Electronic Structure: from BlackBoard to Source Code

Stefano de Gironcoli
Scuola Internazionale Superiore di Studi Avanzati
Trieste-Italy

Density Functional Theory in a nutshell

Every observable quantity of a stationary quantum mechanical system is determined by the system ground-state density alone

The ground-state density of the interacting system of interest can be calculated as ground-state density of an auxiliary non-interacting system in an effective potential

There are prescriptions to determine the auxiliary effective potential with useful accuracy

There is nothing so practical as a good theory

-– Kurt Lewin

founder of social
psychology

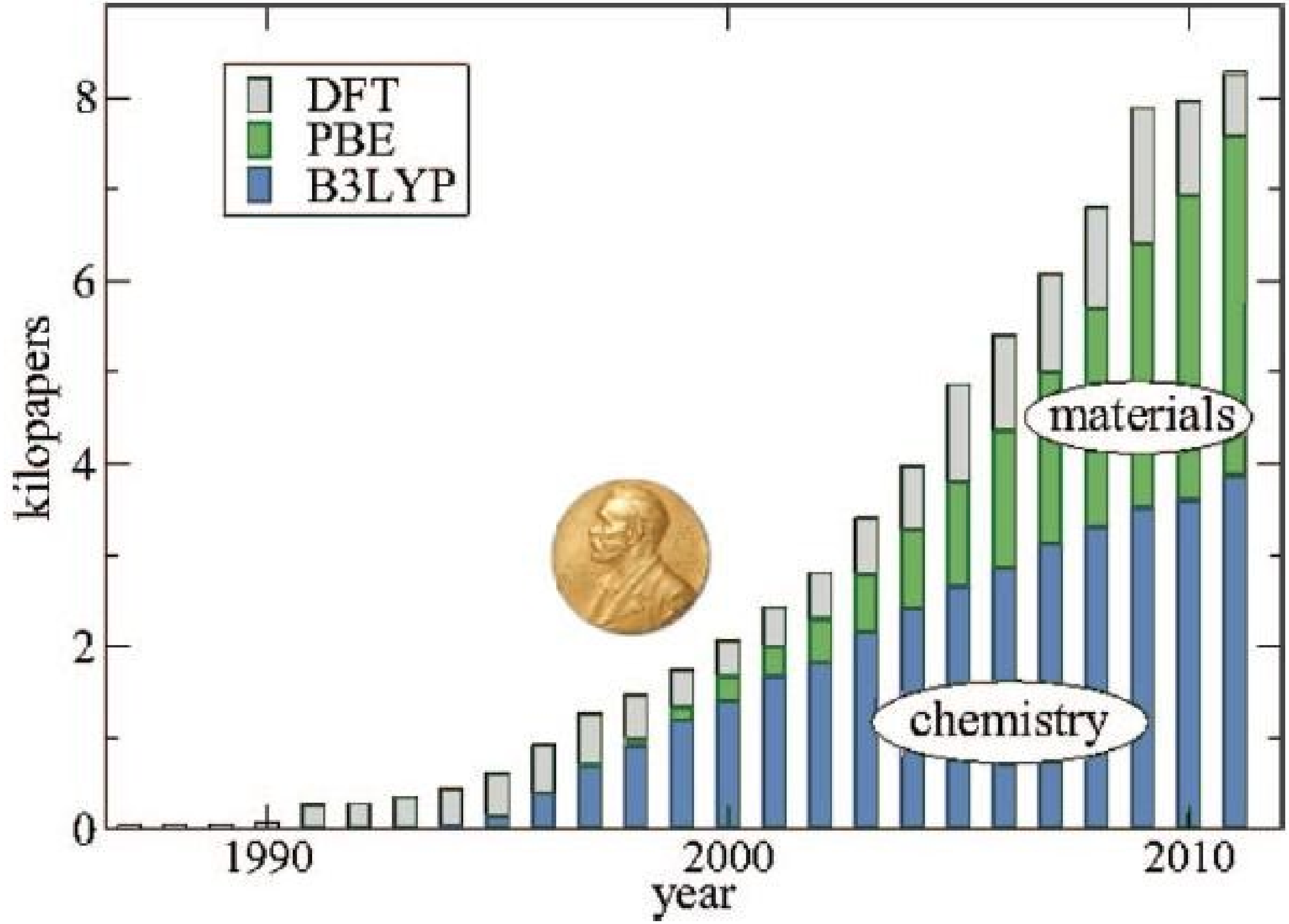


FIG. 1. Numbers of papers when DFT is searched as a topic in Web of Knowledge (grey), B3LYP citations (blue), and PBE citations (green, on top of blue).

