

General Structure of a PW code

Self-Consistent KS eqs.

or

Global Minimization approach



## QUANTUM ESPRESSO

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25 May 2011 Version 4.3.1 of Quantum ESPRESSO is available for download.

**05 May 2011**

The first GPU-enabled beta release of Quantum ESPRESSO is available for download.

**01 April 2011**

The new release, v.4.3, of the Quantum ESPRESSO distribution is available for download.

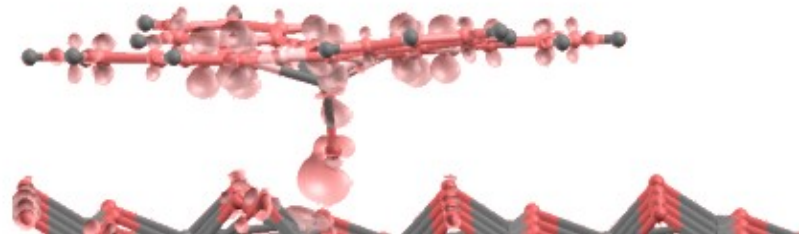
**13 July 2010**

Bugfix release v.4.2.1 of the Quantum ESPRESSO distribution is available for download.

**10 May 2010**

A new version, v.4.2, of the

Quantum ESPRESSO is an integrated suite of computer codes for electronic-structure calculations and materials modeling at the nanoscale. It is based on density-functional theory, plane waves, and pseudopotentials (both norm-conserving and ultrasoft).



<http://www.quantum-espresso.org/>



## KS self-consistent equations

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

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

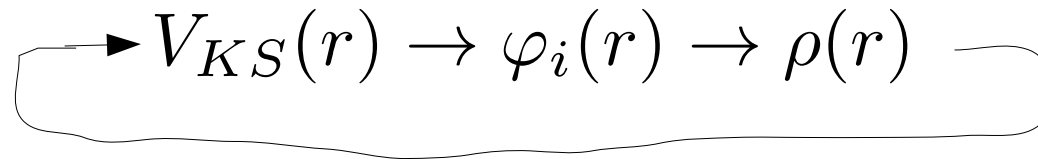
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$$\rightarrow V_{KS}(r) \rightarrow \varphi_i(r) \rightarrow \rho(r)$$

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

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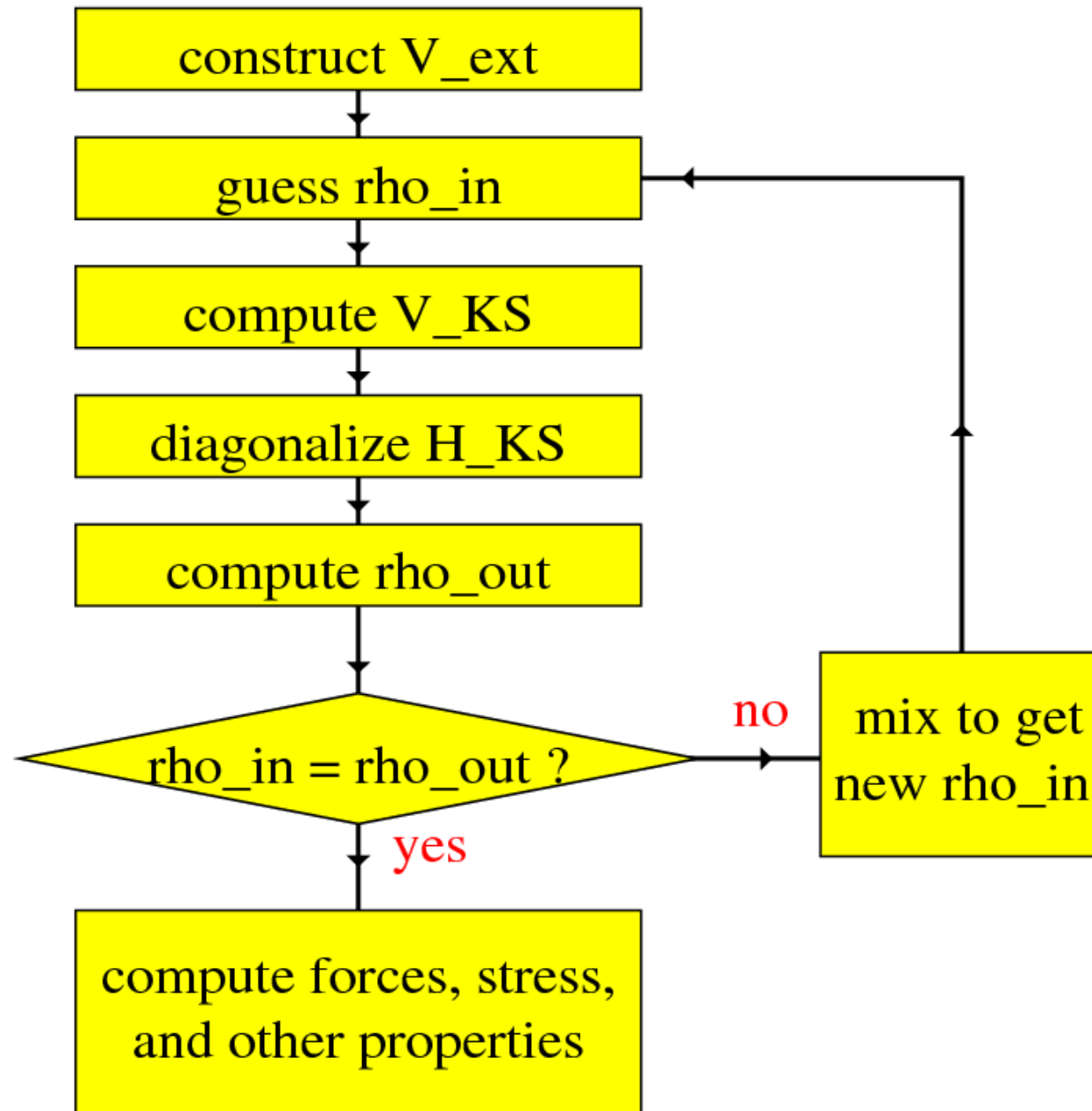
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$$F_{el}^{I\alpha} = -\frac{\partial E_{el}}{\partial R_{I\alpha}} = -\int \frac{\partial V_{ext}(r)}{\partial R_{I\alpha}} \rho(r) dr$$



