

Basics and some details of the SIESTA method

José M. Soler

Univ. Autónoma de Madrid



Outline



Specifications:

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

Methods:

- Norm-conserving pseudopotentials
- Basis of numerical atomic orbitals
- Uniform real-space grid
- Order-N functional

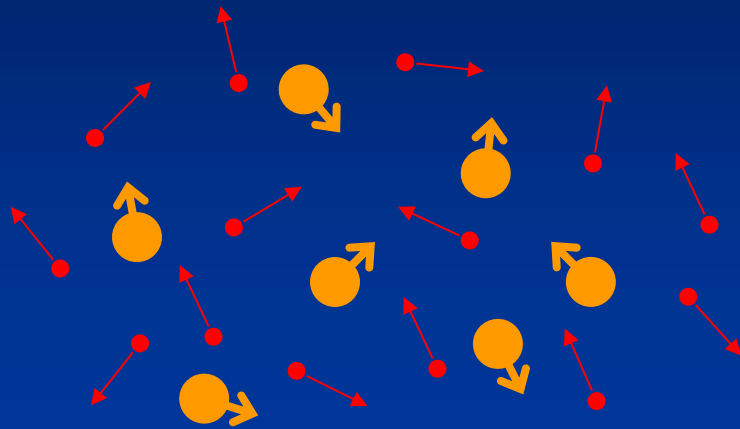
First principles

- Schrödinger equation
- Coulomb's law

$$\frac{\partial \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t)}{\partial t} = \frac{i}{\hbar} \mathbf{H} \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t)$$

$$\mathbf{H} = - \sum_{i=1}^N \frac{\hbar \nabla_i^2}{2m_i} + \sum_{i \neq j} \frac{q_i q_j}{r_{ij}}$$

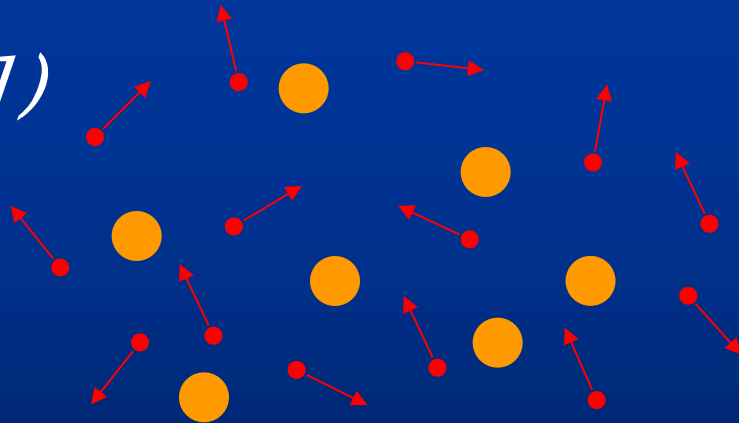
Born–Oppenheimer approximation



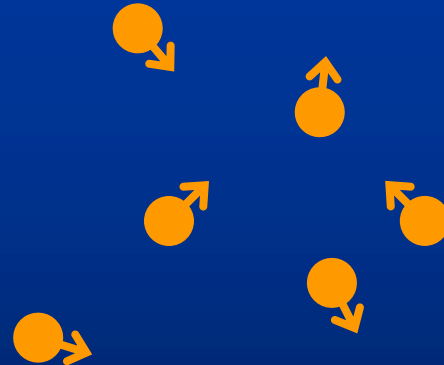
$$m_n \gg m_e$$

⇒ Nuclei are much slower than electrons

(1)



(2)



Decoupling of electrons and nuclei

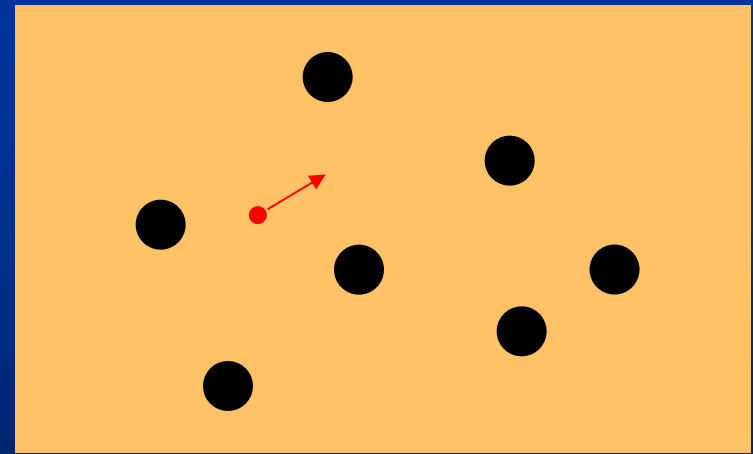
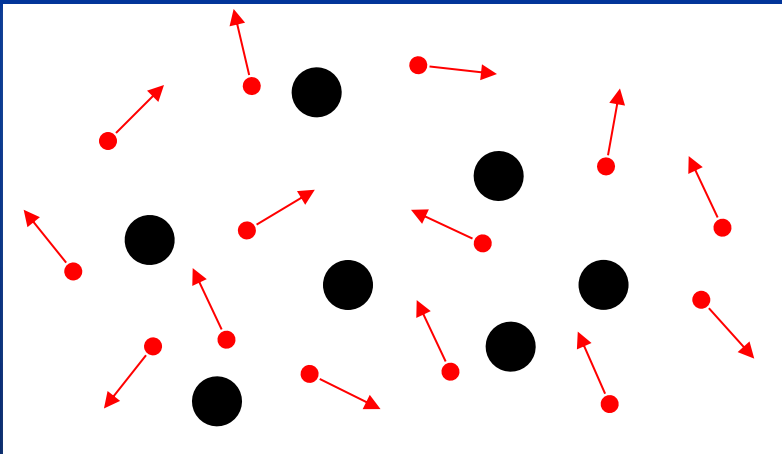
Density functional theory (DFT)

$$H = \sum_{i=1}^{n_e} \left[-\frac{\hbar^2}{2m_e} \nabla_i^2 + V_N(\mathbf{r}_i) \right] + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{n_e} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$H_{DFT} = \sum_{i=1}^{n_e} \left[-\frac{\hbar^2}{2m_e} \nabla_i^2 + V_N(\mathbf{r}_i) + V_H(\mathbf{r}_i) + V_{XC}(\mathbf{r}_i) \right]$$

