# Basics and some details of the SIESTA method


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# Outline


## Main characteristics

- Standard DFT
- Fast for large systems => Order-N
- From quick & dirty to highly accurate

## Methods and approximations

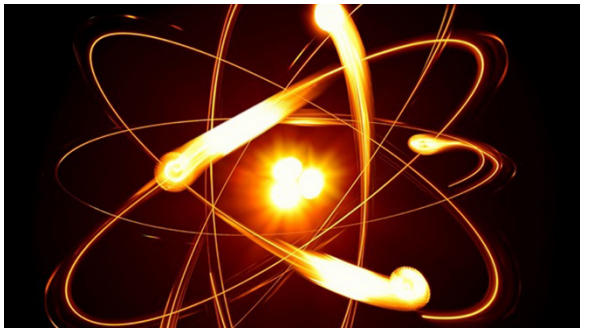
- Norm-conserving pseudopotentials
- Basis of numerical atomic orbitas
- Uniform real-space grid
- Order-N functional (solver)

Introduction to basics only

(SIESTA can do many more things than presented here!)

# The physics of low-energy matter

Made of electrons & nuclei
(interacting with photons)



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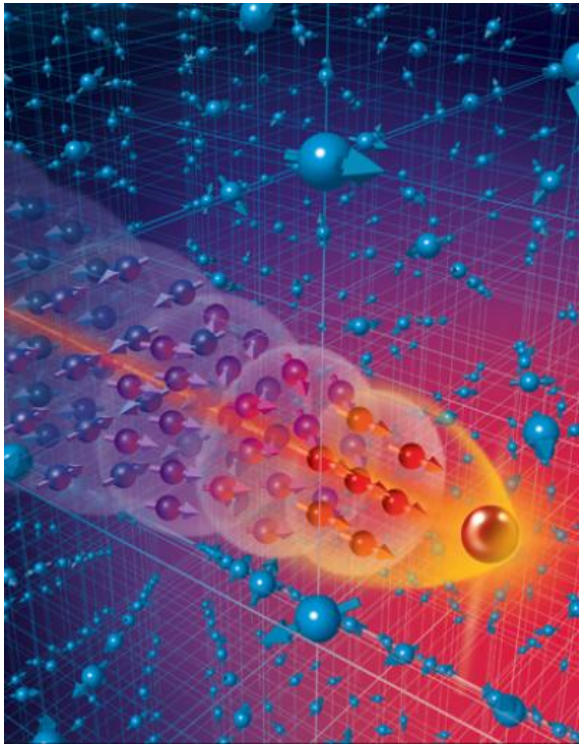
matter at T up to several millon K

(except for nuclear fission and radioactive decay)

- Atomic & molecular physics
- Condensed matter physics (solids, liquids)
- Plasma physics

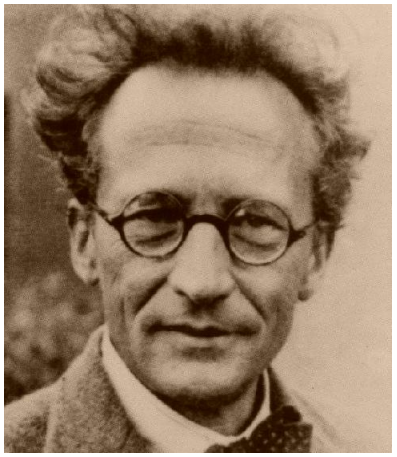
Low energy in the sense of
not probing inner structure of nuclei



Ali Yazdani's group, Princeton

# First principles

## Quantum Mechanics



$$H\Psi(s_1, s_2 \ldots s_N, t) = i\hbar\,\partial_t \Psi(s_1, s_2 \ldots s_N, t)$$

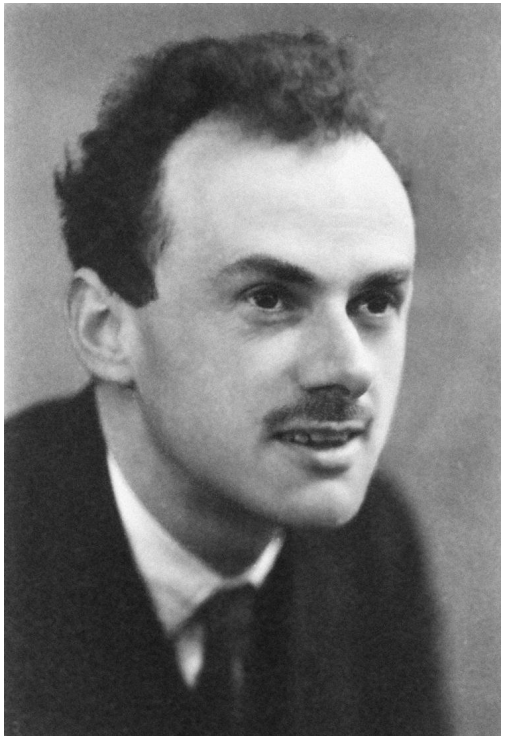
$$s_i = (\mathbf{r}_i, \sigma_i)$$

Coulomb's law

$$H = -\sum_i^N \frac{\hbar^2}{2m_i}\nabla_i^2 + \sum_{i,j<i}^N \frac{q_i q_j}{r_{ij}}$$

Just electrons and nuclei

# Just electrons and nuclei

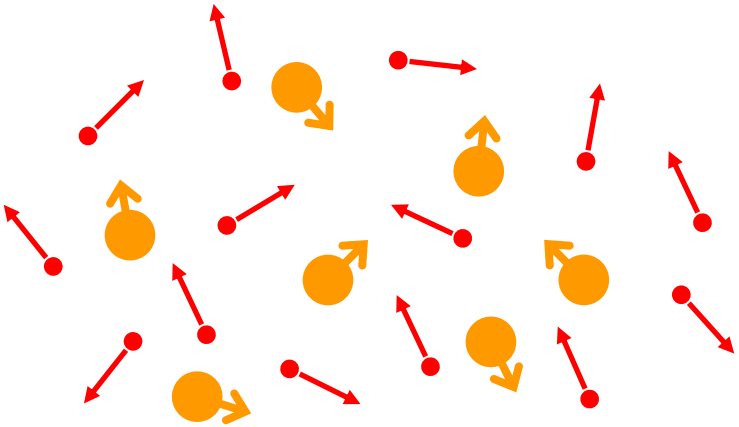


The underlying physical laws necessary for the mathematical theory of . . . the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

Paul Dirac, 1929

=> Approximations

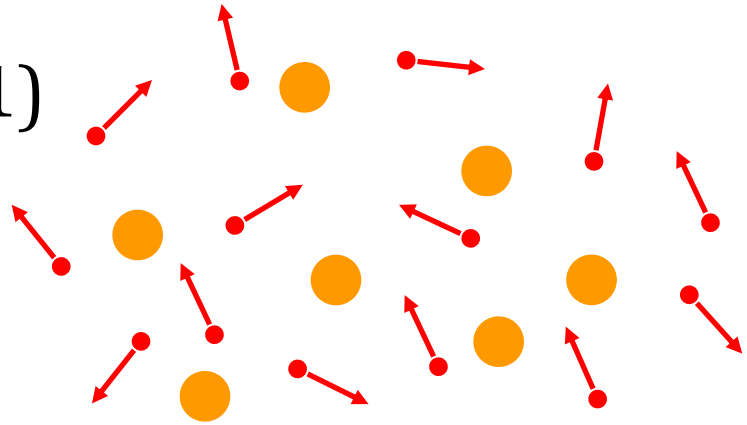
# Born-Oppenheimer approximation



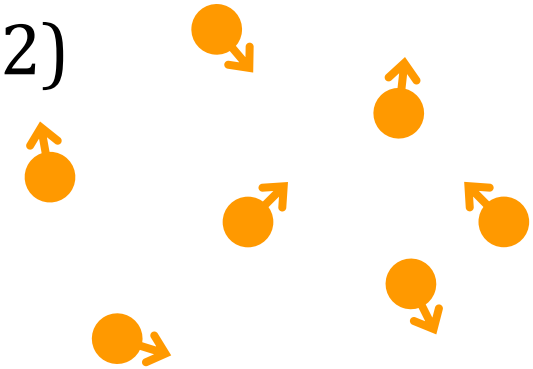
$$m_n \gg m_e$$

$\Rightarrow$ Nuclei are much slower than electrons

(1)



(2)



Decoupling of electrons and nuclei

# Many electrons: Density-Functional Theory (DFT)

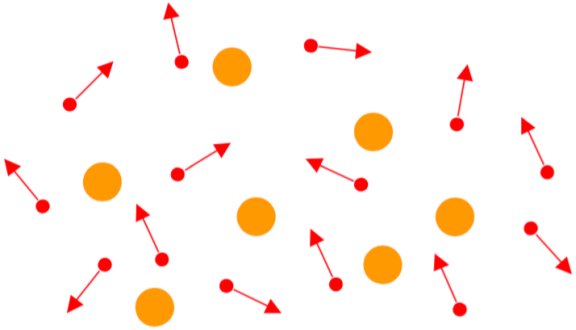
Ground state theory for the electronic problem

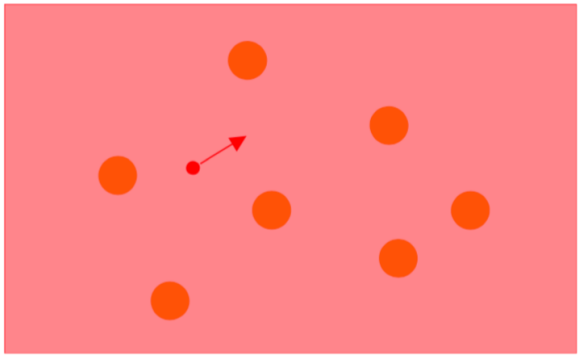
- Twist on variational principle

$$E[\Psi] = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle \longrightarrow \min_{n} E[n]$$

