FIRESIDE CHATS FOR LOCKDOWN TIMES
Density-functional practice (Part 2)

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OUTLINE

- What is density-functional theory? (Part I)
- What does it take to perform these calculations? (Part II)
- Why is it relevant for science and technology? (Part III)
- What can it do? and cannot do? (Part III)

(to keep in touch, info in the Learn section of the Materials Cloud website, and https://bit.ly/3eqighg)

References

Online resources

- The open-access class (videos, slides, readings) on simulations that Gerd Ceder and myself ran at MIT for 10 years: http://ocw.mit.edu/3-320S05
- The Learn section of the Materials Cloud: https://www.materialscloud.org/learn

Quantum mechanics

- B.H. Bransden and C.J. Joachain, *Physics of Atoms and Molecules,* Pearson (2003)
- B.H. Bransden and C.J. Joachain, *Quantum Mechanics,* Pearson (2000)

Density-functional theory and advanced electronic-structure methods

- R.G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules,* Oxford University Press (1989)
- Richard M. Martin, *Electronic Structure: Basic Theory and Practical Methods,* Cambridge University Press (2004)
- Richard M. Martin, Lucia Reining, David M. Ceperley, *Interacting Electrons: Theory and Computational Approaches,* Cambridge University Press (2016)

Materials simulations

- Efthimios Kaxiras, *Atomic and Electronic Structure of Solids,* Cambridge University Press (2003)
- Jorge Kohanoff, *Electronic Structure Calculations for Solids and Molecules,* Cambridge University Press (2006)
- Feliciano Giustino, *Materials Modelling Using Density-Functional Theory,* Oxford University Press (2014)

Kohn-Sham energy functional

- Kohn-Sham mapping into non-interacting electrons allows to define a non-interacting kinetic energy T_s
- Unknown functional: known T_s + known Hartree + unknown E_{xc}

$$E[\{\psi_i\}] = \sum_{i=1}^{N} -\frac{1}{2}\int \psi_i^{\star}(\mathbf{r})\nabla^2\psi_i(\mathbf{r})\ d\mathbf{r} + E_H[n(\mathbf{r})] +$$

$$+E_{xc}[n(\mathbf{r})] + \int v_{ext}(\mathbf{r})n(\mathbf{r})\ d\mathbf{r}$$

The Kohn-Sham equations

- Euler-Lagrange equations (i.e. Kohn-Sham)

$$\left[-\frac{1}{2}\nabla^2 + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) + v_{ext}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \hat{H}_{KS}\ \psi_i(\mathbf{r}) = \epsilon_i\ \psi_i(\mathbf{r})$$

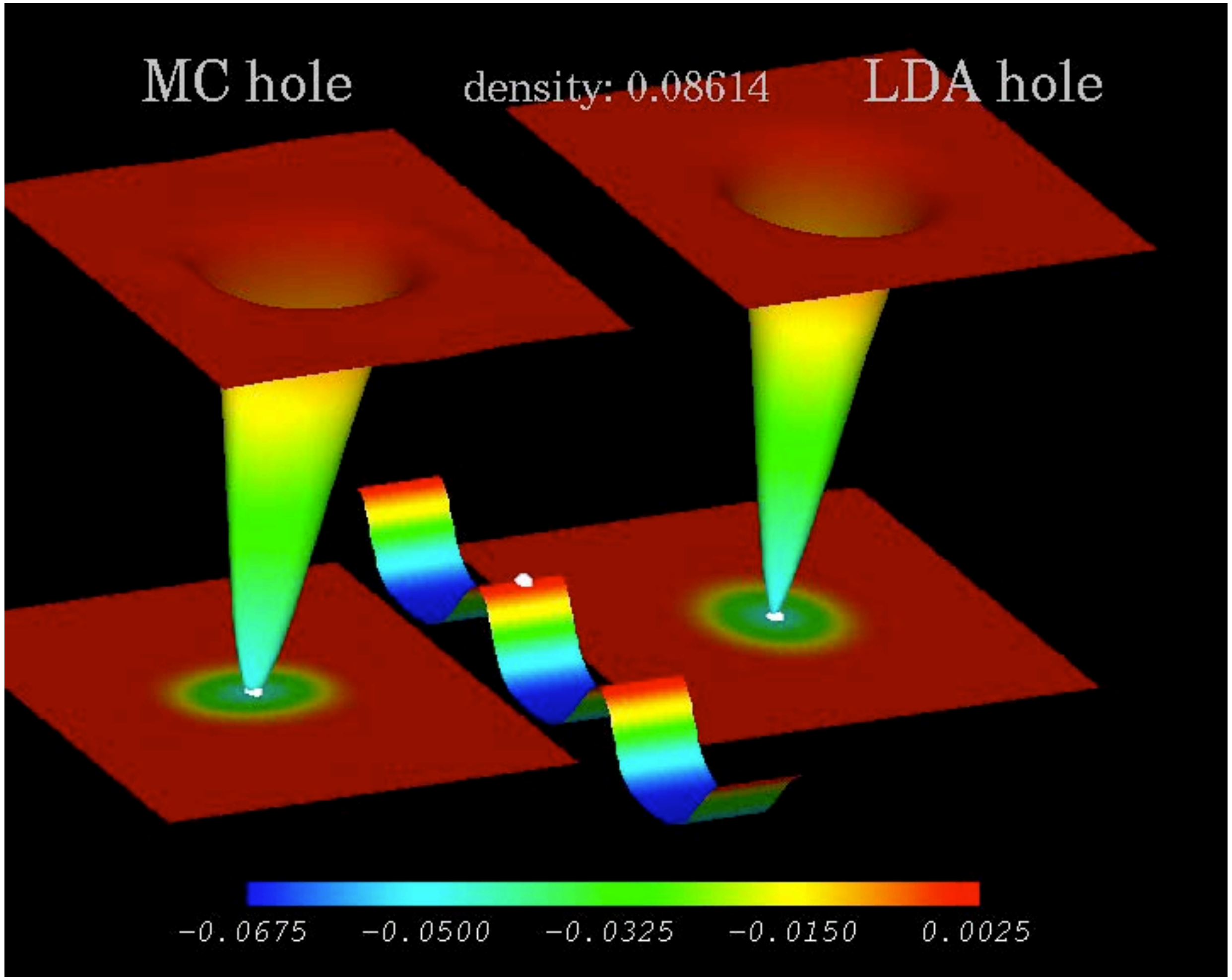
$$v_H(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}', \qquad v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})}$$

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2.$$

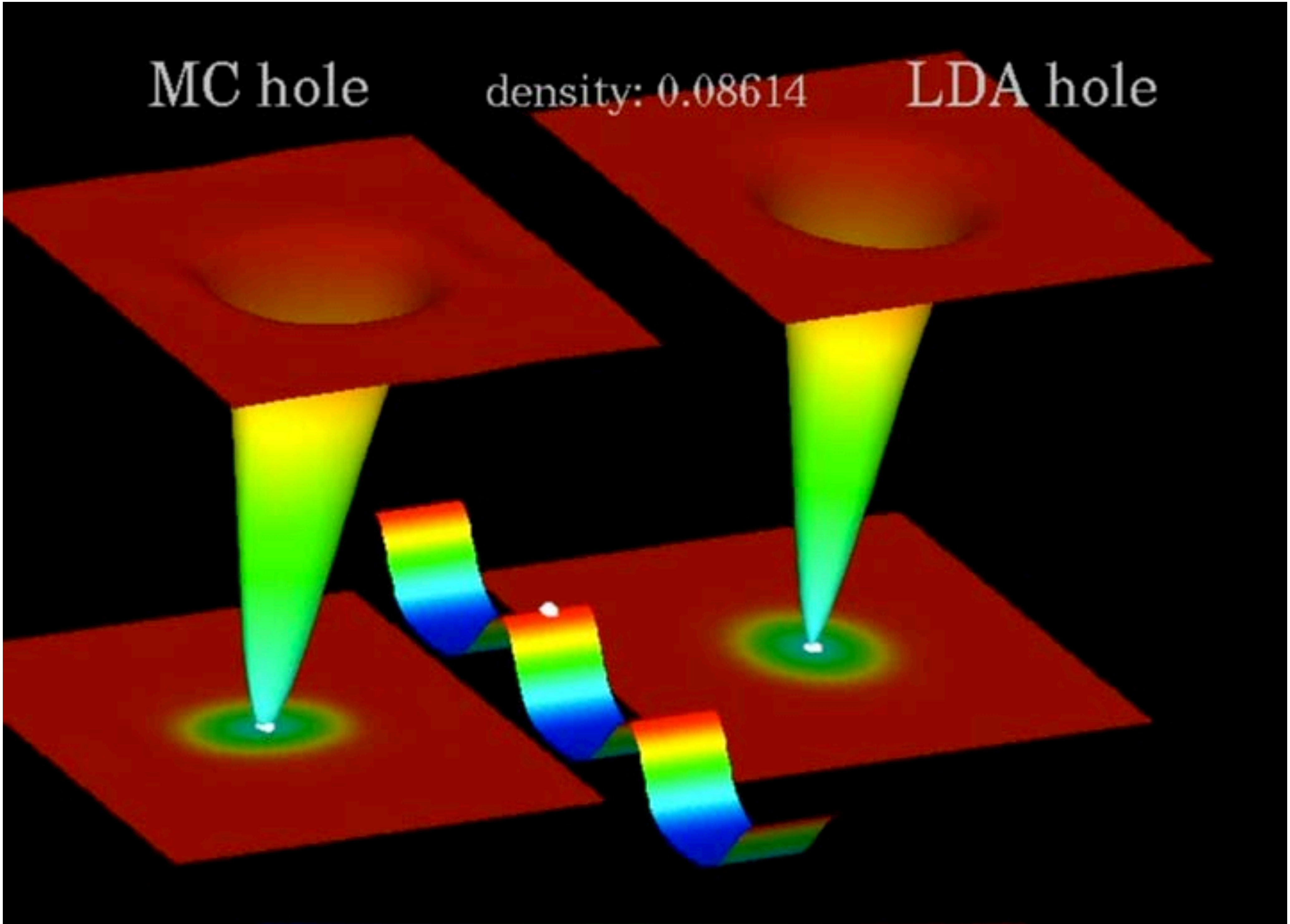
- LDA for the last unknown piece

XC hole in a model insulator

$$\int n_{xc}^{LDA}(\mathbf{r},\mathbf{r}'-\mathbf{r}) = \int n_{xc}(\mathbf{r},\mathbf{r}'-\mathbf{r})d\mathbf{r}' = -1,$$



Courtesy of RJ Needs 2001


MC hole
density: 0.08614
LDA hole

Spherical average saves LDA!

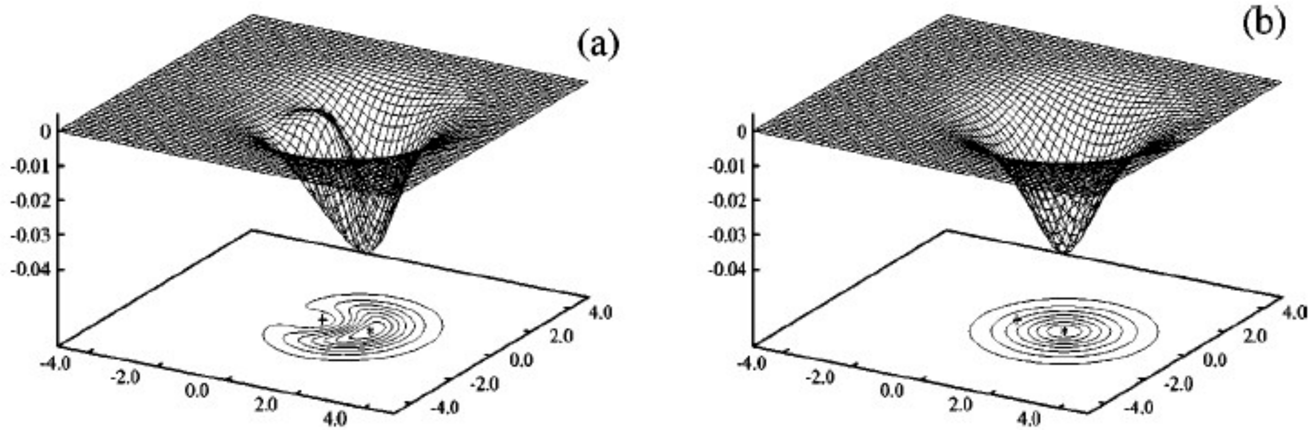


FIG. 3. (a) The Monte Carlo exchange-correlation hole with the fixed electron set at the charge density maximum (0,1.36), marked by a star, and the ion set at the origin, marked by a cross. All quantities are in atomic units. (b) The same quantity spherically averaged. Each contour line represents a change of 0.005 starting at -0.035 and going to -0.005. Each graph shows one plane in position space.

