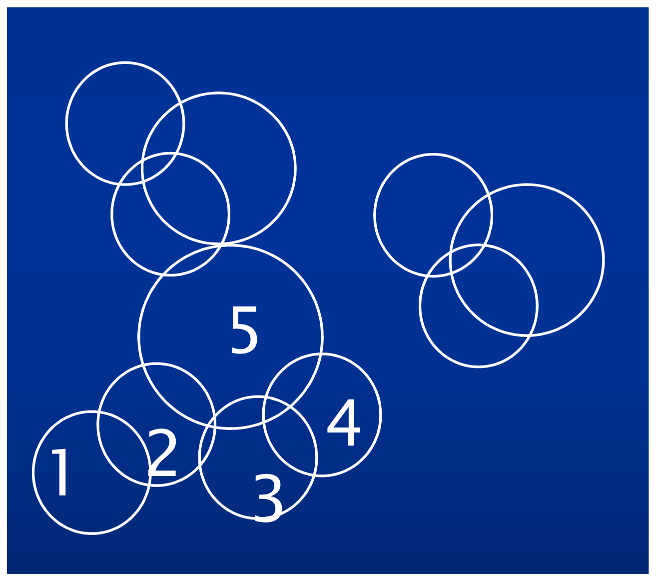
Insulators vs Metals:



Goedecker & Teter, PRB 51, 9455 (1995)

Linear Scaling

Localization + Truncation



- Sparse Matrices

$$\hat{H}_{ij} = \left\langle \chi_i \middle| \hat{H} \middle| \chi_j \right\rangle$$

- Truncation errors

$$Error \approx \exp(-\alpha R_c)$$

In systems with a gap.
Decay rate α depends on gap E_g

Linear Scaling Approaches

(Localized) object which is computed:

- wave functions $\chi(r) \approx \exp(-\alpha r)$
- density matrix $\rho(r-r') \approx \exp(-\beta(r-r'))$

Approach to obtain the solution:

- minimization
- projection
- spectral

Reviews on O(N) Methods: Goedecker, RMP ’98

Ordejón, Comp. Mat. Sci.’98

Basis sets for linear-scaling DFT

- LCAO: – Gaussian based + QC machinery

  M. Challacombe, G. Scuseria, M. Head-Gordon …

  – Numerical atomic orbitals (NAO)

  SIESTA

  S. Kenny &. A Horsfield (PLATO)

  OpenMX
- Hybrid PW – Localized orbitals
  - Gaussians J. Hutter, M. Parrinello
  - "Localized PWs"

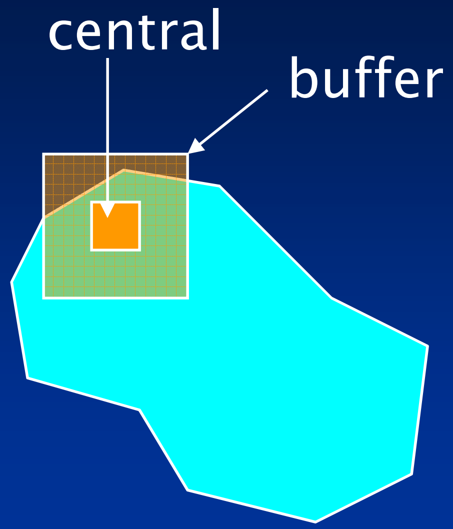
  C. Skylaris, P, Haynes & M. Payne
- B-splines in 3D grid

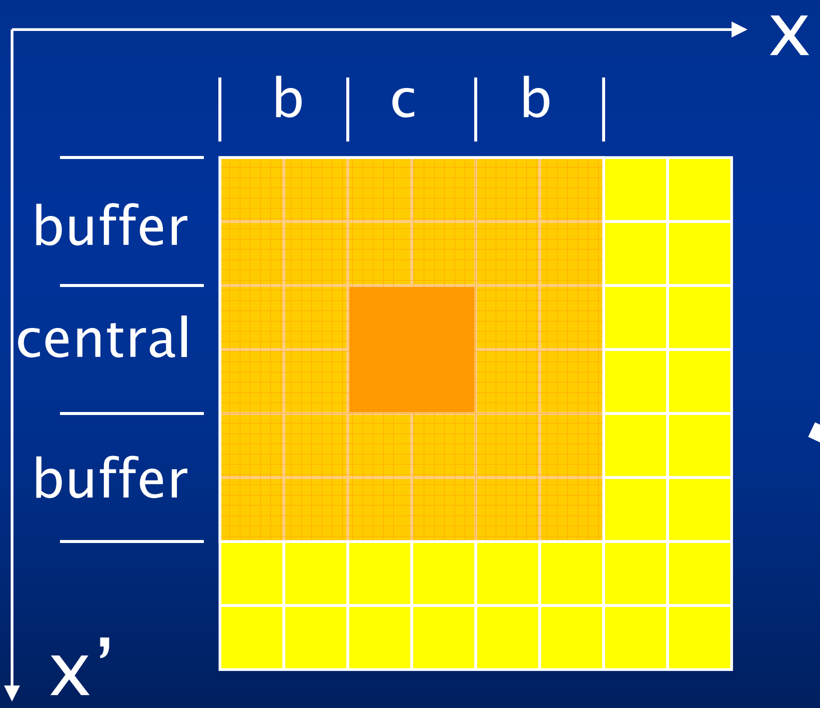
  D. Bowler & M. Gillan
- Finite-differences (nearly O(N))