Hohenberg-Kohn theorems. *No longer exponential complexity!*

- Map $\min_n E[n]$ into solving mean-field-like problem





Kohn-Sham formulation. *Self-consistent single-particle as in HF*

# Kohn-Sham DFT

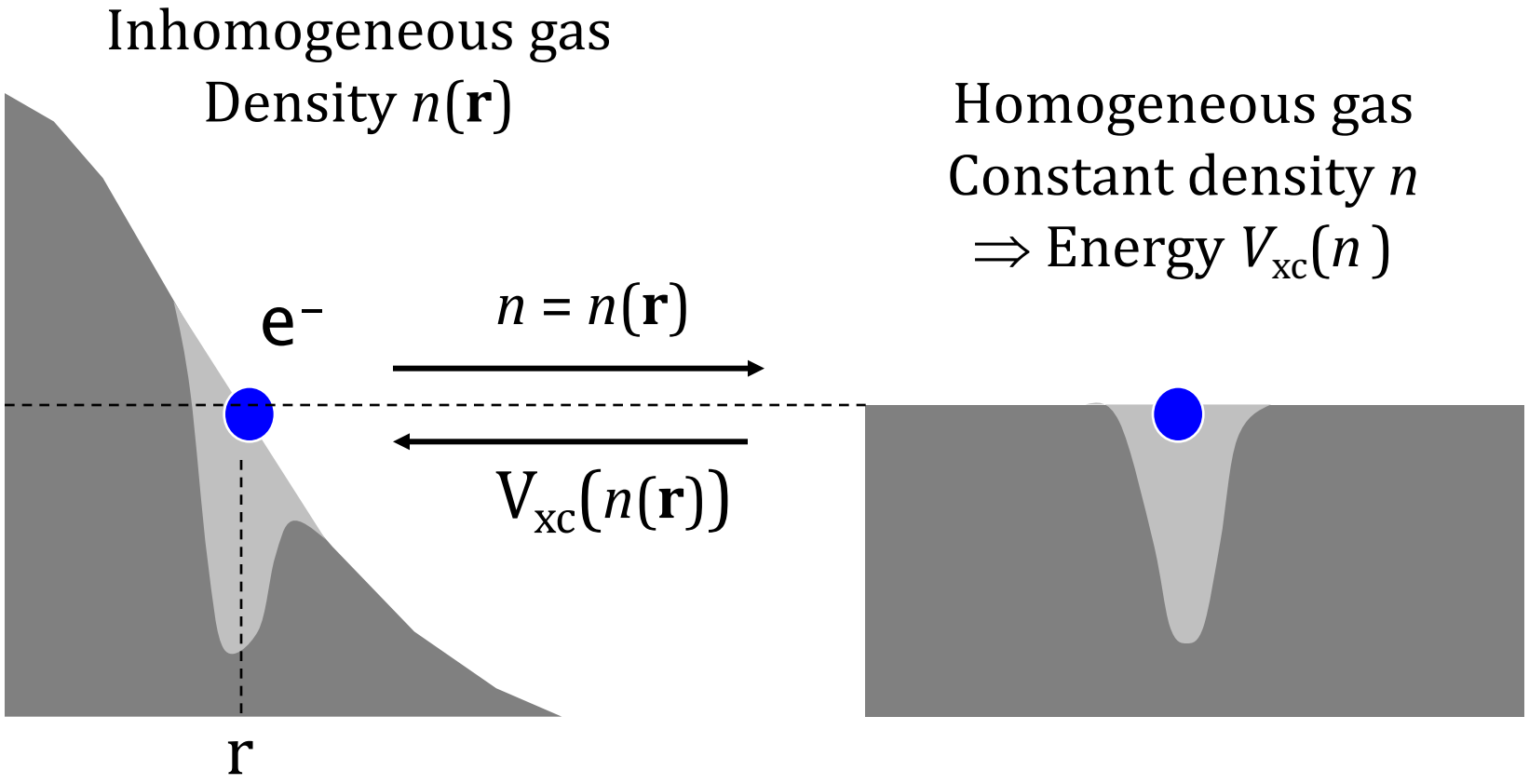
Non-interacting electrons in a self-consistent effective potential

$$h^{\mathrm{KS}} = -\frac{1}{2}\nabla^2 + V_{\mathrm{ext}}(\mathbf{r}) + \Phi(\mathbf{r}) + V_{\mathrm{xc}}(\mathbf{r})$$

$$\Phi(\mathbf{r}) = \int \mathrm{d}^3\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \qquad V_{\mathrm{XC}}(\mathbf{r}) = \frac{\delta E[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$

$$h^{\mathrm{KS}}\psi_n(\mathbf{r}) = \epsilon_n \psi_n(\mathbf{r}) \qquad n(\mathbf{r}) = \sum_n^{\mathrm{occ}} |\psi_n(\mathbf{r})|^2$$

# Local density approximation (LDA)




Generalized gradient approximation (GGA): $V_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}))$

Van der Waals xc functionals: $V_{xc}(n(\mathbf{r}),\nabla n(\mathbf{r}); n(\mathbf{r}'),\nabla n(\mathbf{r}'))$

# Expand KS states in a basis

**Basis set:** $\{|e_\mu\rangle,\ \mu = 1 \ldots \mathcal{N}\}$ $\quad \phi_\mu(\mathbf{r}) = \langle \mathbf{r}|e_\mu\rangle$

Schrödinger (Kohn-Sham) eq. $H|\psi_n\rangle = E_n|\psi_n\rangle$ becomes

$$\sum_\nu H_{\mu\nu} C_{\nu n} = E_n \sum_\nu S_{\mu\nu} C_{\nu n}$$

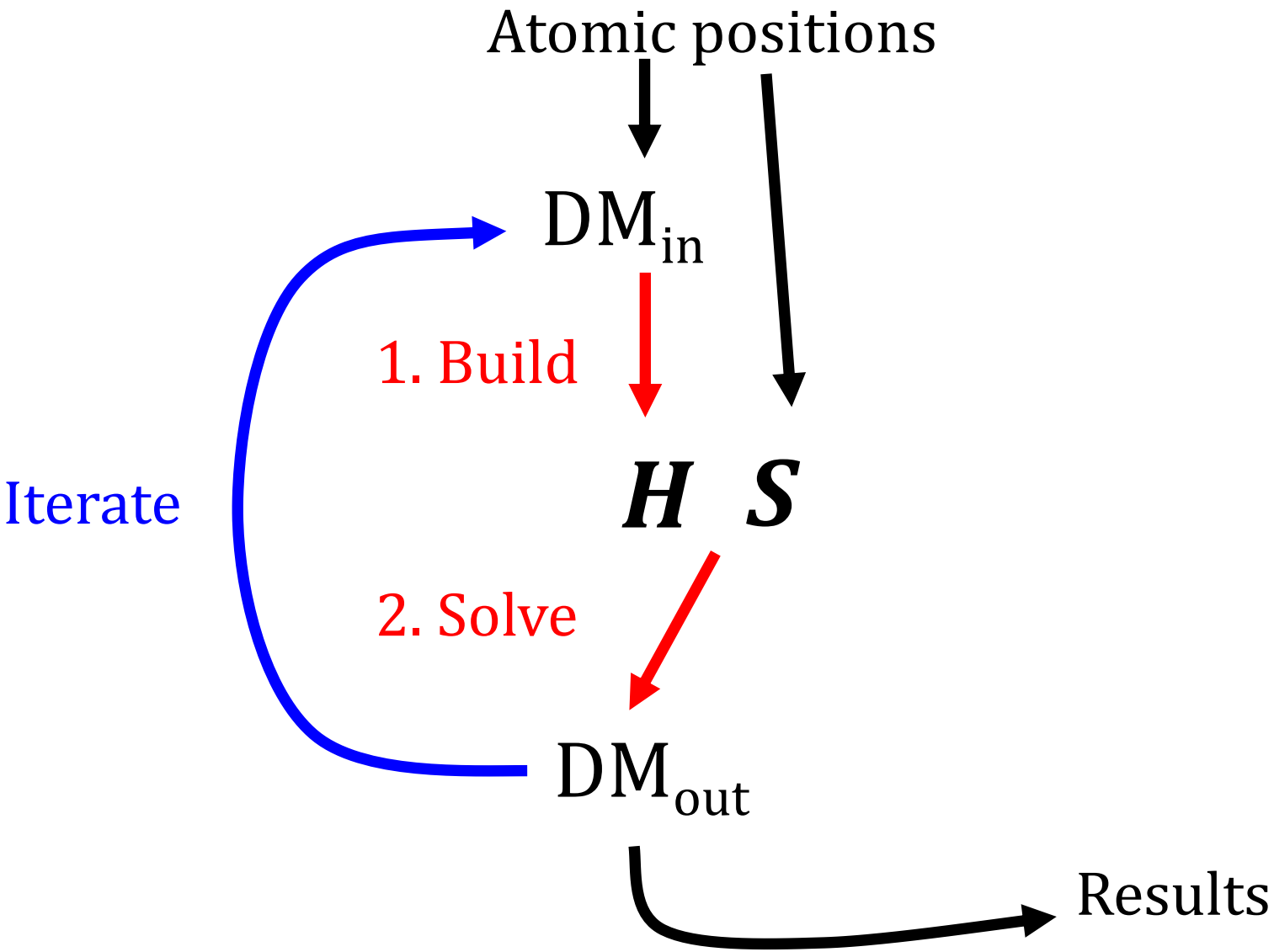
where

$$|\psi_n\rangle = \sum_\mu |e_\mu\rangle\, C_{\mu n}\,, \quad H_{\mu\nu} = \langle e_\mu|H|e_\nu\rangle\,, \quad \text{and } S_{\mu\nu} = \langle e_\mu|e_\nu\rangle\,,$$

$$n(\mathbf{r}) = \sum_n^{\text{occ}} |\psi_n(\mathbf{r})|^2 = \sum_n^{\text{occ}} \psi_n(\mathbf{r})\psi_n^*(\mathbf{r}) = \sum_n^{\text{occ}} \sum_{\mu,\nu} C_{\mu n}\phi_\mu(\mathbf{r})\, C_{\nu n}^*\phi_\nu^*(\mathbf{r})$$