W. M. C. Foulkes, L. Mitas, R. J. Needs, and G. Rajagopal, Rev. Mod. Phys. 73, 33 (2001)
A. Puzder, M. Y. Chou, and R. Q. Hood, Phys. Rev. A 64, 022501 (2001)

LDA across materials space

Material	Expt	Theory	Delta	Type
LaBi	6.57	6.648	1.2%	alloy
CaF_2	5.4626	5.496	0.6%	halide
Ag	4.086	4.112	0.6%	metal
V	3.028	3.019	-0.3%	metal
ZrN	4.62	4.634	0.3%	misc
NbO	4.2103	4.2344	0.6%	oxide
GaAs	5.653	5.663	0.2%	semiconductor
$CoSi_2$	5.36	5.3	-1.1%	silicide

C. J. Pickard 2002

Well, not always…

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Generalized Gradient Theory for Silica Phase Transitions

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(Received 16 October 1995)

Density functional theory based on the generalized gradient approximation to the exchange and correlation energy is shown to correct a qualitative error of the local density approximation in describing a high-pressure phase transition of SiO_2. Advantages of an adaptive curvilinear coordinate method for such generalized gradient calculations are discussed.

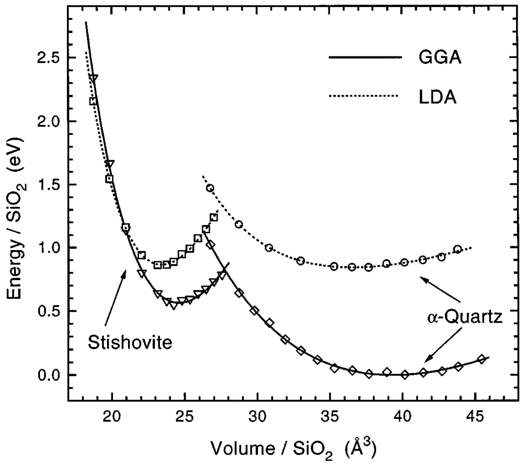


FIG. 3. Energy vs volume for GGA and LDA showing calculated points and fits by the Murnaghan equation of state [22].

TABLE I. Structural and elastic properties of α-quartz.

Parameter	Experiment	GGA	LDA
a (Å)	4.92[a]	4.97	4.84
c (Å)	5.41[a]	5.52	5.41
Si-O(1) (Å)	1.605[a]	1.622	1.611
Si-O(2) (Å)	1.614[a]	1.625	1.617
Si-O-Si (deg)	143.7[a]	145.5	140.2
B_0 (GPa)	38[a]	48	45
B_0'	6[a]	3.0	4.9

[a]Reference [25].

Summary on xc

- LDA (local density approximation)
- GGA (generalized gradient approximation): BP88, PW91, PBEsol, BLYP, …
- WDA (weighted density approximation – good, not much used)
- Meta-GGA: Laplacian (TPSS, SCAN)
- Hybrids (B3LYP, PBE0PBE, HSE): part of Fock exchange

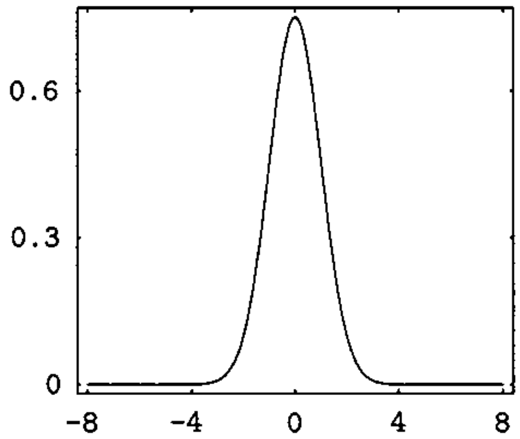
Back to the one-electron problem

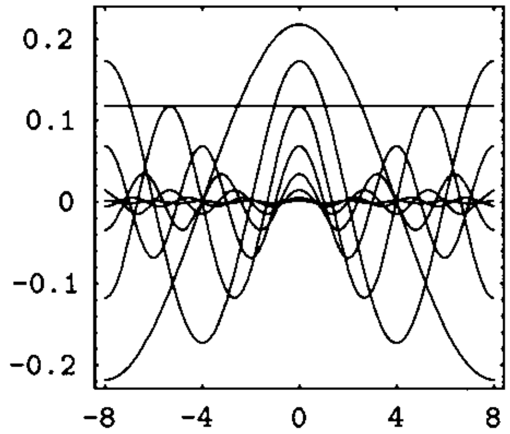
- How do we solve the set of one-particle differential equations that come from Hartree, Hartree-Fock, or density-functional theory ?

$$\left[-\frac{1}{2}\nabla^2+\sum_I V(\vec{R}_I-\vec{r})+\text{Mean Field Term}\right]\varphi(\vec{r})=\varepsilon\varphi(\vec{r})$$

Expansion in a basis

$$\psi(\vec{r}) = \sum_{n=1,k} c_n \varphi_n(\vec{r})$$





Differential eqs. as a linear algebra problem

$$\hat{H}\left|\psi\right\rangle = E\left|\psi\right\rangle$$

$$\left|\psi\right\rangle = \sum_{n=1,k} c_n \left|\varphi_n\right\rangle \qquad \left\{\left|\varphi_n\right\rangle\right\} \text{ orthogonal}$$

$$\left\langle\varphi_m\right|\hat{H}\left|\psi\right\rangle = E\left\langle\varphi_m\middle|\psi\right\rangle$$

$$\sum_{n=1,k} c_n \left\langle\varphi_m\right|\hat{H}\left|\varphi_n\right\rangle = E c_m$$

Differential eqs. as a linear algebra problem

$$\sum_{n=1,k} H_{mn} c_n = E c_m$$

$$\begin{pmatrix} H_{11} & \cdots\cdots & H_{1k} \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \cdot & & \cdot \\ H_{k1} & \cdots\cdots & H_{kk} \end{pmatrix} \cdot \begin{pmatrix} c_1 \\ \cdot \\ \cdot \\ \cdot \\ c_k \end{pmatrix} = E \begin{pmatrix} c_1 \\ \cdot \\ \cdot \\ \cdot \\ c_k \end{pmatrix}$$

Differential eqs. as a linear algebra problem

$$\det\begin{pmatrix} H_{11}-E & \ldots\ldots & & H_{1k} \\ . & H_{22}-E & & . \\ . & & & . \\ . & & & . \\ H_{k1} & \ldots\ldots & & H_{kk}-E \end{pmatrix}=0$$

Variational principle as a non-linear minimization

$$E[\{\psi_i\}] = \sum_{i=1}^{N} -\frac{1}{2}\int \psi_i^*(\vec{r})\,\nabla^2\psi_i(\vec{r})\,d\vec{r} + E_H[n(\vec{r})] +$$

$$+ E_{xc}[n(\vec{r})] + \int V_{ext}(\vec{r})\,n(\vec{r})\,d\vec{r}$$

$$E\left[\{\psi_i\}\right] = E\left[\sum_{n=1,k} c_n^i \varphi_n(\vec{r})\right] = E(c_1, c_2, \cdots, c_k)$$

What choice for a basis ?

- For molecules: often atomic orbitals, or localized functions as Gaussians

- For solids, periodic functions such as sines and cosines (plane waves)

Bravais lattices

- Infinite array of points with an arrangement and orientation that appears exactly the same regardless of the point from which the array is viewed.

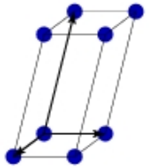
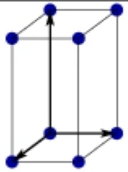
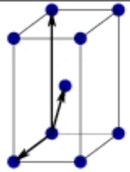
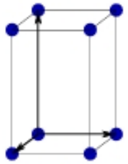
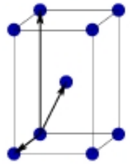
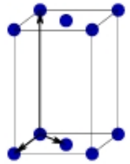
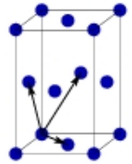
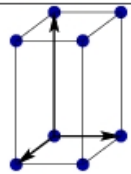
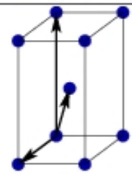
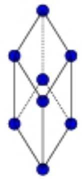
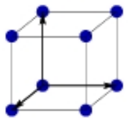
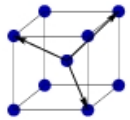
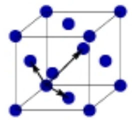
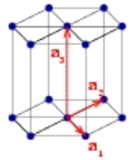
$$\vec{R} = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3 \quad \text{l,m and n integers}$$

$$\vec{a}_1,\ \vec{a}_2 \text{ and } \vec{a}_3 \text{ primitive lattice vectors}$$

- 14 Bravais lattices exist in 3 dimensions (1848)

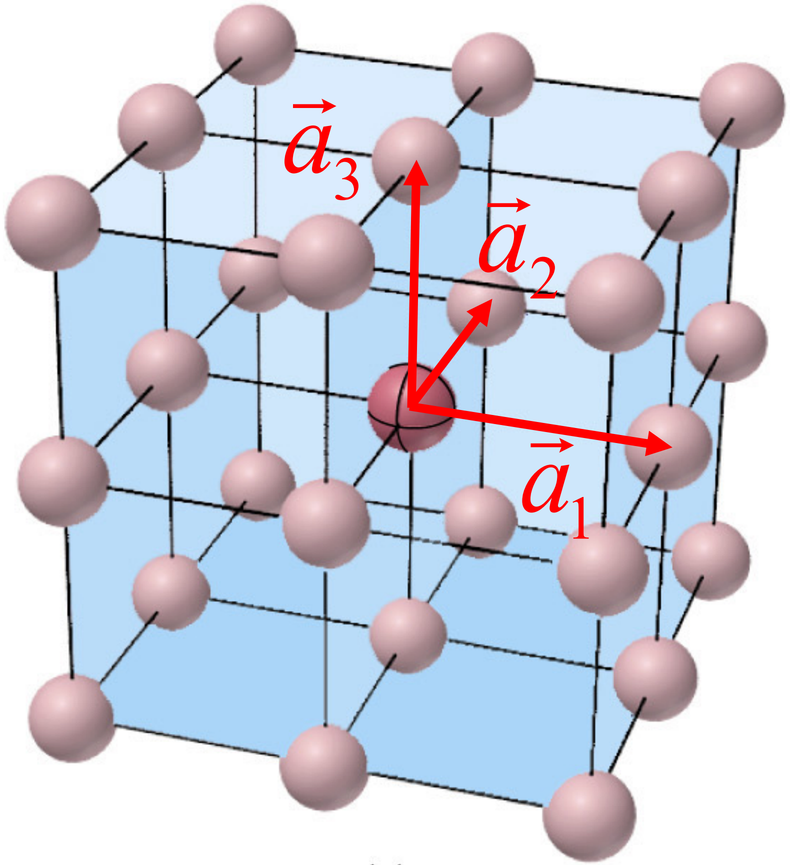
4 Lattice types

7 Crystal classes

14 Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90^\circ$ $\alpha_{12} \neq 90^\circ$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120^\circ$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120^\circ$ $\alpha_{23} = \alpha_{31} = 90^\circ$				

Reciprocal lattice (I)

- Let's start with a Bravais lattice, defined in terms of its primitive lattice vectors…



$$\vec{R} = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3$$

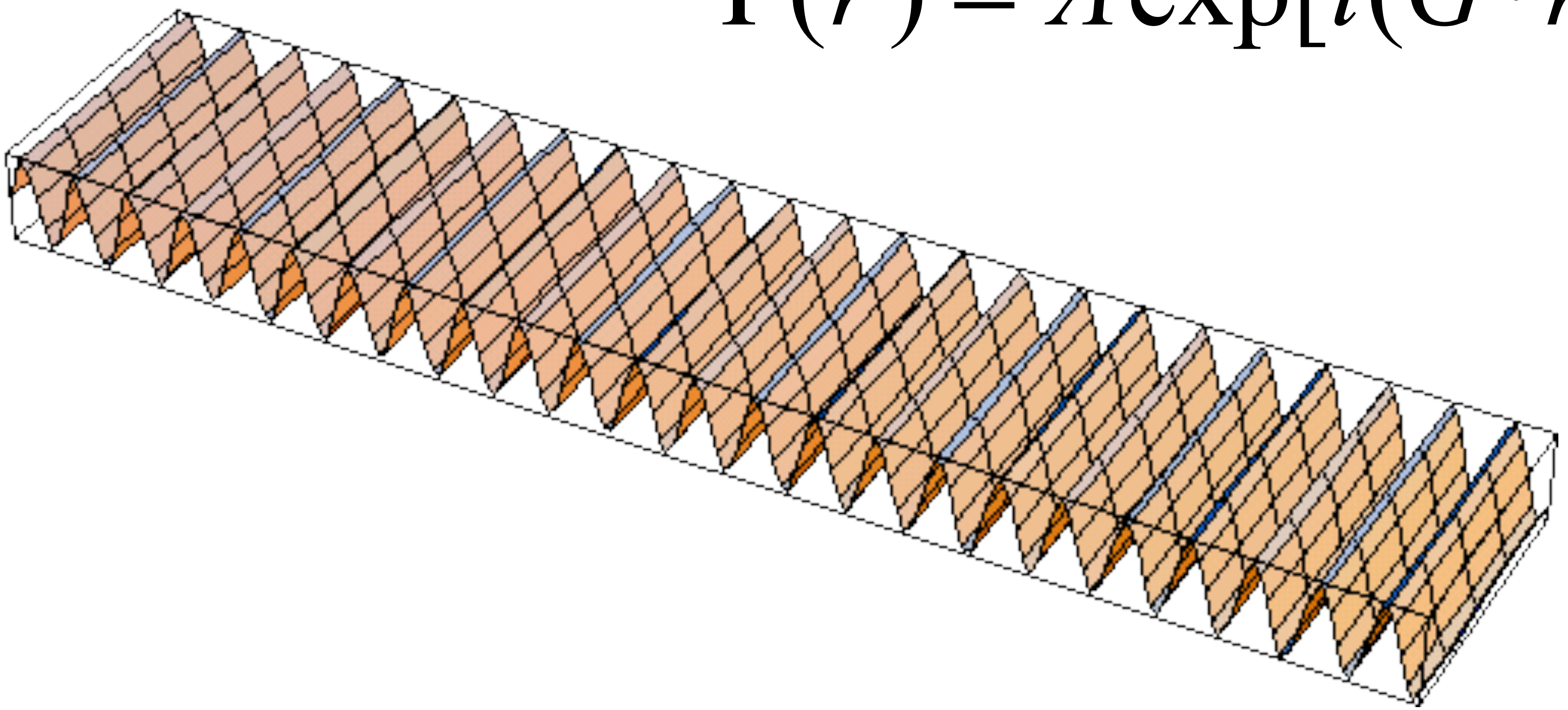
l, m, n integer numbers

$$\vec{R} = (l, m, n)$$

Reciprocal lattice (II)