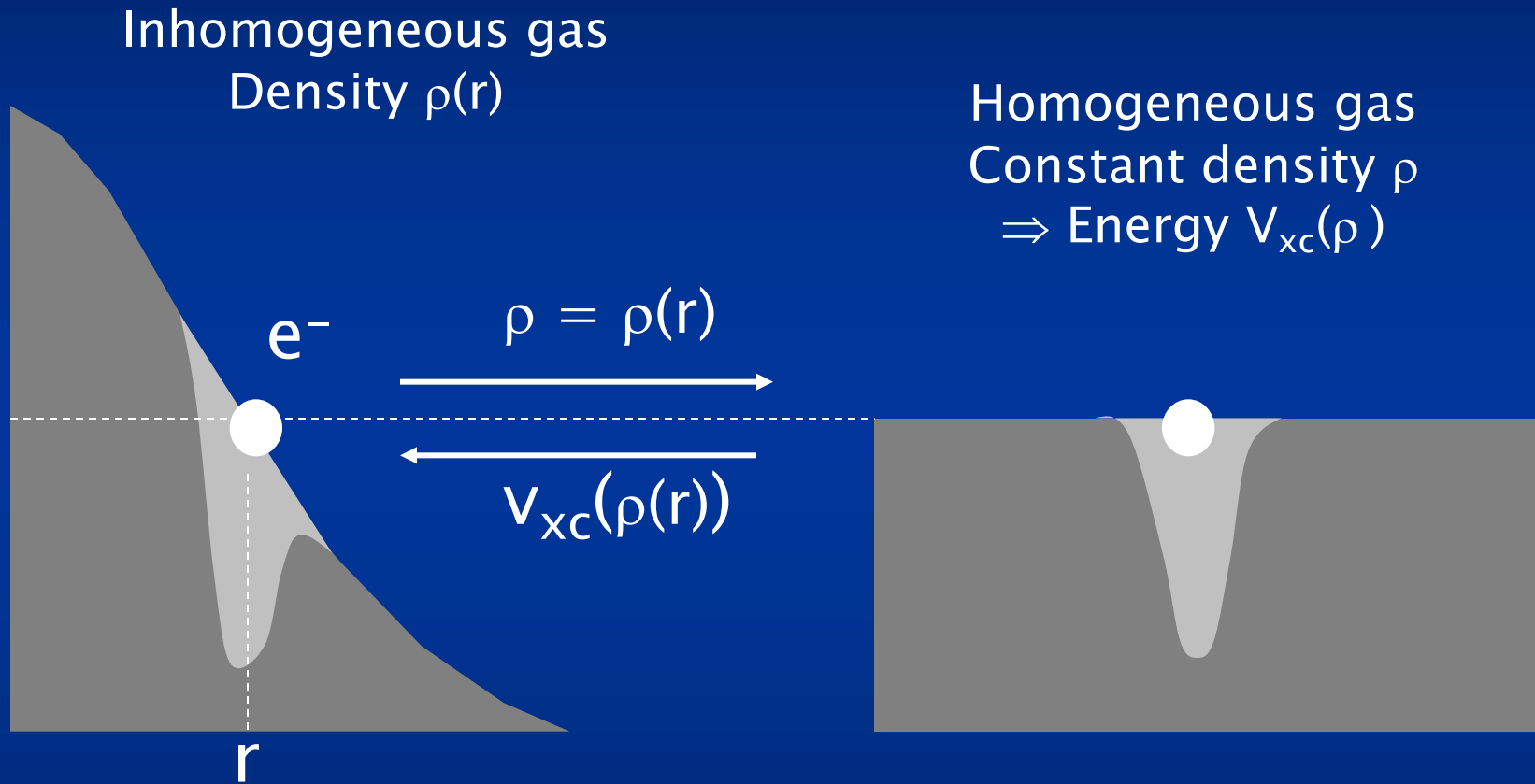
$$V_H(\mathbf{r}) = \int d^3\mathbf{r}' \frac{\rho_e(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Non-interacting electrons in a self-consistent effective potential



$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \rightarrow \psi_1(\mathbf{r}_1) \psi_2(\mathbf{r}_2) \dots \psi_N(\mathbf{r}_N)$$

Local density approximation (LDA)



- Generalized gradient approximation (GGA): $V_{xc}(\rho(r), \nabla\rho(r))$
- Van der Waals xc functionals: $V_{xc}(\rho(r), \nabla\rho(r); \rho(r'), \nabla\rho(r'))$

Kohn-Sham method

Initial electron density

$$\rho(\mathbf{r}) = \sum_{\text{atoms}} \rho_{\text{atom}}(\mathbf{r})$$

Effective electron potential

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{nuclei}}(\mathbf{r}) + V_{\text{H}}[\rho(\mathbf{r})] + V_{\text{xc}}(\rho(\mathbf{r}))$$

Schrödinger equation

$$[-(1/2) \nabla^2 + V_{\text{eff}}(\mathbf{r})] \psi_i(\mathbf{r}) = E_i \psi_i(\mathbf{r})$$

$$\psi_i(\mathbf{r}) = \sum_{\mu} c_{i\mu} \phi_{\mu}(\mathbf{r}) \quad \Rightarrow \quad \sum_{\nu} H_{\mu\nu} c_{i\nu} = E_i c_{i\mu}$$