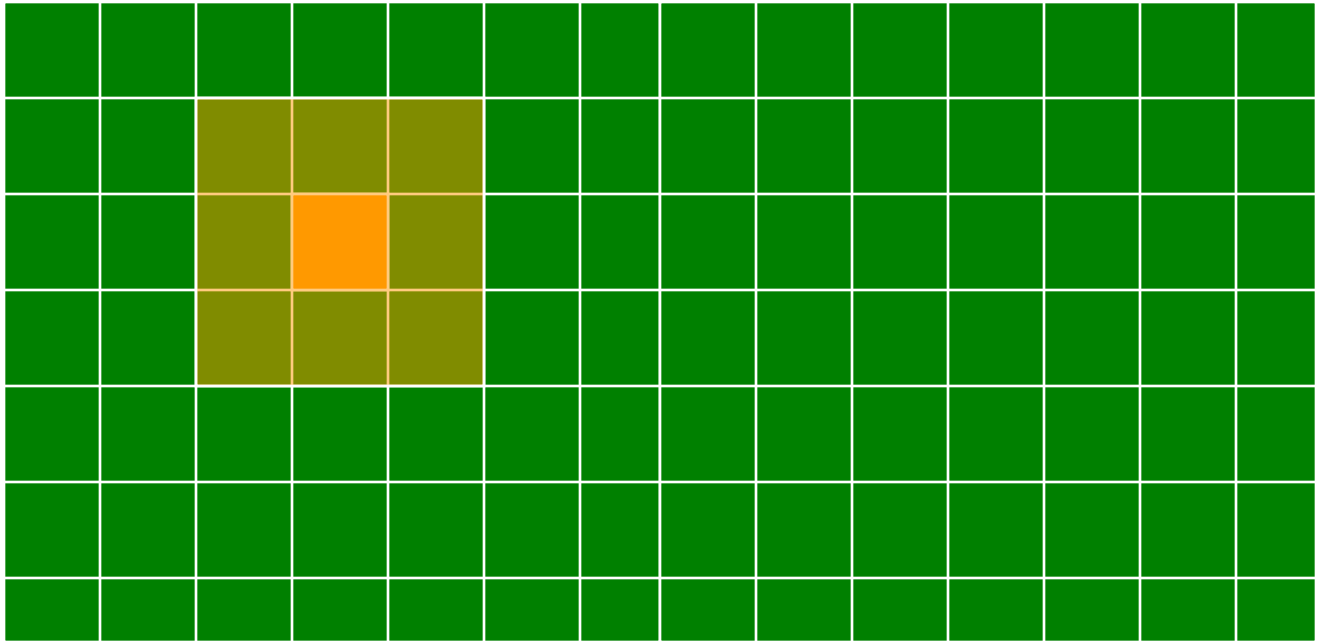
$$= \sum_{\mu,\nu} \rho_{\mu\nu}\phi_\mu(\mathbf{r})\,\phi_\nu^*(\mathbf{r}) \quad \text{where} \quad \rho_{\mu\nu} \equiv \sum_n^{\text{occ}} C_{\mu n} C_{\nu n}^*$$

# Two steps and SCF cycle



# Linear Scaling
# KEY: LOCALITY

Large system



**x 2**

"Divide and Conquer"

W. Yang, Phys. Rev. Lett. 66, 1438 (1992)

# Basis set – LCAO – atomic orbitals

Numerical (pseudo)atomic orbitals (PAOs)
& real spherical harmonics

$$\phi_{\zeta lm}(r,\theta,\varphi) = R_{\zeta}(r)Y_{lm}(\theta,\varphi)$$

$$Y_{lm}(\theta,\varphi) = C_{lm}P_l^m(\cos\theta)\times\begin{cases}\sin(m\varphi) & \text{if } m<0\\ \cos(m\varphi) & \text{if } m\geq 0\end{cases}$$

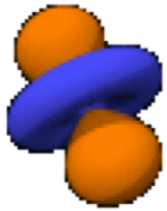
$$l=1,\ \ m=-1,0,+1 \quad\Rightarrow\quad p_y, p_z, p_x$$

# Finite-support atomic orbitals as basis

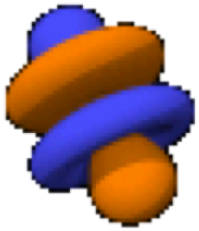
s

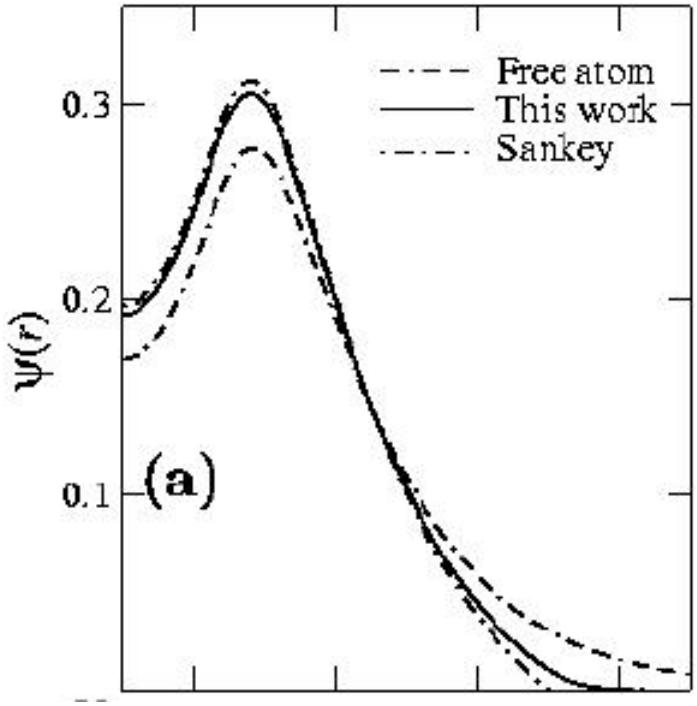
p

d



f






Strictly localised

(zero beyond cut-off radius)

Hard vs smooth confinement

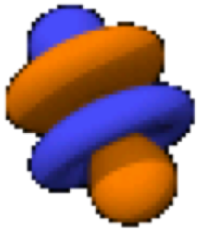
# Finite-support atomic orbitals as basis

s

p

d

f



Only 2 conditions

1. $\phi_{\zeta lm}(r,\theta,\varphi) = R_{\zeta}(r)Y_{lm}(\theta,\varphi)$
2. Finite range

User decides

- How many centres
- Where to put them (on atoms or not)
- How many angular momenta
- How many for each angul momentum
- Each  radial shape

# Finite-support atomic orbitals as basis

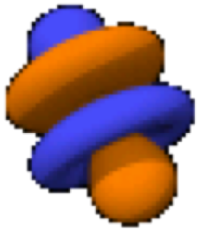
$$\phi_{\zeta lm}(r,\theta,\varphi) = R_{\zeta}(r)Y_{lm}(\theta,\varphi)$$