- …and then let's take a plane wave

$$\Psi(\vec{r}) = A \exp[i(\vec{G} \cdot \vec{r})]$$



Reciprocal lattice (III)

- What are the wavevectors for which our plane wave has the same amplitude at all lattice points ?

$$\exp[i(\vec{G}\cdot\vec{r})] = \exp[i(\vec{G}\cdot(\vec{r}+\vec{R}))]$$
$$\exp[i(\vec{G}\cdot\vec{R})] = 1$$
$$\exp[i(\vec{G}\cdot(l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3))] = 1$$

$\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$ define the primitive unit cell

$\vec{G} = h\vec{b}_1 + i\vec{b}_2 + j\vec{b}_3$ with h, i, j integers,

provided $\vec{b}_1 = 2\pi \dfrac{\vec{a}_2\times\vec{a}_3}{\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)}$ $\vec{b}_2 = 2\pi \dfrac{\vec{a}_3\times\vec{a}_1}{\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)}$ $\vec{b}_3 = 2\pi \dfrac{\vec{a}_1\times\vec{a}_2}{\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)}$

Bravais lattices in INPUT_PW

ibrav is the structure index:

ibrav	structure	celldm(2)-celldm(6)
1	cubic P (sc)	not used

2	cubic F (fcc)	not used
6	tetragonal P (st)	celldm(3)=c/a

14	triclinic P	celldm(2)= b/a, celldm(3)= c/a, celldm(4)= cos(bc), celldm(5)= cos(ac), celldm(6)= cos(ab)
-------------------------------		

fcc bravais lattice.

a1=(a/2)(-1,0,1), a2=(a/2)(0,1,1), a3=(a/2)(-1,1,0).

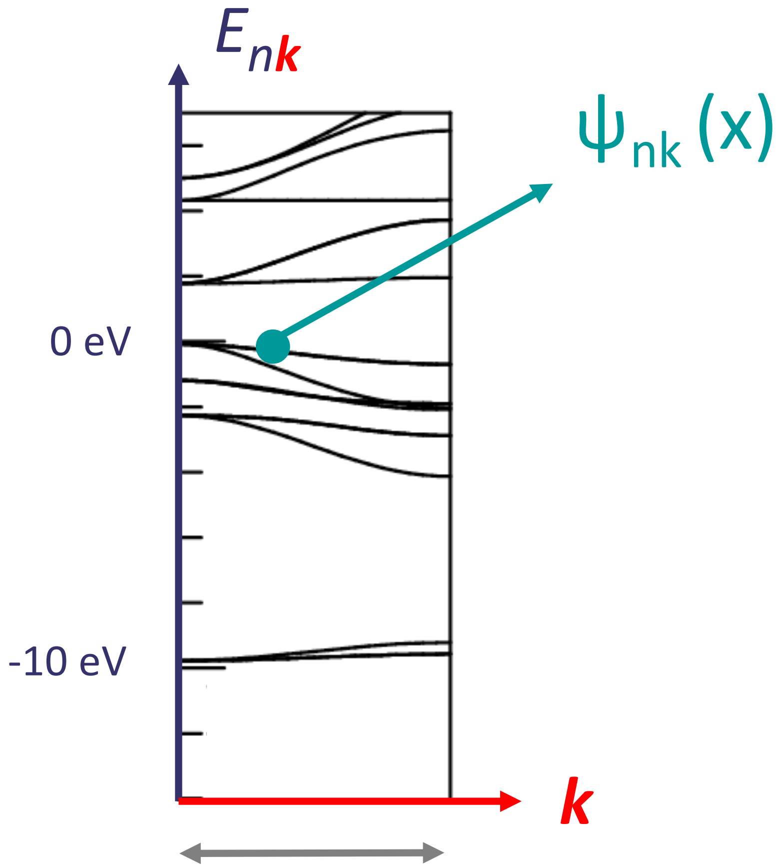
Bloch theorem

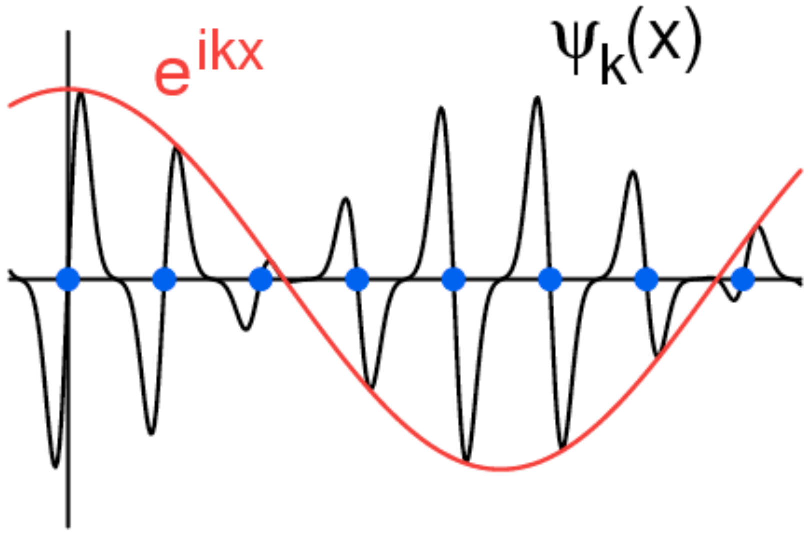
$$[\,\hat{H},\,\hat{T}_{\mathrm{R}}\,] = 0 \;\Rightarrow\; \Psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})\,e^{i\mathbf{k}\cdot\mathbf{r}}$$

- *n, **k*** are the quantum numbers (band index *n* and crystal momentum ***k***)
- *u* is periodic (same periodicity as Hamiltonian)

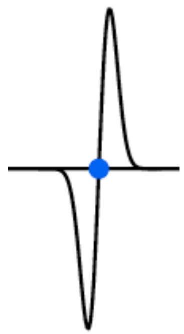
Bands and Bloch theorem

Bloch wavefunction





Ingredient:
Atomic
wavefunction



Plane wave expansion

$$\psi_{n\vec{k}}(\vec{r}) = u_{n\vec{k}}(\vec{r})\exp\left(i\vec{k}\cdot\vec{r}\right)$$

periodic *u* is expanded in planewaves, labeled according to the reciprocal lattice vectors

$$u_{n\vec{k}}(\vec{r}) = \sum_{\vec{G}} c_{n\vec{k}}^{\vec{G}} \exp(i\vec{G}\cdot\vec{r})$$

The plane waves basis set

1. Systematic improvement of completeness/resolution
2. Huge number of basis elements – only possible because of pseudopotentials
3. Allows for easy evaluation of gradients and Laplacian
4. Kinetic energy in reciprocal space, potential in real space
5. Basis set does not depend on atomic positions: there are no Pulay terms in the forces

The cutoff sphere

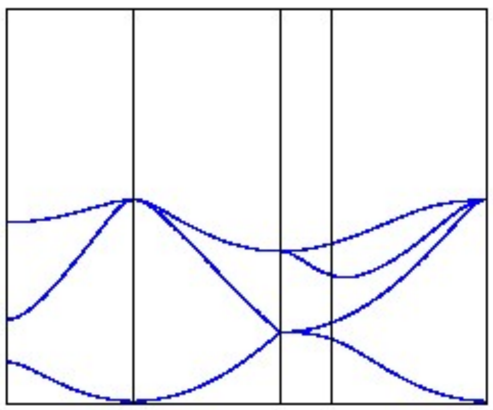
Laplacians are easy: Poisson equation

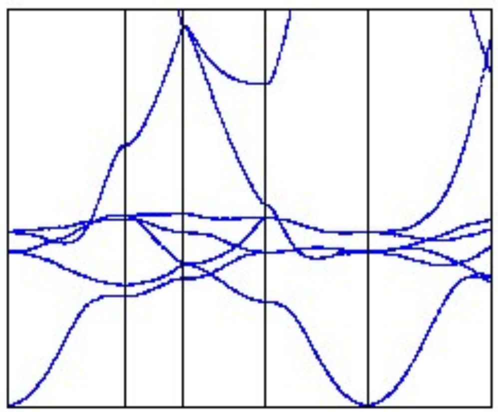
Other possibilities - many

- Gaussian basis sets (Hartree-Fock codes)
- Real space representations
- LCAO
- LMTO, LAPW

Brillouin zone integrations

1. Sampling at one point (the best – Baldereschi point, or the simplest – Gamma point)
2. Sampling at regular meshes (Monkhorst-Pack grids)
3. For metallic systems, integration of the discontinuity is improved introducing a fictitious electronic temperature

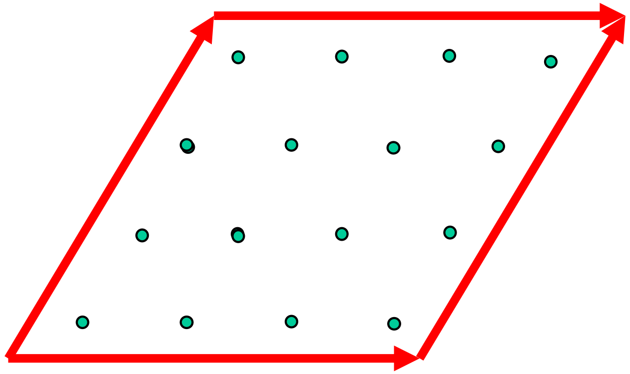




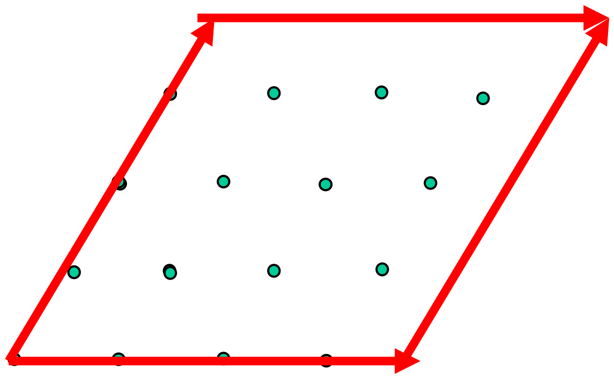
Monkhorst-Pack meshes

- Regular, equispaced meshes in the Brillouin Zone (generated automatically by PWscf – "automatic" keyword)

(4,4,4) shifted



(4,4,4) unshifted

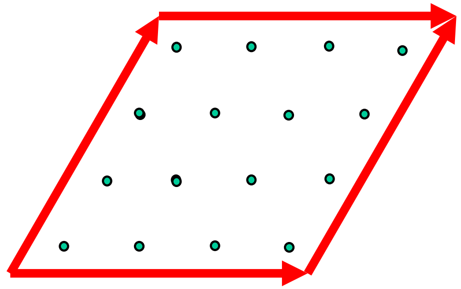


Symmetry

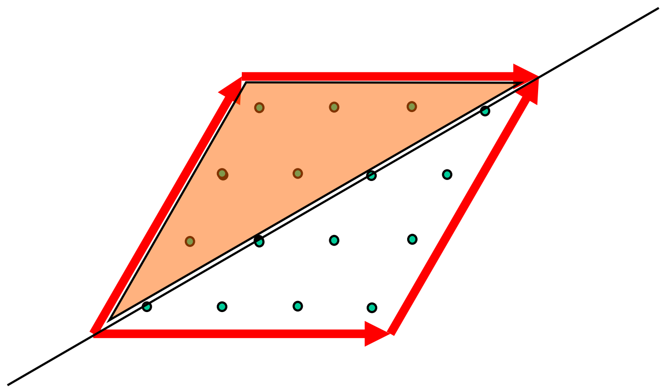
- Symmetry operations: actions that transform an object into a new but undistinguishable configuration
- Symmetry elements: geometric entities (axes, planes, points…) around which we carry out the symmetry operations