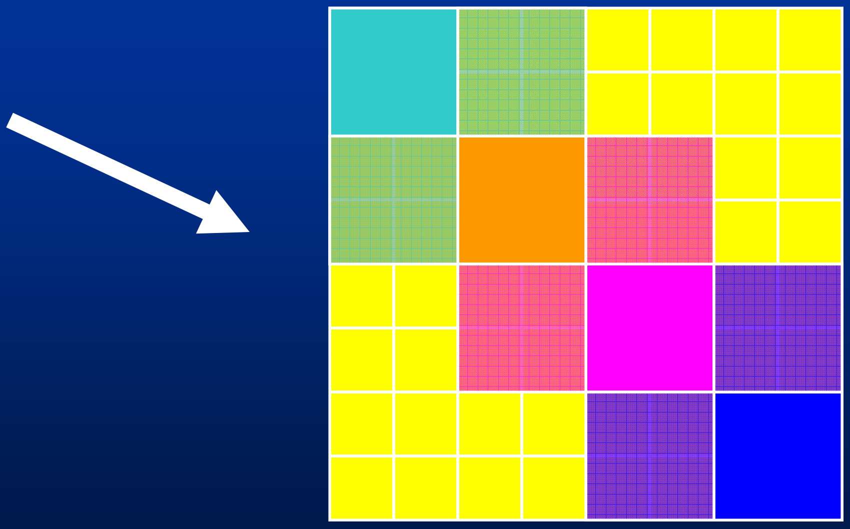
  J. Bernholc

Divide and conquer

Weitao Yang (1992)



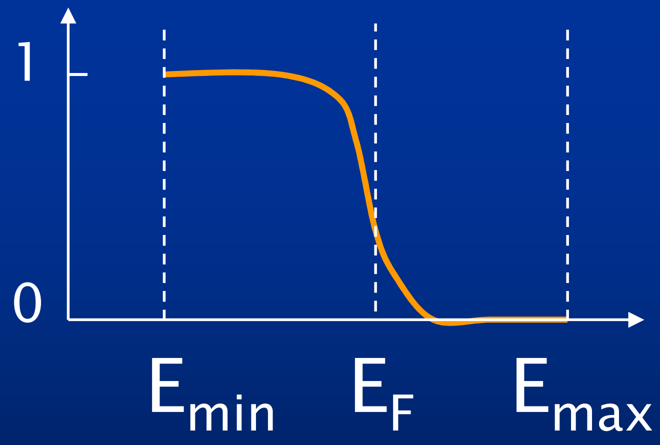




Fermi operator/projector

Goedecker & Colombo (1994)

$$f(E) = 1/(1+e^{E/kT}) \approx \sum_n c_n E^n$$



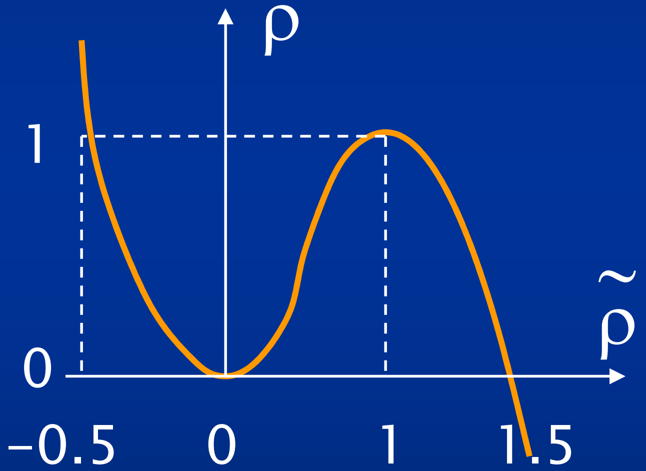
$$\hat{F} \approx \sum c_n \hat{H}^n$$

$$E_{tot} = \mathrm{Tr}[\,\hat{F}\,\hat{H}\,]$$

$$N_{tot} = \mathrm{Tr}[\,\hat{F}\,]$$

Density matrix functional

Li, Nunes & Vanderbilt (1993)



$$\rho_{\mu\nu} = 3\,\tilde{\rho}^2_{\mu\nu} - 2\,\tilde{\rho}^3_{\mu\nu}$$

$$E_{tot}(\tilde{\rho}_{\mu\nu}) = \Sigma_{\mu\nu}\,\rho_{\mu\nu}H_{\nu\mu} = \min$$