WIEN2k

elk

www.flapw.de

fleur

CASTEP

Abinit

siesta

QUANTUM ESPRESSO

VASP
b-initio
ackage
ienna
imulation

https://www.quantum-espresso.org

NEWS

04.02.20

SCIENTIFIC SOFTWARE ENGINEER POSITION

A software developer position in the field of electronic structure is available at IOM-CNR,funded...

21.01.20

DEVELOPERS' MEETING 2020

Slides, discussion material and reports of the 2020 developers' meeting are available in the develo...

15.01.20

QE DEVELOPERS' MEETING 2020

The 2020 Quantum ESPRESSO developers' meeting will be held on January 16, in Giambiagi room (Adriat...

Zn induced structural aggregation patterns of β-amyloid peptides. Metallomics, 2012 Courtesy of G. La Penna.

QUANTUM ESPRESSO

is an integrated suite of Open-Source computer codes for electronic-structure calculations and materials modeling at the nanoscale. It is based on density-functional theory, plane waves, and pseudopotentials.

What I cannot compute, I do not understand (adapted from Richard P. Feynman)

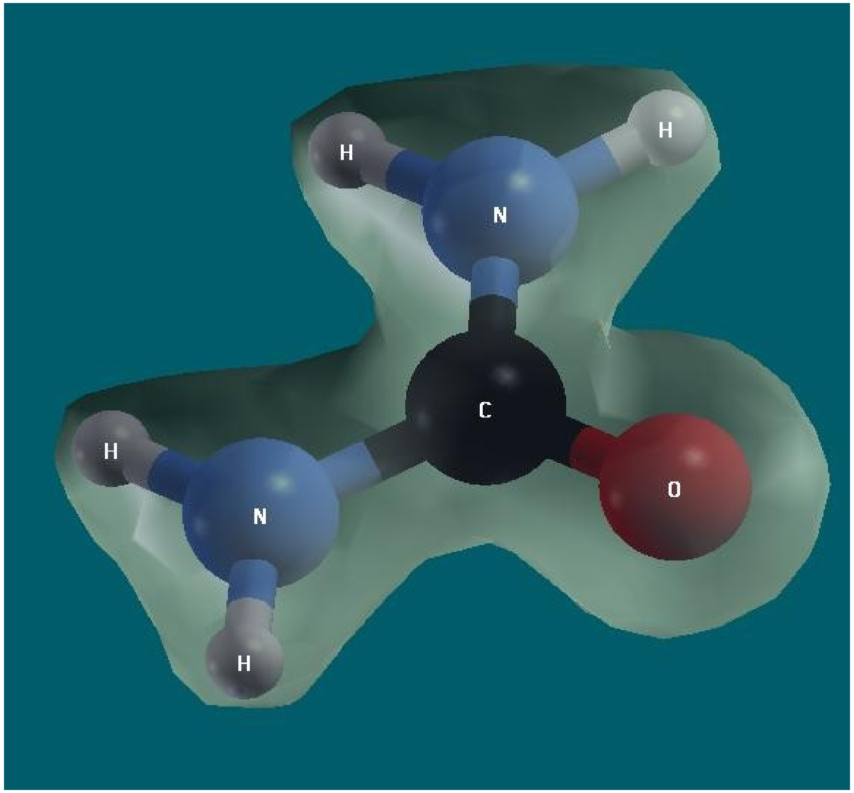
Adiabatic approximation

Independent electrons in an effective potential

Hartree–Fock

Density Functional Theory

MBPT - GW



General Structure of a PW code

Self-Consistent KS eqs.
or
Global Minimization approach

KS self-consistent equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r) - \varepsilon_i\right]\varphi_i(r) = 0$$

$$\rho(r) = \sum_i |\varphi_i(r)|^2$$

$$V_{KS}(r) = V_{ext}(r) + V_H(r) + v_{xc}(r)$$

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$$\begin{tikzcd} V_{KS}(r) \arrow[r] & \varphi_i(r) \arrow[r] & \rho(r) \arrow[ll, bend left] \end{tikzcd}$$