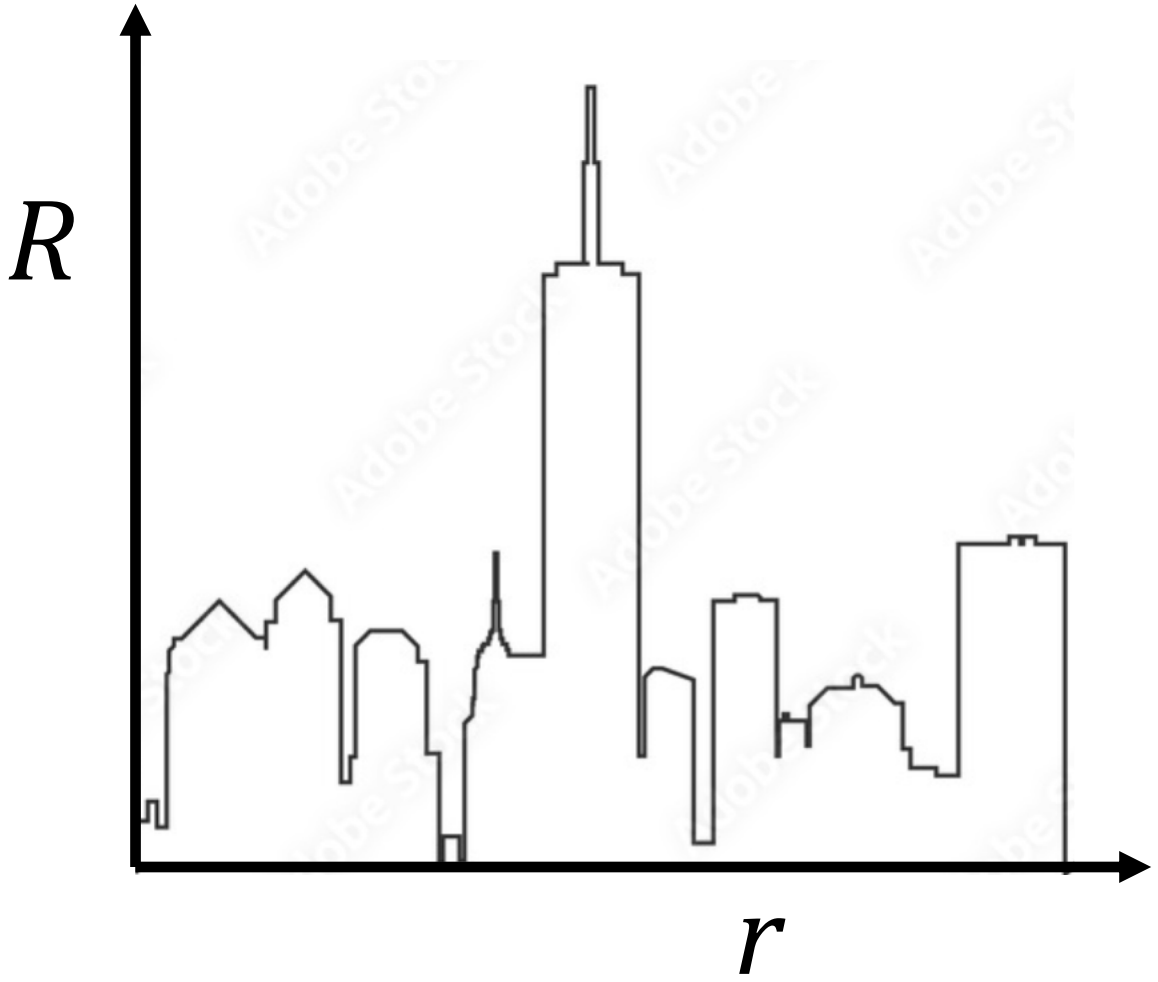
s

p

d

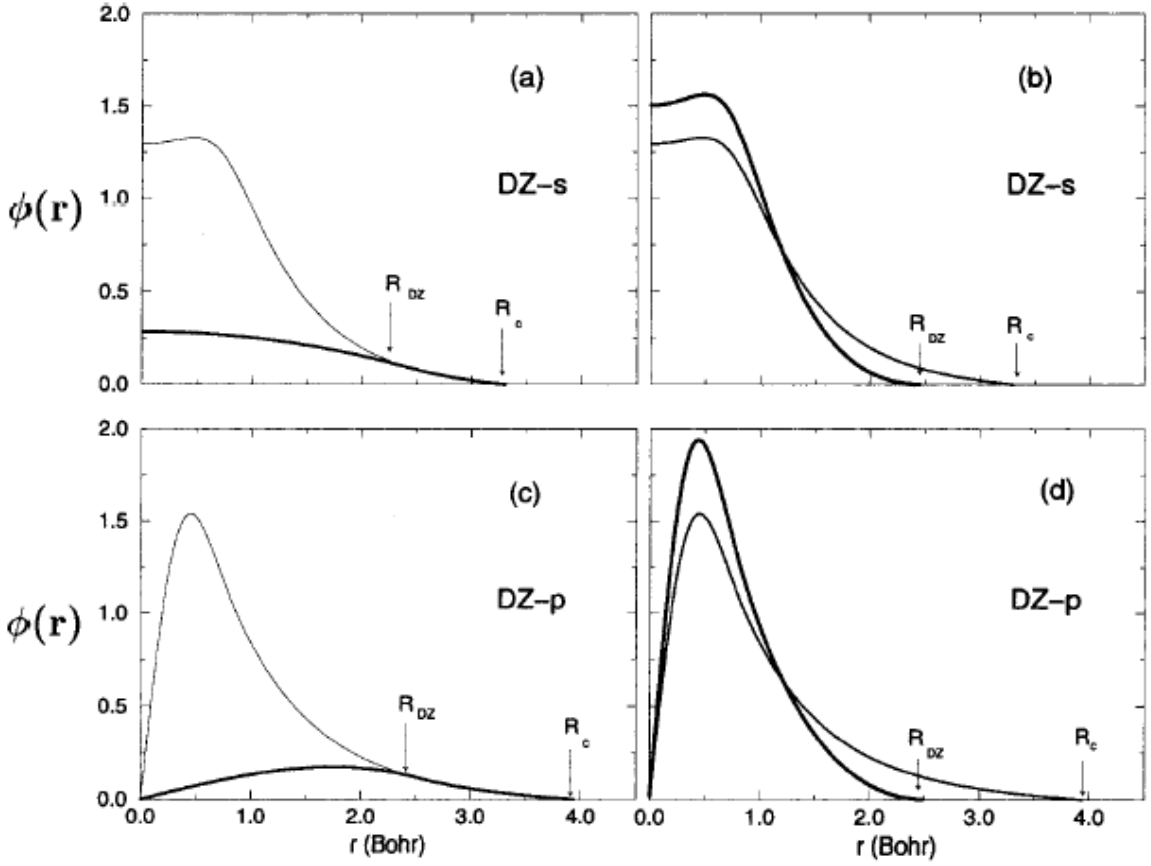
f





# Finite-range basis orbitals – Multiple zeta

- First $\zeta$: $\Delta\varepsilon_{PAO} \Rightarrow R_c$
- Second $\zeta$: Split-valence $\Rightarrow$ Split-norm




O. F. Sankey and D. J. Niklewski, *Phys. Rv. B* ***40****, 3979 (1989)*

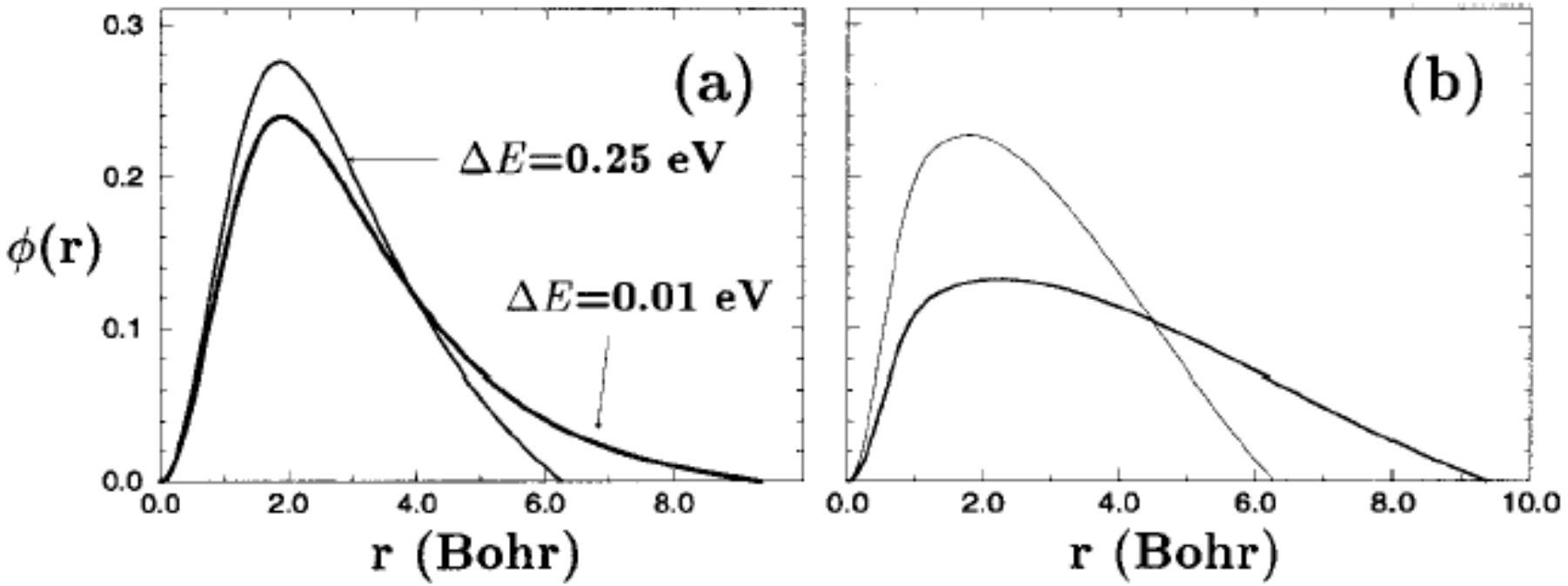
E. Artacho et al, *Phys. Stat. Sol (b)* ***215****, 809 (1999)*