Wannier O(N) functional

- Mauri, Galli & Car, PRB **47**, 9973 (1993)
- Ordejón et al, PRB **48**, 14646 (1993)

$$S_{ij} = < \psi_i \mid \psi_j > \qquad\qquad \mid \psi'_k > = \Sigma_j \mid \psi_j > S_{jk}^{-1/2}$$

$$E_{KS} = \Sigma_k < \psi'_k \mid \hat{H} \mid \psi'_k >$$

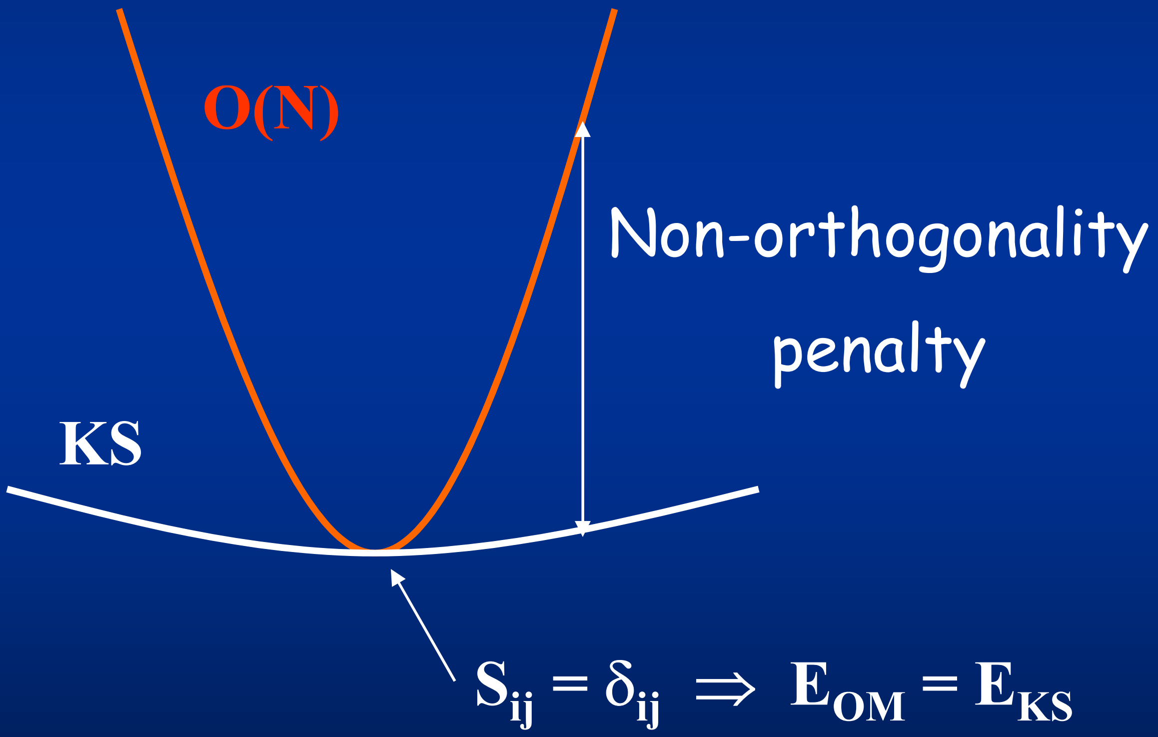
$$= \Sigma_{ijk} S_{ki}^{-1/2} < \psi_i \mid \hat{H} \mid \psi_j > S_{jk}^{-1/2}$$

$$= Tr_{occ}[\, S^{-1}\, H \,] \qquad \textbf{Kohn-Sham}$$

$$E_{OM} = Tr_{occ}[\, (2I-S)\, H \,] \qquad \textbf{Order-N}$$

$$= Tr_{occ}[\, H] + Tr_{occ}[(I-S)\, H \,]$$

Order-N vs KS functionals



$S_{ij} = \delta_{ij} \Rightarrow E_{OM} = E_{KS}$

Chemical potential

Kim, Mauri & Galli, PRB **52**, 1640 (1995)

$$\rho(\mathbf{r}) = 2\Sigma_{ij}\ \psi_i(\mathbf{r})\ (2\delta_{ij}-S_{ij})\ \psi_j(\mathbf{r})$$

$E_{OM} = \mathrm{Tr}_{occ}[\ (2I\text{-}S)\ H\ ]$ **# states = # electron pairs**

$\Rightarrow$ **Local minima**

$E_{KMG} = \mathrm{Tr}_{occ+}[\ (2I\text{-}S)\ (H-\eta S)\ ]$ **# states > # electron pairs**