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$$E_{el} = -\frac{\hbar^2}{2m}\sum_i \langle\varphi_i|\nabla^2|\varphi_i\rangle + \int V_{ext}(r)\rho(r)dr + E_H[\rho] + E_{xc}[\rho]$$

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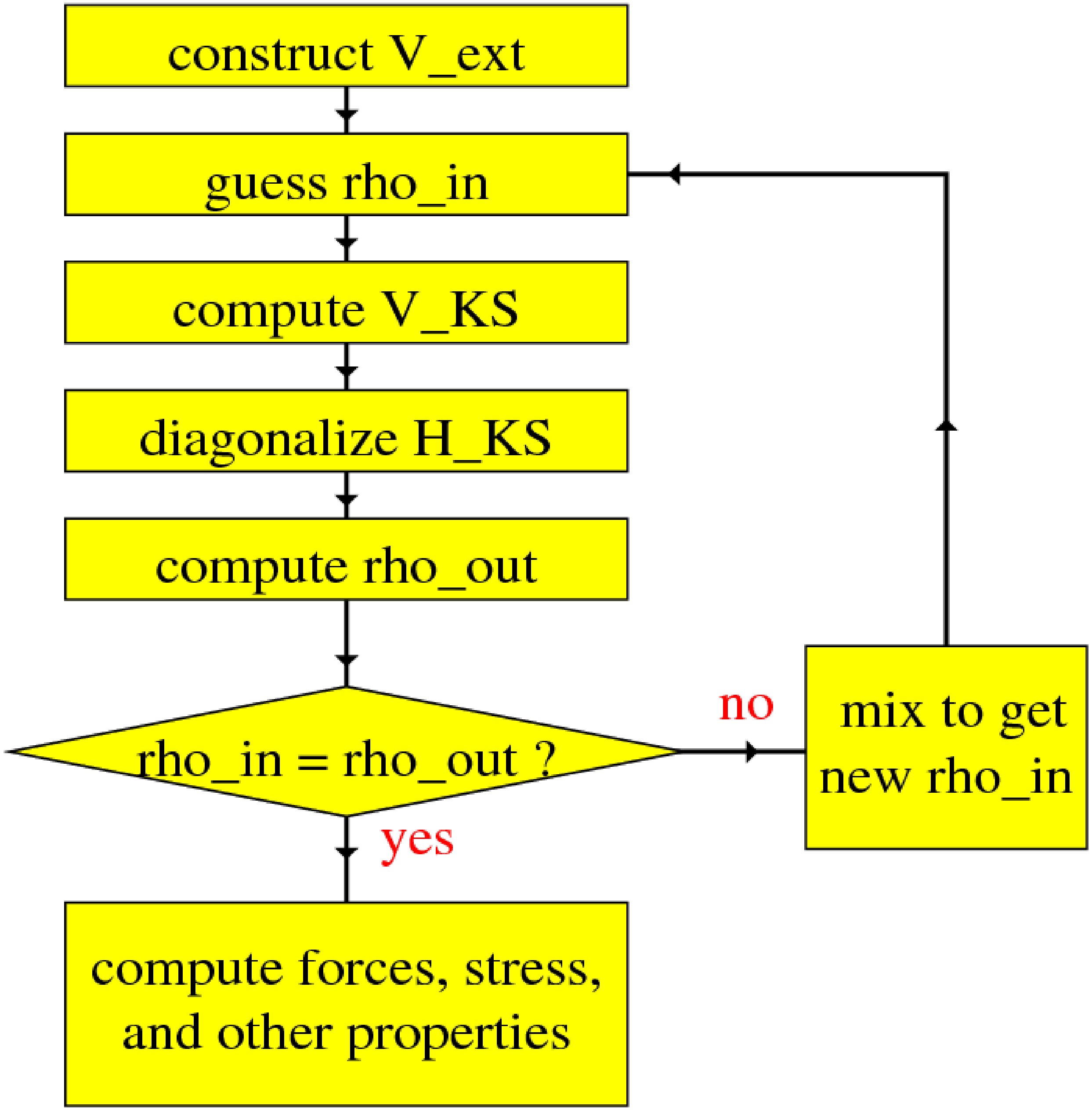
$$\begin{aligned} E_{el} = -\frac{\hbar^2}{2m}\sum_i \langle\varphi_i|\nabla^2|\varphi_i\rangle + \int V_{ext}(r)\rho(r)dr &+ \\ E_H[\rho] + E_{xc}[\rho] \end{aligned}$$

$$F_{el}^{I\alpha} = -\frac{\partial E_{el}}{\partial R_{I\alpha}} = -\int \frac{\partial V_{ext}(r)}{\partial R_{I\alpha}}\rho(r)dr$$

