

Quantum ESPRESSO

Guide to running simulations for DLS Spectroscopy

Joshua D Elliott

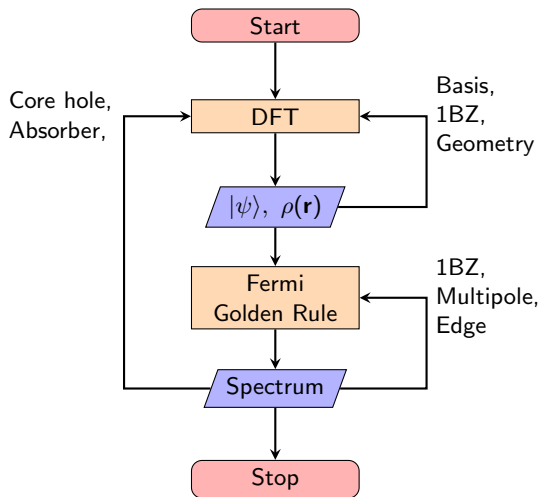
Diamond Light Source Ltd.

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Introduction

Quantum ESPRESSO

opEn Source Package for Research in Electronic Structure Simulations and Optimization



Open Source Software Package

Where to get help?

At Diamond:

Email: joshua.elliott@diamond.ac.uk; Office: 1.12 Z02 (Ring); Ext:

Email: mihai.duta@diamond.ac.uk (installation/compilation problems)

Online:

Web-site: www.quantum-espresso.org

Literature:

Journal of Physics: Condensed Matter 2009, 21 (39), 395502.

Journal of Physics: Condensed Matter 2017, 29 (46), 465901.

Journal of Chemical Physics 2020, 152 (15), 154105.

Source Code:

Doc folder under quantum espresso distribution

Mailing List:

Email: users@lists.quantum-espresso.org

Archive of questions/issues dating back to 2011.

Web-site: <https://www.mail-archive.com/users@lists.quantum-espresso.org/>

A Software Suite

Important: QE is not a single executable file, rather a collected distribution of several executable programs.

- PWscf** Ground state electronic structure, structural optimization.
- CP** Carr-Parrinello molecular dynamics.
- PHonon** Linear-response calculations.
- PostProc** Post processing, graphs and visualization.
- PWneb** Nudged-Elastic Band driver from reaction paths.
- atomic** Generation of pseudopotentials.
- PWGui** Graphical User Interface for input.
- PWcond** Ballistic conductance calculations.
- XSpectra** Core-level excitation spectra based on Fermi-Golden Rule.
- GWL** Quasiparticle and Exciton energies based on GW/BSE approximation.
- TD-DFPT** Time-dependent Density Functional Perturbation Theory.
- EPW** Electron-phonon coupling.
- HP** Automation of linear-response DFT+U parameters.

All these packages and others share: (i) installation method, (ii) input file format, (iii) pseudopotential file format, (iv) output format (v) source code.

Density Functional Theory - Theory

Quantum mechanics in terms of the electron density

The total energy of the ground state of a system of electrons may be written as a functional of the electron density.

$$E^{\text{DFT}}[n]; \quad \int n(\mathbf{r}) \, d\mathbf{r} = N; \quad n(\mathbf{r}) \geq 0 \quad (1)$$

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We can prove mathematically that the functional exists, but the form is unknown. Within Kohn-Sham formalism we write the functional:

$$E^{\text{DFT}}[n] = T_s[\{\psi_i\}] + E_{\text{ext}}[n] + E_{\text{Hartree}}[n] + E_{\text{xc}}[n] + E_{\text{ions}} \quad (2)$$

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$$n(\mathbf{r}) = \sum_i^M |\psi_i(\mathbf{r})|^2 \quad (3)$$

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These are used to approximate the kinetic energy

$$T_s[\{\psi_i\}] = -\frac{1}{2} \sum_i^N \int d\mathbf{r} \, \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) \quad (4)$$

Quantum mechanics in terms of the electron density

The other terms are functionals of the density:

$$E_{\text{ext}}[n] = \int d\mathbf{r} n(\mathbf{r}) V_{\text{ext}}(\mathbf{r}), \quad (5)$$

$$E_{\text{Hartree}}[n] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (6)$$

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The Ionic term is the pairwise interaction of the charged nuclei

$$E_{\text{ions}} = \sum_{I, J \neq I} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \quad (7)$$

There difficulty with the approach lies in the exchange-correlation energy, whose form remains unknown.

