



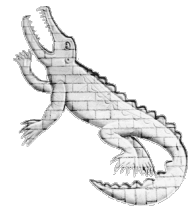
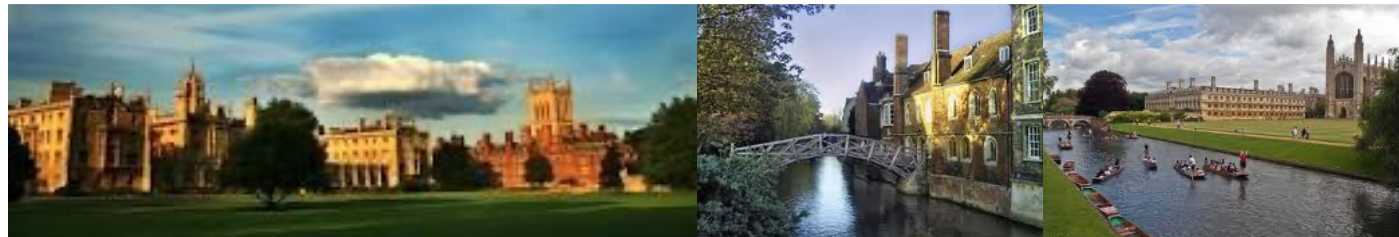
Basics and some details of the SIESTA method



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Cavendish Laboratory, University of Cambridge*



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 orbitals
- Uniform real-space grid
- Order-N functional (solver)

Introduction to basics only (main engine)

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

The physics of low-energy matter

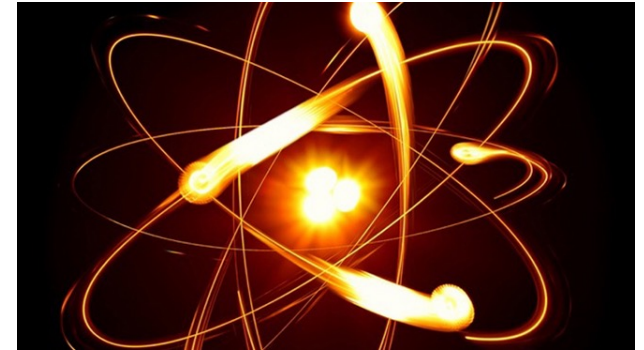
Made of electrons & nuclei
(interacting with photons)

matter at T up to several million K

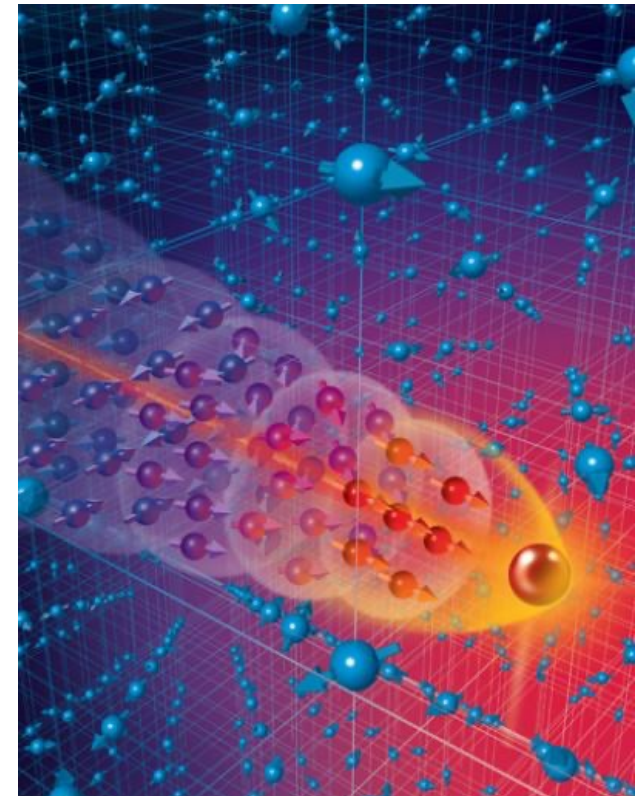
(except for nuclear fission and radioactive decay)

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

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



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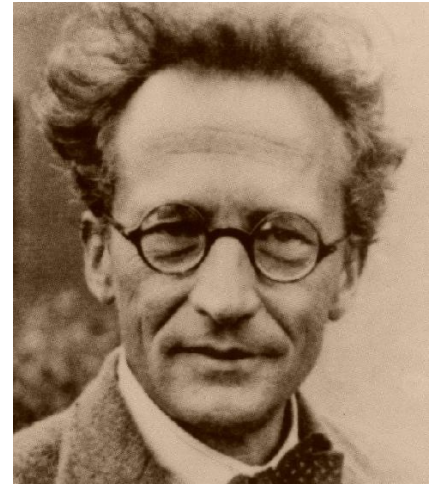


Ali Yazdani's group, Princeton



First principles

Quantum Mechanics

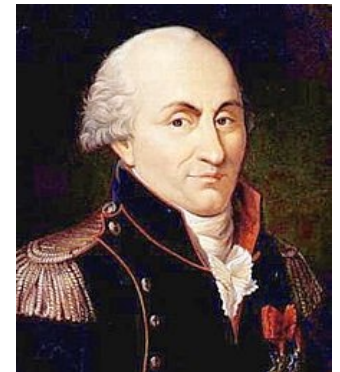


$$H\Psi(s_1, s_2 \dots s_N, t) = i\hbar \partial_t \Psi(s_1, s_2 \dots s_N, t)$$

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

Coulomb's law

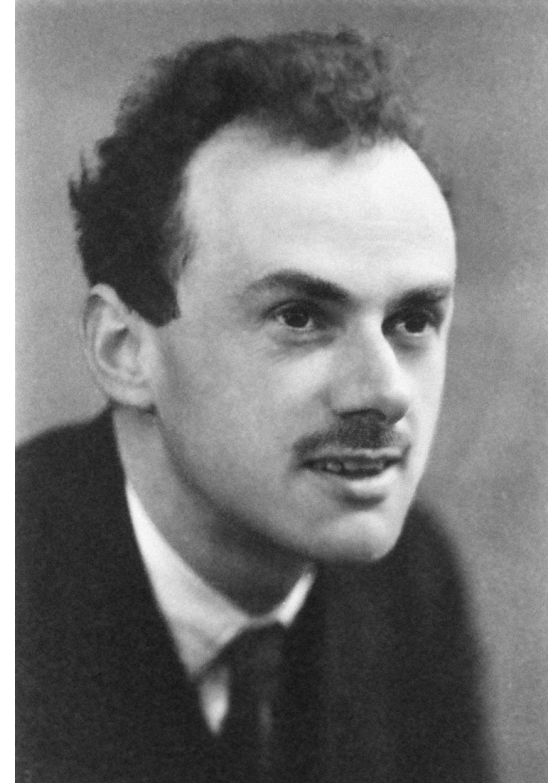
$$H = - \sum_i^N \frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_{i,j < i}^N \frac{q_i q_j}{r_{ij}}$$



Just electrons and nuclei

Just electrons and nuclei

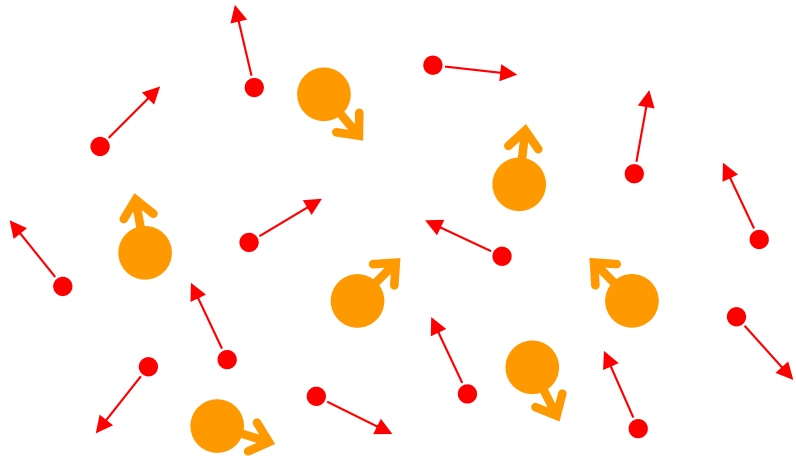
The underlying physical laws necessary for the mathematical theory of . . . the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.



Paul Dirac, 1929

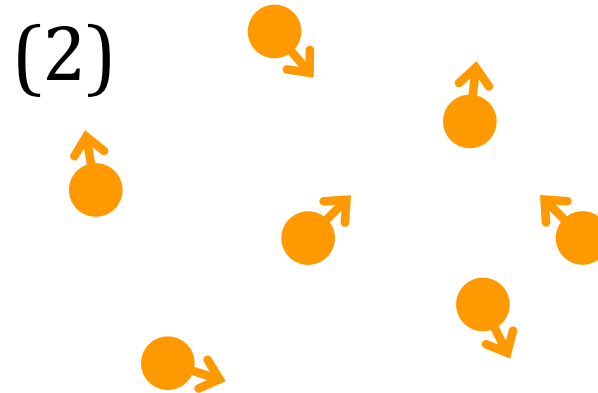
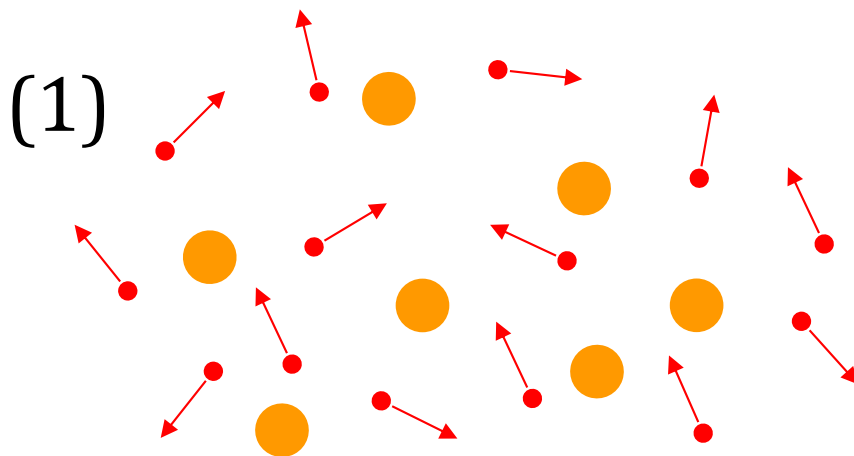
=> Approximations