Structure of a self-consistent type code


construct V_ext

guess rho_in

compute V_KS

diagonalize H_KS

compute rho_out

rho_in = rho_out ?

no

mix to get new rho_in

yes

compute forces, stress, and other properties

DFT solution as global minimization problem

$$E_{el} = -\frac{\hbar^2}{2m}\sum_i \langle\varphi_i|\nabla^2|\varphi_i\rangle + \int V_{ext}(r)\rho(r)dr + E_H[\rho] + E_{xc}[\rho] - \sum_{i,j}\lambda_{ij}\left(\langle\varphi_i|\varphi_j\rangle - \delta_{ij}\right)$$

where $\rho(r) = \sum_i |\varphi_i(r)|^2$

DFT solution as global minimization problem

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$$+ E_H[\rho] + E_{xc}[\rho]$$
$$- \sum_{i,j} \lambda_{ij} \left(\langle \varphi_i | \varphi_j \rangle - \delta_{ij} \right)$$

where $\rho(r) = \sum_i |\varphi_i(r)|^2$

E_{el} *is minimized when*

$$0 = \frac{\partial E_{el}}{\partial \varphi_i^*(r)} = \left[-\frac{\hbar^2}{2m}\nabla^2 + V_{ext}(r) + V_H[\rho](r) + v_{xc}[\rho](r) \right] \varphi_i(r)$$
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the same as solving the KS eqs !

DFT solution as global minimization problem

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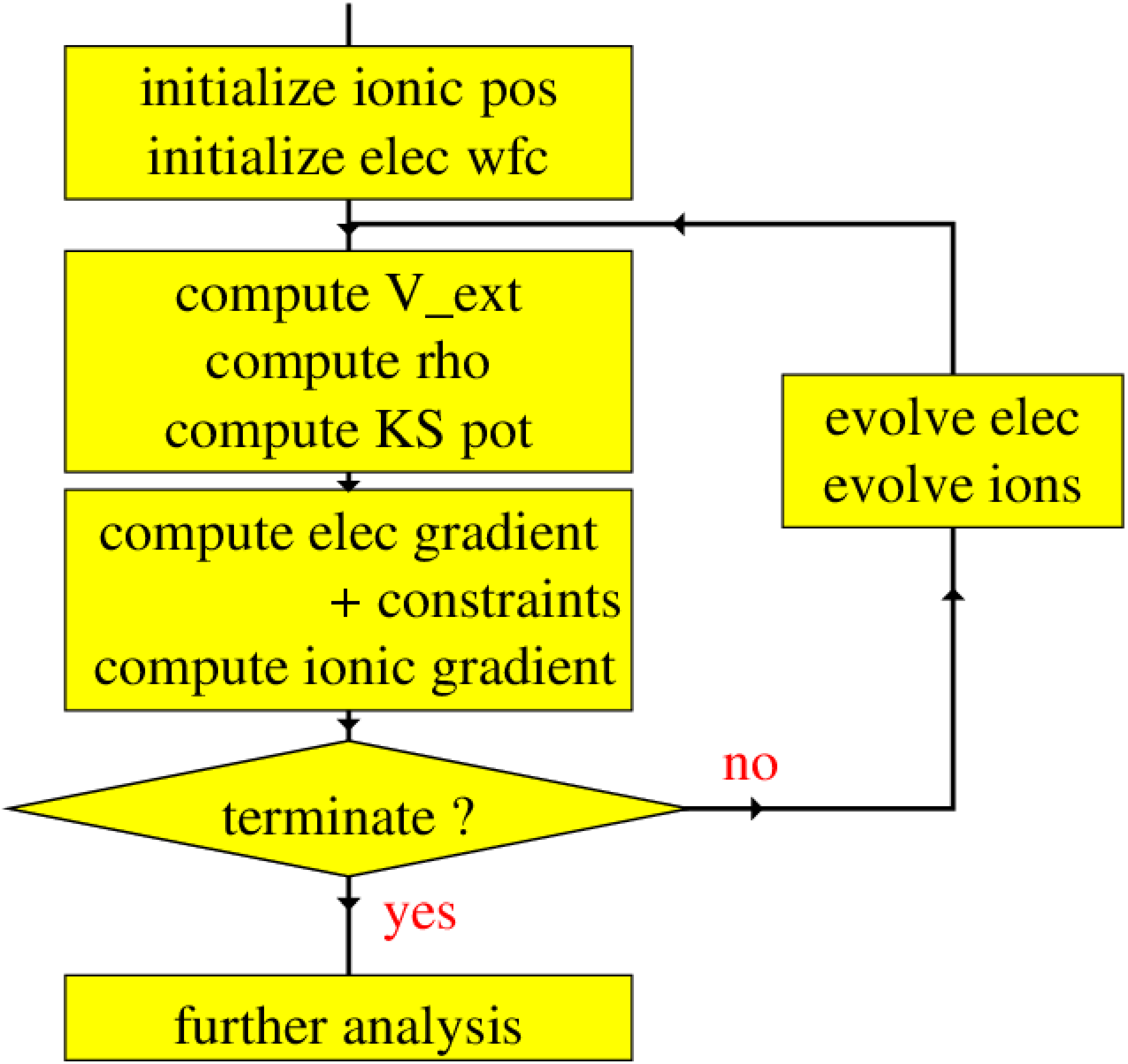
the same as solving the KS eqs !

