

# *Some internals of the SIESTA method*

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# *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

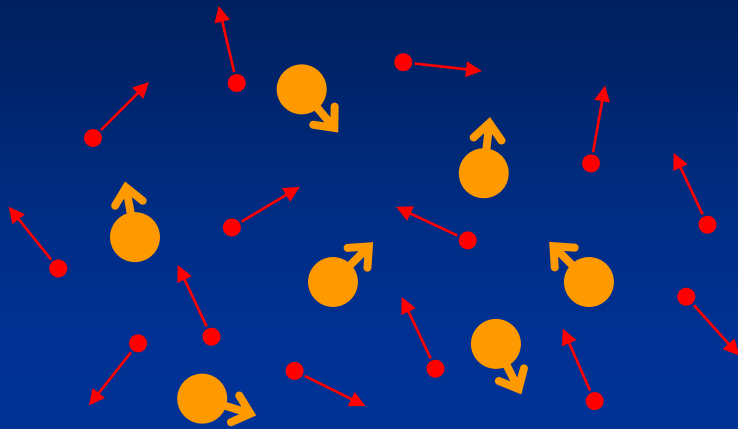
# *First principles*

- Schrödinger equation
- Coulomb's law

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

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

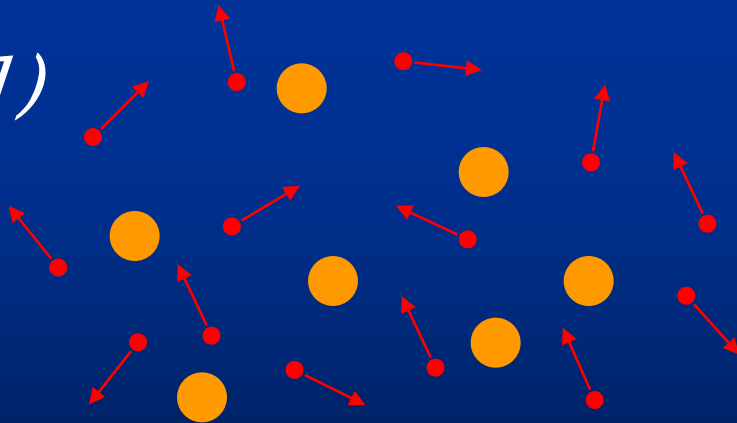
# *Born–Oppenheimer approximation*



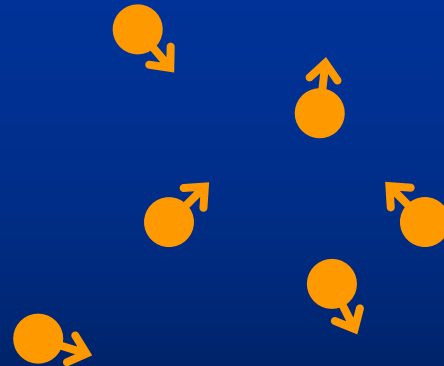
$$m_n \gg m_e$$

*⇒ Nuclei are much slower than electrons*

*(1)*



*(2)*

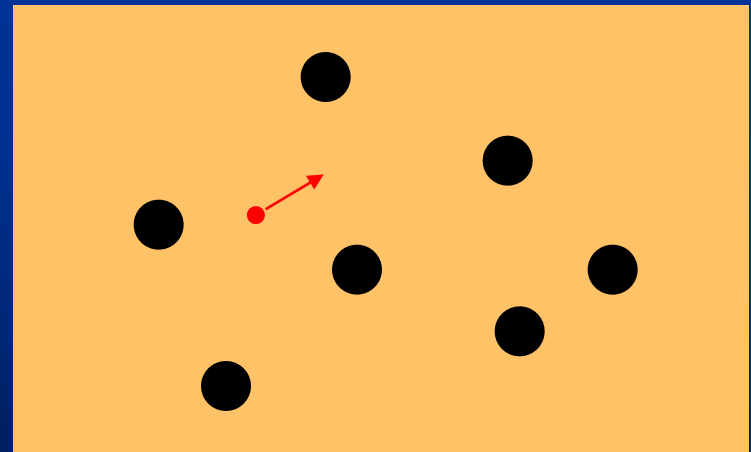
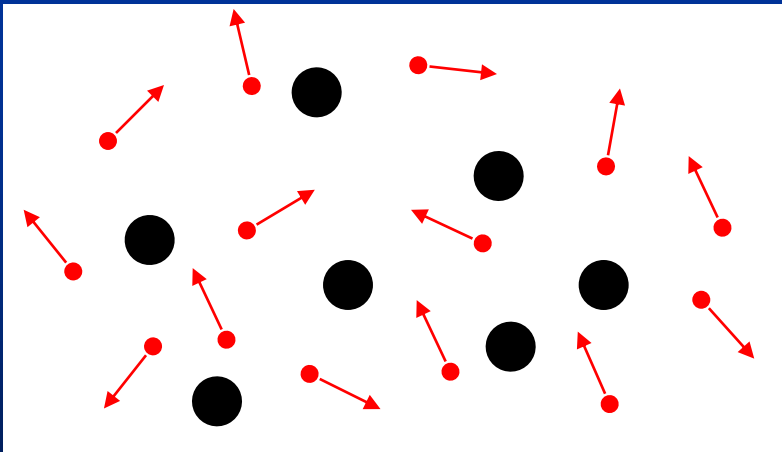