New density

$$\rho(\mathbf{r}) = \sum_i | \psi_i(\mathbf{r}) |^2$$

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

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

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

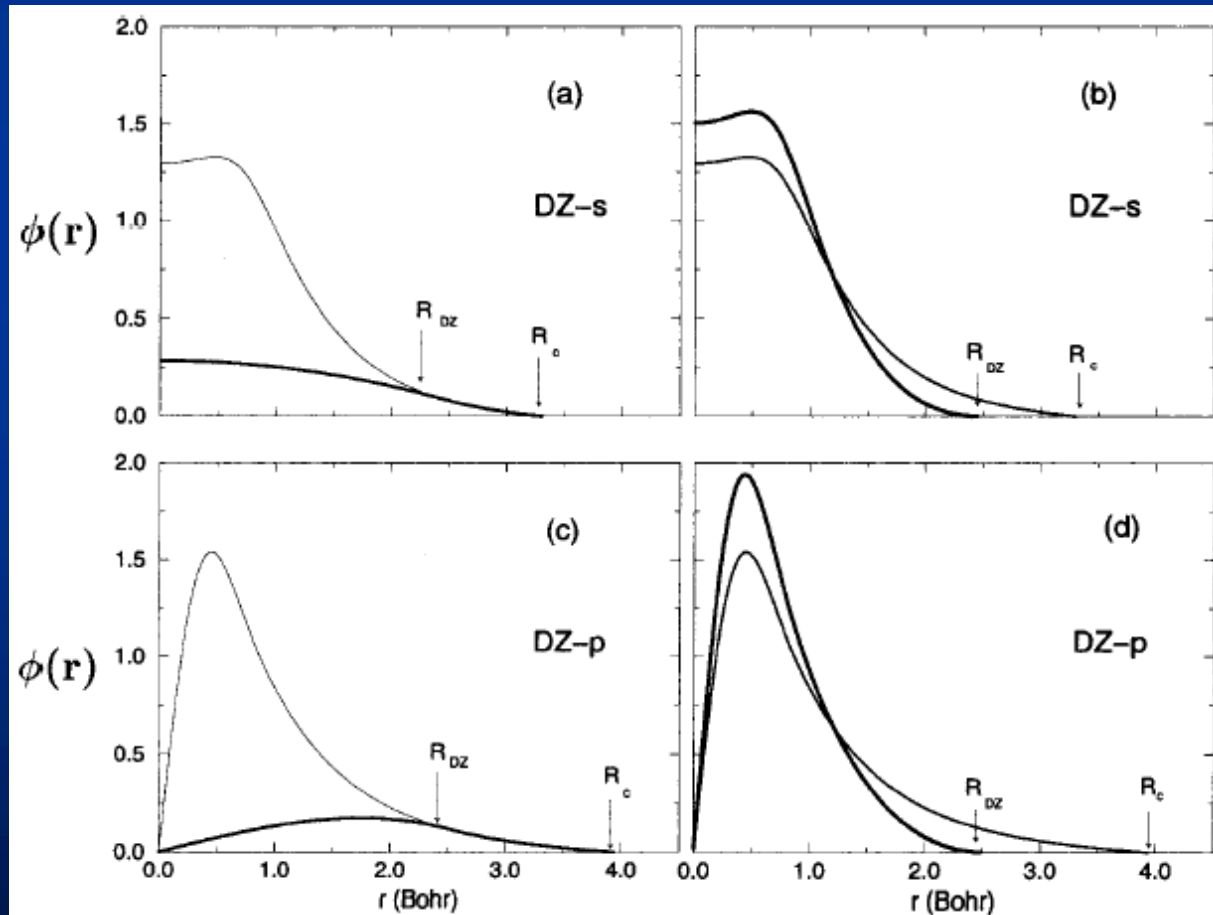
$$l = 1, m = -1, 0, +1 \quad \Rightarrow \quad p_y, p_z, p_x$$