# Structure of a self-consistent type code



## DFT solution as global minimization problem

$$E_{el} = -\frac{\hbar^2}{2m} \sum_i \langle \varphi_i | \nabla^2 | \varphi_i \rangle + \int V_{ext}(r) \rho(r) dr$$
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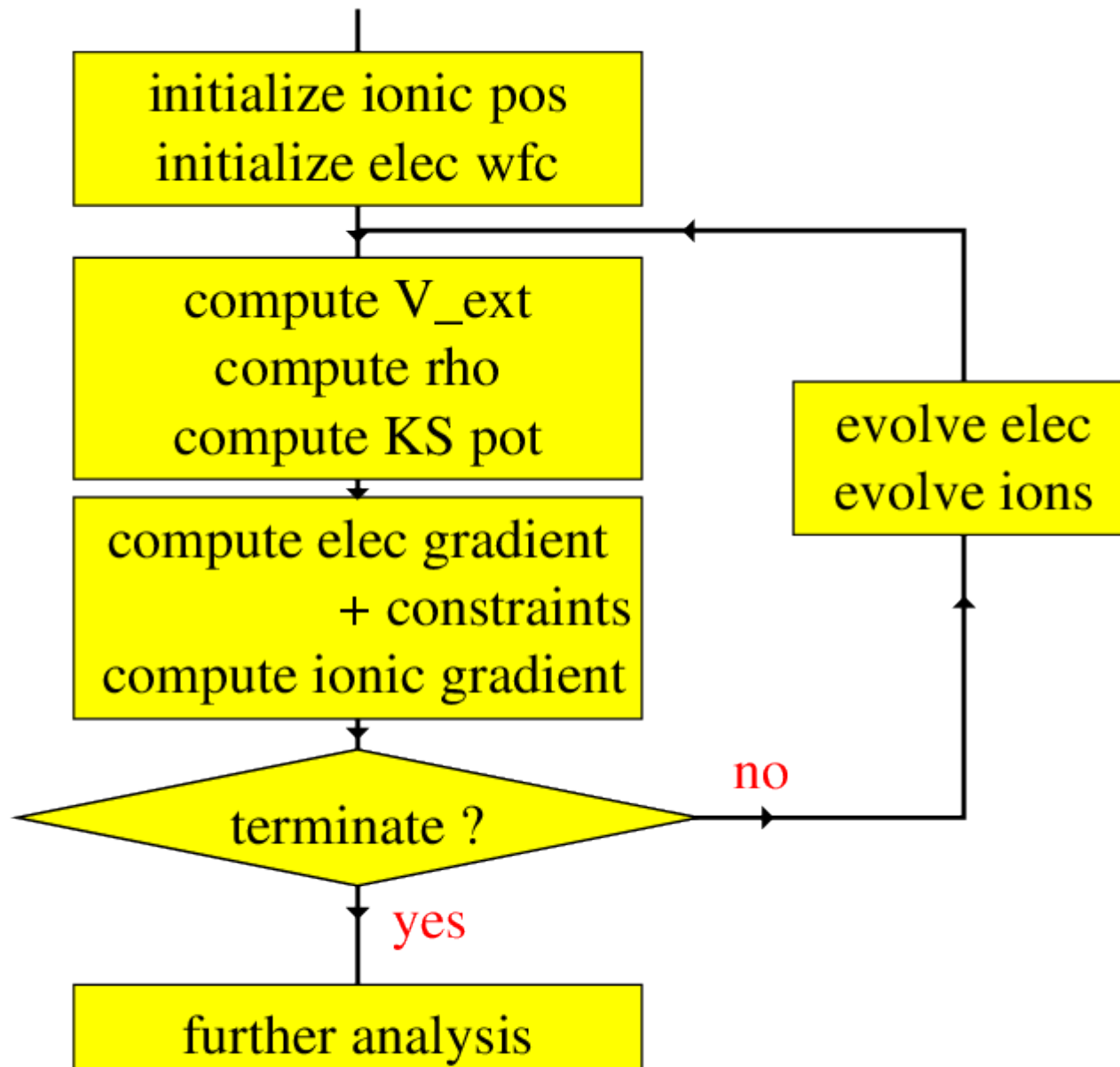
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the same as solving the KS eqs !