ionic and electronic minimization can be done together

Structure of a global minimization code



initialize ionic pos
initialize elec wfc

compute V_ext
compute rho
compute KS pot

compute elec gradient
+ constraints
compute ionic gradient

terminate ?

no

evolve elec
evolve ions

yes

further analysis

The Building Blocks

Diagonalize the hamiltonian/Compute the gradient

Build the density

Calculate the KS potential

The Building Blocks

Diagonalize the hamiltonian/Compute the gradient

*needs an efficient computation of H*psi*

Build the density

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Build the density

needs an efficient BZ sampling and fast psi(r)

Calculate the KS potential

The Building Blocks

Diagonalize the hamiltonian/Compute the gradient

*needs an efficient computation of H*psi*

Build the density

needs an efficient BZ sampling and fast psi(r)

Calculate the KS potential

needs Poisson's solver and xc functionals

Initialization and termination

evaluation of the external potential

forces/stress and ionic evolution

The wfc and the KS hamiltonian in a PW basis set

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r)\right]\varphi_i(r) = \varepsilon_i\varphi_i(r)$$

The system is periodic: $V_{KS}(r+R) = V_{KS}(r)$

It is convenient to consider the Fourier transform

$$V_{KS}(r) = \sum_G V_{KS}(G)\exp(iGr)$$

$$\begin{aligned} V_{KS}(G) &= \frac{1}{\mathcal{V}}\int_{\mathcal{V}} V_{KS}(r)\exp(-iGr)dr \\ &= \frac{1}{\Omega}\int_{\Omega} V_{KS}(r)\exp(-iGr)dr \end{aligned}$$

$$\mathcal{V} = \mathcal{N}\Omega$$

The KS hamiltonian and the wfc in a PW basis set

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r)\right]\varphi_i(r) = \varepsilon_i \varphi_i(r)$$

thanks to Bloch theorem $i \rightarrow kv$

$$|\varphi_{kv}\rangle = \sum_{k+G} c^v_{k+G}\, |k+G\rangle$$

$$|k+G| < G_{max}$$

$$\varphi_{kv}(r) = \langle r|\varphi_{kv}\rangle = \sum_{k+G} c^v_{k+G}\, \langle r|k+G\rangle$$

$$= \sum_{k+G} c^v_{k+G}\, \frac{e^{i(k+G)r}}{\sqrt{\mathcal{V}}}$$

the KS eq. becomes a matrix eigenvalue problem

$$\sum_{k+G'} \langle k+G|H_{KS}|k+G'\rangle\, c^v_{k+G'} = \varepsilon_{kv}\, c^v_{k+G}$$

The KS hamiltonian and the wfc in a PW basis set

$$\sum_{k+G'} \langle k+G|H_{KS}|k+G'\rangle \; c^{v}_{k+G'} = \varepsilon_{kv} \; c^{v}_{k+G}$$

$$\langle k+G| -\frac{\hbar^2}{2m}\nabla^2|k+G'\rangle = \frac{\hbar^2}{2m}(k+G)^2 \; \delta_{GG'}$$

diagonal in reciprocal space

The KS hamiltonian and the wfc in a PW basis set

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diagonal in reciprocal spacec

$$\begin{aligned}
\langle k+G|V_{KS}(r)|k+G'\rangle \quad &= \frac{1}{\mathcal{V}}\int_{\mathcal{V}} V_{KS}(r) \;\; e^{-i(G-G')r} \; dr \\
&= \frac{1}{\Omega}\int_{\Omega} V_{KS}(r) \;\; e^{-i(G-G')r} \; dr \\
&= V_{KS}(G-G')
\end{aligned}$$

a local potential becomes a convolution
*as such its application to a vector would require N**2 ops*