Finite-range basis orbitals

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

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

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

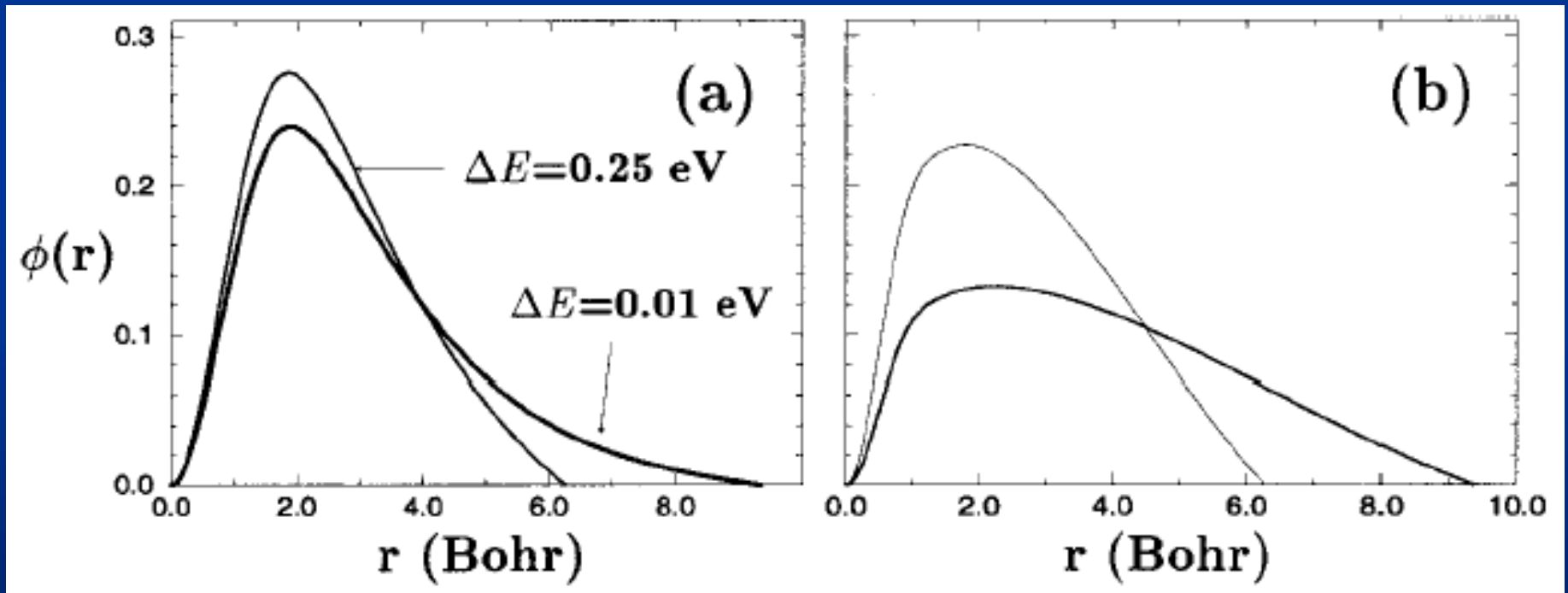


Polarization orbitals

Si *d* orbitals

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 momentum 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)

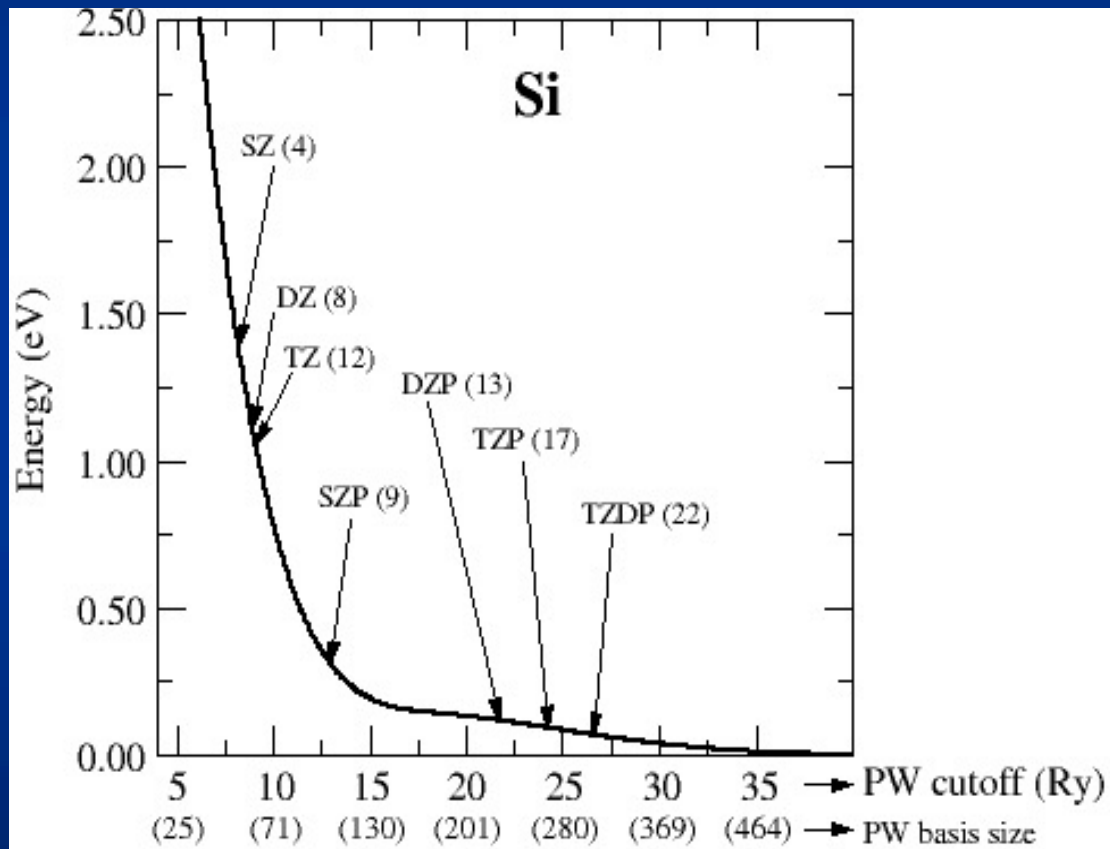
isc = Unit cell indexes to which orbital belongs:

center(io) = center(iuo) + sum_(i=1:3) cell_vec(i) * isc(i)

iuo = Equivalent orbital in first unit cell

Basis set convergence

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



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

Schrödinger equation

$$H\psi_i(\mathbf{r}) = E_i\psi_i(\mathbf{r})$$

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

$$\sum_{\nu} (H_{\mu\nu} - E_i S_{\mu\nu}) c_{i\nu} = 0$$

$$H_{\mu\nu} = \langle \phi_{\mu} | H | \phi_{\nu} \rangle$$

$$S_{\mu\nu} = \langle \phi_{\mu} | \phi_{\nu} \rangle$$

Kohn-Sham hamiltonian

$$H = T + V_{PS} + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})$$

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

$$V_{PS} = V_{ion}(\mathbf{r}) + V_{nl}$$

$$V_{ion}(\mathbf{r}) \rightarrow -Z_{val} / r \quad \text{Local pseudopotential}$$

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

$$V_H(\mathbf{r}) = \int d\mathbf{r}' \rho(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'| \quad \text{Hartree potential}$$

$$V_{xc}(\mathbf{r}) = v_{xc}(\rho(\mathbf{r})) \quad \text{Exchange \& correlation}$$

Long-range potentials

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

Long range

$$V_{\text{na}}(\mathbf{r}) = V_{\text{ion}}(\mathbf{r}) - V_{\text{H}}[\rho_{\text{ions}}(\mathbf{r})] \quad \text{Neutral-atom potential}$$