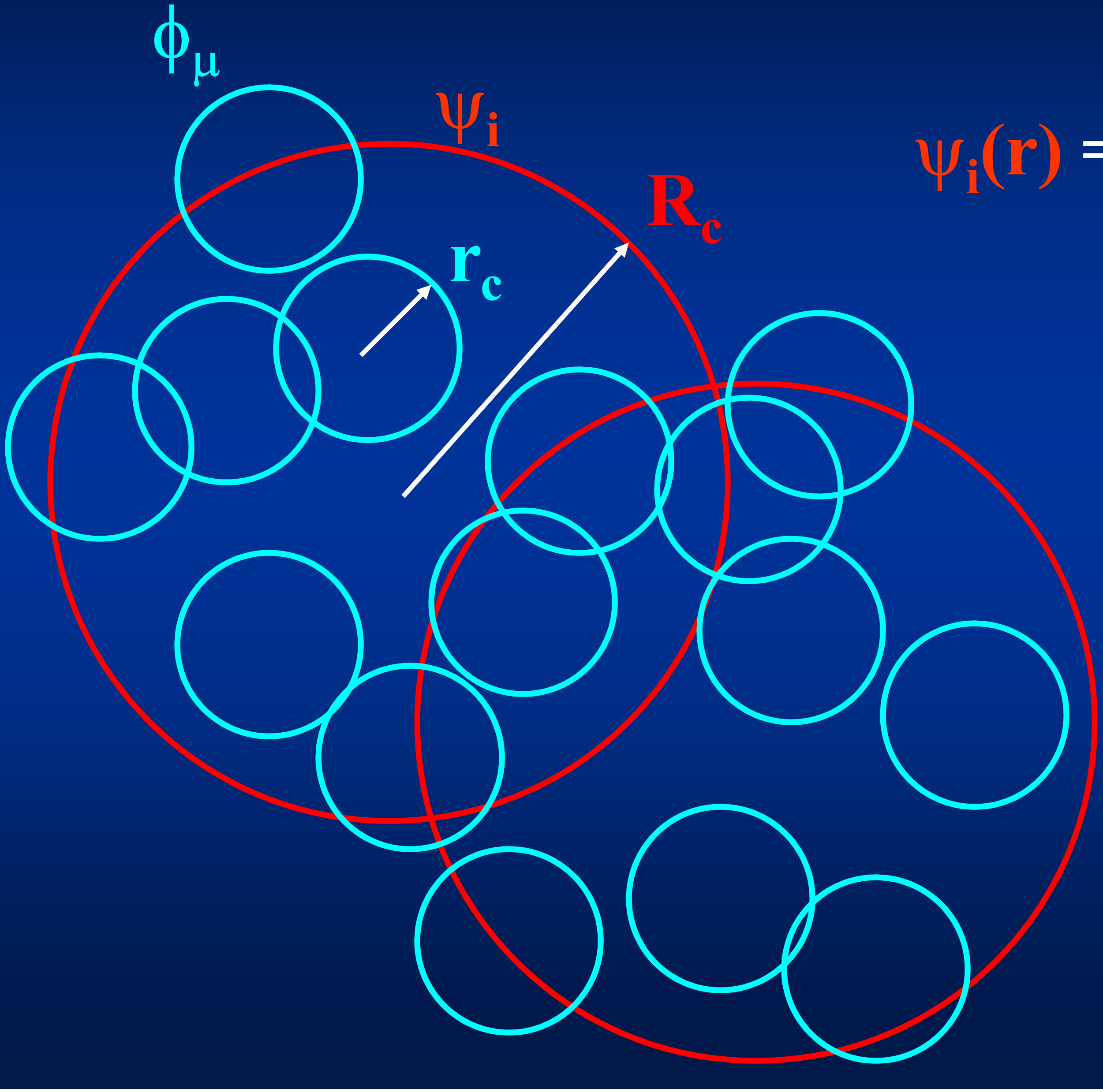
η = **chemical potential (Fermi energy)**

$E_i > \eta \quad \Rightarrow \quad |\psi_i| \approx 0$

$E_i < \eta \quad \Rightarrow \quad |\psi_i| \approx 1$

Difficulties	**Solutions**
Stability of N(η)	Initial diagonalization / Estimate of η
First minimization of E_{KMG}	Reuse previous solutions