The Kohn-Sham Equations

Minimization of the functional derivative of E^{DFT} with respect to the density n gives

$$H^{\text{KS}}\psi_i(\mathbf{r}) = \left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \quad (8)$$

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$$V_{\text{Hartree}} = \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (9)$$

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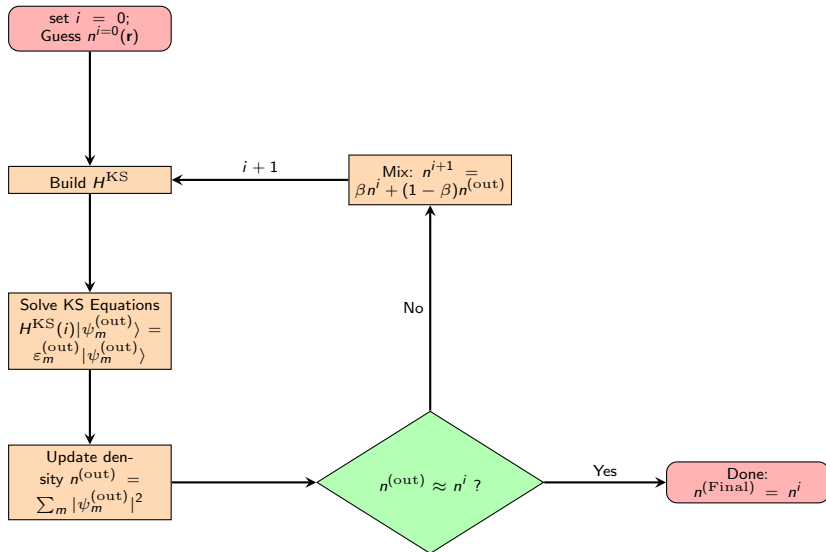
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The issue with the formalism is that the Hamiltonian depends explicitly on the orbitals and density.

The self-consistency cycle



The self-consistency cycle

```
02_Espresso -- scarf1097@cn1062 -- jnab23632/xspectrum/XSpectra-CONEXSw...
.../simulationGuides/02_Espresso -- ssh -- ssh -Y nab23632@uclscarf.ac.uk +
120 Initial potential from superposition of free atoms
121
122 starting charge 27.99999, renormalised to 32.00000
123 Starting wfcs are 64 randomized atomic wfcs
124
125 total cpu time spent up to now is 0.6 secs
126
127 Self-consistent Calculation
128
129 iteration # 1 ecut= 40.00 Ry beta= 0.30
130 Davidson diagonalization with overlap
131 ethr = 1.00E-02, avg # of iterations = 2.0
132
133 Threshold (ethr) on eigenvalues was too large:
134 Diagonalizing with lowered threshold
135
136 Davidson diagonalization with overlap
137 ethr = 4.54E-04, avg # of iterations = 1.0
138
139 total cpu time spent up to now is 0.9 secs
140
141 total energy = -91.08182670 Ry
142 Harris-Foulkes estimate = -91.08620067 Ry
143 estimated scf accuracy < 0.14661758 Ry
144
145 iteration # 2 ecut= 40.00 Ry beta= 0.30
146 Davidson diagonalization with overlap
147 ethr = 4.58E-04, avg # of iterations = 1.0
148
149 total cpu time spent up to now is 1.0 secs
150
151 total energy = -91.07558874 Ry
152 Harris-Foulkes estimate = -91.08299144 Ry
153 estimated scf accuracy < 0.06454221 Ry
154
155 iteration # 3 ecut= 40.00 Ry beta= 0.30
156 Davidson diagonalization with overlap
157 ethr = 2.02E-04, avg # of iterations = 1.0
158
159 total cpu time spent up to now is 1.1 secs
160
161 total energy = -91.07920271 Ry
162 Harris-Foulkes estimate = -91.07922257 Ry
163 estimated scf accuracy < 0.00076087 Ry
120,1 45%
```