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

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

Two-center
integrals

Grid integrals

Two-center integrals

Convolution theorem

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

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

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

Grid work

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

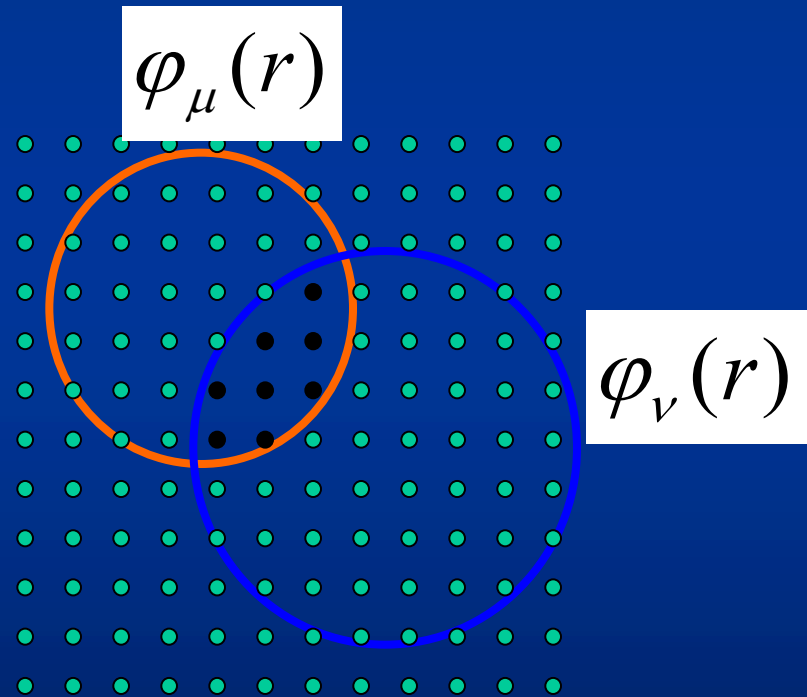
$$\rho_{\mu\nu} = \sum_i c_{i\mu} c_{i\nu}$$

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

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

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

$$\delta\rho(\mathbf{r}) \xrightarrow{\text{FFT}} \delta V_{\text{H}}(\mathbf{r})$$



Poisson equation

$$\nabla^2 V_H(\mathbf{r}) = -4\pi \rho(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_{\mathbf{G}} \rho_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \Rightarrow V_H(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}$$

$$V_{\mathbf{G}} = -4\pi \rho_{\mathbf{G}} / \mathbf{G}^2$$

$$\rho(\mathbf{r}) \xrightarrow{\text{FFT}} \rho_{\mathbf{G}} \rightarrow V_{\mathbf{G}} \xrightarrow{\text{FFT}} V_H(\mathbf{r})$$

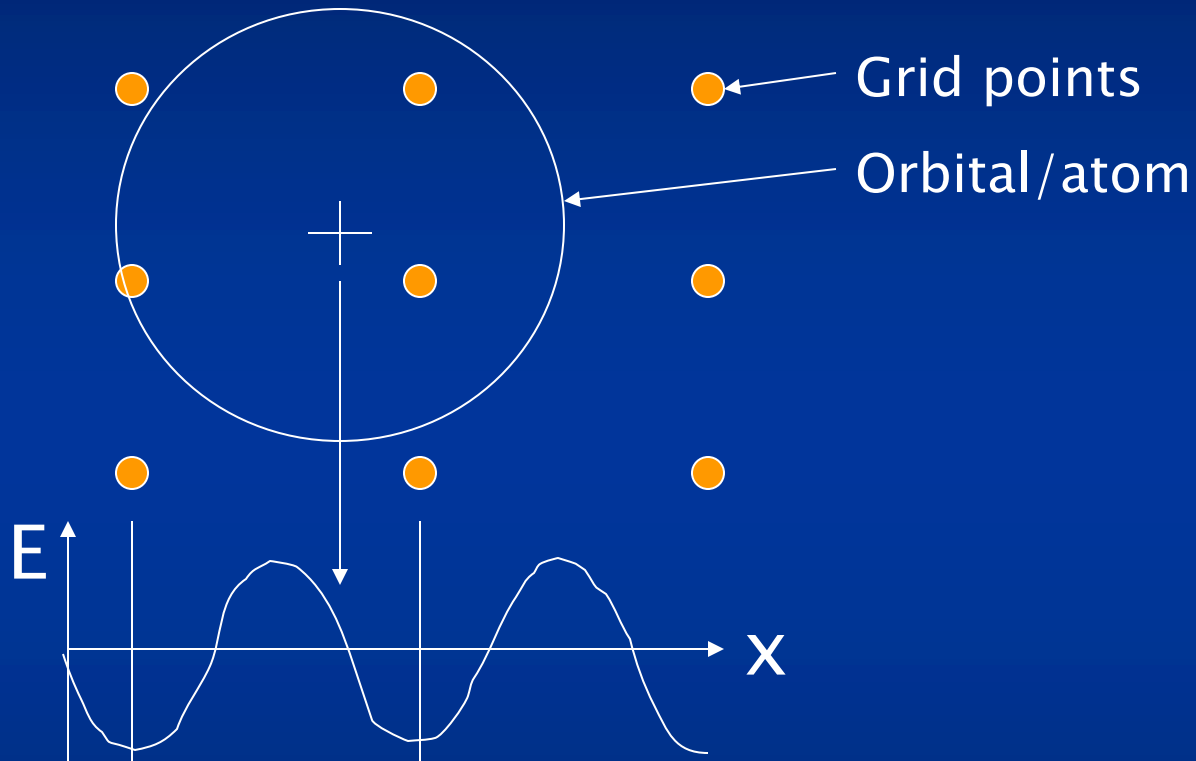
- SIESTA always uses periodic boundary conditions
- Net charge compensated by uniform background
- Spurious interactions between 'images'

GGA

$$\begin{aligned} v_{xc}(r) &= \frac{\delta E_{GGA}[\rho(r'), |\nabla \rho(r')|]}{\delta \rho(r)} \\ &= V_{GGA}(\rho(r), |\nabla \rho(r)|, \nabla^2 \rho(r), \nabla \rho(r) \cdot \nabla |\nabla \rho(r)|) \end{aligned}$$