*Decoupling of electrons and nuclei*

# Density functional theory (DFT)

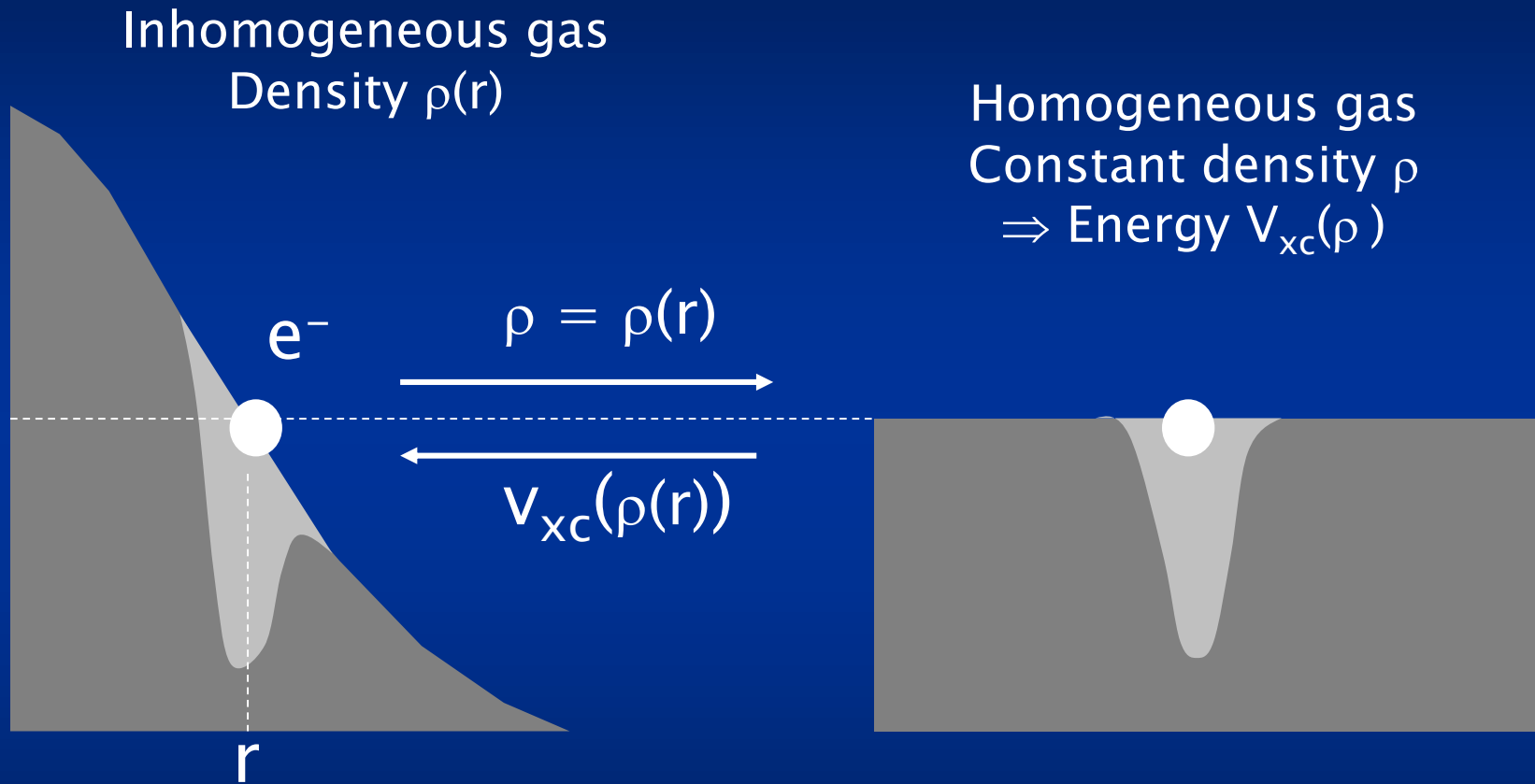
$$H = \sum_{i=1}^{n_e} \left[ -\frac{\hbar^2}{2m_e} \nabla_i^2 + V_N(\mathbf{r}_i) \right] + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{n_e} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$
$$H_{DFT} = \sum_{i=1}^{n_e} \left[ -\frac{\hbar^2}{2m_e} \nabla_i^2 + V_N(\mathbf{r}_i) + V_H(\mathbf{r}_i) + V_{XC}(\mathbf{r}_i) \right]$$
$$V_H(\mathbf{r}) = \int d^3\mathbf{r}' \frac{\rho_e(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