Born-Oppenheimer approximation



$$m_n \gg m_e$$

$\Rightarrow$ Nuclei are much slower than electrons



Decoupling of electrons and nuclei

Many electrons: Density-Functional Theory (DFT)

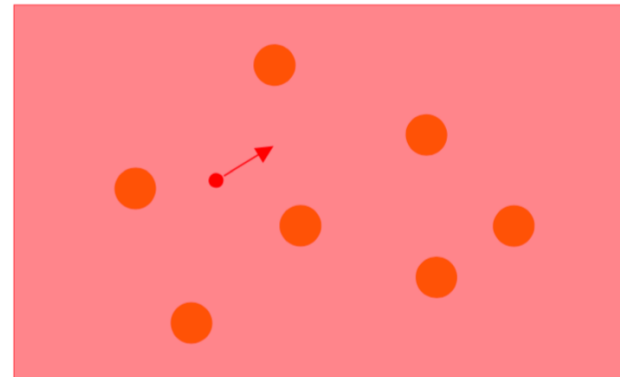
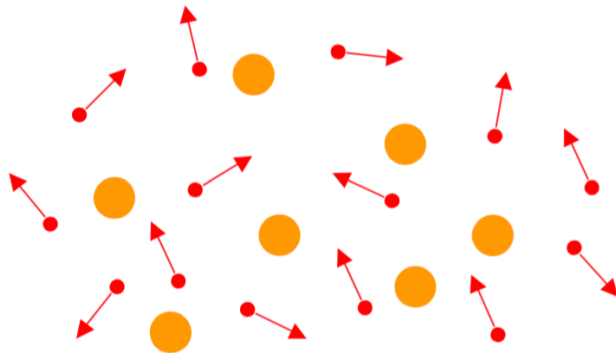
Ground state theory for the electronic problem

- 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

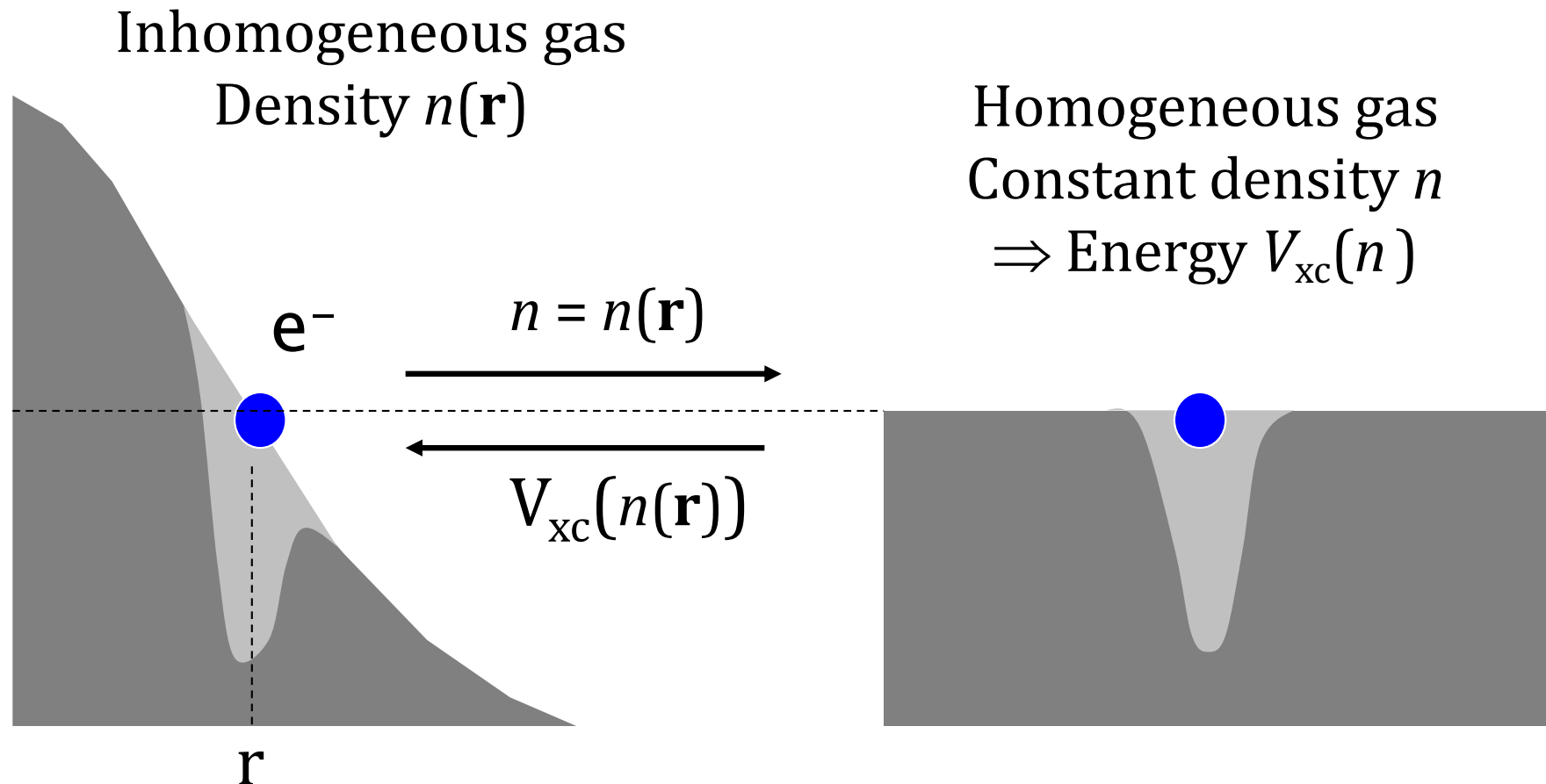
Non-interacting electrons in a self-consistent effective potential

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

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

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

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: $\{|e_\mu\rangle, \mu = 1 \dots \mathcal{N}\}$ $\phi_\mu(\mathbf{r}) = \langle \mathbf{r} | e_\mu \rangle$

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

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

$$\begin{aligned} n(\mathbf{r}) &= \sum_n^{\text{occ}} |\psi_n(\mathbf{r})|^2 = \sum_n^{\text{occ}} \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}) = \sum_n^{\text{occ}} \sum_{\mu, \nu} C_{\mu n} \phi_\mu(\mathbf{r}) C_{\nu n}^* \phi_\nu^*(\mathbf{r}) \\ &= \sum_{\mu, \nu} \rho_{\mu\nu} \phi_\mu(\mathbf{r}) \phi_\nu^*(\mathbf{r}) \quad \text{where} \quad \rho_{\mu\nu} \equiv \sum_n^{\text{occ}} C_{\mu n} C_{\nu n}^* \end{aligned}$$

Basis set – LCAO – atomic orbitals

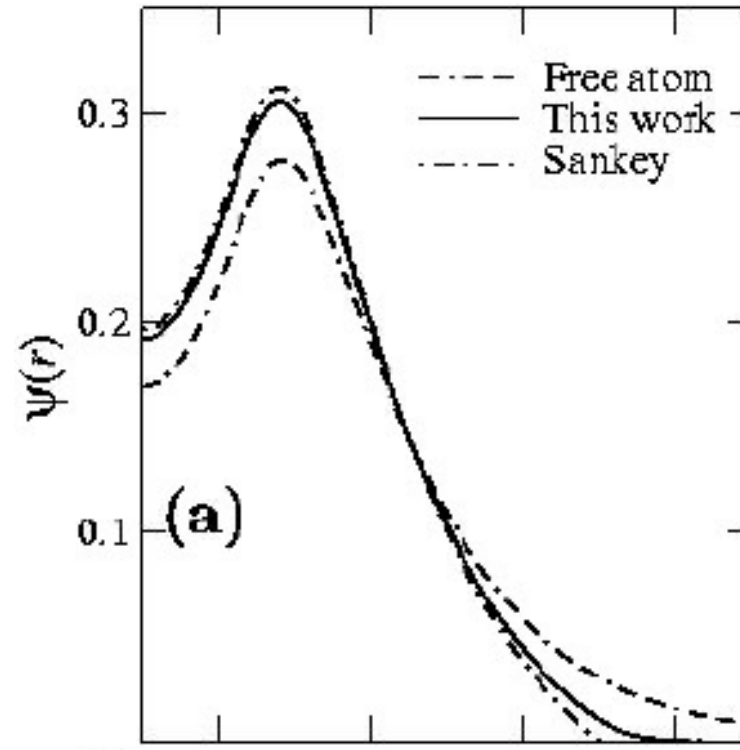
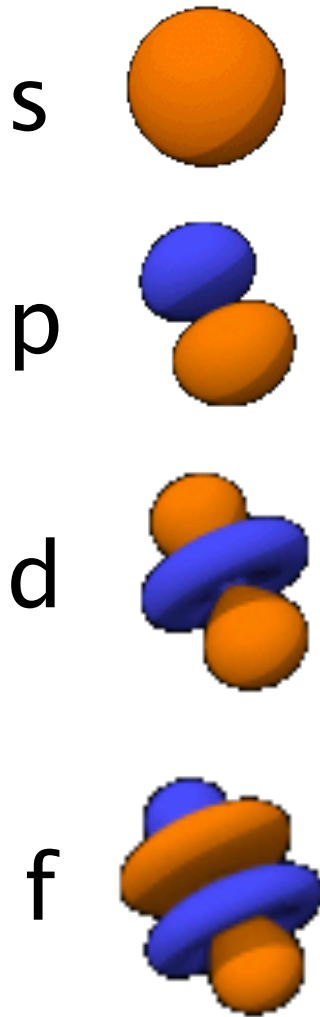
Numerical (pseudo)atomic orbitals (PAOs)
& real spherical harmonics