The KS hamiltonian and the wfc in a PW basis set

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a local potential becomes a convolution

if $|k+G|, |k+G'| < G_{max}$ *then* $|G-G'| < 2G_{max}$

The Fast Fourier Transform and the dual space formalism

a uniform N point sampling in real space (1D)

$$x_j = \frac{j}{N}a, \quad j = 0, 1, 2, ..., N-1$$

describes exactly f(r) if its Fourier components are such that

$$G_k = k\frac{2\pi}{a}, \quad N/2 \leq k < N/2$$

Discrete Fast Fourier Transforms allow to go back and forth…

$$\tilde{f}(G_k) = \frac{1}{\Omega}\int_\Omega f(r)\exp(-iG_k r)dr = \frac{1}{N}\sum_j f(r_j)e^{-i2\pi\frac{jk}{N}}$$ fwfft

$$f(x_j) = \sum_k \tilde{f}(G_k)\exp(iG_k x_j) = \sum_k \tilde{f}(G_k)e^{i2\pi\frac{jk}{N}}$$ invfft

… in N log N operations

The Fast Fourier Transform and the dual space formalism

*H * psi can be computed very efficiently*

psi(r) = invfft[psi(k+G)]

vpsi(r) = v(r) * psi(r)

vpsi(k+G) = fwfft[vpsi(r)]

hpsi(k+G) = h2/2m (k+G)**2 * psi(k+G) + vpsi(k+G)

The result is exact if the FFT grid can describe Fourier components up to $2G_{max}$ *where psi is limited to* G_{max}

NB: *this is also the required grid to describe correctly the charge density (i.e. the square of the wavefunctions) and the Hartree potential.*

Exact diagonalization is expensive

find eigenvalues & eigenfunctions of H k+G,k+G’

Typically, NPW > 100 x number of atoms in unit cell.

Expensive to store H matrix: NPW^2 elements to be stored

Expensive (CPU time) to diagonalize matrix exactly, ~ NPW^3 operations required.

Note, NPW >> Nb = number of bands required = Ne/2 or a little more (for metals).

So ok to determine just lowest few eigenvalues.

How things scale with system size ?

N_{at}	number of atoms	Ω system volume $\propto N_{at}$
N_{elec}	number of electrons	$\propto N_{at}$
N_{band}	number of bands	$\approx N_{elec}$
N_{PW}	number of plane waves	$\propto \quad \Omega\, G_{max}^3, \qquad \Omega E_{cut}^{3/2}$
N_r	number of FFT grid points	$\approx 10 N_{PW}$
N_K	number of BZ k-points	$\propto \quad 1/\Omega$

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computational cost

1 Hpsi	$\propto N_{PW} + N_r \log N_r + N_r$
Iter. Diag.	$\propto N_{band}\, \texttt{Hpsi} + N^2_{band} N_{PW} + N^3_{band}$
new rho	$\propto N_K\, (N_r \log N_r + N_r)$
new pot	$\propto N_r \log N_r + N_r$

strongly dependent on N_{elec} *and* N_{PW} (E_{cut})

The external potential

Electrons experience experience a Coulomb potential due to the nuclei

This has a known simple form

$$V_{nuc} = -\frac{Z}{r}$$

But this leads to computational problems !

Problems for Plane-Wave basis

Core wavefunctions:
Sharply peaked close to nuclei due to deep Coulomb potential.

Valence wavefunctions:
Lots of wiggles near nuclei due to orthogonality to core wavefunctions

High Fourier component are present
i.e. large kinetic energy cutoff needed

$$r_{1s} \approx 1/Z \qquad Ecut \approx \left(\frac{2\pi}{r_{1s}}\right)^2 \approx 40Z^2$$

An analogy!

Use

PseudoPotentials

- cement agencies!
- ng as it works

- Obviously it can't reproduce all the functions of a real cop, but should be convincing enough to produce desired results….