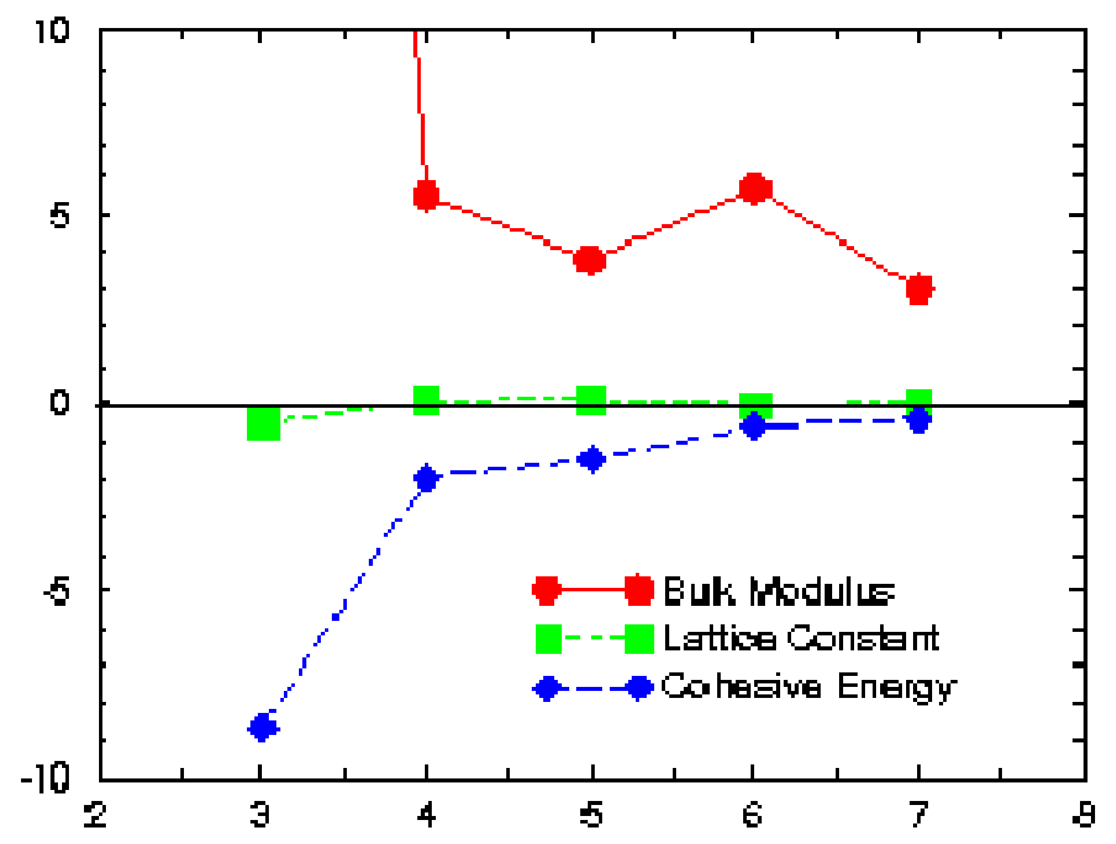
Orbital localization



$$\psi_i(\mathbf{r}) = \Sigma_\mu\, \mathbf{c}_{i\mu}\, \phi_\mu(\mathbf{r})$$

Convergence with localisation radius

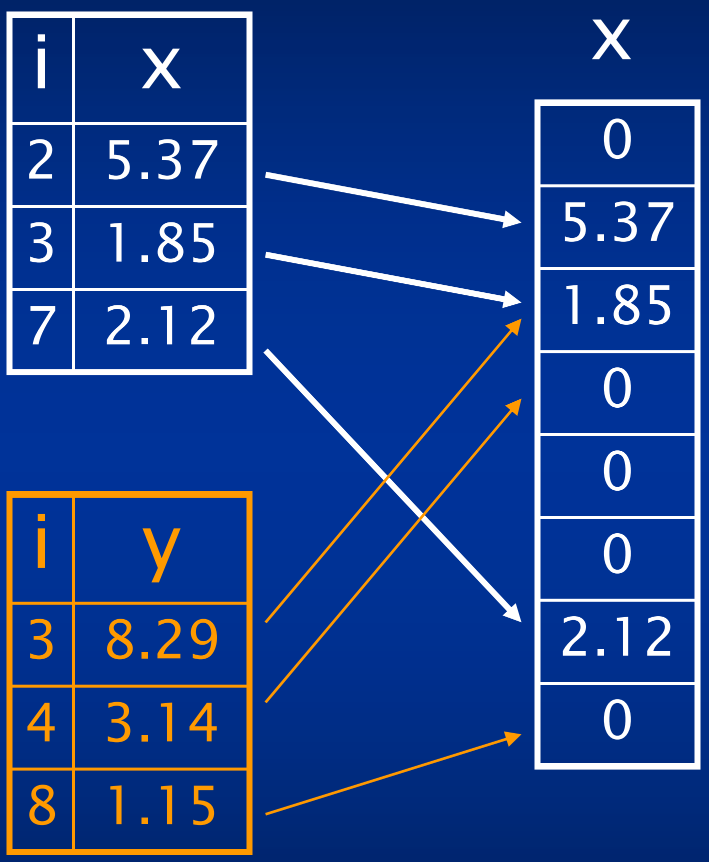
Si supercell, 512 atoms



Relative Error (%)

R_c (Ang)