Exploiting symmetry

$$\rho(\vec{r}) = \sum_{n,\vec{k}} \left\| \Psi_{n,\vec{k}}\left(\vec{r}\right) \right\|^2$$



$$\Psi_{n,\vec{k}}\left(S^{-1}\vec{r}\right) = \Psi_{n,S\vec{k}}\left(\vec{r}\right)$$



$$\rho(\vec{r}) = \sum_{n,\vec{k}} \left\| \Psi_{n,\vec{k}}\left(\vec{r}\right) \right\|^2 = \sum_{n,S,\vec{k}_{irr}} \left\| \Psi_{n,S\vec{k}_{irr}}\left(\vec{r}\right) \right\|^2 =$$

$$= \sum_{n,S,\vec{k}_{irr}} \left\| \Psi_{n,\vec{k}_{irr}}\left(S^{-1}\vec{r}\right) \right\|^2$$

One symmetry that's always there

Periodic Hamiltonian for u_{nk} (apply H to $u_{nk}\, e^{ikr}$)

$$\frac{1}{2}\left(\frac{1}{i}\nabla + k\right)^2 + V(\vec{r})$$

$$u_{nk}(\vec{r}) = u^*_{n\,-k}(\vec{r})$$

K-points in PWSCF

K_POINTS { tpiba | automatic | crystal | gamma

gamma : use k = 0 (do not read anything after this card)

Note that a set of subroutines optimized for calculations at
the gamma point are used so that both memory and cpu requirements
are reduced

automatic: automatically generated uniform grid of k-points

next card:

nk1, nk2, nk3, k1, k2, k3

generates (nk1, nk2, nk3) mesh with (k1, k2, k3) offset
nk1, nk2, nk3 as in Monkhorst-Pack grids
k1, k2, k3 must be 0 (no offset) or 1 (grid displaced
by half a grid step in the corresponding direction)
The mesh with offset may not work with tetrahedra.

crystal : read k-points in crystal coordinates

K-points in PWSCF

tpiba : read k-points in 2pi/a units (default)

next card:

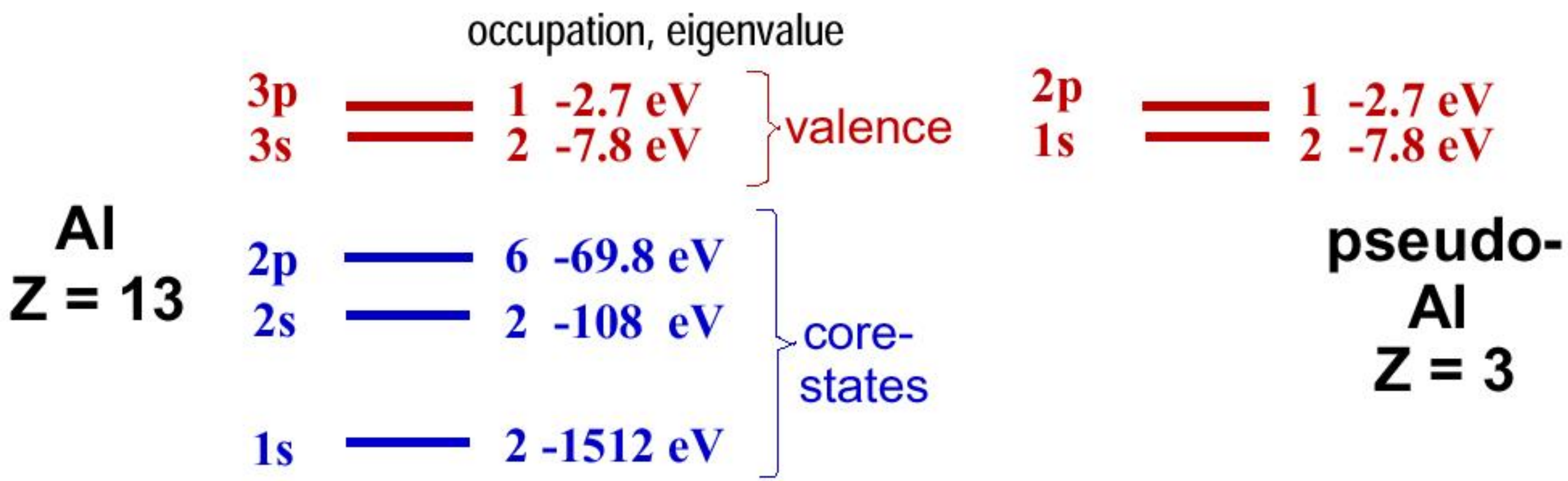
nks

number of supplied special points

xk_x, xk_y, xk_z, wk

special points in the irreducible Brillouin Zone
of the lattice (with all symmetries) and weights
If the symmetry is lower than the full symmetry
of the lattice, additional points with appropriate
weights are generate

Pseudopotentials (I)



$$(-\frac{1}{2}\nabla^2 + v_{\text{eff}})\psi_j = \varepsilon_j \psi_j$$

$$(-\frac{1}{2}\nabla^2 + v_{\text{eff}}^{(\text{ps})})\psi_j^{(\text{ps})} = \varepsilon_j \psi_j^{(\text{ps})}$$

From Eckhard Pehlke lecture notes – Fritz-Haber Institut
http://www.fhi-berlin.mpg.de/th/Meetings/FHImd2001/pehlke1.pdf

Pseudopotentials (II)

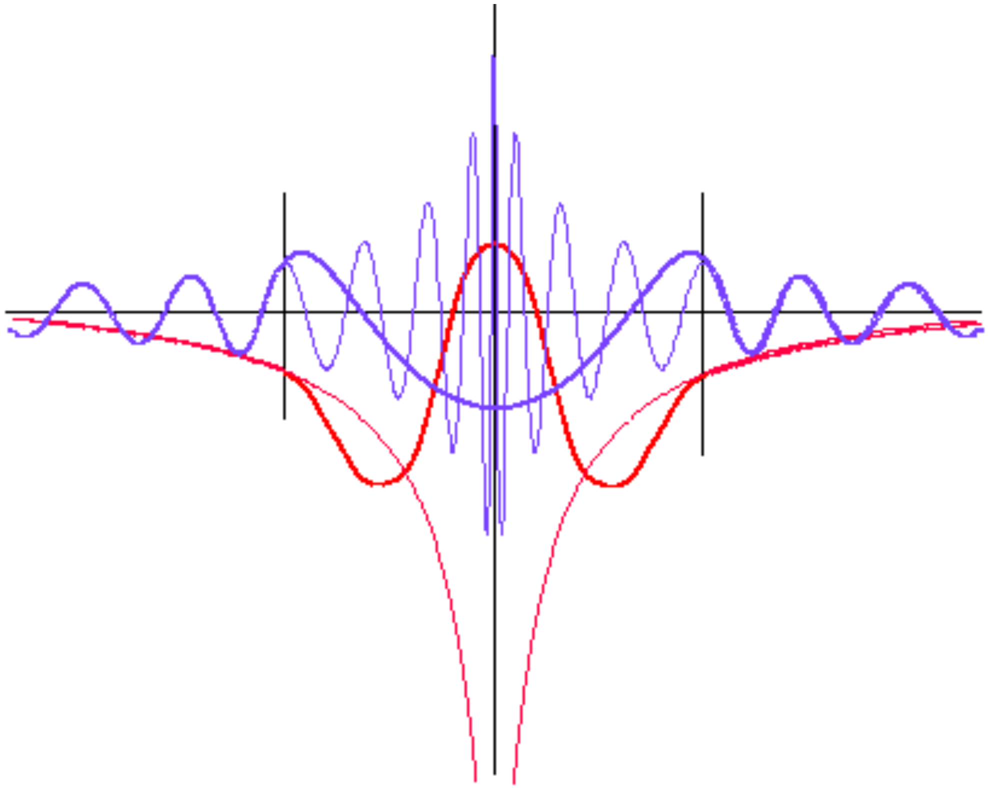


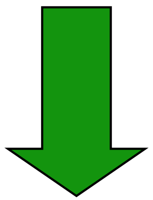
Figure 2.3: A schematic representation of the potentials (red lines) and wavefunctions (blue lines) for an atom. The real potential and wavefunction are shown with thin lines, while the pseudopotential and wavefunction are shown in thick lines. Outside the cutoff region (vertical black lines) the two are identical. *Picture courtesy of Chris Goringe.*

Norm-conserving pseudopotentials

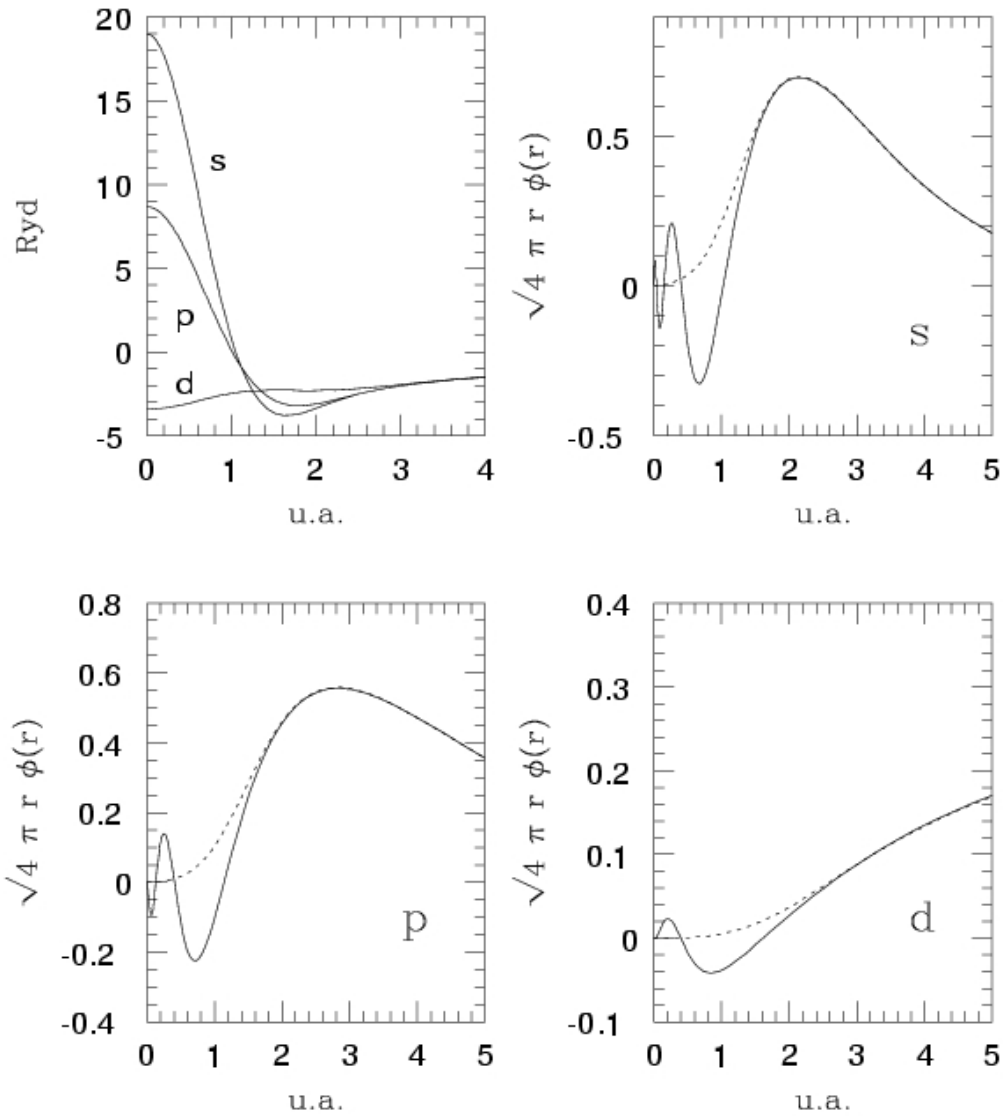
- Real and pseudo valence eigenvalues agree for a chosen atomic configuration
- Real and pseudo wavefunctions agree beyond a core radius
- The integral of real and pseudo charge from 0 to a distance greater than core radius agree
- The logarithmic derivatives of the real and pseudo wavefunctions, and their first energy derivatives, agree for distances greater than the core radius

Non-local, norm conserving

Different **angular momenta** scatter differently from the core (states that have shell below them with same angular momentum are repelled more)