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

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

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

Atomic orbitals as basis



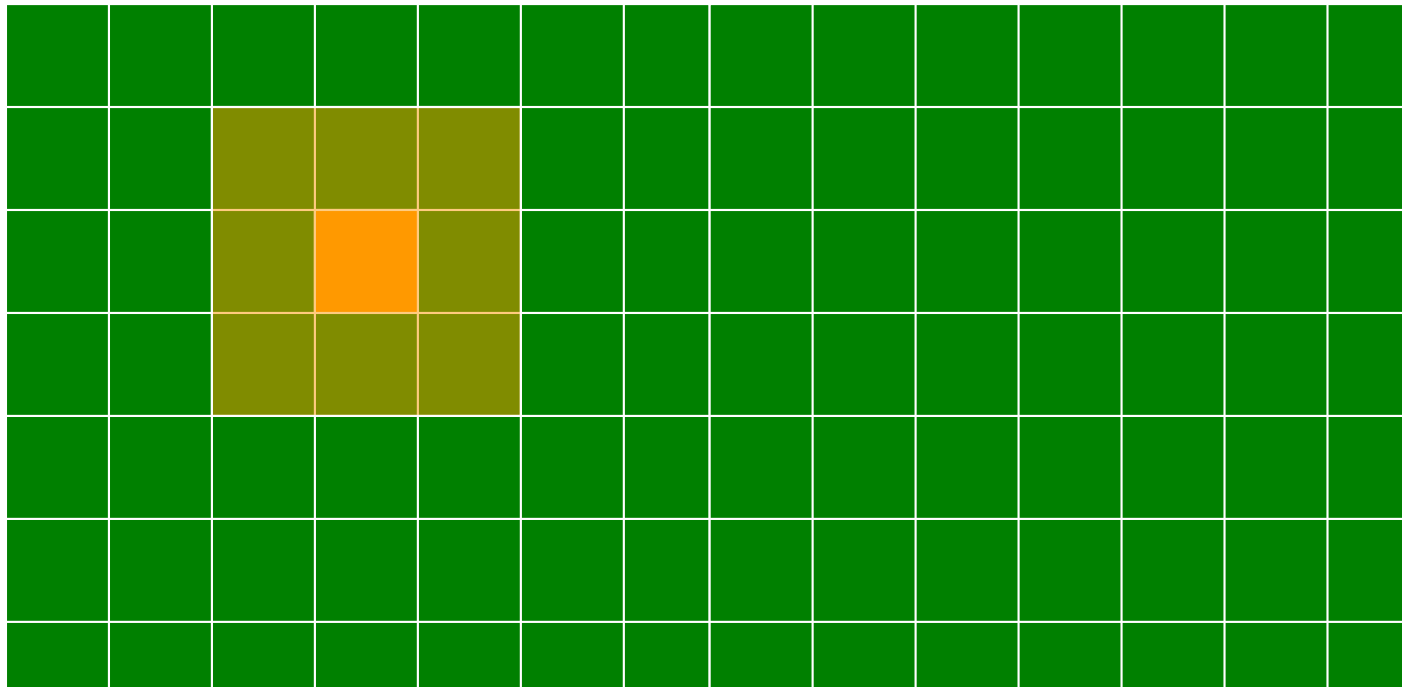
Radial functions

← Angular functions

Linear Scaling

KEY: LOCALITY

Large system

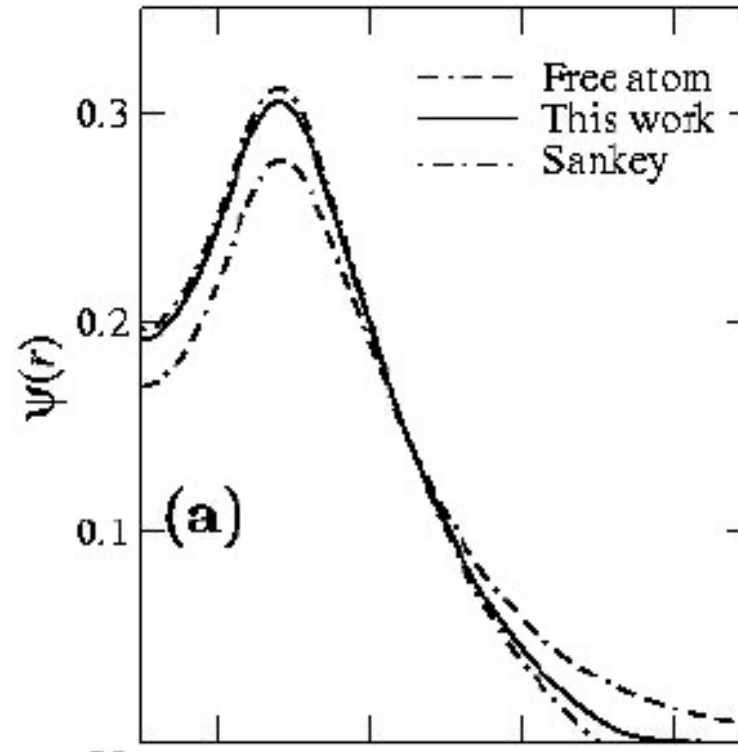


x 2

“Divide and Conquer”

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

Finite-support atomic orbitals



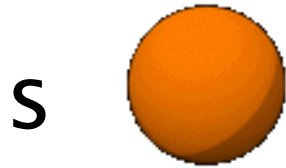
Strictly localised

(zero beyond cut-off radius)

Hard vs smooth confinement

Finite-support atomic orbitals as basis

Only 2 conditions

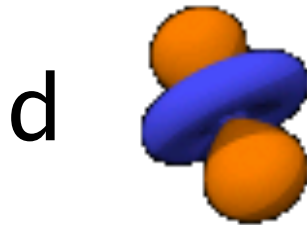


1. $\phi_{\zeta lm}(r, \theta, \varphi) = R_{\zeta}(r)Y_{lm}(\theta, \varphi)$

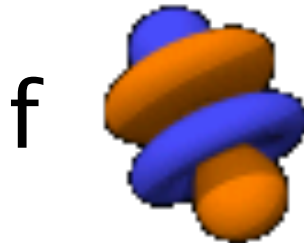


2. Finite range

User decides



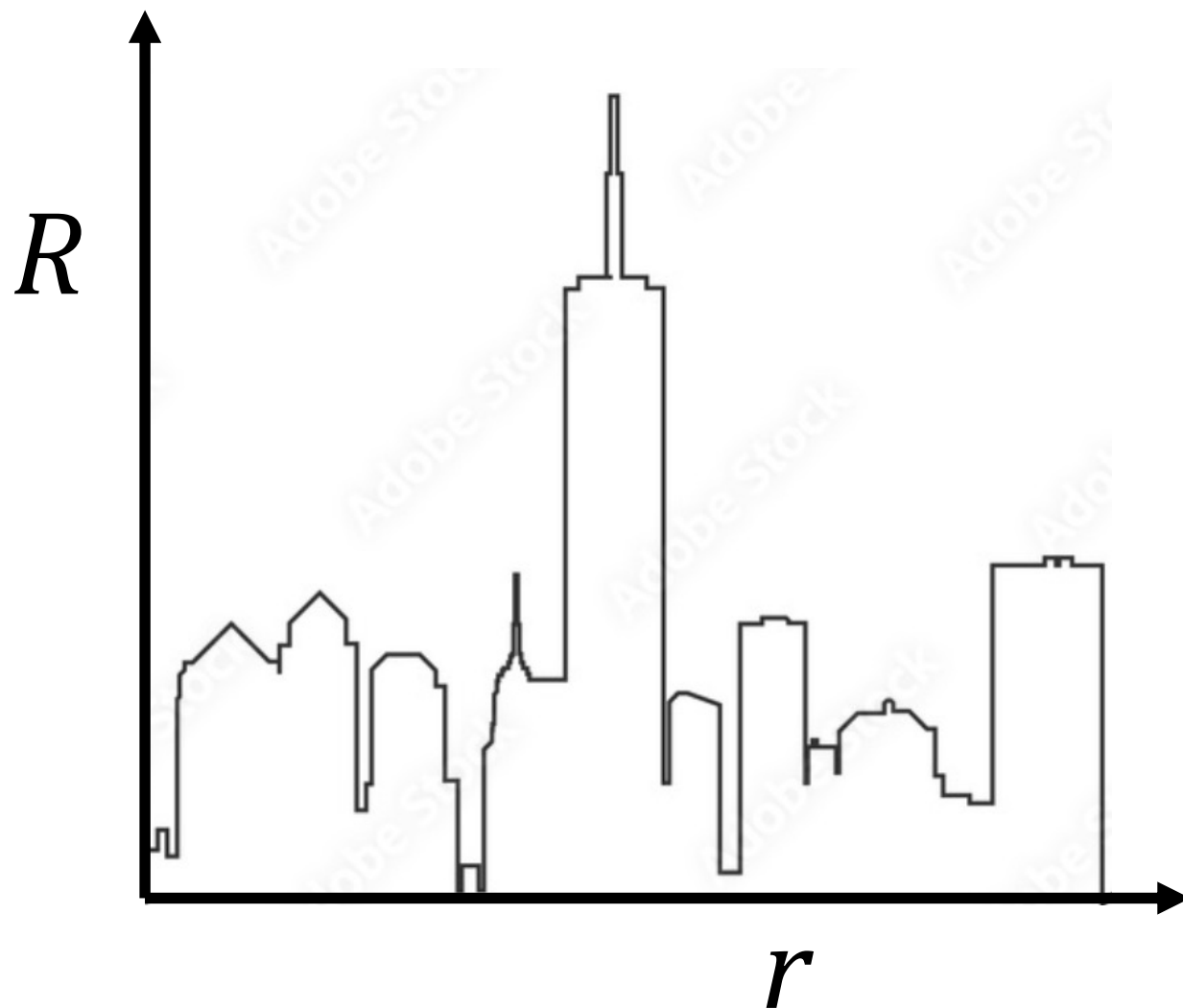
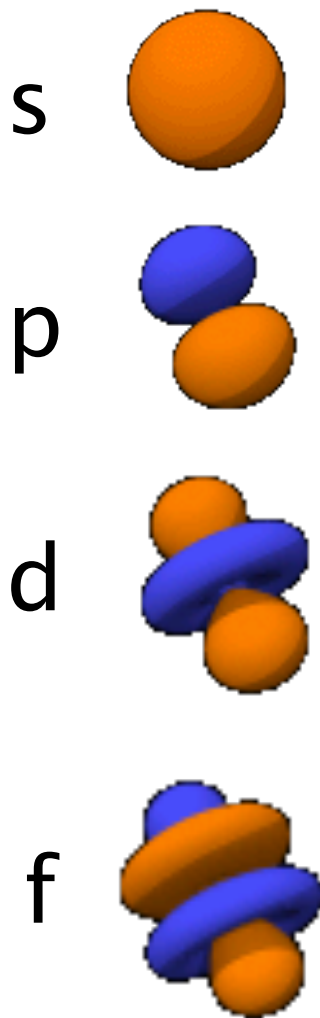
- How many centres
- Where to put them (on atoms or not)