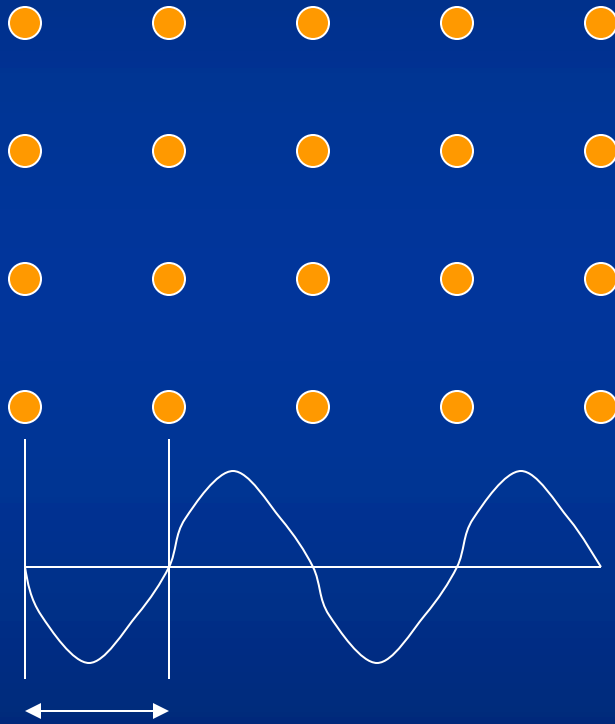
$$\begin{aligned} \frac{\partial \rho}{\partial x} &\equiv \frac{\rho_{i+1} - \rho_{i-1}}{x_{i+1} - x_{i-1}} \quad \Rightarrow \quad E_{xc} \equiv E_{GGA}(\rho_1, \rho_2, \dots) \\ &\quad \Rightarrow \quad v_{xc}(r_i) \equiv \frac{\partial E_{xc}}{\partial \rho_i} \end{aligned}$$

Egg-box effect



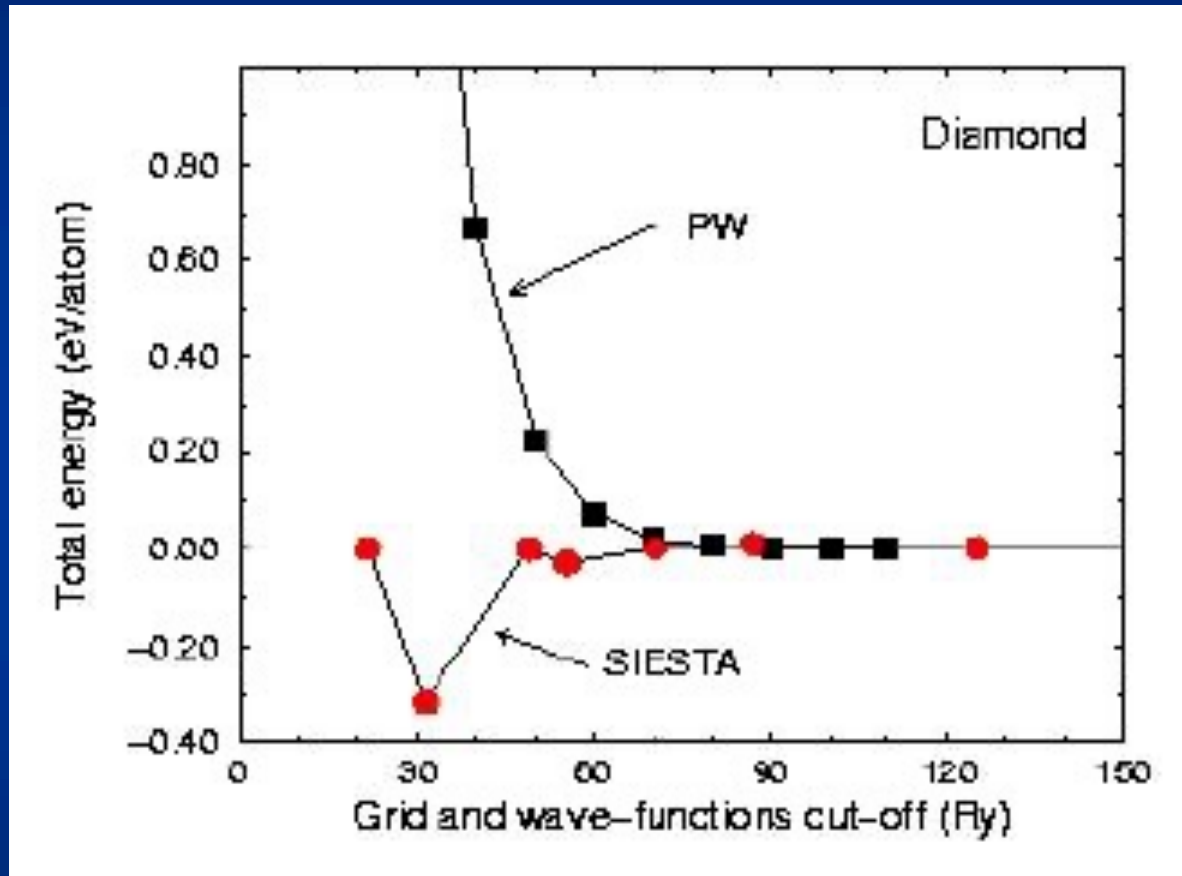
- Affects more to forces than to energy
- Grid-cell sampling

Grid fineness: 'mesh cutoff'



$$\Delta x \Rightarrow k_c = \pi / \Delta x \Rightarrow E_{\text{cut}} = \hbar^2 k_c^2 / 2m_e$$