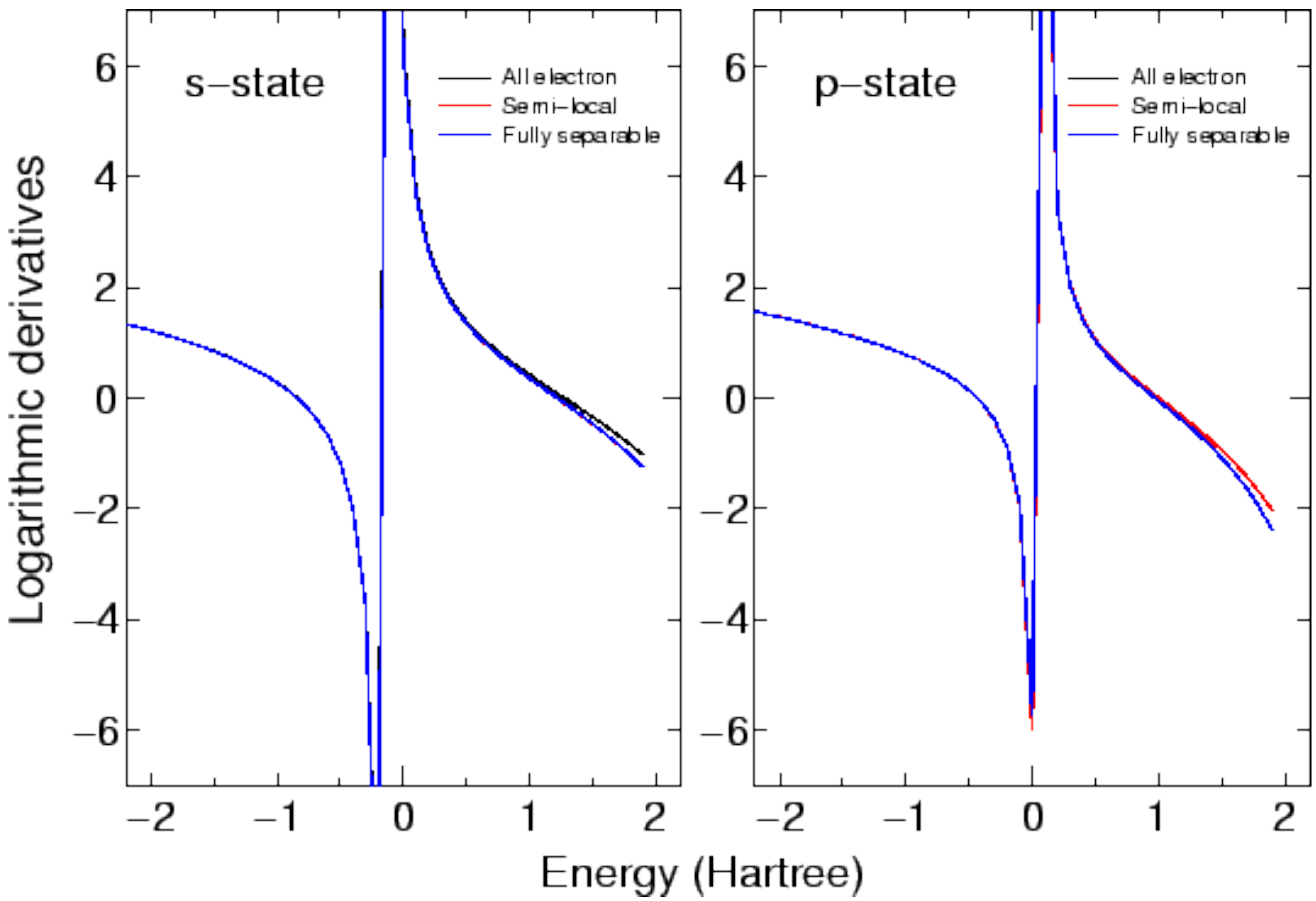


Non-local PP



Logarithmic derivatives

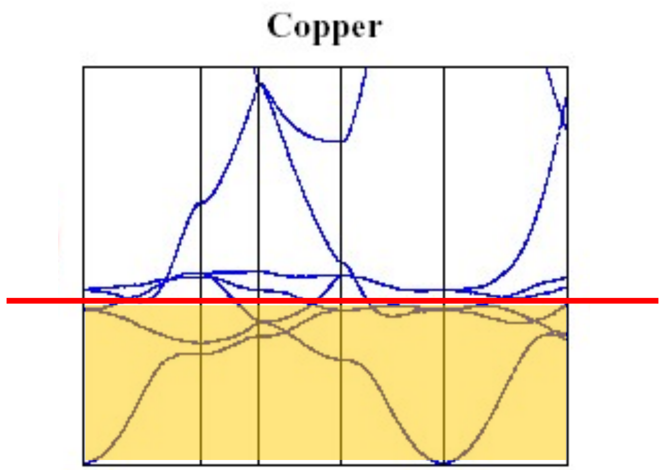
$$\frac{d}{dr}\ln u_l(E,r)$$



Note on ultrasoft pseudopotentials

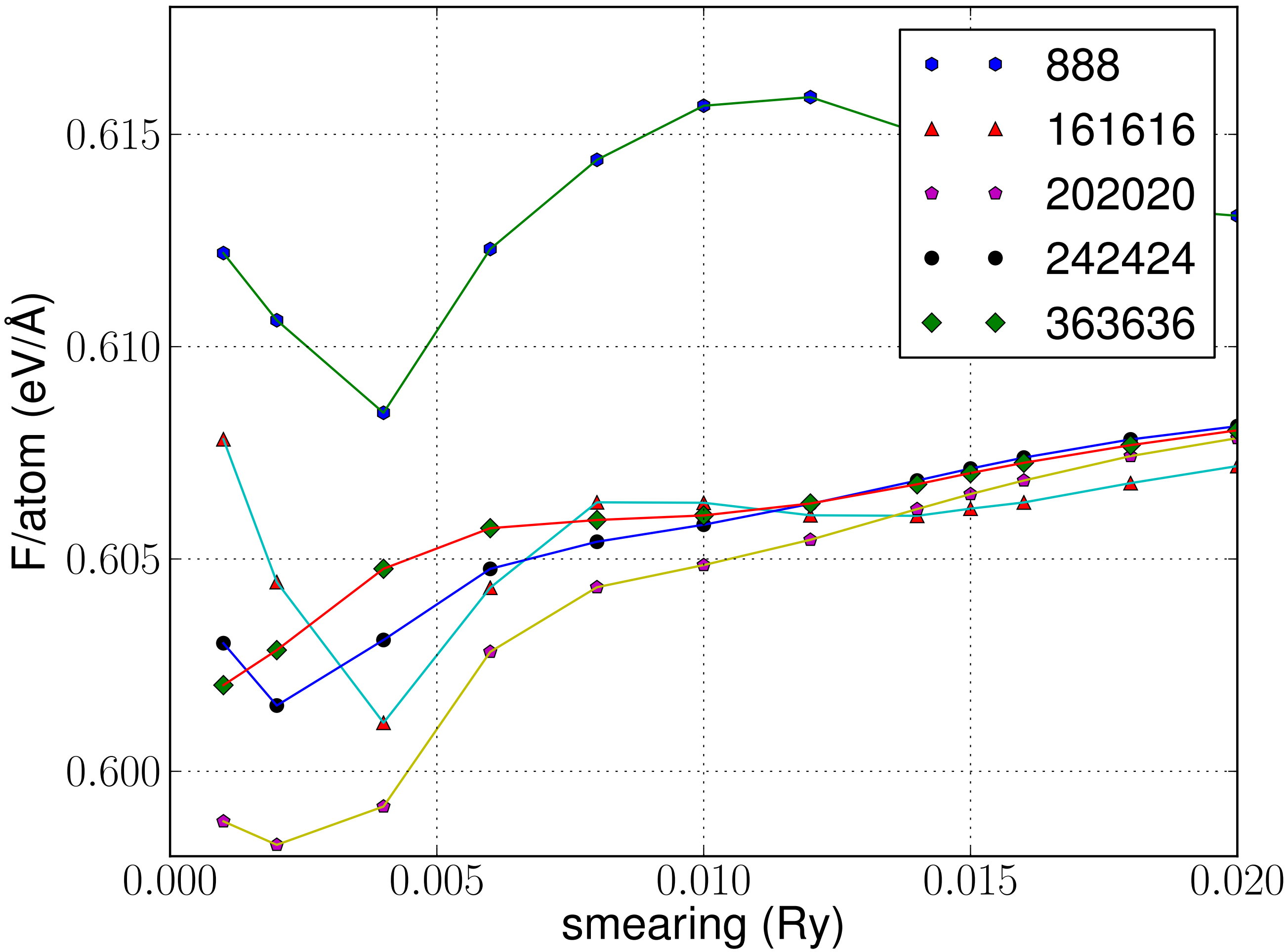
Temperature and smearing

$$\rho(\vec{r}) = \sum_{n,\vec{k}} f_{n,\vec{k}} \left\| \Psi_{n,\vec{k}}(\vec{r}) \right\|^2$$



$$A\left[\sigma;\{\psi_i\},\{f_i\}\right] = \sum_i f_i \langle \psi_i | \hat{T}_e + \hat{V}_{nl} | \psi_i \rangle + E_{\mathrm{Hxc}}[n] - \sigma S[\{f_i\}]\,.$$

Temperature and smearing



Generalized smearing/entropic formulations

$$A\,[\sigma\,;\{\psi_i\},\{f_i\}] \;=\; \sum_i f_i \,\langle\psi_i|\hat{T}_e+\hat{V}_{nl}|\psi_i\rangle + E_{\mathrm{Hxc}}[n] - \sigma S[\,\{f_i\}\,]$$

$$+\;\; \mu\,(N-\sum_i f_i) + \sum_i f_i\epsilon_{\,i}\,(\langle\psi_i|\psi_i\rangle - 1)$$

$$n(\mathbf{r}) = \sum_i f_i\,\psi_i^*(\mathbf{r})\psi_i(\mathbf{r}) \quad ,$$

$$\frac{\delta A}{\delta\psi_i^\star} = 0 \quad\Rightarrow\quad f_i\hat{H}\psi_i = f_i\epsilon_i\psi_i$$

$$\frac{\partial A}{\partial\lambda_i} = 0 \quad\Rightarrow\quad \langle\psi_i|\psi_i\rangle = 1$$

$$\frac{\partial A}{\partial f_i} = 0 \quad\Rightarrow\quad \langle\psi_i|H|\psi_i\rangle - \mu = T\frac{\partial S}{\partial f_i}$$

$$\frac{\partial A}{\partial\mu} = 0 \quad\Rightarrow\quad \sum_i f_i = N$$

Generalized smearing/entropic formulations

$$f(x) = \int_{-\infty}^{x} g(t)\, dt$$

$$S[\{f_i\}] = \sum_i S_i = \sum_i S(f_i)$$

$$\frac{dS}{df} = \frac{\epsilon - \mu}{\sigma} = -x \Rightarrow \frac{dS}{dx} = -x \frac{df}{dx}$$

$$f(x) = \int_{-\infty}^{x} g(t)\, dt \Rightarrow S_i = \int_{-\infty}^{x_i} -t\, g(t)\, dt$$

Generalized smearing/entropic formulations

$$\int_{-\infty}^{\infty} \tilde{\delta}(x)\, dx = 1 \qquad \text{normalization}$$

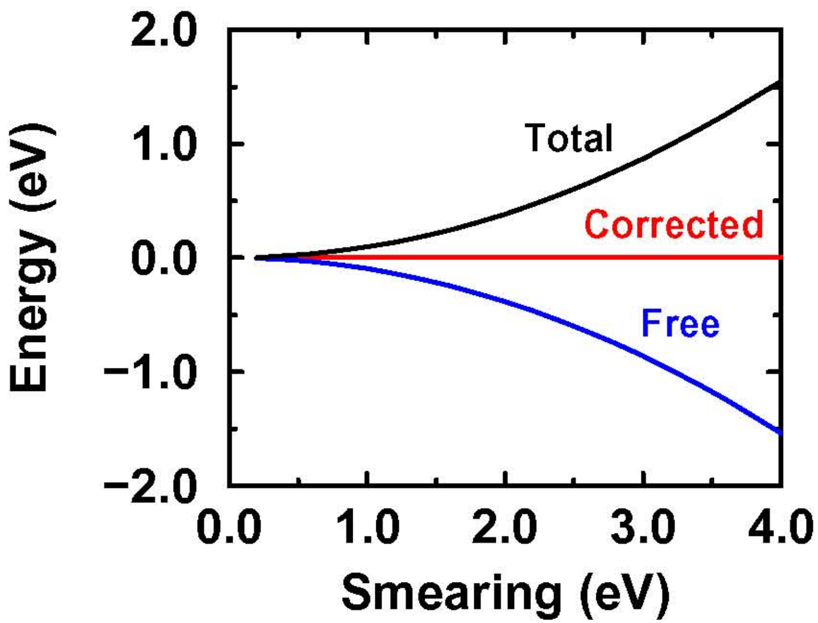
$$\int_{-\infty}^{\infty} x\, \tilde{\delta}(x)\, dx = 0 \qquad \mathrm{S}(0) = 0$$