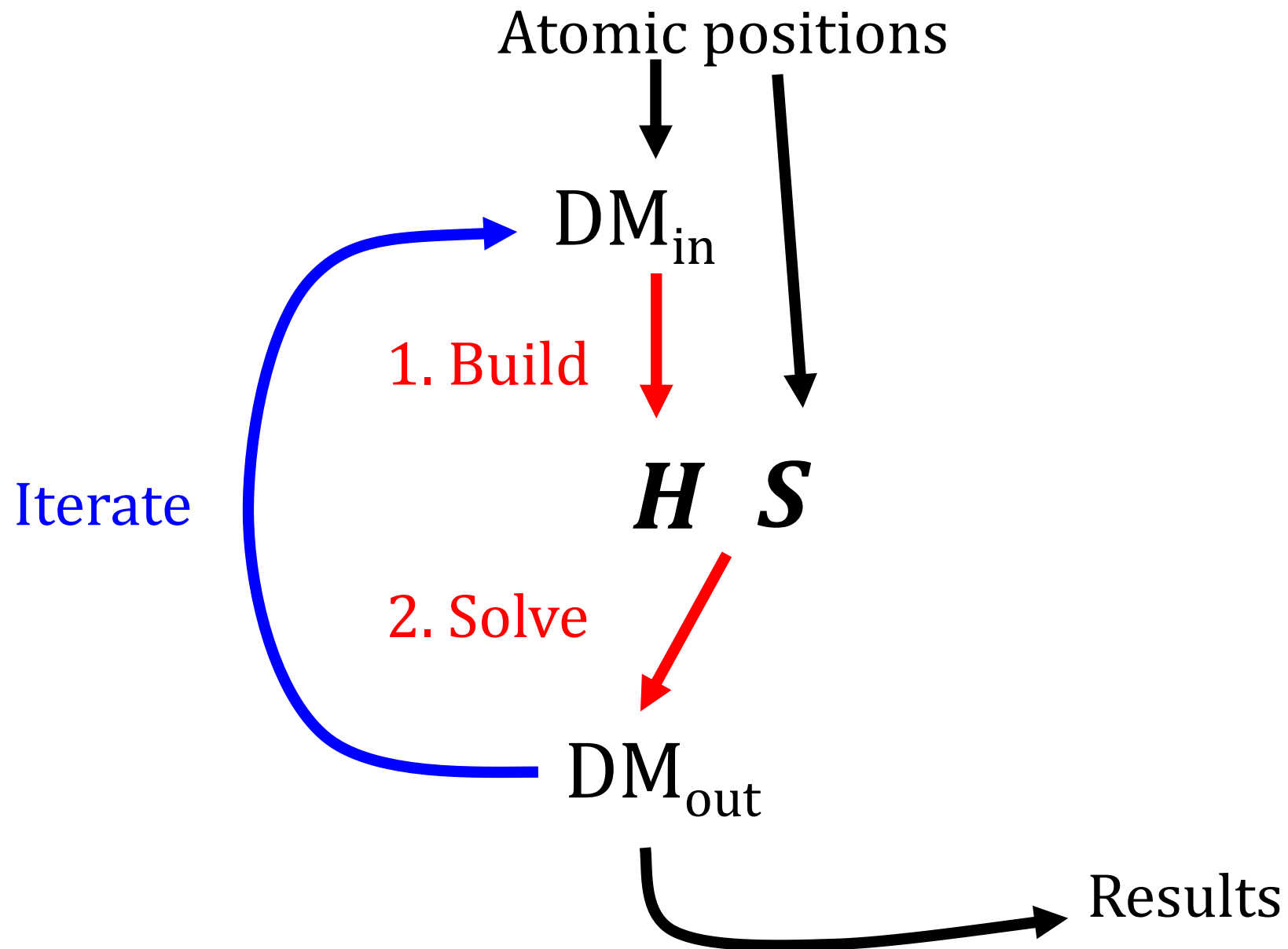
- How many angular momenta
- How many for each angular momentum
- Each radial shape

Finite-support atomic orbitals as basis

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



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

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

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

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


Two-center
integrals


Grid integrals

1. Building (a)

Two-center integrals

Convolution theorem

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

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

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

In addition to overlap:

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

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

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

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

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

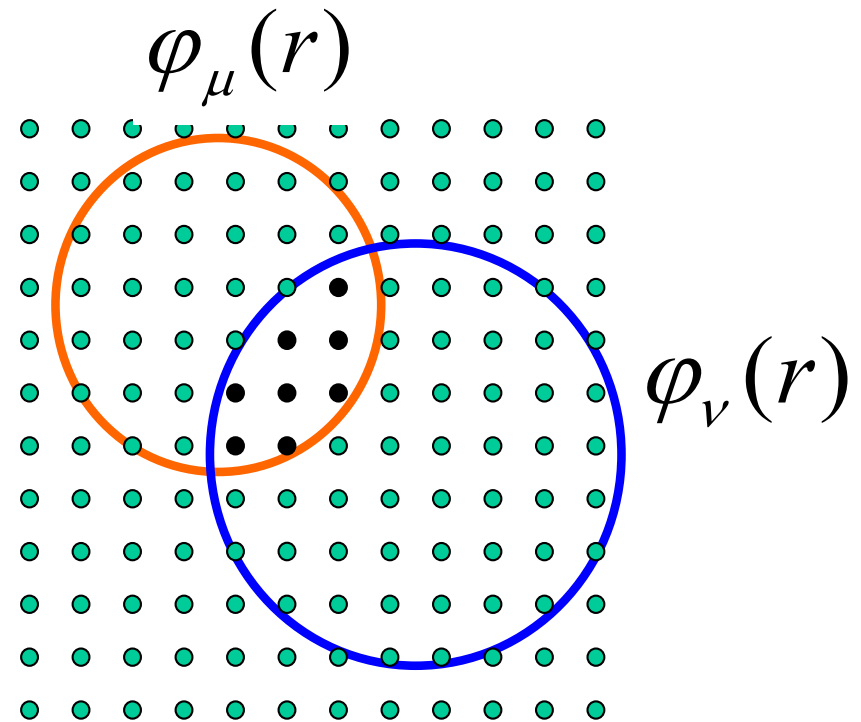
$$\rho_{\mu\nu} = \sum_i c_{i\mu} c_{i\nu}$$

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

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

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

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



Poisson equation

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

$$\rho(\mathbf{r}) = \sum_G \rho_G e^{i\mathbf{G}\cdot\mathbf{r}} \Rightarrow V_H(\mathbf{r}) = \sum_G V_G e^{i\mathbf{G}\cdot\mathbf{r}}$$

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

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

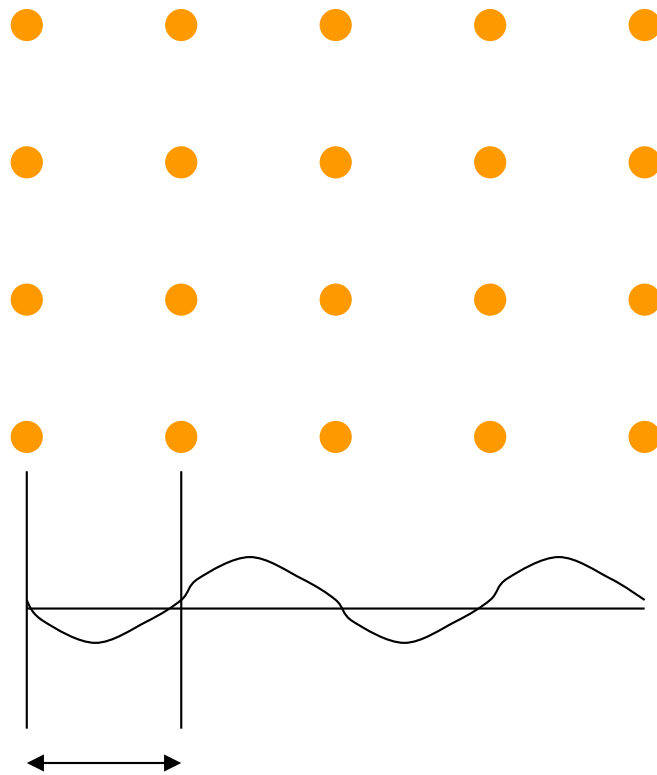
- SIESTA (normally) uses periodic boundary conditions
- Net charge compensated by uniform background
- Spurious interactions between ‘images’