Sparse vectors and matrices



i	x
2	5.37
3	1.85
7	2.12

i	y
3	8.29
4	3.14
8	1.15

x
0
5.37
1.85
0
0
0
2.12
0

$8.29 \times 1.85 = 15.34$

$3.14 \times 0 = 0$

$1.15 \times 0 = 0$

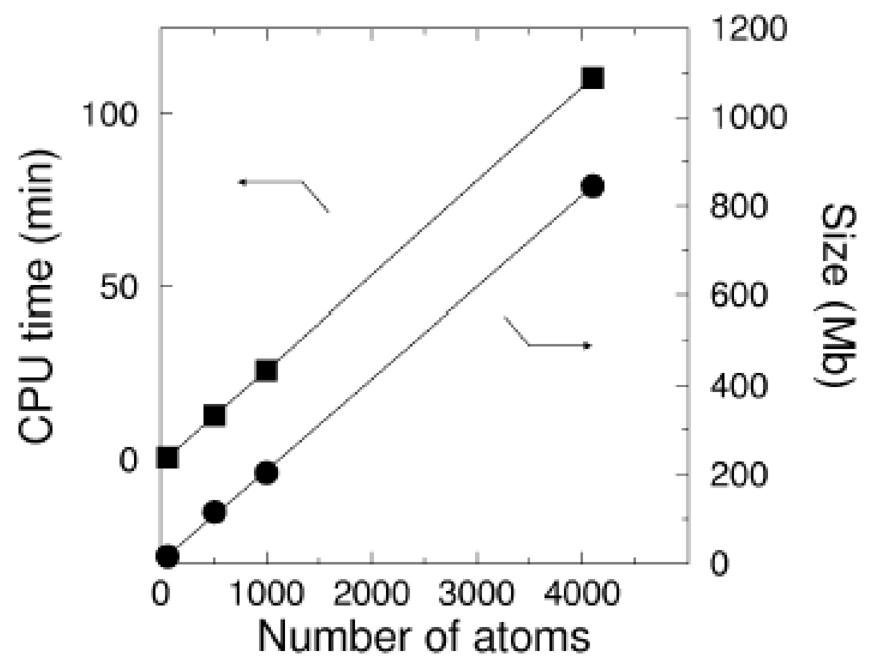
\-------

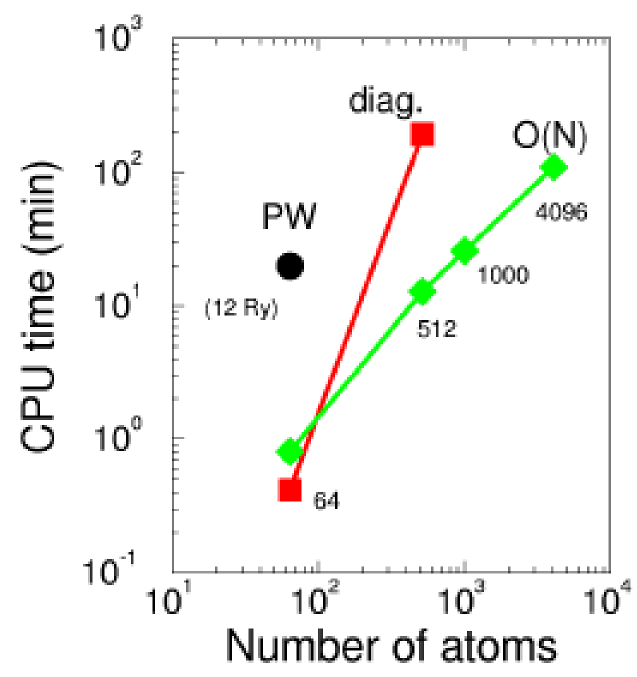
Sum 15.34

Restore to zero $x_i \neq 0$ only

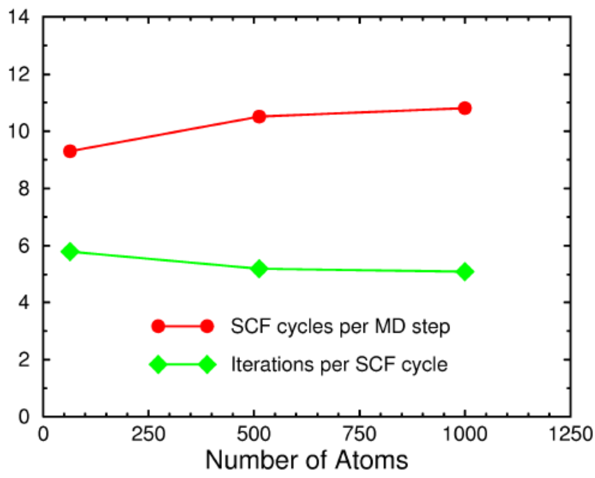
Actual linear scaling

c-Si supercells, single-ζ





Single Pentium III 800 MHz. 1 Gb RAM



132.000 atoms in 64 nodes

Linear scaling solver: practicalities in SIESTA

P. Ordejón

Institut de Ciència de Materials de Barcelona (CSIC)

Order-N in SIESTA (1)

SCF

Calculate Hamiltonian

Minimize E_{KS} with respect to WFs (GC minimization)

Build new charge density from WFs

Energy Functional Minimization

- **Start from initial LWFs** (from scratch or from previous step)