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

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

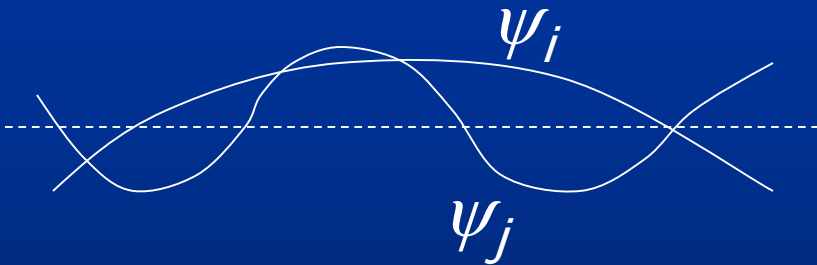
$$\psi_i(\mathbf{r}) = \sum_{\mu} c_{i\mu} \phi_{\mu}(\mathbf{r}) \quad \Rightarrow \quad \sum_{\nu} H_{\mu\nu} c_{i\nu} = E_i c_{i\mu}$$

New density

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

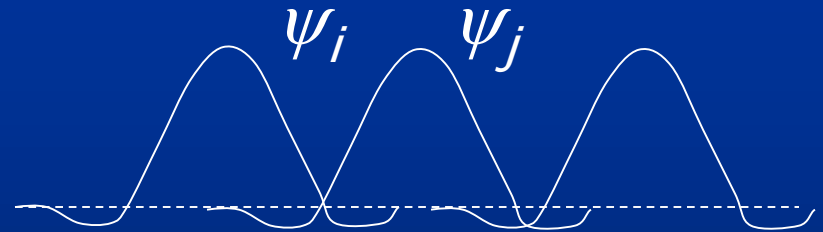
# *Pauli exclusion principle*

$$\int \psi_i(r) \psi_j(r) d^3r = \delta_{ij}$$



Bloch functions

CPU  $\propto N^3$

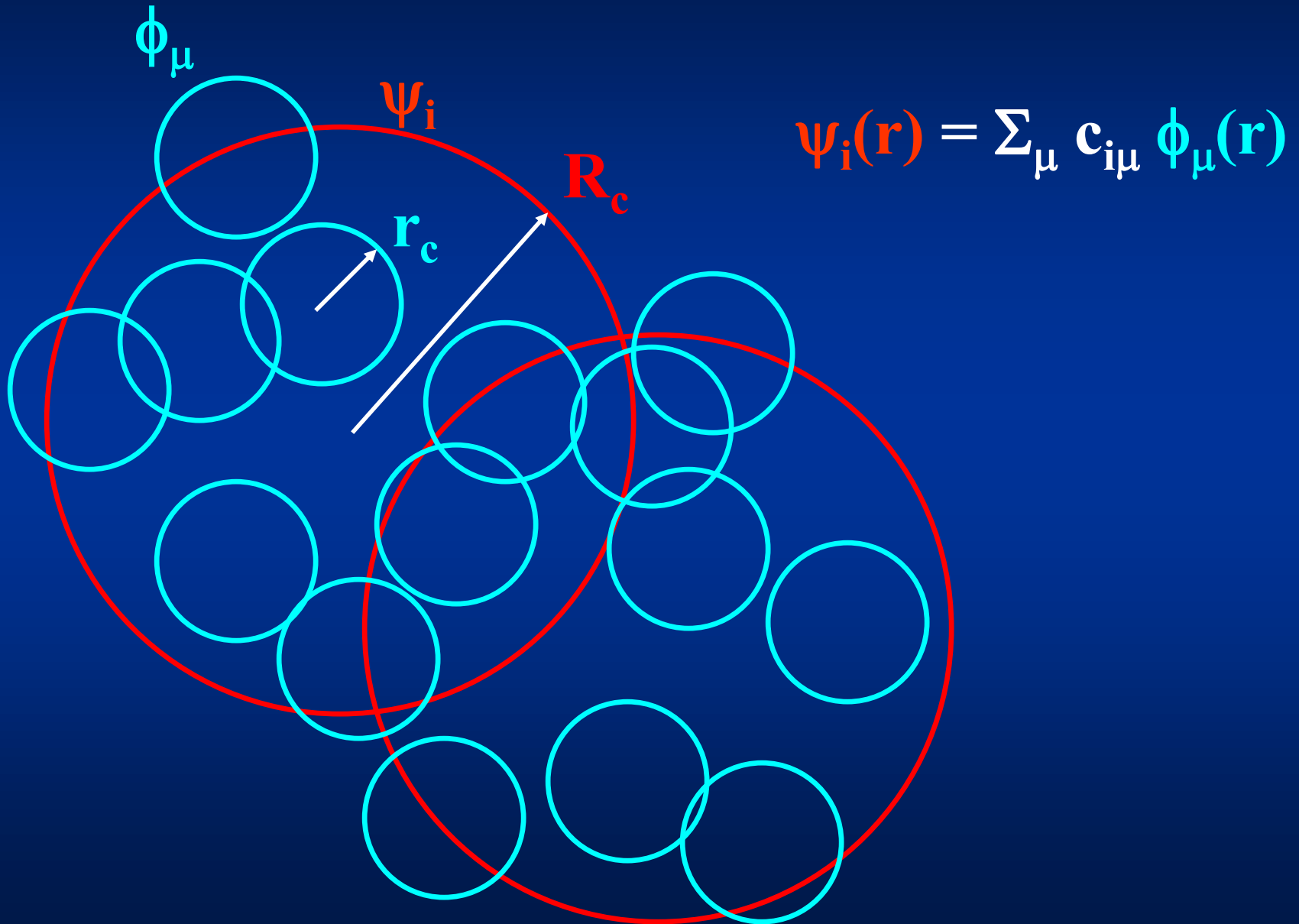


Wannier functions

CPU  $\propto N$



# Orbital localization



# *Real spherical harmonics*

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

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