GGA

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

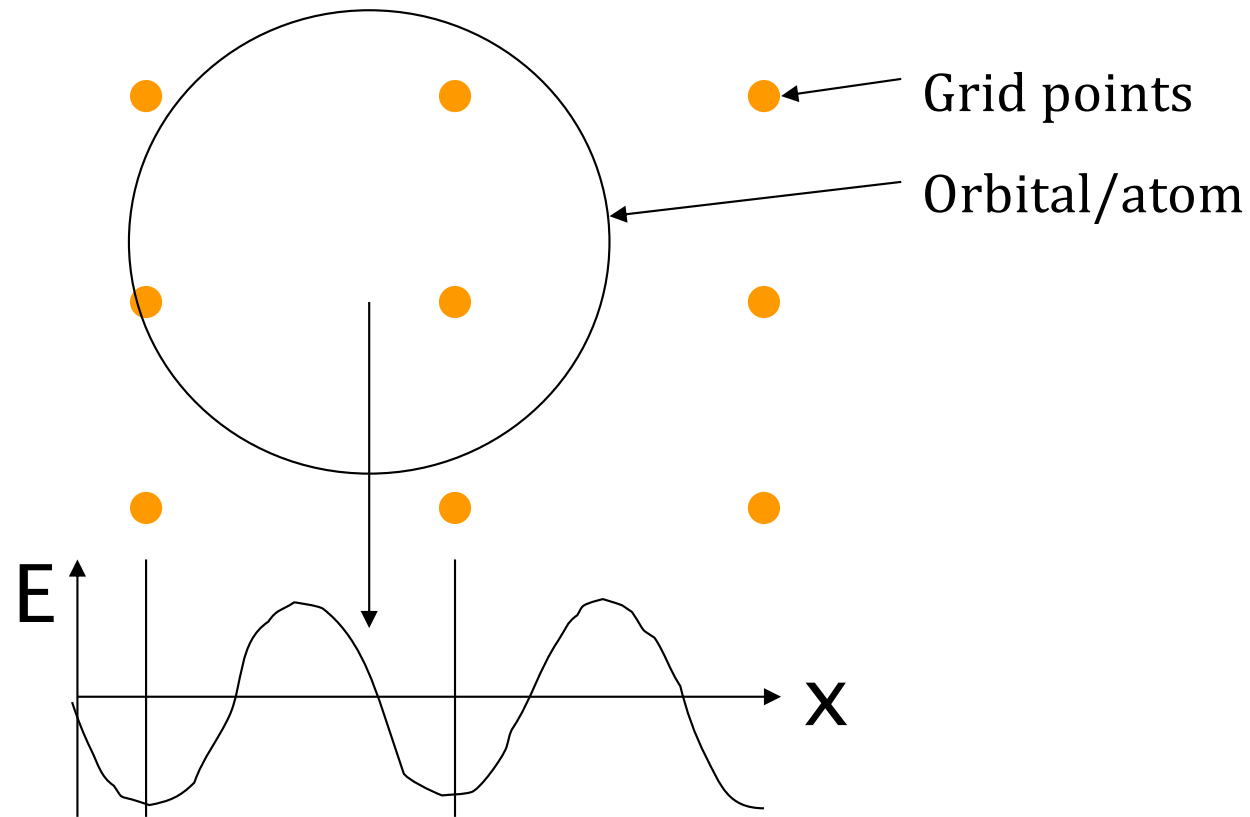
$$\begin{aligned} \frac{\partial \rho}{\partial x} &\equiv \frac{\rho_{i+1} - \rho_{i-1}}{x_{i+1} - x_{i-1}} \quad \Rightarrow \quad E_{xc} \equiv E_{GGA}(\rho_1, \rho_2, \dots) \\ &\Rightarrow v_{xc}(r_i) \equiv \frac{\partial E_{xc}}{\partial \rho_i} \end{aligned}$$

Grid fineness: 'mesh cutoff'