# Polarization orbitals

3*d* orbitals of Si

*p* PAO perturbed by electric field

*d* PAO



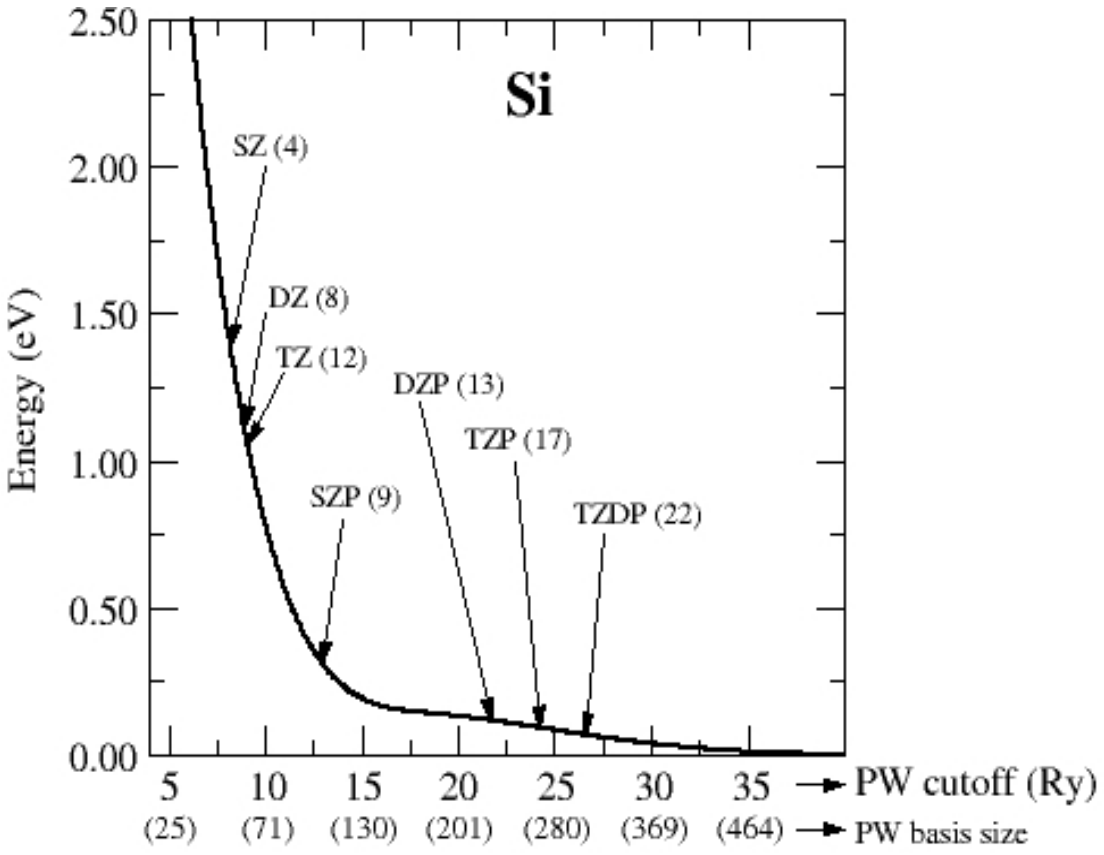
# NaCl.ORB_INDX file

```
     18      18 = orbitals in unit cell and supercell. See end of file.

    io     ia is    spec iao  n  l  m  z  p          sym       rc     isc      iuo
     1      1  1      Na   1  3  0  0  1  F            s   11.046   0  0  0      1
     2      1  1      Na   2  3  0  0  2  F            s    8.821   0  0  0      2
     3      1  1      Na   3  3  1 -1  1  T          Ppy   11.046   0  0  0      3
     4      1  1      Na   4  3  1  0  1  T          Ppz   11.046   0  0  0      4
     5      1  1      Na   5  3  1  1  1  T          Ppx   11.046   0  0  0      5
     6      2  2      Cl   1  3  0  0  1  F            s    4.912   0  0  0      6
     7      2  2      Cl   2  3  0  0  2  F            s    3.212   0  0  0      7
     8      2  2      Cl   3  3  1 -1  1  F           py    6.152   0  0  0      8
     9      2  2      Cl   4  3  1  0  1  F           pz    6.152   0  0  0      9
    10      2  2      Cl   5  3  1  1  1  F           px    6.152   0  0  0     10
    11      2  2      Cl   6  3  1 -1  2  F           py    3.594   0  0  0     11
    12      2  2      Cl   7  3  1  0  2  F           pz    3.594   0  0  0     12
    13      2  2      Cl   8  3  1  1  2  F           px    3.594   0  0  0     13
    14      2  2      Cl   9  3  2 -2  1  T         Pdxy    6.152   0  0  0     14
    15      2  2      Cl  10  3  2 -1  1  T         Pdyz    6.152   0  0  0     15
    16      2  2      Cl  11  3  2  0  1  T         Pdz2    6.152   0  0  0     16
    17      2  2      Cl  12  3  2  1  1  T         Pdxz    6.152   0  0  0     17
    18      2  2      Cl  13  3  2  2  1  T      Pdx2-y2    6.152   0  0  0     18

Column codes:
  io = Orbital index in supercell
  ia = Atom to which orbital belongs
  is = Atomic species index
spec = Atomic species label
 iao = Orbital index within atom
   n = Principal quantum number
   l = Angular mumentum quantum number
   m = Magnetic quantum number of (real) orbital:
       m<0 => sin(m*phi), m>=0 => cos(m*phi)
   z = Zeta index of orbital
   p = Is this a polarization orbital? (False|True)
 sym = Symmetry name of real orbital
  rc = Cutoff radius of orbital (Bohr)
 isc = Unit cell indexes to which orbital belongs:
       center(io) = center(iuo) + sum_(i=1:3) cell_vec(i) * isc(i)
 iuo = Equivalent orbital in first unit cell
```

# Basis set convergence

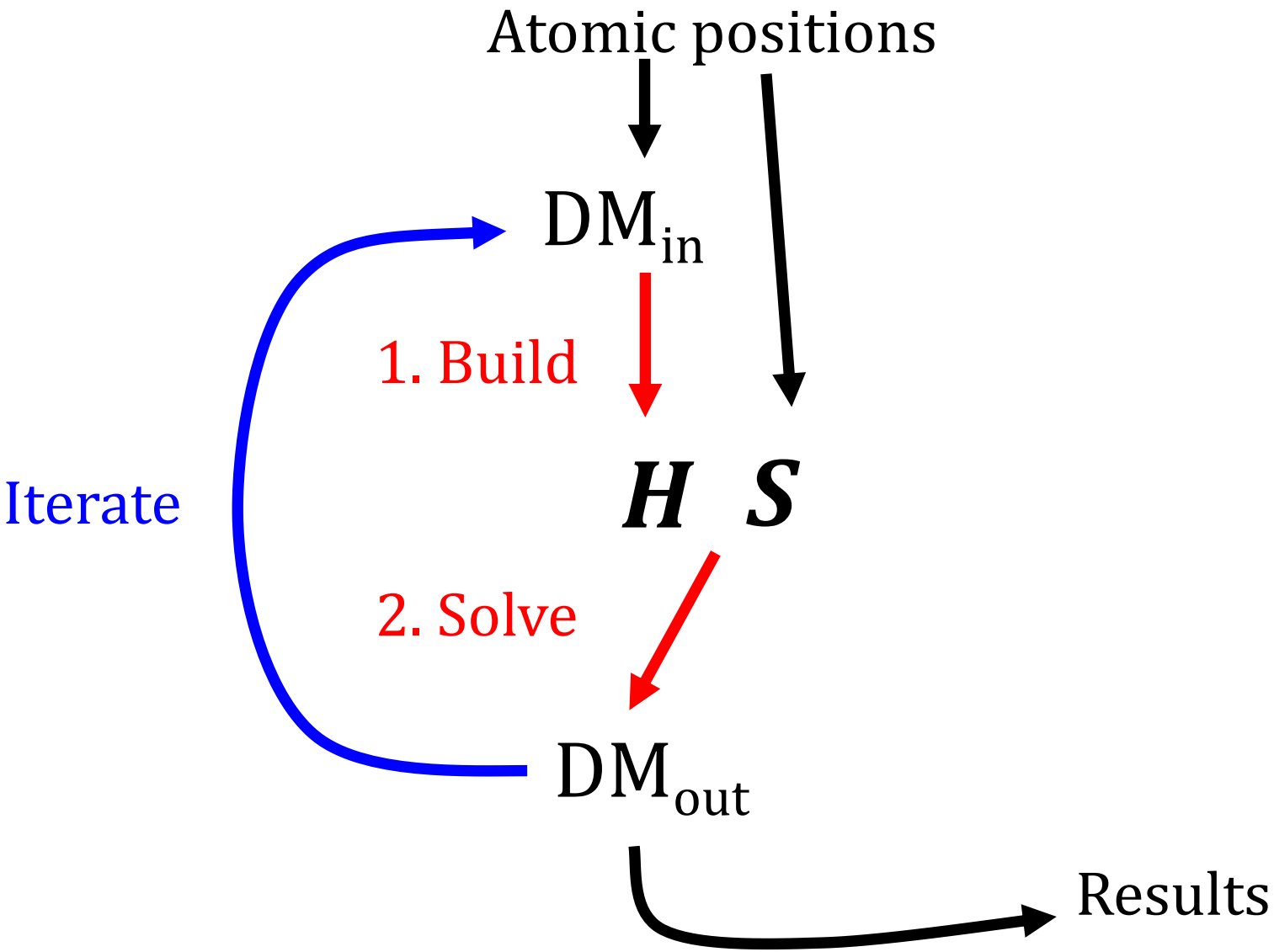



Equivalent PW cutoffs (Ry) for basis optimized in

| | Atom | Solid |
|---|---|---|
| SZ | 7.3 | 7.9 |
| DZ | 8.4 | 8.5 |
| TZ | 8.5 | 8.7 |
| SZP | 8.6 | 12.5 |
| DZP | 11.9 | 16.0 |
| TZP | 12.5 | 16.8 |
| TZDP | 13.1 | 17.8 |

J. Junquera et al. Phys. Rev. B, 64, 235111 (2001)

# Two steps and SCF cycle



# 1. Building: Computing H (and S)

$$H = T + V_{\text{ion}}(\mathbf{r}) + V_{\text{nl}} + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})$$

Long range

$$V_{\text{na}}(r) = V_{\text{ion}}(r) + V_{\text{H}}[\rho_{\text{o}}(r)]$$

Neutral-atom potential

$$\delta V_{\text{H}}(\mathbf{r}) = V_{\text{H}}[\rho_{\text{SCF}}(\mathbf{r})] - V_{\text{H}}[\rho_{\text{o}}(\mathbf{r})]$$

$$H = T + V_{\text{nl}} + V_{\text{na}}(\mathbf{r}) + \delta V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})$$

Two-center integrals

Grid integrals

# 1. Building (a)

## Two-center integrals

### Convolution theorem

$$S(\mathbf{R}) \equiv \langle \phi_1 | \phi_2 \rangle = \int \phi_1(\mathbf{r})\, \phi_2(\mathbf{r}-\mathbf{R})\, d\mathbf{r}$$

$$\phi(\mathbf{k}) = \frac{1}{(2\pi)^{2/3}} \int \phi(\mathbf{r})\, e^{-i\mathbf{kr}}\, d\mathbf{r}$$

$$S(\mathbf{R}) = \int \phi_1(\mathbf{k})\, \phi_2(\mathbf{k})\, e^{i\mathbf{kR}}\, d\mathbf{k}$$

$T = -(1/2)\,\nabla^2$

$V_{nl} = \sum_\alpha |\chi_\alpha\rangle\, \varepsilon_\alpha\, \langle\chi_\alpha|$ Kleinman-Bylander