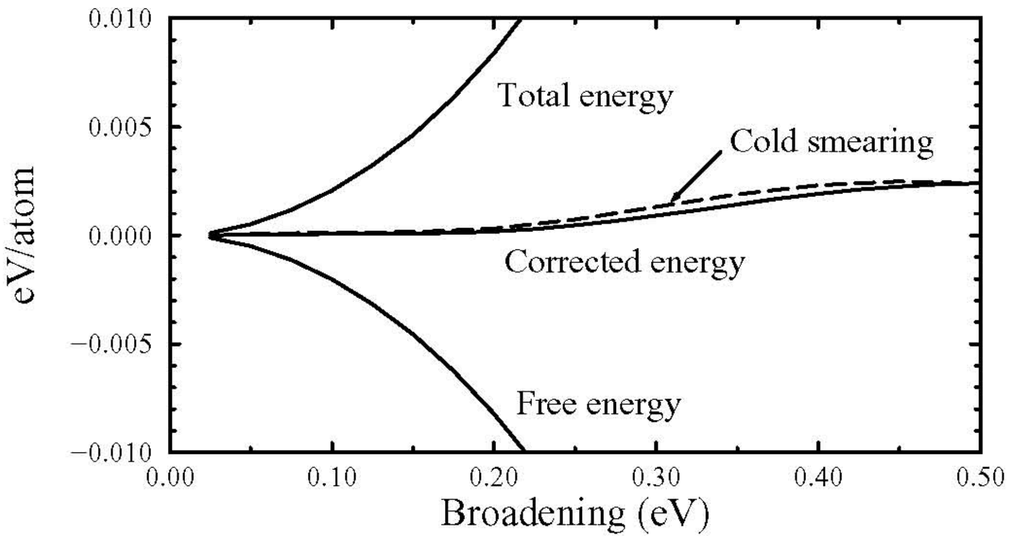
$$\int_{-\infty}^{\infty} x^2 \tilde{\delta}(x)\, dx = 0 \qquad \text{cold smearing}$$

$$\int_{-\infty}^{t} \tilde{\delta}(x)\, dx \geq 0 \qquad \text{positive occupancies}$$

$$\tilde{\delta}(x) = \frac{2}{\sqrt{\pi}}\, e^{-[x-(1/\sqrt{2})]^2}(2 - \sqrt{2}\, x)$$

Generalized smearing/entropic formulations



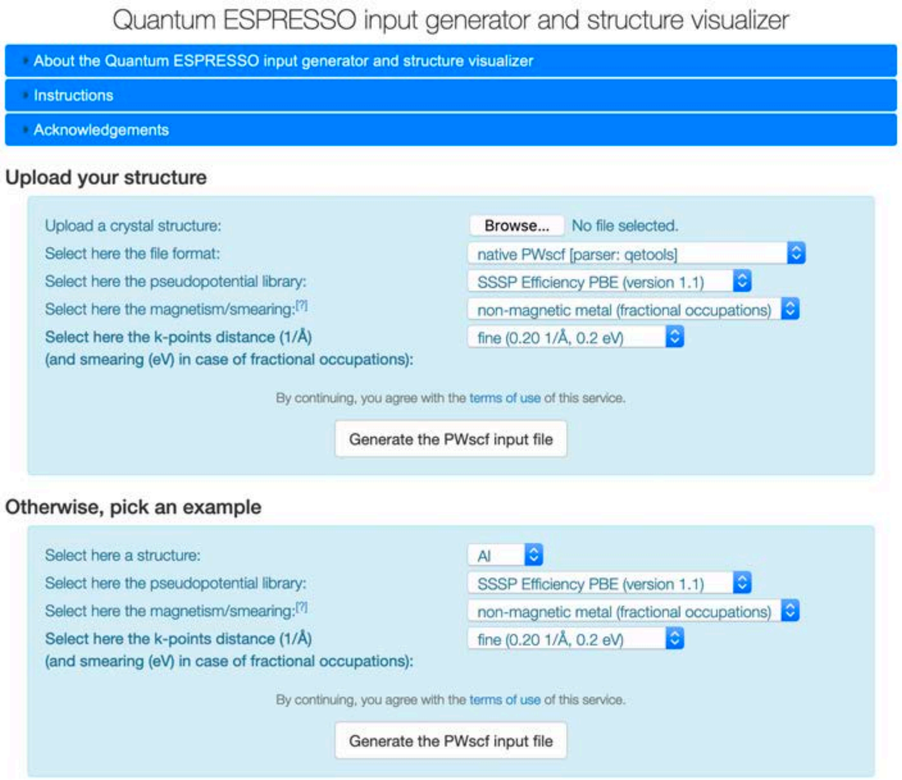


Summary

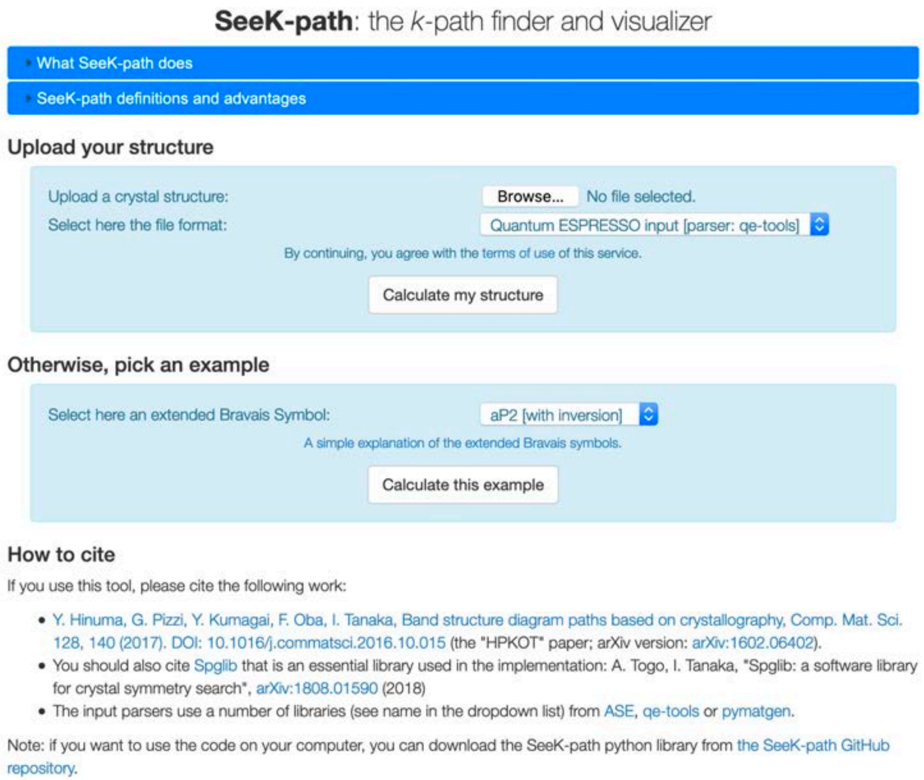
- Bravais lattice
- Atoms in the basis
- Cutoff energy for the wavefunctions (and for the charge density – 4x-12x)
- K-point sampling
- Metal: fictitious temperature (smearing)
- Self-consistency recipe

Materials Cloud Work tools

QE input generator



SeeK-path



Iterations to selfconsistency

• Construct the external potential (array of non-local pseudopotentials)

• Choose the plane-wave basis set cutoff, k-point sampling

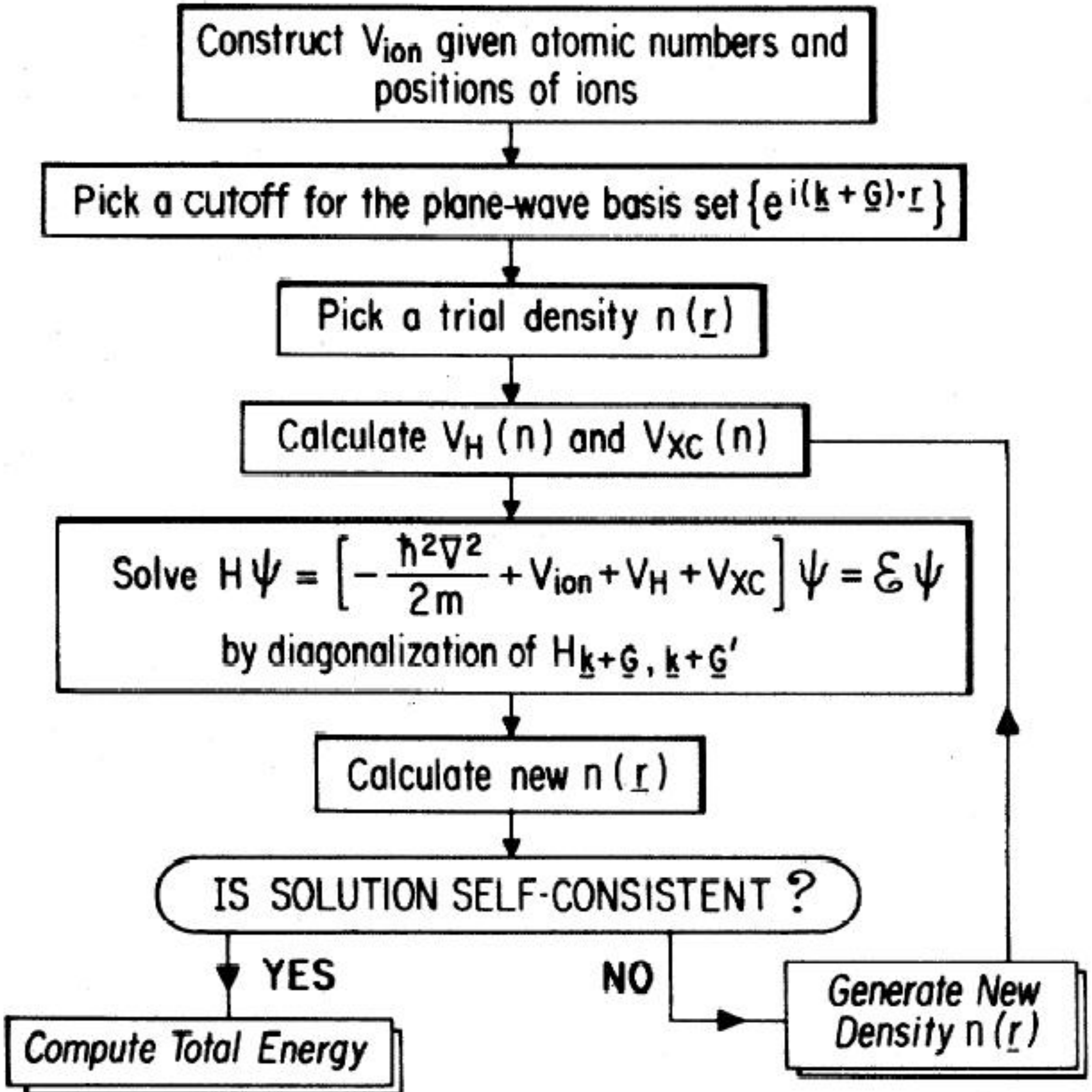
• Pick a trial electronic density

• Construct the Hamiltonian operator: Hartree and exchange-correlation

• Solve Kohn-Sham equations for the given Hamiltonian (e.g. by diagonalization)

• Calculate the new charge density

• Iterate


Construct V_{ion} given atomic numbers and positions of ions
Pick a cutoff for the plane-wave basis set $\{e^{i(\underline{k}+\underline{G})\cdot\underline{r}}\}$
Pick a trial density $n(\underline{r})$
Calculate $V_H(n)$ and $V_{XC}(n)$
Solve $H\psi = \left[-\frac{\hbar^2\nabla^2}{2m} + V_{ion} + V_H + V_{XC}\right]\psi = \mathcal{E}\psi$
by diagonalization of $H_{\underline{k}+\underline{G},\,\underline{k}+\underline{G}'}$
Calculate new $n(\underline{r})$
IS SOLUTION SELF-CONSISTENT ?
YES
NO
Compute Total Energy
Generate New Density $n(\underline{r})$

Let's go variatonal: kinetic energy

$$E_{kin} = \sum_n \langle \psi_n | -\frac{1}{2}\nabla^2 | \psi_n \rangle \qquad \psi_n(\vec{r}) = \sum_{\vec{G}} c^n_{\vec{G}} \exp(i\vec{G}\cdot\vec{r})$$

$$\left\langle G \left| -\frac{1}{2}\nabla^2 \right| G' \right\rangle = \int dr \exp(-iGr)\left[-\frac{1}{2}\nabla^2\right]\exp(iG'r) = \frac{1}{2}G^2\delta_{G,G'}$$

$$E_{kin} = \sum_n \frac{1}{2}\sum_{\vec{G}} \left\| c^n_{\vec{G}} \right\|^2 G^2$$