ionic and electronic minimization can be done together



# Structure of a global minimization code



# The Building Blocks

Diagonalize the hamiltonian/Compute the gradient

Build the density

Calculate the KS potential



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Diagonalize the hamiltonian/Compute the gradient

*needs an efficient computation of  $H^*\psi$*

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Diagonalize the hamiltonian/Compute the gradient

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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  $i \rightarrow kv$

$$|\varphi_{kv}\rangle = \sum_{k+G} c_{k+G}^v |k+G\rangle \quad |k+G| < G_{max}$$

$$\begin{aligned} \varphi_{kv}(r) = \langle r | \varphi_{kv} \rangle &= \sum_{k+G} c_{k+G}^v \langle r | k+G \rangle \\ &= \sum_{k+G} c_{k+G}^v \frac{e^{i(k+G)r}}{\sqrt{\mathcal{V}}} \end{aligned}$$

the KS eq. becomes a matrix eigenvalue problem

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



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*diagonal in reciprocal space*

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*diagonal in reciprocal space*

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

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



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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)*

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

*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..*

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

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

*... in  $N \log N$  operations*



# The Fast Fourier Transform and the dual space formalism

*$H * \psi$  can be computed very efficiently*

$$\psi(r) = \text{invfft}[\psi(k+G)]$$

$$v\psi(r) = v(r) * \psi(r)$$

$$v\psi(k+G) = \text{fwfft}[v\psi(r)]$$

$$h\psi(k+G) = \hbar^2/2m (k+G)^{**2} * \psi(k+G) + v\psi(r)$$

*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,  $NPW > 100 \times$  number of atoms in unit cell.

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

**Expensive (CPU time) to diagonalize** matrix exactly,  
 $\sim NPW^3$  operations required.

Note,  $NPW \gg Nb$  = number of bands required =  $N_e/2$   
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           | $\Omega$                    | 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     | $\propto \Omega G_{max}^3,$ | $\Omega E_{cut}^{3/2}$ |                  |
| $N_r$      | number of FFT grid points | $\approx 10N_{PW}$          |                        |                  |
| $N_K$      | number of BZ k-points     | $\propto 1/\Omega$          |                        |                  |

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### *computational cost*

|             |  |
|-------------|--|
| 1 Hpsi      | $\propto N_{PW} + N_r \log N_r + N_r$                        |
| Iter. Diag. | $\propto N_{band} N_{Hpsi} + N_{band}^2 N_{PW} + N_{band}^3$ |
| 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 a **Coulomb potential** due to the nuclei

This has a known simple form

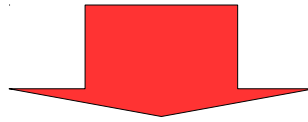
$$V_{nuc} = -\frac{Z}{r}$$

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

$$r_{1s} \approx 1/Z \quad E_{cut} \approx \left( \frac{2\pi}{r_{1s}} \right)^2 \approx 40Z^2$$

# An analogy!

- Use

- PseudoPotentials

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

placement agencies!

ng as it works