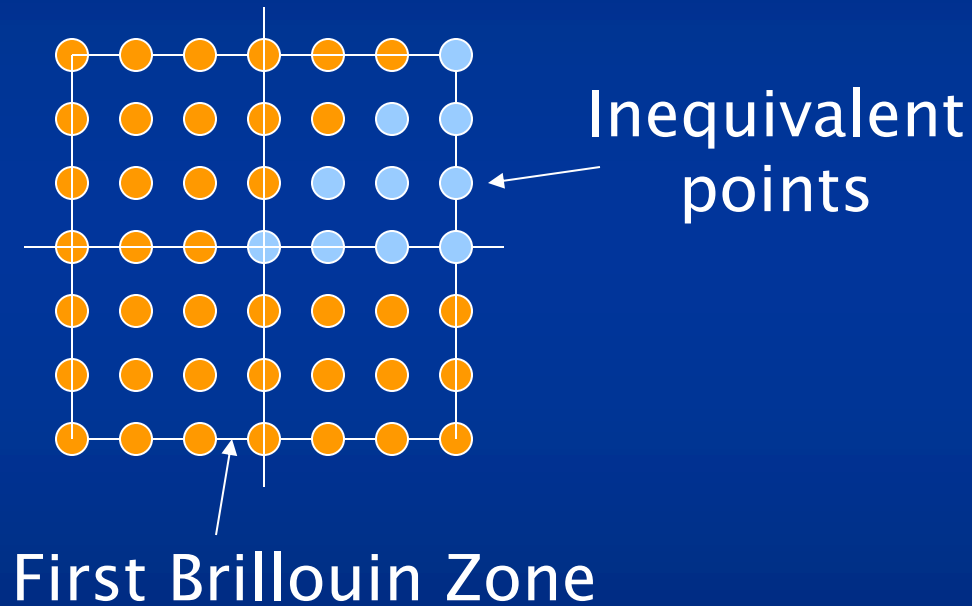
Grid fineness convergence



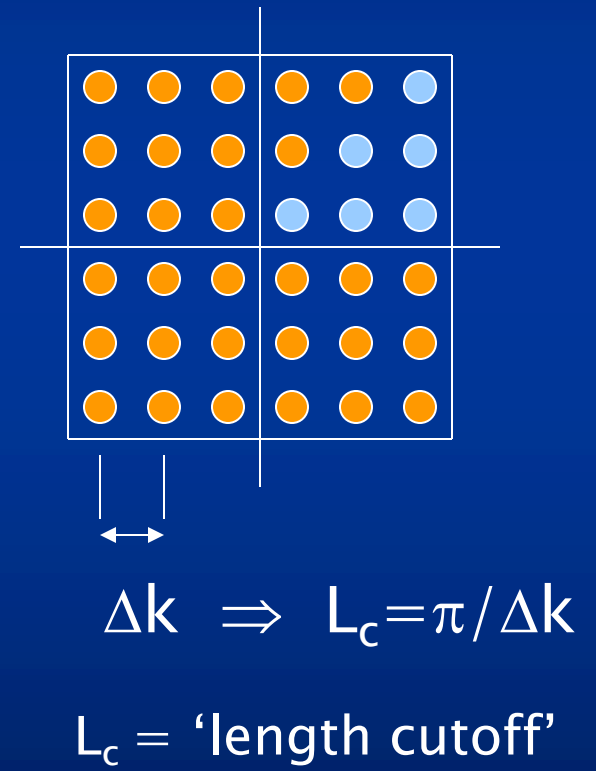
$$E_{cut} = (\pi / \Delta x)^2$$

K-point sampling

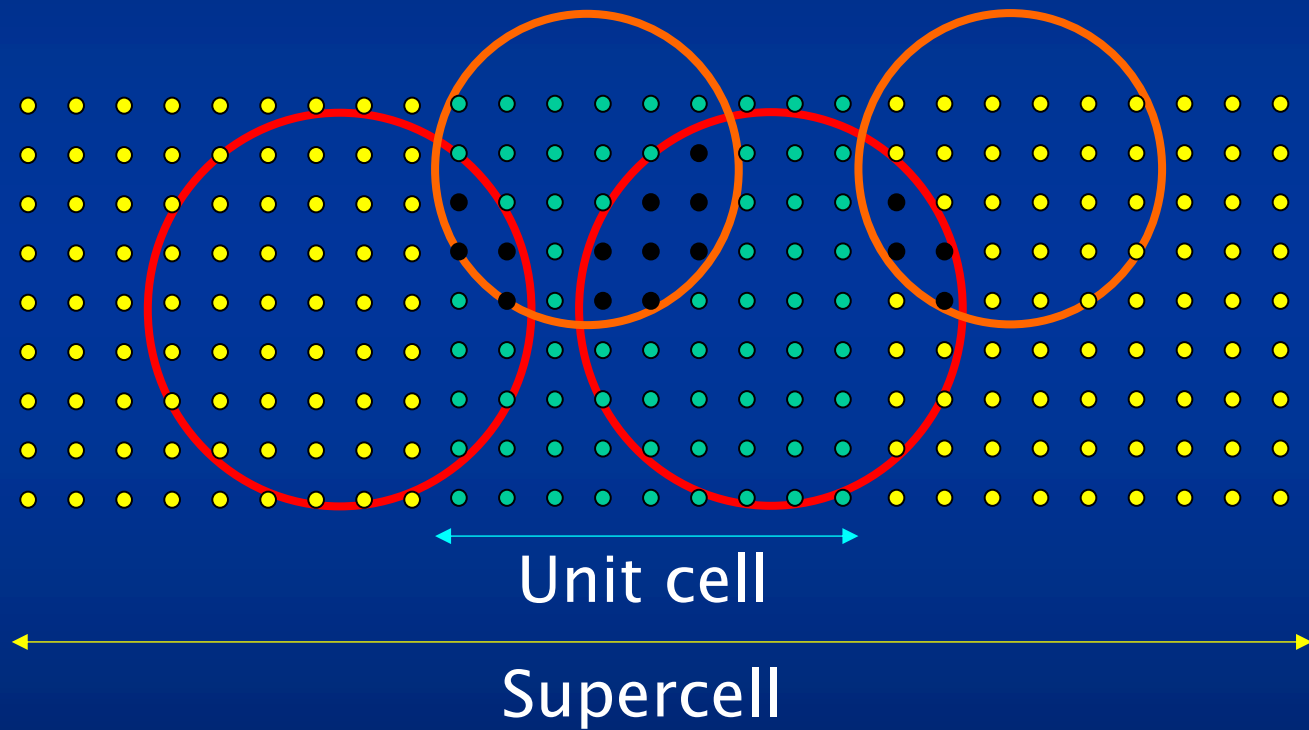
Regular k-grid



Monkhorst-Pack



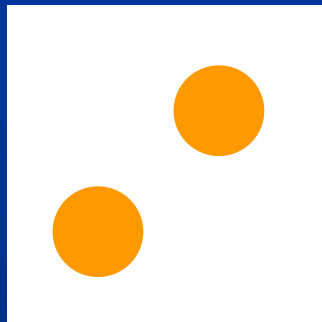
Internal supercell



'Molecular' vs 'solid' pressure

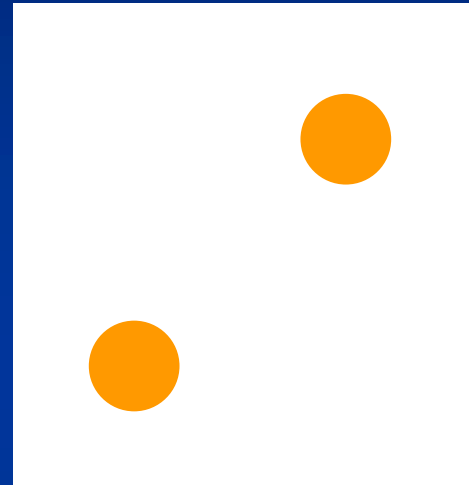
$$T_{ij} = +dE/d\varepsilon_{ij}$$

$$P = -dE/dV$$

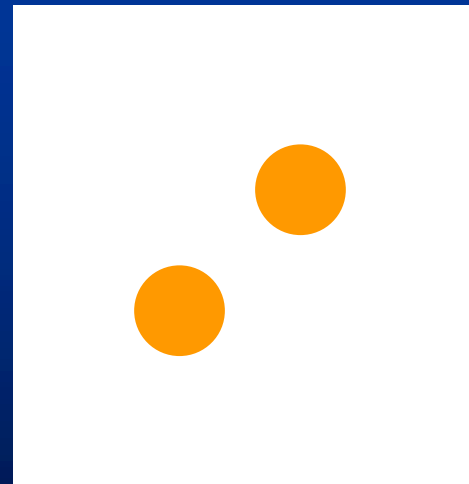