Potential energy (non-SCF)

$$E_{pot} = \sum_n \left\langle \psi_n \middle| V\left(\vec{r}\right) \middle| \psi_n \right\rangle \qquad \psi_n(\vec{r}) = \sum_{\vec{G}} c_{\vec{G}}^n \exp(i\vec{G}\cdot\vec{r})$$

$$\left\langle G \middle| V(r) \middle| G' \right\rangle = \int dr \exp(-iGr) V(r) \exp(iG'r) = V(G-G')$$

$$E_{tot} = \sum_n \left(\frac{1}{2} \sum_{\vec{G}} \left\| c_{\vec{G}}^n \right\|^2 G^2 + \sum_{\vec{G},\vec{G}'} c_{\vec{G}}^{*n} c_{\vec{G}'}^n V(\vec{G}-\vec{G}') \right)$$

Total energy (non-SCF)

$$E = \sum_n \varepsilon_n = \sum_n \left\langle \psi_n \right| -\frac{1}{2}\nabla^2 + V \left| \psi_n \right\rangle$$

$$E = \sum_n \left(\frac{1}{2} \sum_{\vec{G}} \left\| c_{\vec{G}}^n \right\|^2 G^2 + \sum_{\vec{G},\vec{G}'} c_{\vec{G}}^{n*} c_{\vec{G}'}^n V(\vec{G} - \vec{G}') \right)$$

Dynamical evolution of c's

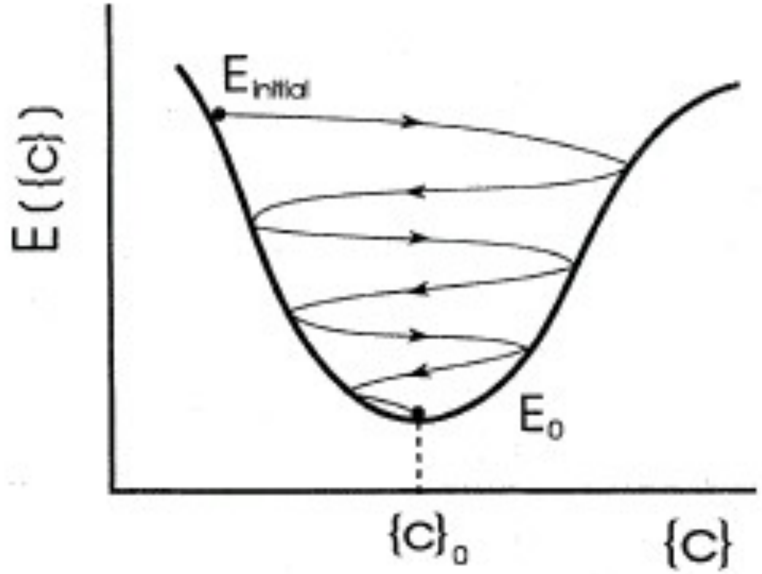


FIG. 9. Schematic representation of the damping of wave-function coefficients $\{c\}$ and the evolution of the Kohn-Sham energy functional $E[\{c\}]$ to its ground-state value E_0.

$$E_{tot} = \sum_n \left(\frac{1}{2} \sum_{\vec{G}} \left\| c^n_{\vec{G}} \right\|^2 G^2 + \sum_{\vec{G},\vec{G}'} c^{*n}_{\vec{G}} c^n_{\vec{G}'} V(\vec{G} - \vec{G}') \right)$$

We need the force

$$E = E[\{\psi_i\}] \longrightarrow F_i = -\frac{\delta E[\{\psi_i\}]}{\delta \psi_i}$$

$$= -\hat{H}\psi_i$$

Skiing down a valley

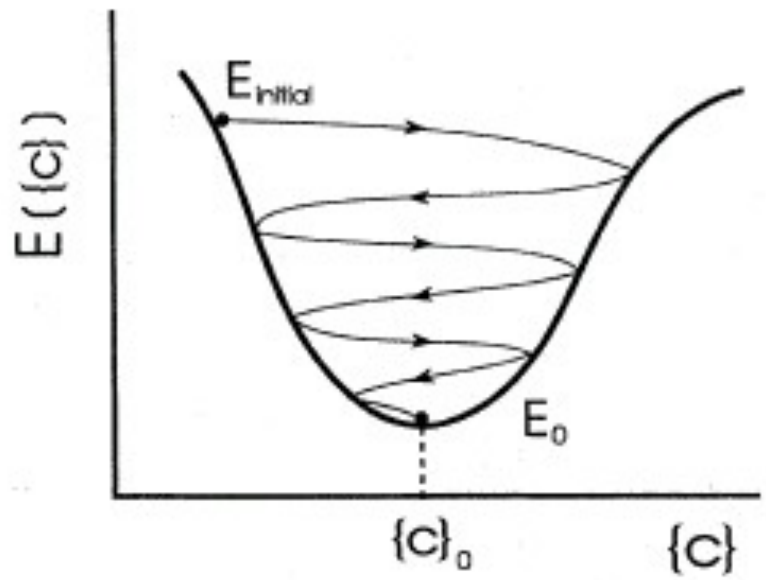


FIG. 9. Schematic representation of the damping of wave-function coefficients $\{c\}$ and the evolution of the Kohn-Sham energy functional $E[\{c\}]$ to its ground-state value E_0.

$$\mu \ddot{\psi}_i = F_i(= -H\psi)_i$$

$$\dot{\psi}_i = F_i(= -H\psi_i)$$

SD or CG skiing

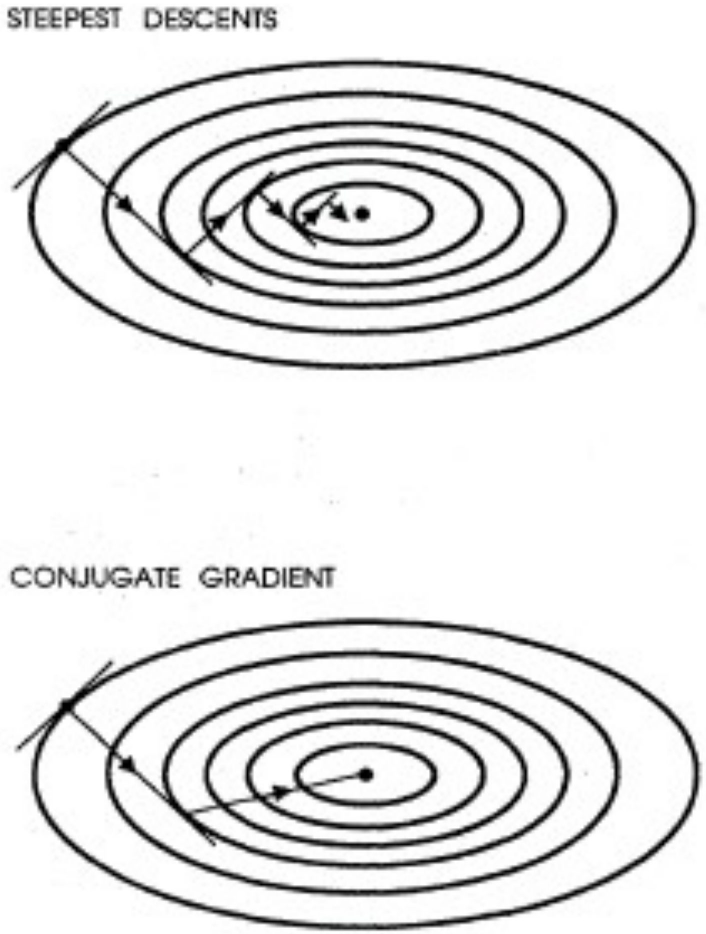
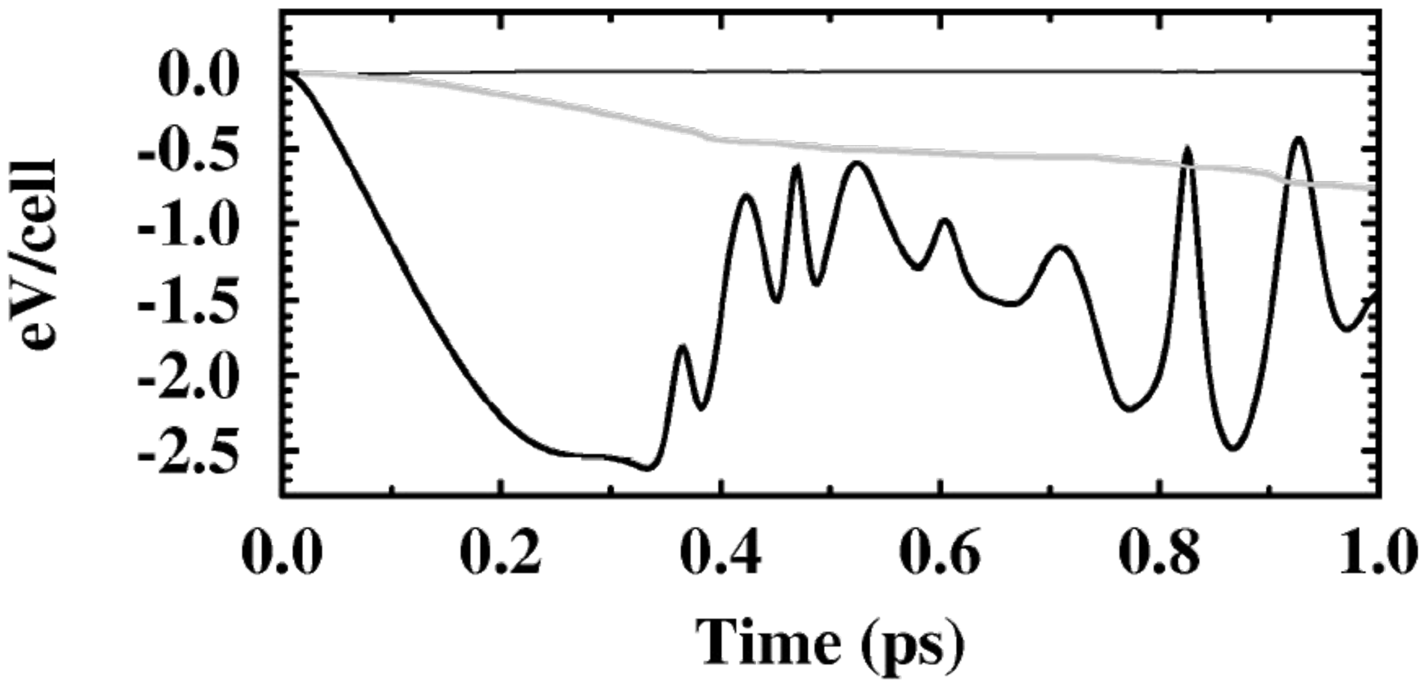


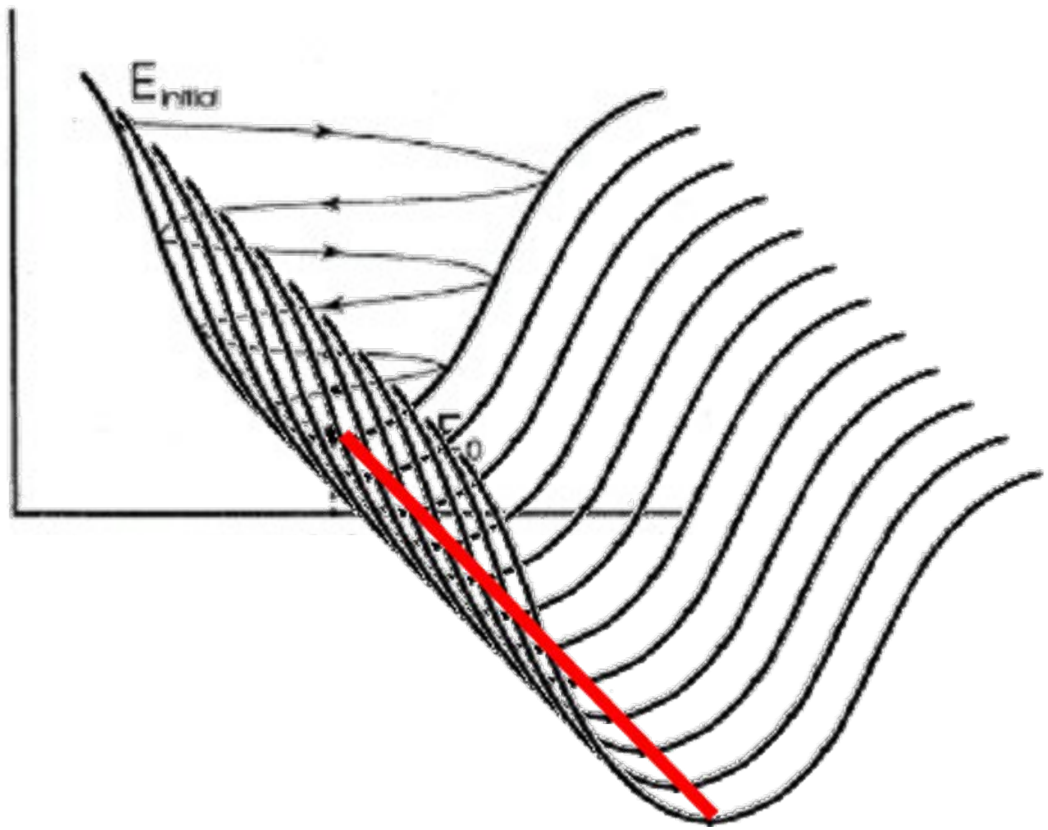
FIG. 14. Schematic illustration of two methods of convergence to the center of an anisotropic harmonic potential. Top: steepest-descents method requires many steps to converge. Bottom: Conjugate-gradients method allows convergence in two steps.