# 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)

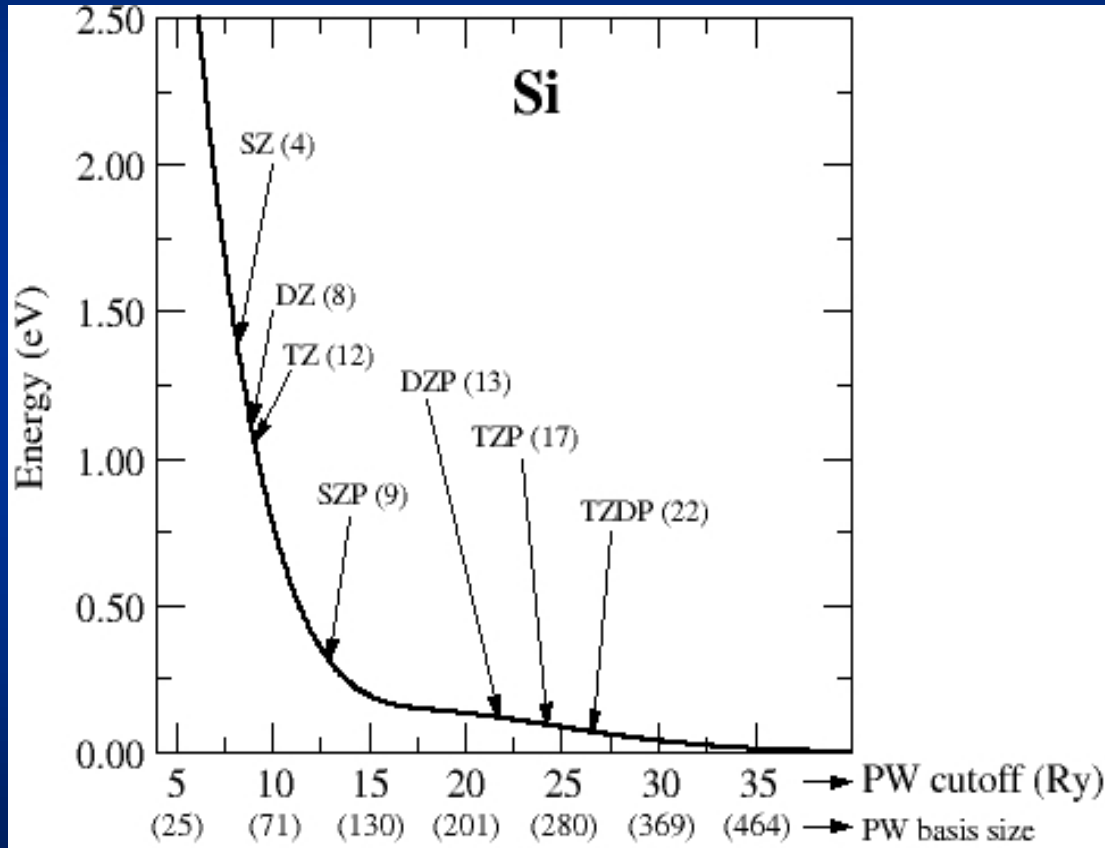
isc = Unit cell indexes to which orbital belongs:

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

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

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

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

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

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

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

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

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

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

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