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

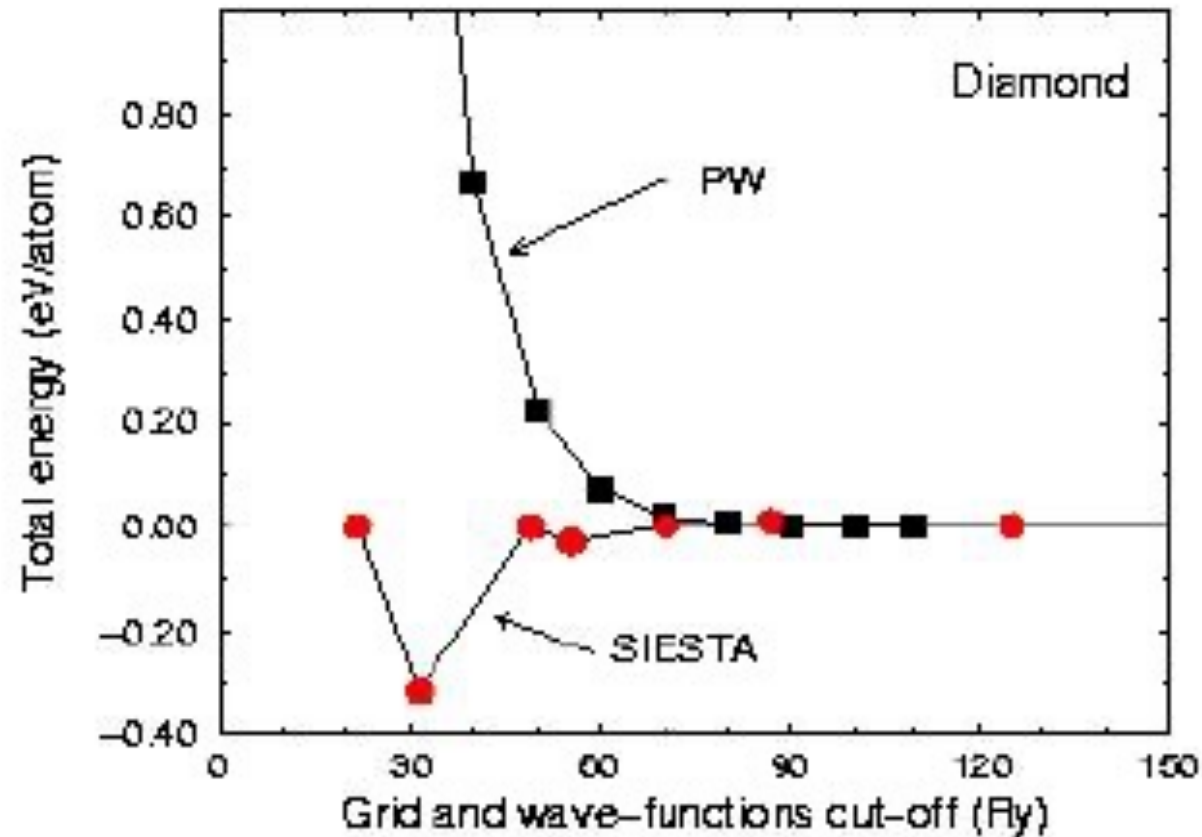
Egg-box effect



Higher effects on forces than on energy

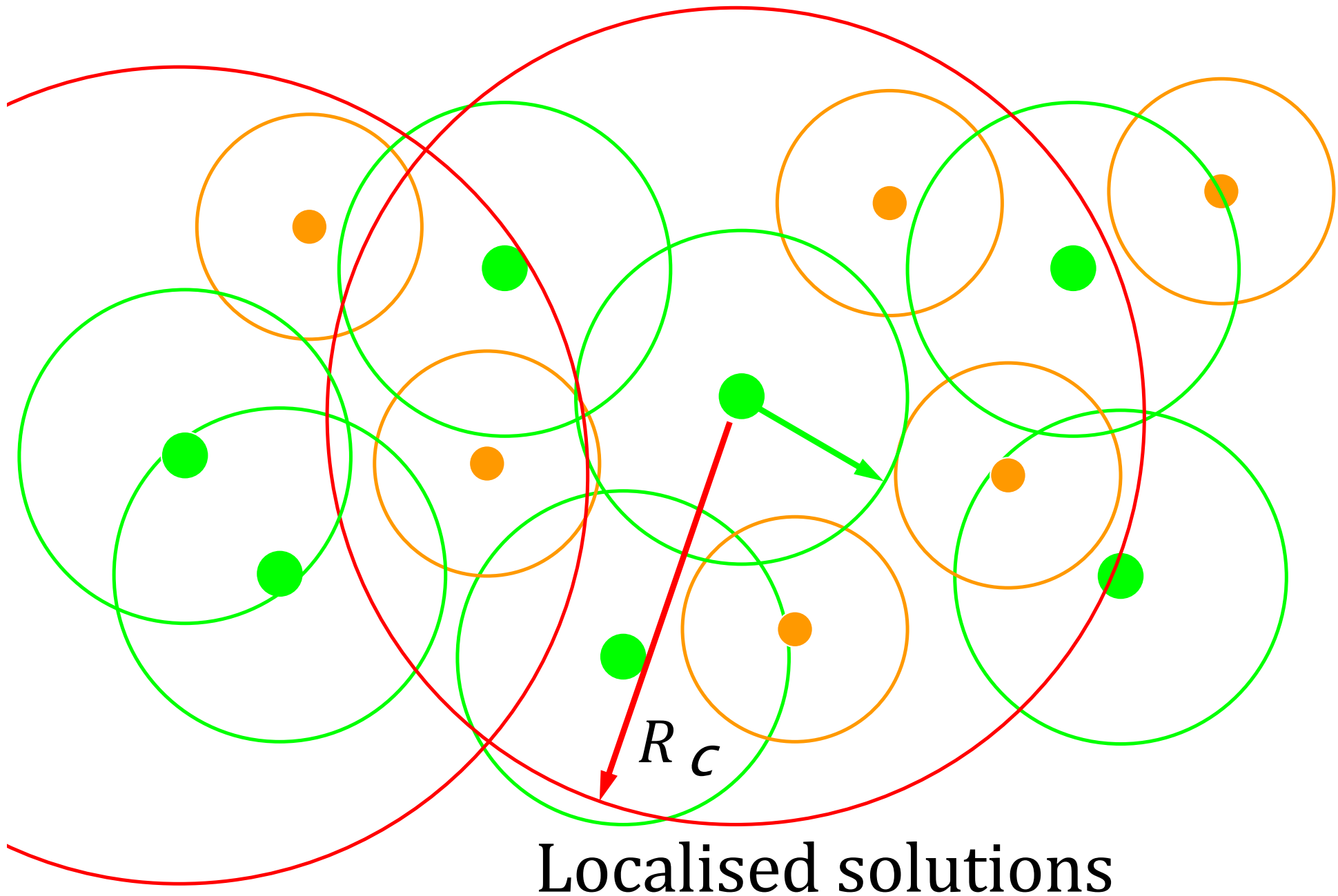
Grid-cell sampling

Grid fineness convergence



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

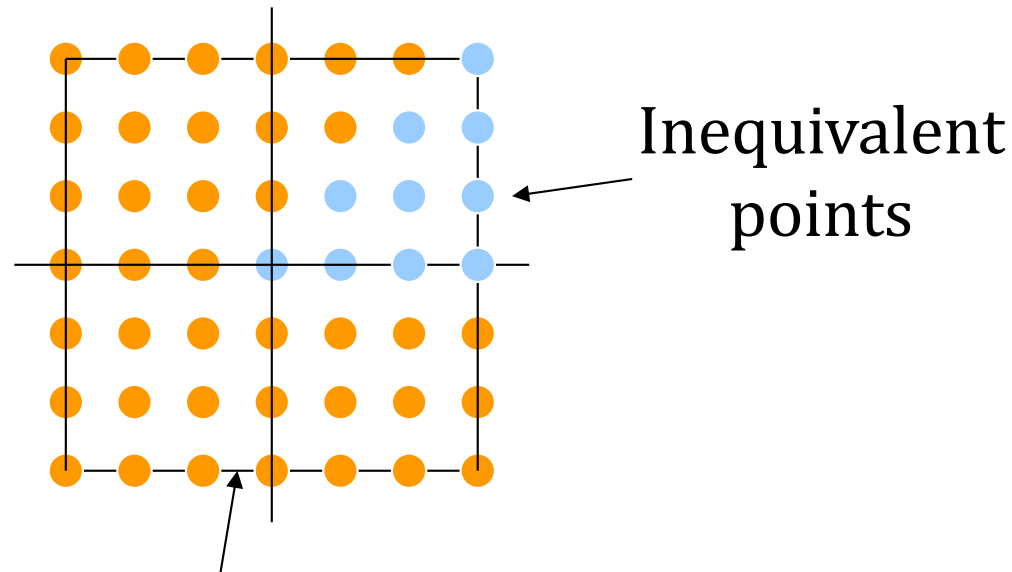
2. Solving: Linear scaling



k -point sampling

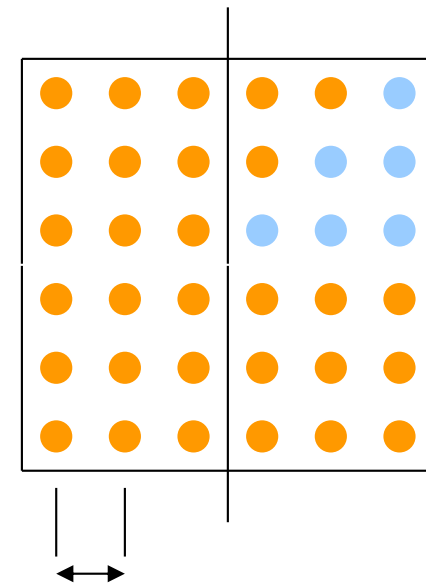
(fineness of grid in k -space)

Regular k-grid



First Brillouin Zone

Monkhorst-Pack



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

L_c = 'length cutoff'

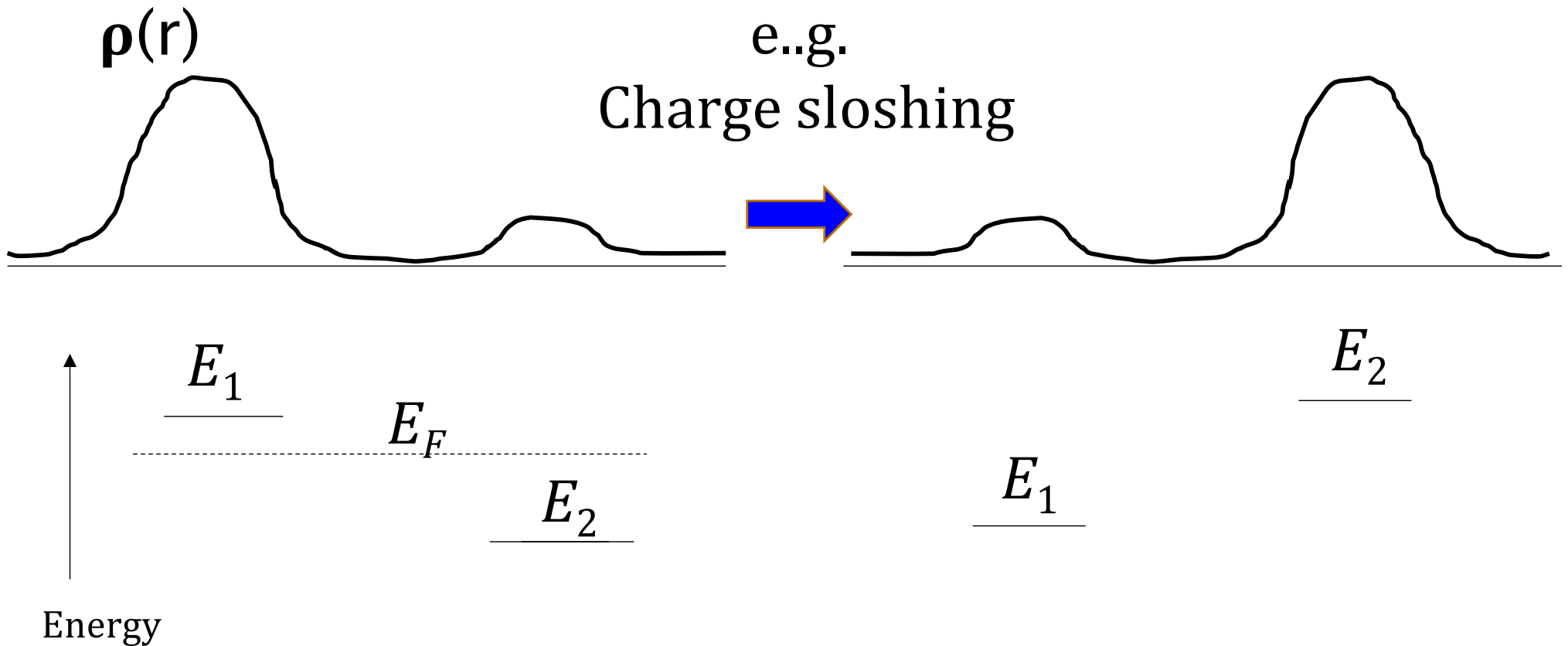
Selfconsistency convergence

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

Can be unstable

e.g.

Charge sloshing



Moderated by electronic temperature

Pulay mixing

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

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

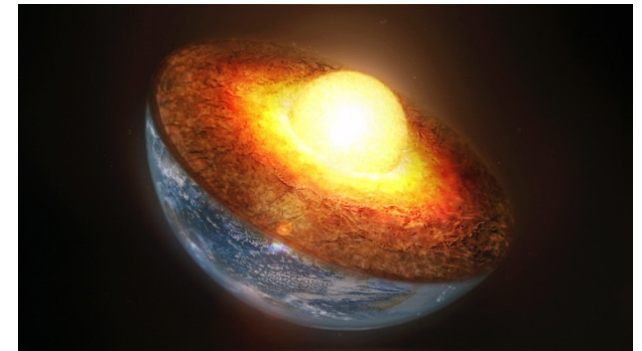
$$\rho_{n+1}(\mathbf{r}) = \sum_{k=n-m}^n c_k \rho_k(\mathbf{r})$$