The self-consistency cycle

```
O2_Espresso -- scarfi097@cn1052:~/nab23632/spectra/XSpectra-CONEXSW...
...ides/simulationGuides/O2_Espresso --ssh d--ssh -Y nab23632@uit.scarfi.ac.uk +
120 Initial potential from superposition of free atoms
121
122 starting charge 27.99999, renormalised to 32.00000
123 Starting wfcs are 64 randomized atomic wfcs
124
125 total cpu time spent up to now is 0.6 secs
126
127 Self-consistent Calculation
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164
165 120,1 45%
```

```
O2_Espresso -- scarfi097@cn1052:~/nab23632/spectra/XSpectra-CONEXSWorkshop2022...
...ONDisides/simulationGuides/O2_Espresso --ssh lamond --ssh -Y nab23632@uit.scarfi.ac.uk +
156 Davidson diagonalization with overlap
157 ethr = 2.02E-04, avg # of iterations = 1.0
158
159 total cpu time spent up to now is 1.1 secs
160
161 total energy = -91.07920271 Ry
162 Harris-Foulkes estimate = -91.07922257 Ry
163 estimated scf accuracy < 0.00076087 Ry
164
165 iteration # 4 ecut= 40.00 Ry beta= 0.30
166 Davidson diagonalization with overlap
167 ethr = 2.38E-06, avg # of iterations = 2.3
168
169 total cpu time spent up to now is 1.2 secs
170
171 total energy = -91.07935896 Ry
172 Harris-Foulkes estimate = -91.07939926 Ry
173 estimated scf accuracy < 0.00011744 Ry
174
175 iteration # 5 ecut= 40.00 Ry beta= 0.30
176 Davidson diagonalization with overlap
177 ethr = 3.67E-07, avg # of iterations = 2.0
178
179 total cpu time spent up to now is 1.3 secs
180
181 total energy = -91.07937378 Ry
182 Harris-Foulkes estimate = -91.07937444 Ry
183 estimated scf accuracy < 0.00000290 Ry
184
185 iteration # 6 ecut= 40.00 Ry beta= 0.30
186 Davidson diagonalization with overlap
187 ethr = 9.07E-09, avg # of iterations = 2.7
188
189 total cpu time spent up to now is 1.5 secs
190
191 End of self-consistent calculation
192
193 k = 0.0000 0.0000 0.0000 ( 1357 PWs) bands (ev):
194
195 -8.1117 0.6223 0.6225 0.6225 0.6227 0.6227 0.6227 7.0449
196 7.0449 7.0449 7.0451 7.0451 7.0451 13.3363 13.3363 13.3363
197
198 k = 0.0000 0.0000 0.2500 ( 1298 PWs) bands (ev):
199
200 156,1 58%
```

The Basis Set

Introduction to basis sets (General)

$$\psi_i(\mathbf{r}) = \sum_{\alpha}^M c_{\alpha} \phi_{\alpha}(\mathbf{r}) \quad (11)$$

$\psi_i(\mathbf{r})$: The function that we want to represent (KS wfn)

$\phi_{\alpha}(\mathbf{r})$: The set of basis functions

- Predefined (known) functions
- Determine choice of code

M : The size of the basis set

C_{α} : Expansion Coefficients

- Information stored on the computer
- Want to keep M as small as possible
- More C_{α} means more complete basis set (more transferable)