$$\chi_i(\mathbf{r}) = \Sigma_\mu\, c_{i\mu}\, \phi_\mu(\mathbf{r})$$

- **Minimize Energy Functional w.r.t. $c_{i\mu}$**

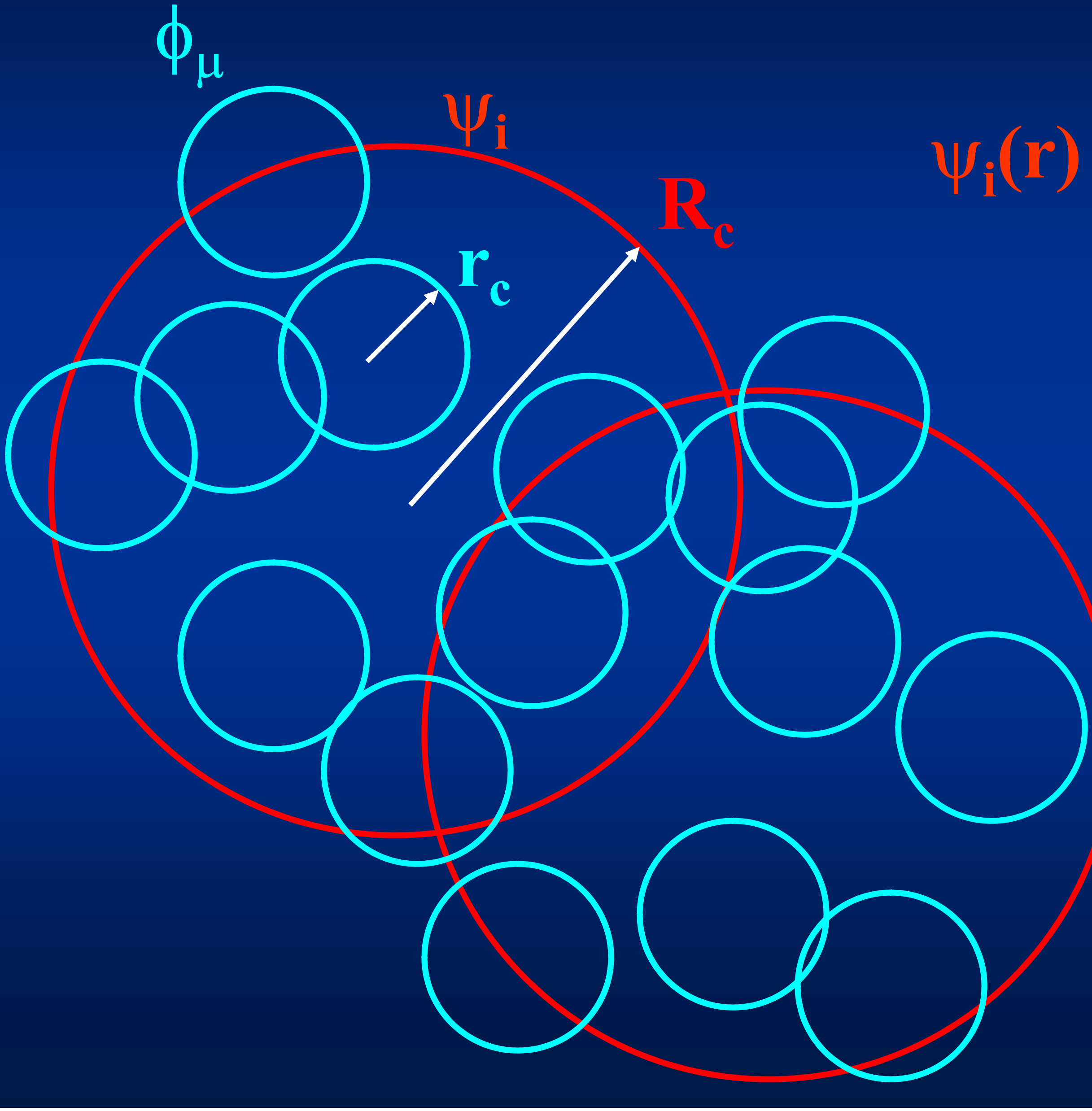
$$E_{OM} = Tr_{occ}[\ (2I\text{-}S)\ H\ ] \qquad \text{or}$$

$$E_{KMG} = Tr_{occ+}[\ (2I\text{-}S)\ (H\text{-}\eta S)\ ]$$

- **Obtain new density**

$$\rho(\mathbf{r}) = 2\Sigma_{ij}\, \psi_i(\mathbf{r})\ (2\delta_{ij}\text{-}S_{ij})\ \psi_j(\mathbf{r})$$

Orbital localization



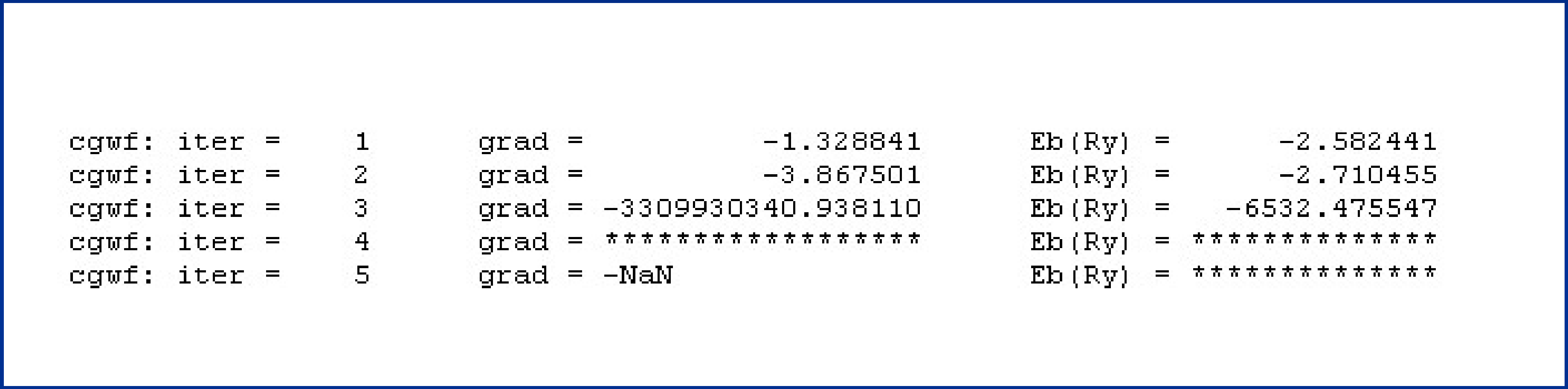
$\psi_i(\mathbf{r}) = \Sigma_\mu \, \mathbf{c}_{i\mu} \, \phi_\mu(\mathbf{r})$

```
siesta: iscf =    7
Eharris(eV) =      -1868.7292  E_KS(eV) =      -1868.9207  dDmax =  0.0072


ordern: enum =     32.0000
cgwf: iter =    1      grad =           -0.000017      Eb(Ry) =      -16.103689
cgwf: iter =    2      grad =           -0.000041      Eb(Ry) =      -16.103690
cgwf: iter =    3      grad =           -0.000005      Eb(Ry) =      -16.103690
cgwf: iter =    4      grad =           -0.000008      Eb(Ry) =      -16.103691
cgwf: iter =    5      grad =           -0.000006      Eb(Ry) =      -16.103691
cgwf: iter =    6      grad =           -0.000001      Eb(Ry) =      -16.103691
cgwf: iter =    7      grad =           -0.000001      Eb(Ry) =      -16.103691
cgwf: iter =    8      grad =           -0.000001      Eb(Ry) =      -16.103691
cgwf: iter =    9      grad =           -0.000001      Eb(Ry) =      -16.103691
cgwf: iter =   10      grad =            0.000000      Eb(Ry) =      -16.103691

cgwf:  CG tolerance reached

denmat: qtot (before DM normalization) =      32.0000
ordern: qtot (after  DM normalization) =      32.0000

siesta: iscf =    8
Eharris(eV) =      -1868.7291  E_KS(eV) =      -1868.8286  dDmax =  0.0046


ordern: enum =     32.0000
cgwf: iter =    1      grad =           -0.000001      Eb(Ry) =      -16.100366
cgwf: iter =    2      grad =           -0.000001      Eb(Ry) =      -16.100366
cgwf: iter =    3      grad =            0.000000      Eb(Ry) =      -16.100366

cgwf:  CG tolerance reached

denmat: qtot (before DM normalization) =      32.0000
ordern: qtot (after  DM normalization) =      32.0000

siesta: iscf =    9
Eharris(eV) =      -1868.7290  E_KS(eV) =      -1868.6741  dDmax =  0.0030


ordern: enum =     32.0000
cgwf: iter =    1      grad =           -0.000001      Eb(Ry) =      -16.096840
cgwf: iter =    2      grad =           -0.000002      Eb(Ry) =      -16.096840
cgwf: iter =    3      grad =            0.000000      Eb(Ry) =      -16.096840

cgwf:  CG tolerance reached

denmat: qtot (before DM normalization) =      32.0000
ordern: qtot (after  DM normalization) =      32.0000

siesta: iscf =   10
Eharris(eV) =      -1868.7290  E_KS(eV) =      -1868.7273  dDmax =  0.0003
```