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

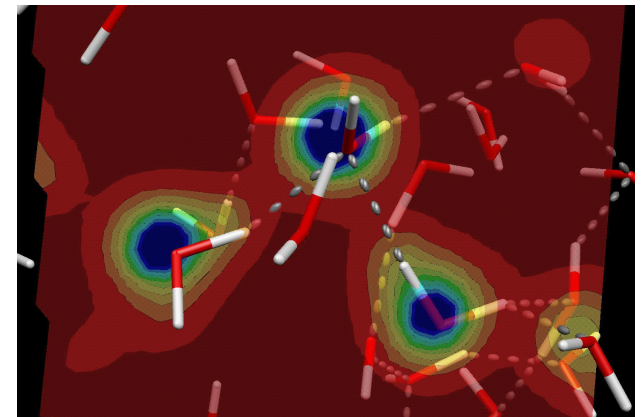
The physics of low-energy matter

Behind properties and processes in

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



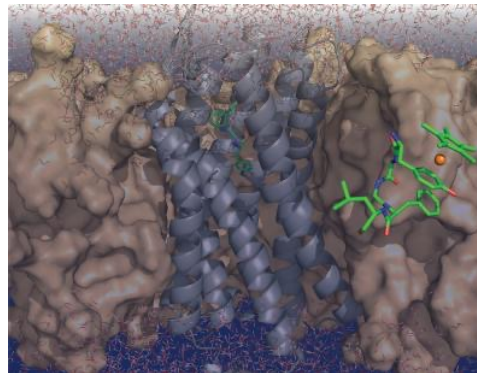
Earth's interior © ASX Canada



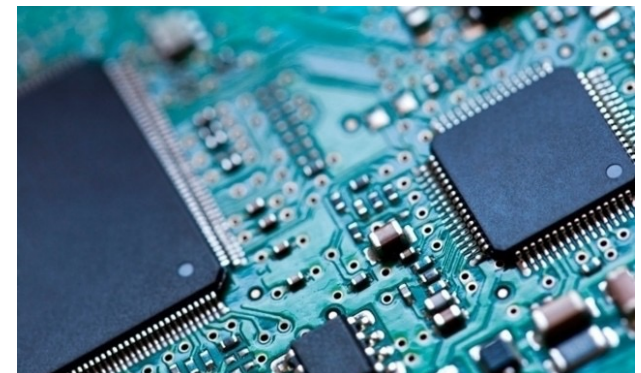
Liquid water © MV Fernandez-Serra



Exoplanets © NASAJPL Caltech, FINESSE Project



Pain receptors in the brain © Univ Bochum



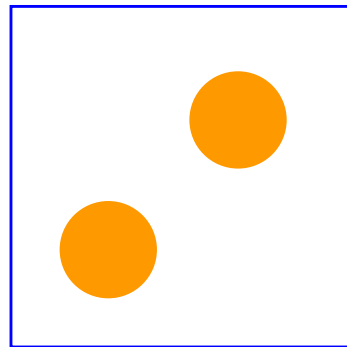
© Getty Images

Thank you

'Molecular' vs 'solid' pressure

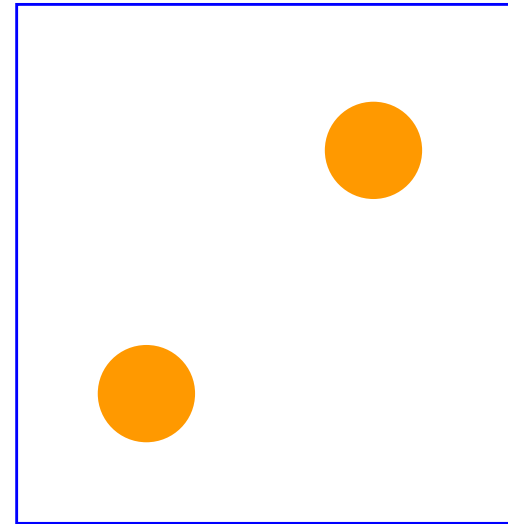
$$T_{ij} = +dE/d\epsilon_{ij}$$

$$P = -dE/dV$$

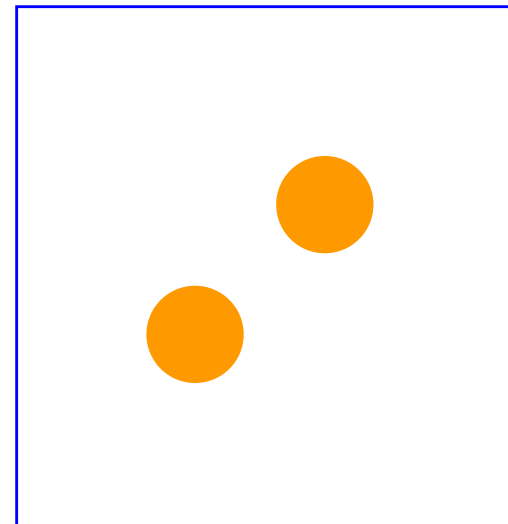


Unit cell

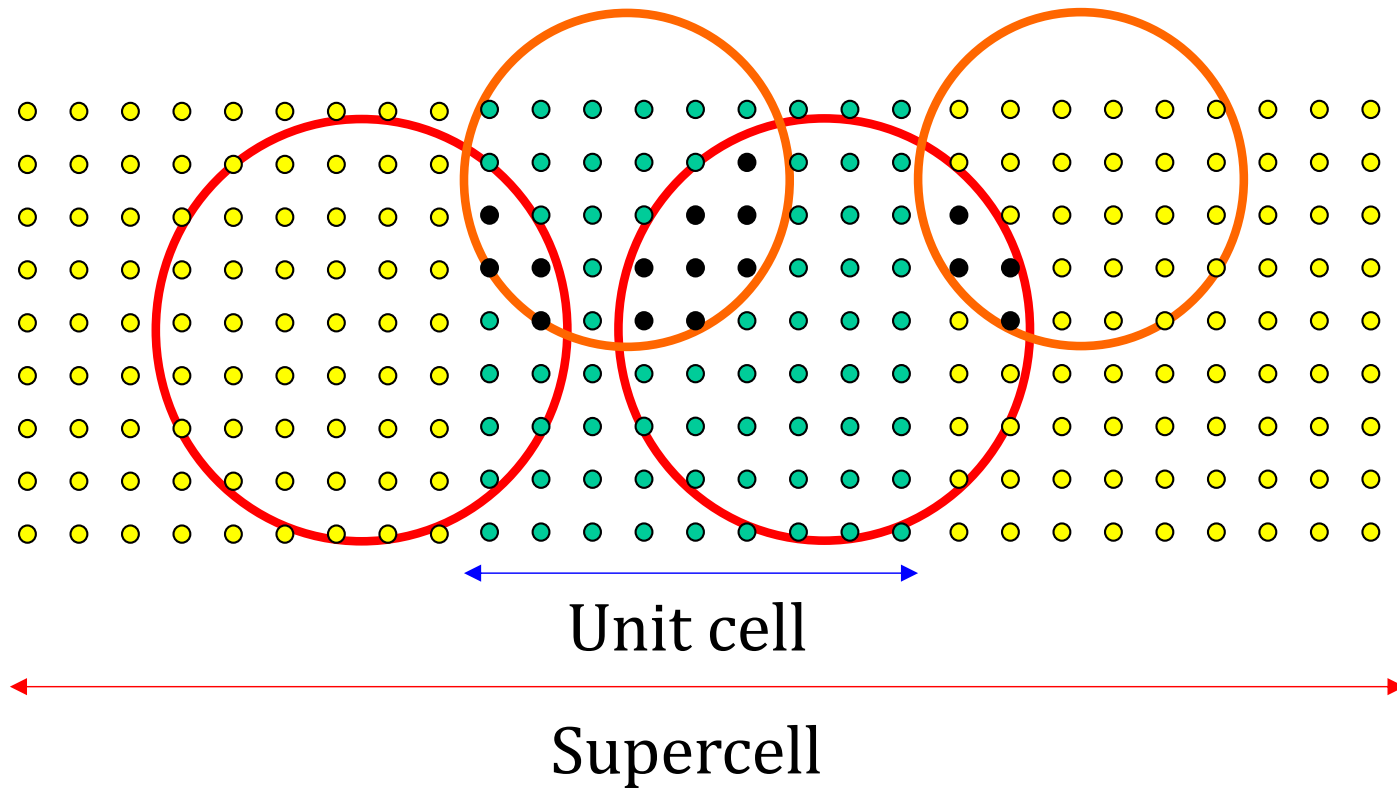
solid



molecule

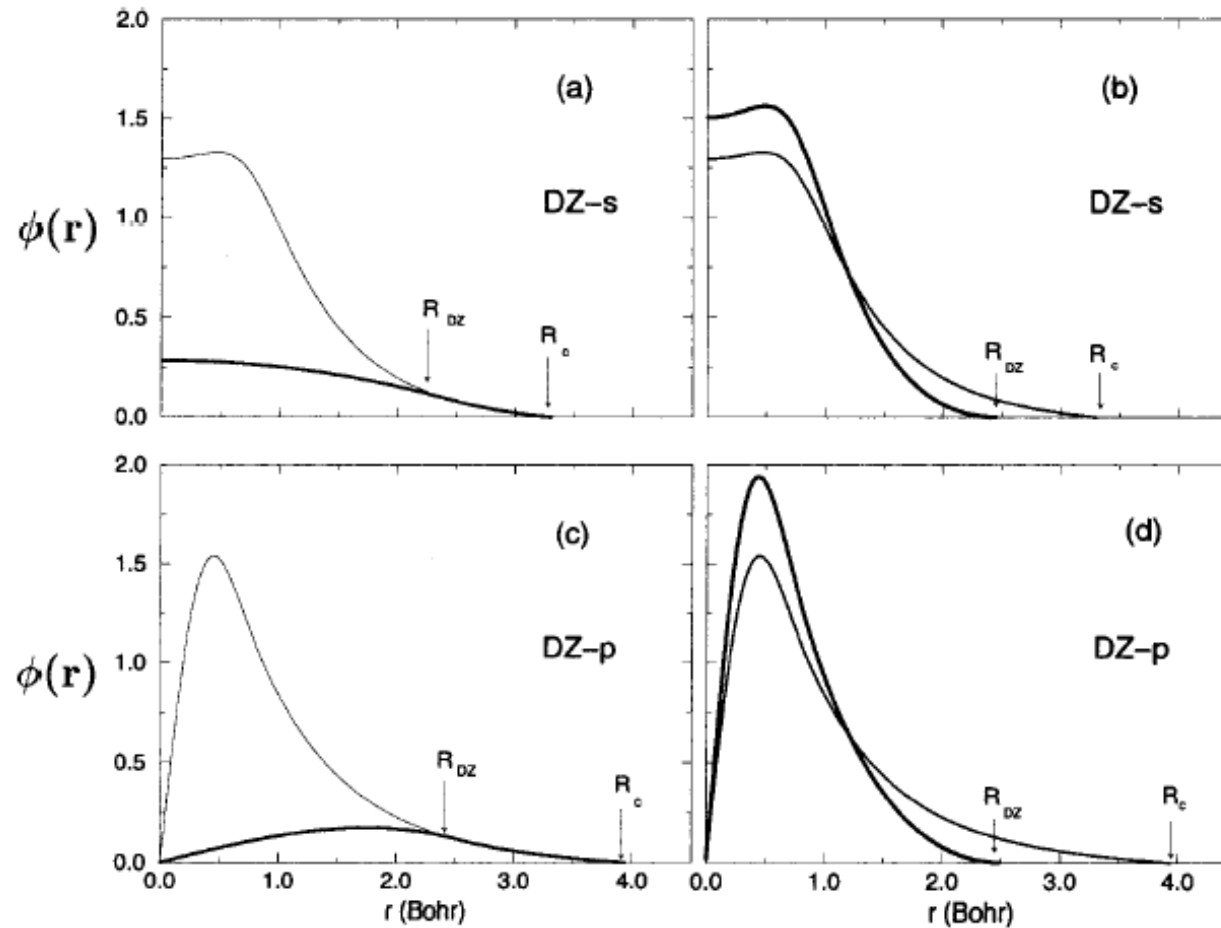


Internal supercell



Finite-range basis orbitals – Multiple zeta