(From $V_{PS} = V_{ion}(r) + V_{nl,}$ but not $V_{ion}(r) \rightarrow -Z_{val}/r$)

# 1. Building (b): on a real-space grid

(discretise space)

$$\psi_i(r) = \sum_\mu c_{i\mu}\varphi_\mu(r)$$

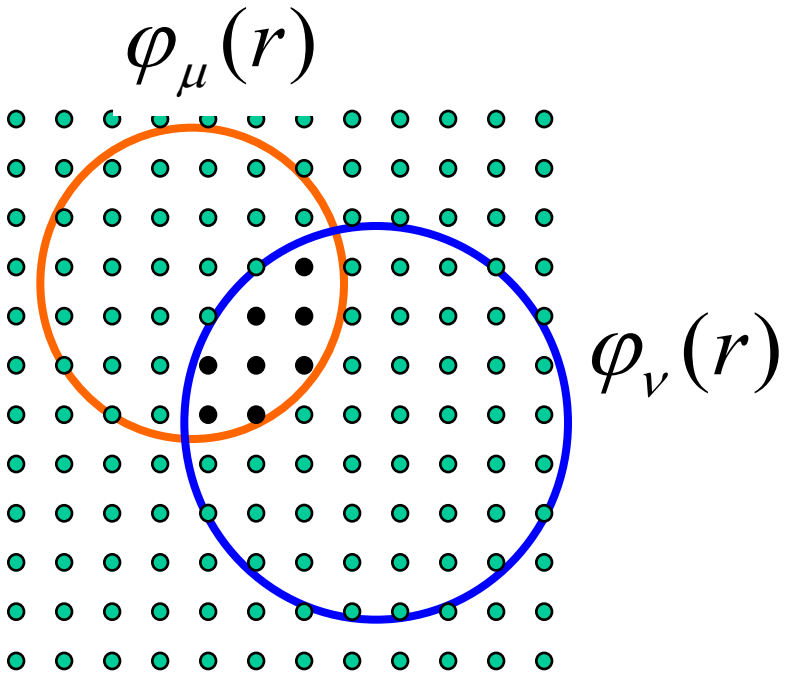
$$\rho_{\mu\nu} = \sum_i c_{i\mu}c_{i\nu}$$

$$\rho(r) = \sum_i \psi_i^2(r) = \sum_{\mu\nu} \rho_{\mu\nu}\varphi_\mu(r)\varphi_\nu(r)$$

$$\delta\rho(r) = \rho_{SCF}(r) - \rho_{atoms}(r)$$

$$\rho(r) \rightarrow V_{xc}(r)$$

$$\delta\rho(r) \overset{FFT}{\rightarrow} \delta V_H(r)$$



# Poisson equation

$$\nabla^2 V_H(r) = -4\pi\,\rho(r)$$

$$\rho(r) = \sum_G \rho_G\, e^{iGr} \quad \Rightarrow \quad V_H(r) = \sum_G V_G\, e^{iGr}$$

$$V_G = -4\pi\,\rho_G / G^2$$

$$\rho(r) \xrightarrow{\text{FFT}} \rho_G \rightarrow V_G \xrightarrow{\text{FFT}} V_H(r)$$

- SIESTA (nrmally) uses periodic boundary conditions
- Net charge compensated by uniform background
- Spurious interactions between ‘images’

# GGA

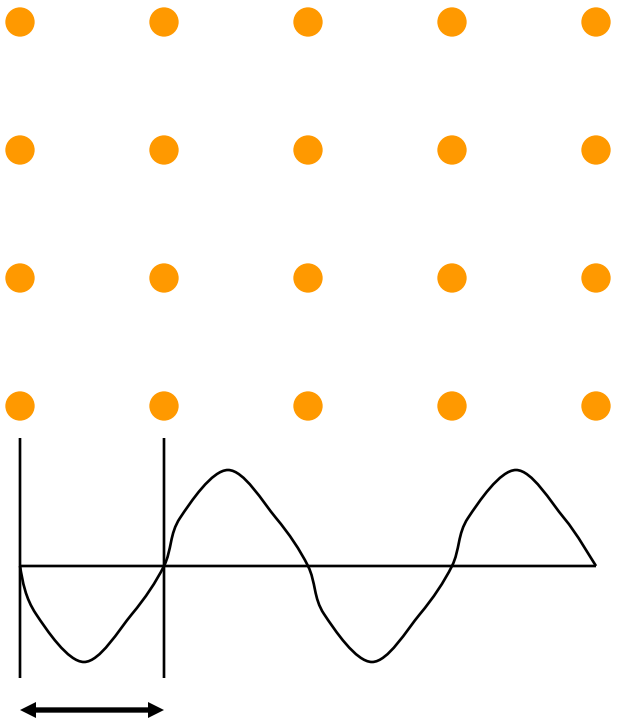
$$v_{xc}(r) = \frac{\delta E_{GGA}[\rho(r'), |\nabla\rho(r')|]}{\delta\rho(r)}$$

$$= V_{GGA}\left(\rho(r), |\nabla\rho(r)|, \nabla^2\rho(r), \nabla\rho(r) \bullet \nabla|\nabla\rho(r)|\right)$$

$$\frac{\partial\rho}{\partial x} \equiv \frac{\rho_{i+1} - \rho_{i-1}}{x_{i+1} - x_{i-1}} \quad \Rightarrow \quad E_{xc} \equiv E_{GGA}(\rho_1, \rho_2, \ldots)$$

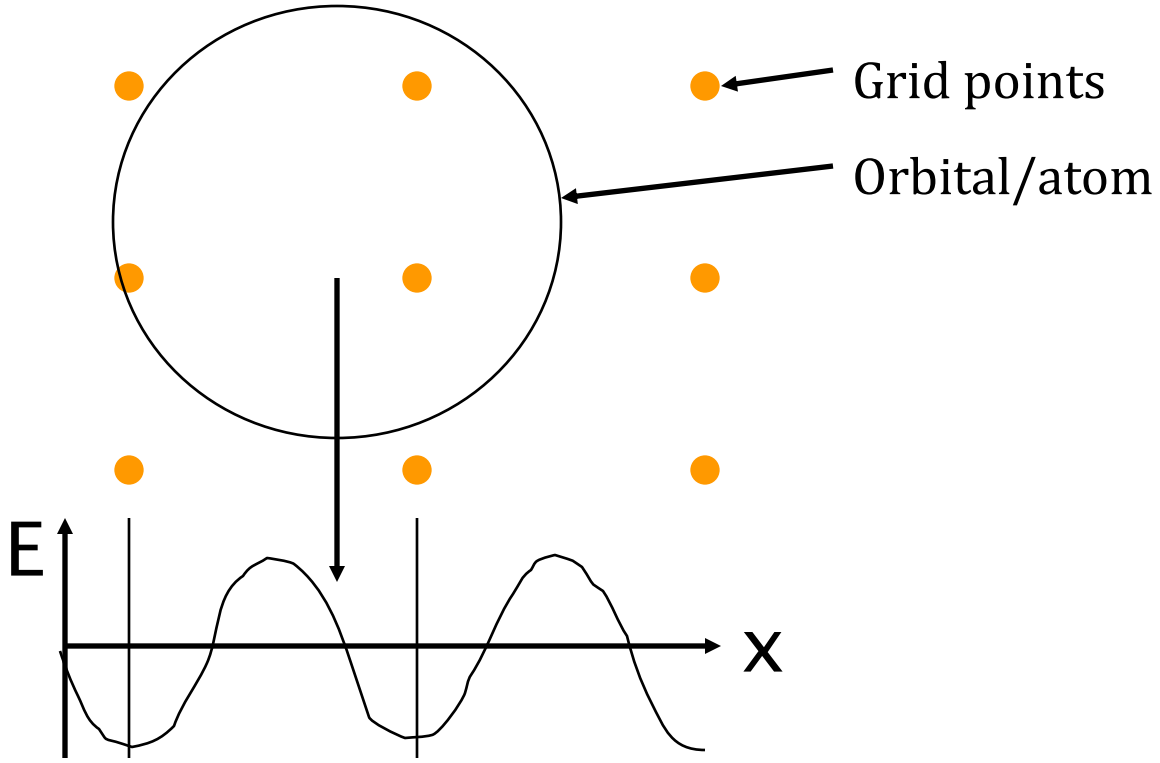
$$\Rightarrow v_{xc}(r_i) \equiv \frac{\partial E_{xc}}{\partial\rho_i}$$

# Grid fineness: ‘mesh cutoff’



$$\Delta x \;\Rightarrow\; k_c = \pi/\Delta x \;\Rightarrow\; E_{cut} = h^2 k_c^{\,2}/2m_e$$