Order–N in SIESTA (2)

- Practical problems:
  - Minimization of E versus WFs:
    - First minimization is hard!!! (~1000 CG iterations)
    - Next minimizations are much faster (next SCF and MD steps)
    - ALWAYS save SystemName.LWF and SystemName.DM files!!!!
  - The Chemical Potential (in Kim’s functional):
    - Data on input (ON.Eta). Problem: can change during SCF and dynamics.
    - Possibility to estimate the chemical potential in O(N) operations
    - If chosen ON.Eta is inside a band (conduction or valence), the minimization often becomes unstable and diverges
    - Solution I: use chemical potential estimated on the run
    - Solution II: do a previous diagonalization

Example of instability related to a wrong chemical potential



```
cgwf: iter =    1      grad =            -1.328841      Eb(Ry) =      -2.582441
cgwf: iter =    2      grad =            -3.867501      Eb(Ry) =      -2.710455
cgwf: iter =    3      grad = -3309930340.938110      Eb(Ry) =   -6532.475547
cgwf: iter =    4      grad = ******************      Eb(Ry) = **************
cgwf: iter =    5      grad = -NaN                    Eb(Ry) = **************
```

Order-N in SIESTA (3)

- SolutionMethod OrderN
- ON.Functional
  Ordejon-Mauri or Kim (def)
- ON.MaxNumIter
  Max. iterations in CG minim. (WFs)
- ON.Etol
  Tolerance in the energy minimization
  $2(E_n - E_{n-1})/(E_n + E_{n-1}) < \text{ON.Etol}$
- ON.RcLWF
  Localisation radius of WFs

Order–N in SIESTA (4)

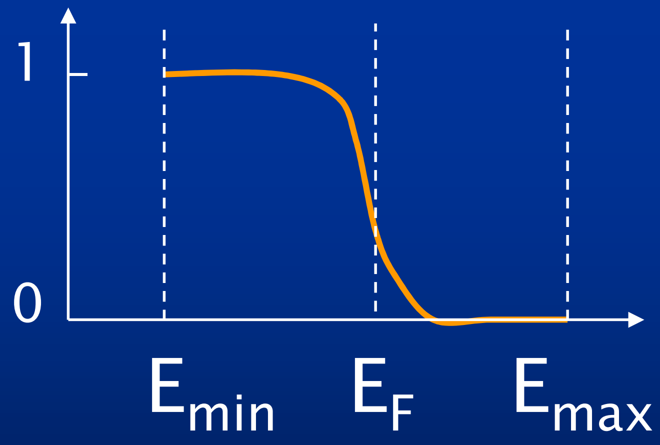
- ON.Eta (energy units)
  Chemical Potential (Kim)
  Shift of Hamiltonian (Ordejon–Mauri)

- ON.ChemicalPotential
- ON.ChemicalPotentialUse
- ON.ChemicalPotentialRc
- ON.ChemicalPotentialTemperature
- ON.ChemicalPotentialOrder

Fermi operator/projector

Goedecker & Colombo (1994)

$$f(E) = 1/(1+e^{E/kT}) \approx \sum_n c_n E^n$$



$$\hat{F} \approx \sum c_n \hat{H}^n$$

$$E_{tot} = \mathrm{Tr}[\,\hat{F}\,\hat{H}\,]$$

$$N_{tot} = \mathrm{Tr}[\,\hat{F}\,]$$