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



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

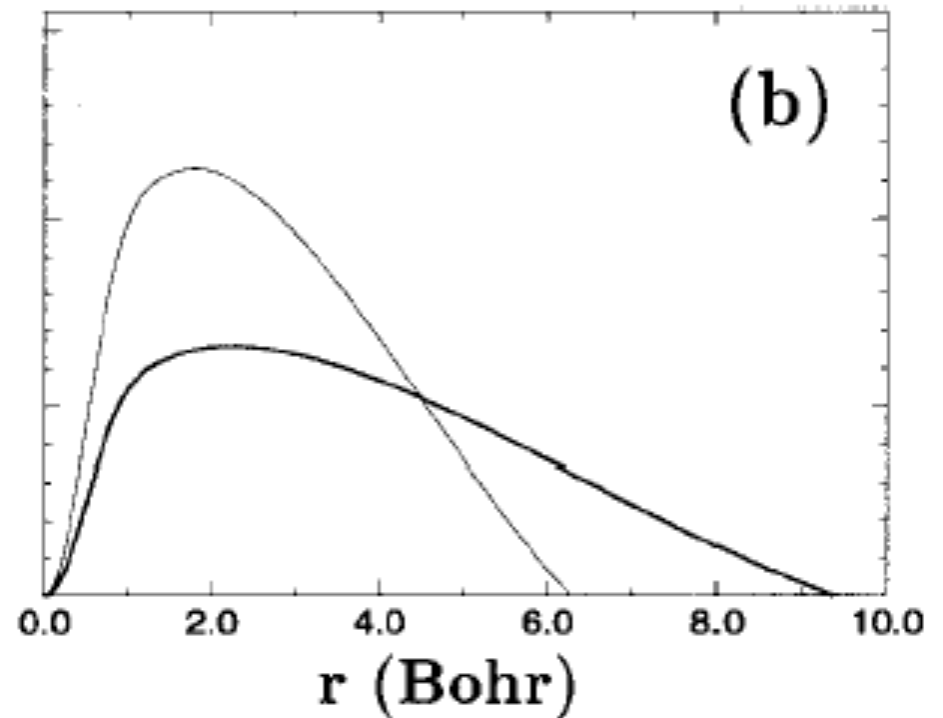
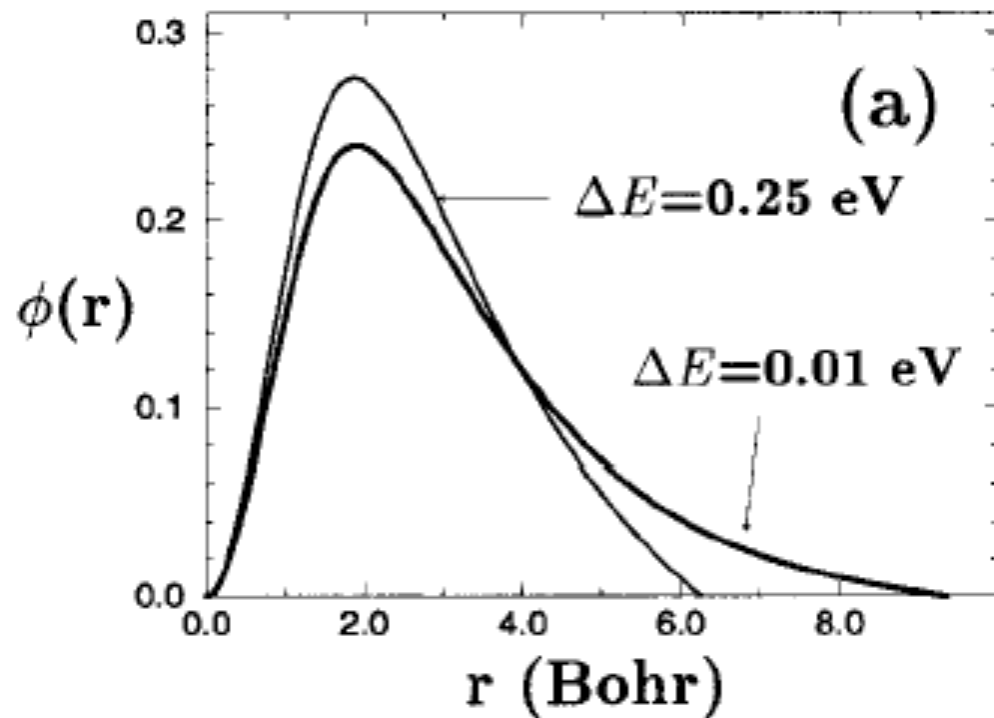
E. Artacho et al, *Phys. Stat. Sol (b)* **215**, 809 (1999)

Polarization orbitals

3d 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 momentum quantum number

m = Magnetic quantum number of (real) orbital:

$m < 0 \Rightarrow \sin(m \cdot \phi)$, $m \geq 0 \Rightarrow \cos(m \cdot \phi)$

z = Zeta index of orbital

p = Is this a polarization orbital? (False|True)

sym = Symmetry name of real orbital

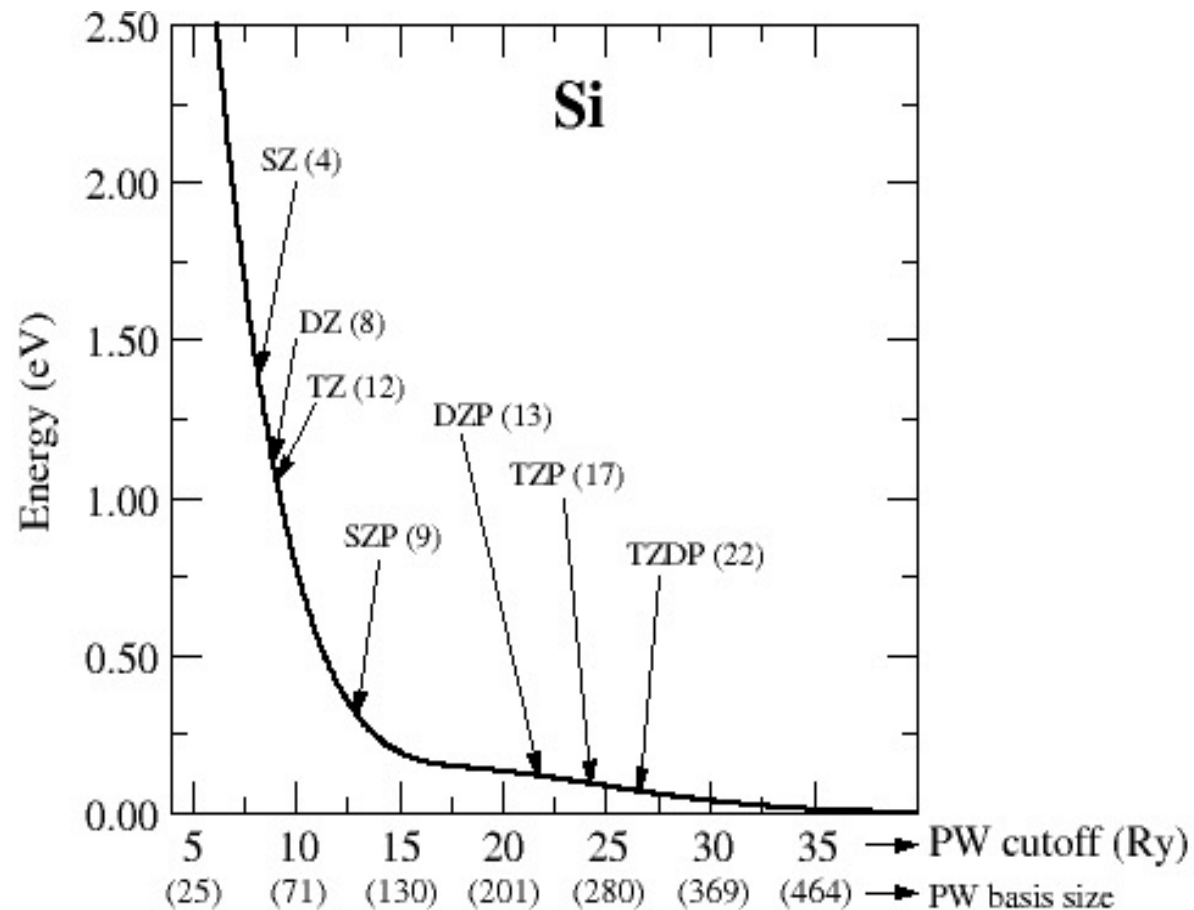
rc = Cutoff radius of orbital (Bohr)

isc = Unit cell indexes to which orbital belongs:

$\text{center}(\text{io}) = \text{center}(\text{iuo}) + \sum_{i=1:3} \text{cell_vec}(i) * \text{isc}(i)$

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