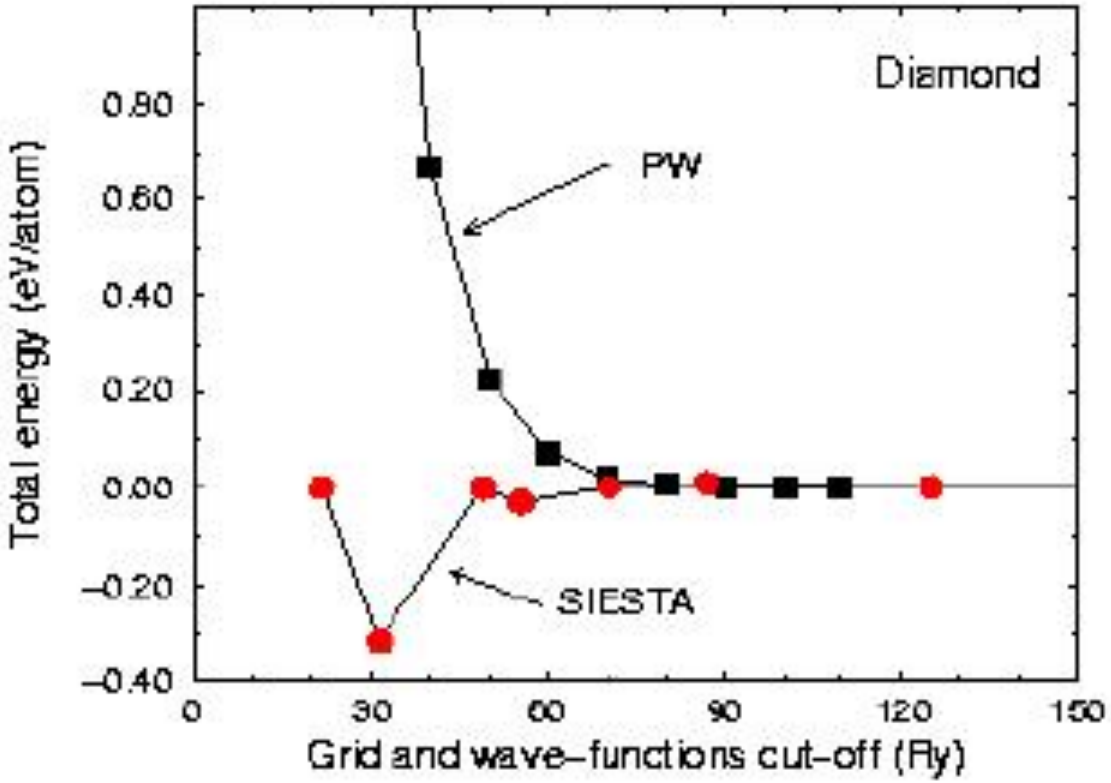
# Egg-box effect




Higher effects on forces than on energy

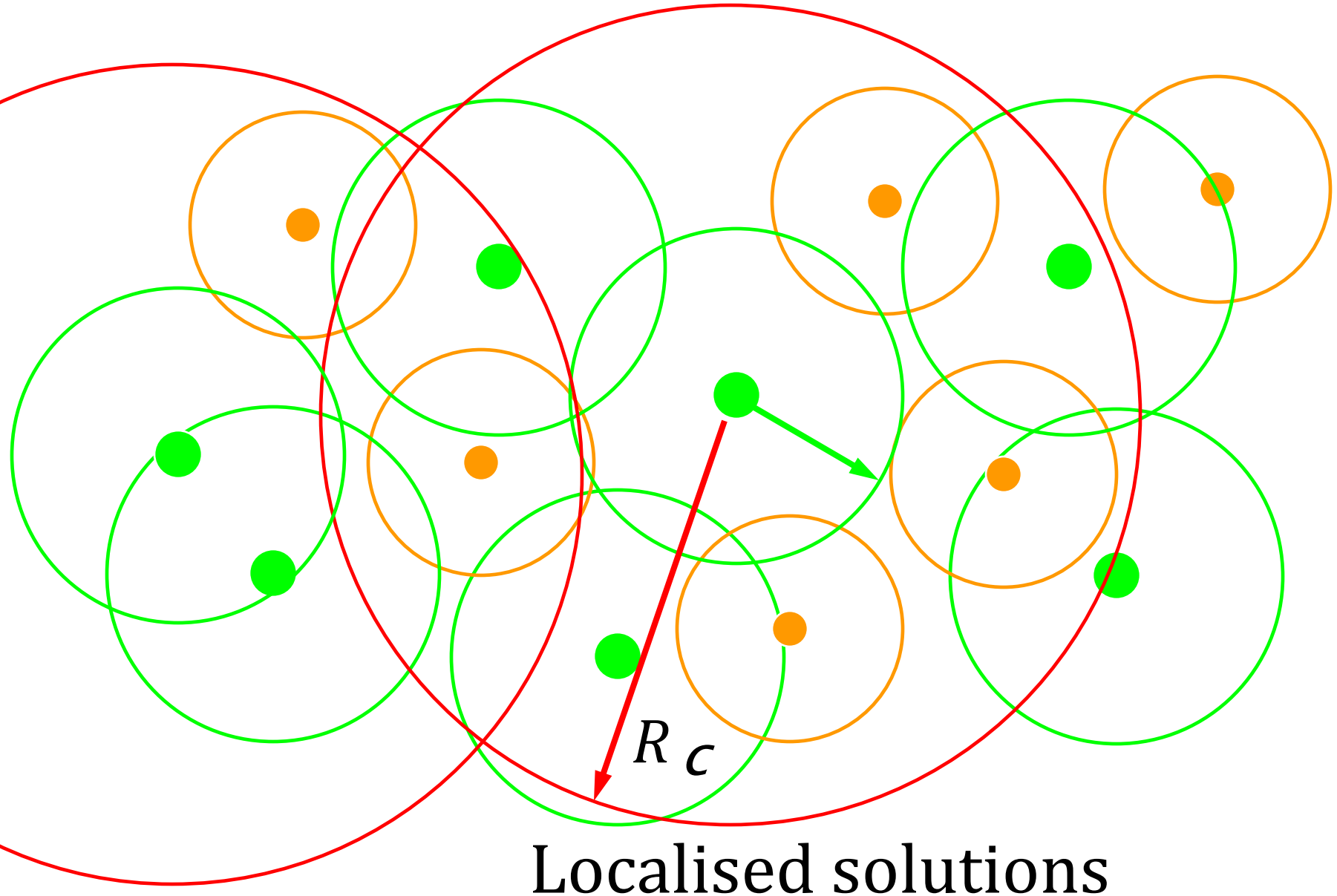
Grid-cell sampling

# Grid fineness convergence




$$E_{cut} = (\pi / \Delta x)^2$$

# 2. Solving: Linear scaling

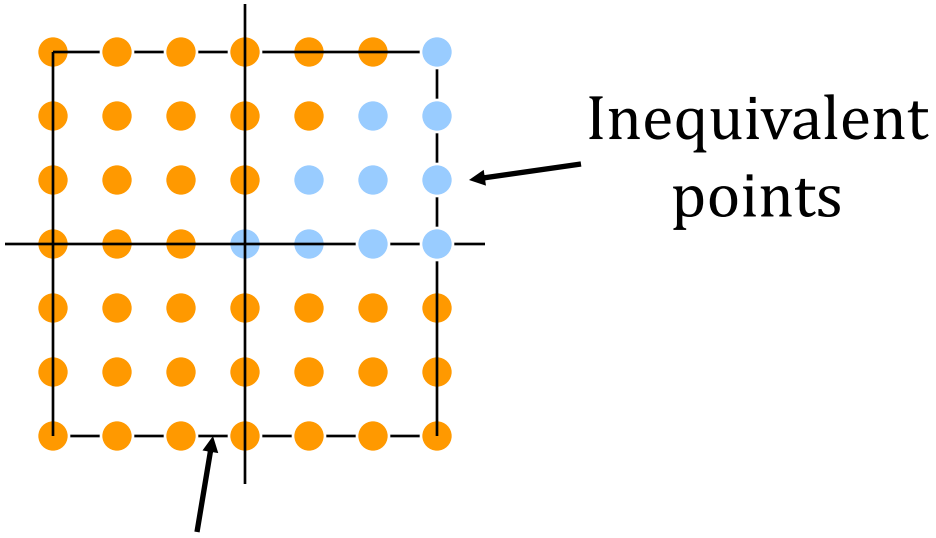



Localised solutions

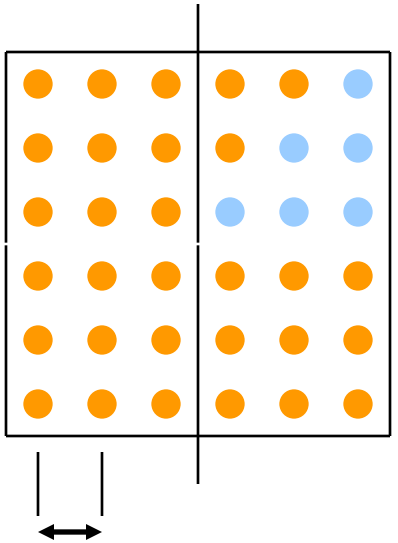
# *k*-point sampling

(fineness of grid in *k*-space)