Born-Oppenheimer Molecular Dynamics

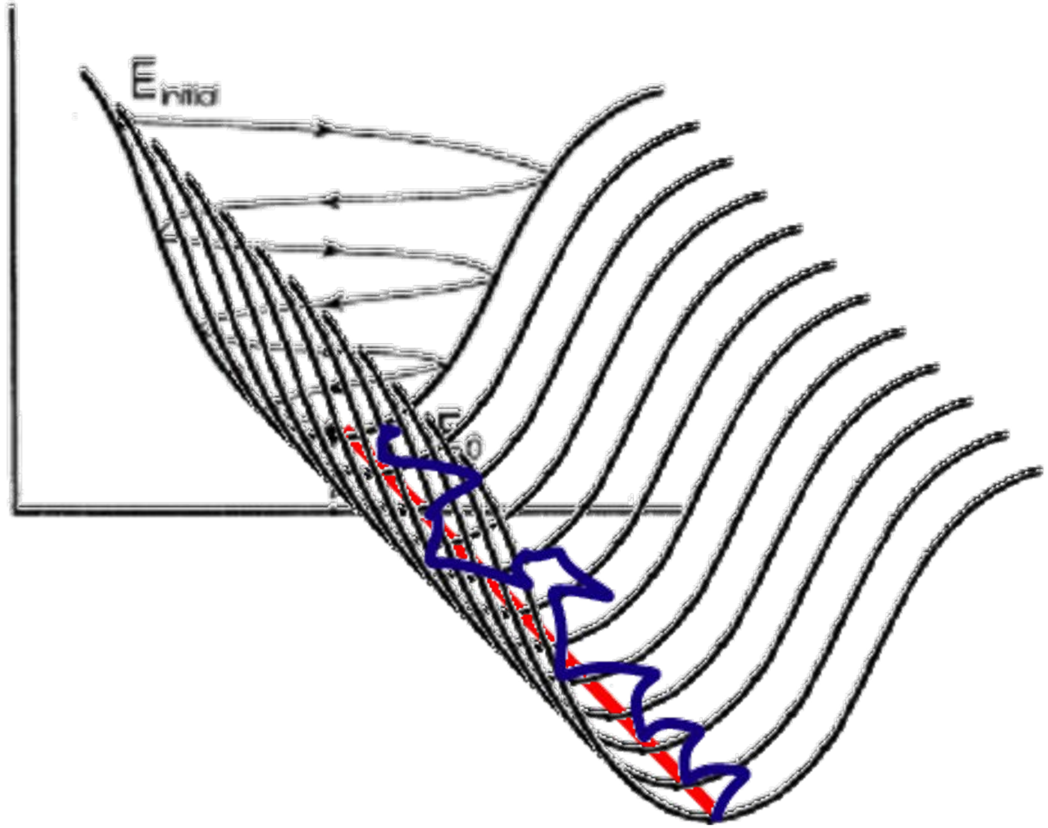
$$m_i \ddot{\vec{R}}_i = \vec{F}_i = \left\langle \Psi \left| -\frac{d\hat{V}}{d\vec{R}_i} \right| \Psi \right\rangle$$



Lots of Skiing if Atoms Move



Lots of Skiing if Atoms Move



The extended Car-Parrinello Lagrangian

$$\mathcal{L}_{\mathrm{CP}} = \underbrace{\sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \frac{1}{2}\mu_i \left\langle \dot{\psi}_i \middle| \dot{\psi}_i \right\rangle}_{\text{kinetic energy}} - \underbrace{\langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle}_{\text{potential energy}} + \underbrace{\mathit{constraints}}_{\text{orthonormality}}$$

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_I} = \frac{\partial \mathcal{L}}{\partial \mathbf{R}_I}$$

$$\frac{d}{dt}\frac{\delta \mathcal{L}}{\delta \dot{\psi}_i^\star} = \frac{\delta \mathcal{L}}{\delta \psi_i^\star}$$

Constant(s) of motion

$$E_{cons} = \sum_i \frac{1}{2}\mu_i \langle \dot{\psi}_i | \dot{\psi}_i \rangle + \sum_I \frac{1}{2} M_I \dot{R}_I^2 + \langle \Psi_0 | \hat{H}_e | \Psi_0 \rangle$$

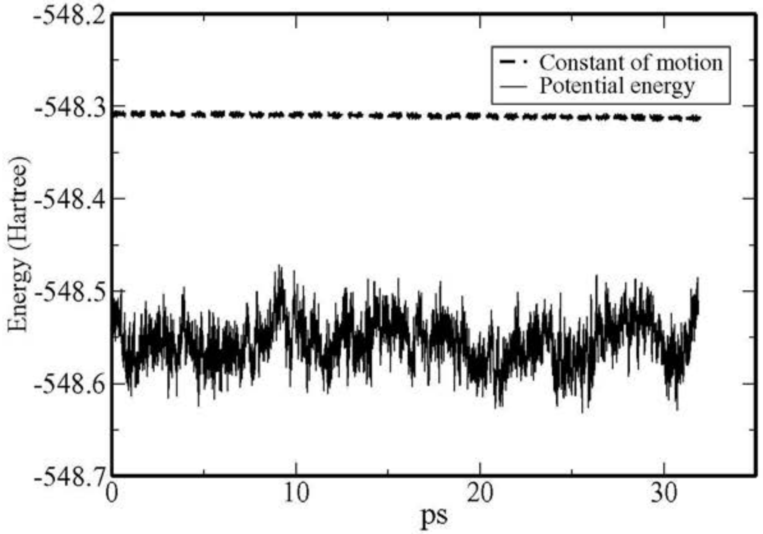
$$E_{phys} = \sum_I \frac{1}{2} M_I \dot{R}_I^2 + \langle \Psi_0 | \hat{H}_e | \Psi_0 \rangle = E_{cons} - T_e$$

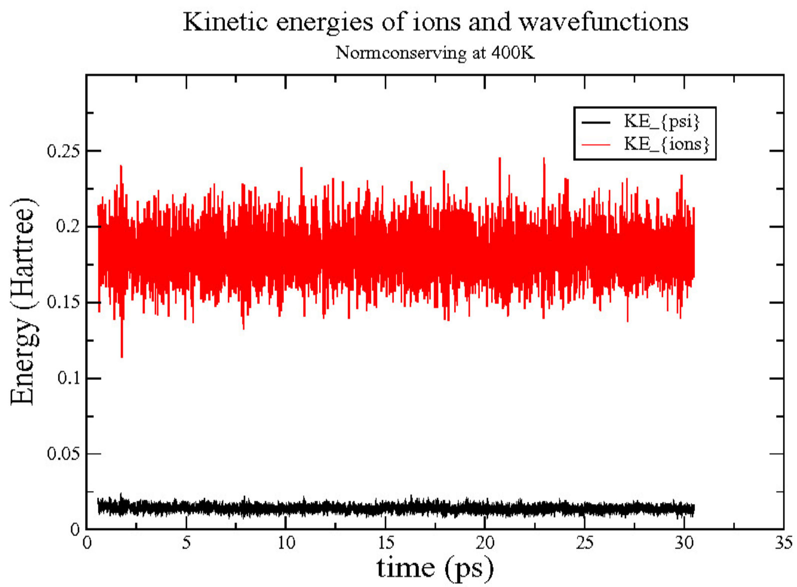
$$V_e = \langle \Psi_0 | \hat{H}_e | \Psi_0 \rangle$$

$$T_e = \sum_i \frac{1}{2}\mu_i \langle \dot{\psi}_i | \dot{\psi}_i \rangle$$

Constant of Motion

$$\underbrace{\sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \frac{1}{2}\mu_i \left\langle \dot{\psi}_i \middle| \dot{\psi}_i \right\rangle}_{\text{kinetic energy}} + \underbrace{\langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle}_{\text{potential energy}}$$





Born-Oppenheimer vs Car-Parrinello

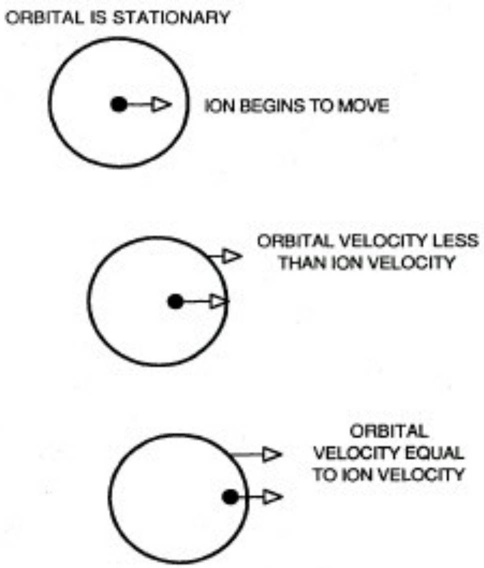


FIG. 24. Schematic illustration of how an orbital will eventually lag behind a moving ion during a simulation with $\mu\dot{\psi}=-[H-\lambda]\psi$, as discussed in the text. Convention the same as in Fig. 23.

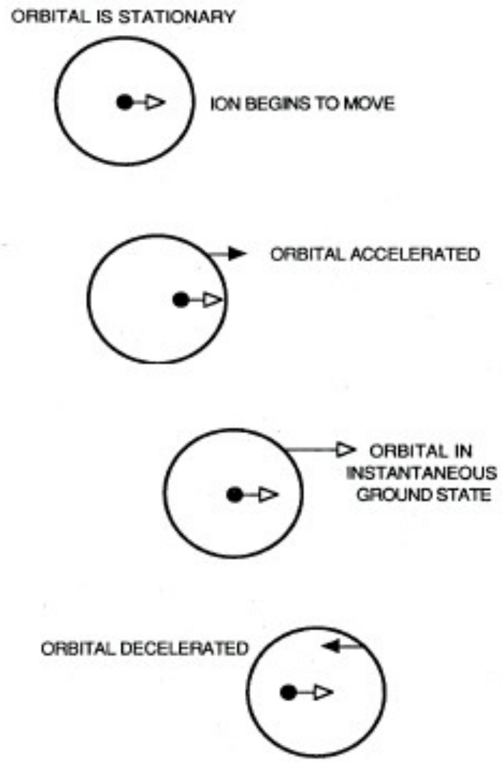


FIG. 23. Schematic illustration of how an orbital will oscillate around a moving ion during a simulation with $\mu\ddot{\psi}=-[H-\lambda]\psi$, as discussed in the text. Velocities and accelerations are designed as open and filled arrows, respectively.

What about metals?

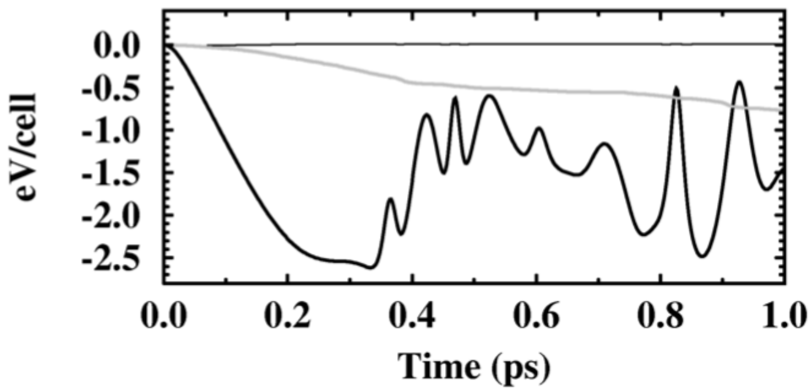
$$A[T;\{\psi_i\},\{f_{ij}\}]$$

$$= \sum_{ij} f_{ji}\langle\psi_i|\hat{T} + \hat{V}_{\text{ext}}|\psi_j\rangle + E_{\text{HXC}}[n] - TS[\{f_{ij}\}];$$

$$n(\mathbf{r}) = \sum_{ij} f_{ji}\, \psi_i^*(\mathbf{r})\psi_j(\mathbf{r})$$

What about metals?

$$G[T;\{\psi_i\}] \coloneqq \min_{\{f_{ij}\}} A[T;\{\psi_i\},\{f_{ij}\}]$$



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Ensemble Density-Functional Theory for *Ab Initio* Molecular Dynamics of Metals and Finite-Temperature Insulators

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