Unit cell

solid

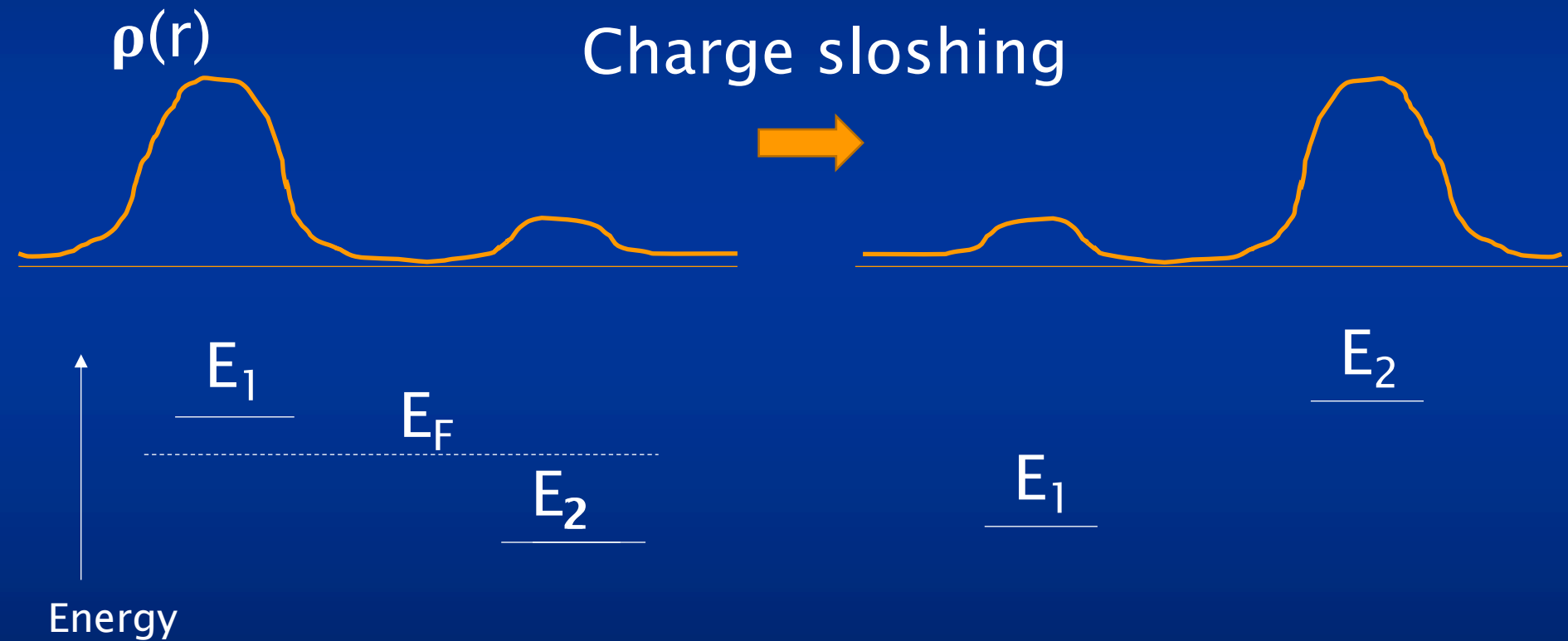


molecule



Selfconsistency convergence

SCF cycle: $\rho(r) \rightarrow v(r) \rightarrow \rho(r)$



Moderated by electronic temperature

Pulay mixing

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

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

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

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

Thank you