Regular k-grid




Monkhorst-Pack

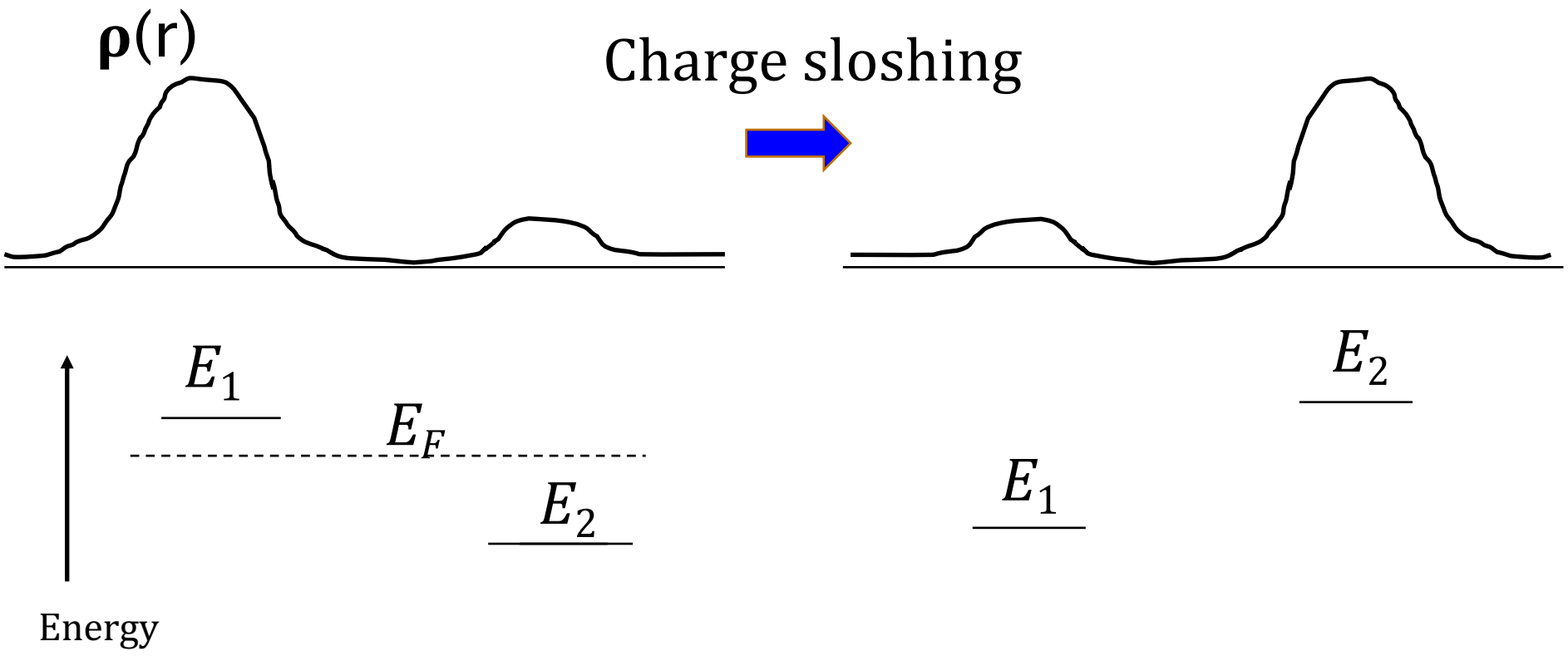


$\Delta k \Rightarrow L_c = \pi/\Delta k$

$L_c$ = 'length cutoff'

# Selfconsistency convergence

SCF cycle: $\boldsymbol{\rho}(r) \rightarrow V(r) \rightarrow \boldsymbol{\rho}(r)$




Moderated by electronic temperature

# Pulay mixing

$$\rho_n(\mathrm{r}) \rightarrow \rho_{out}(\mathrm{r})$$

$$\delta\rho_n(\mathrm{r}) = \rho_{out}(\mathrm{r}) - \rho_n(\mathrm{r})$$

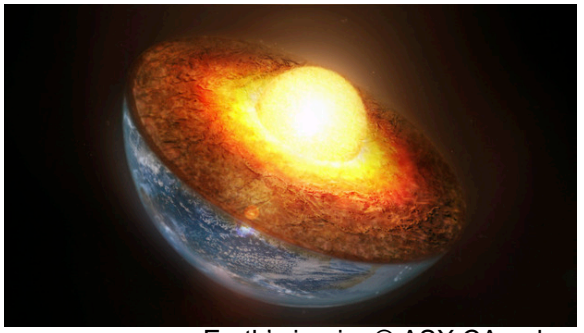
$$\rho_{n+1}(\mathrm{r}) = \sum_{k=n-m}^{n} c_k \rho_k(\mathrm{r})$$

$$\delta\rho_{n+1}(\mathrm{r}) = \sum_{k=n-m}^{n} c_k \delta\rho_k(\mathrm{r}) = min$$

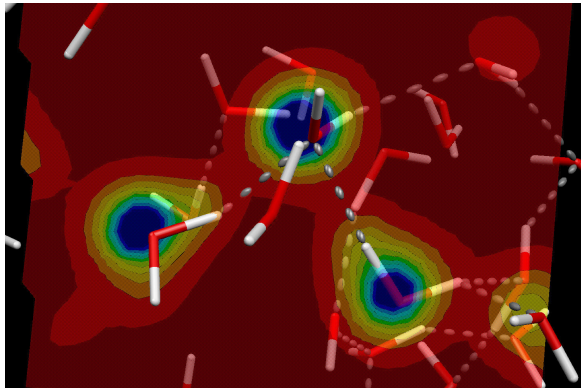
# The physics of low-energy matter

Behind properties and processes in

- Chemistry
- Biomedicine (biochem, biophys, molecular bio)
- Geo (geophyiscs, geochemistry)
- Lots of astrophysics (planets, exoplanets)
- Engineering (materials, electronics …)
- Energy research
- Nanoscience and technlogy

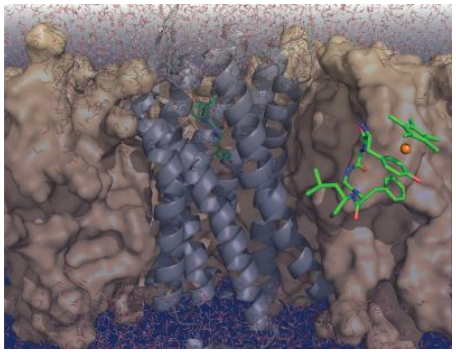


Earth's inerior © ASX CAnada

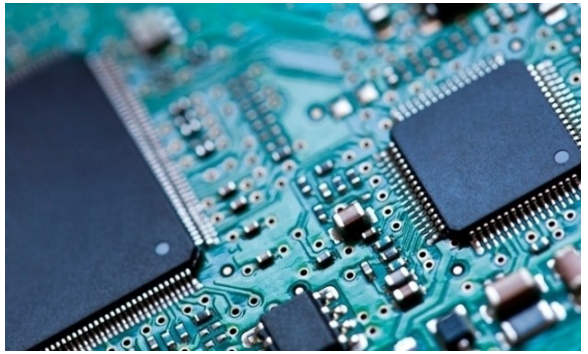


Liquid water © MV Fernandez-Serra

Exoplanets © NASAJPL Caltech, FINESSE Project



Pain receptors in the brain © Univ Bochum



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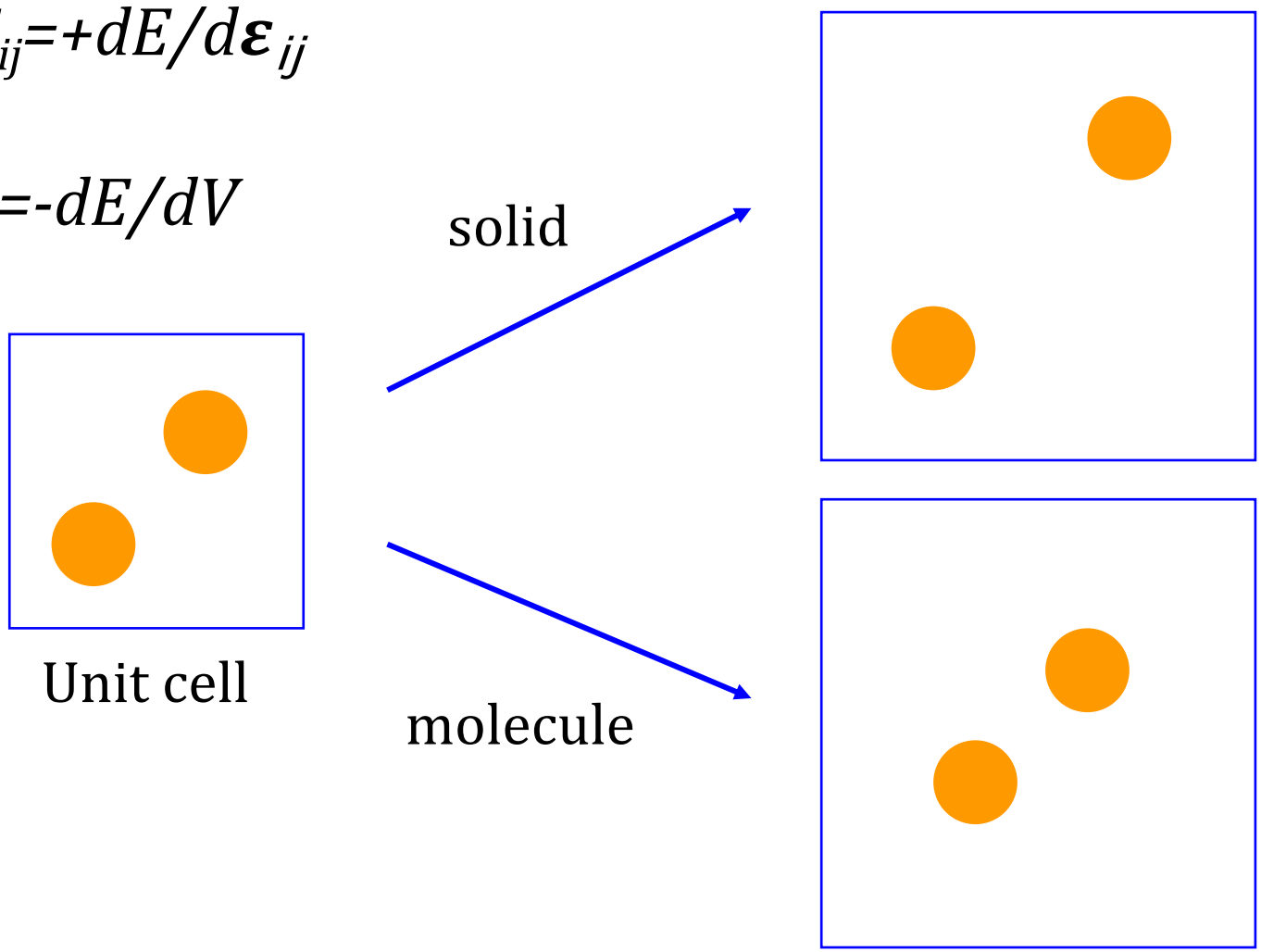
Thank you

# ‘Molecular’ vs ‘solid’ pressure

$T_{ij}=+dE/d\varepsilon_{ij}$

$P=-dE/dV$



# Internal supercell