CRYSCOR09

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Quick Start Manual

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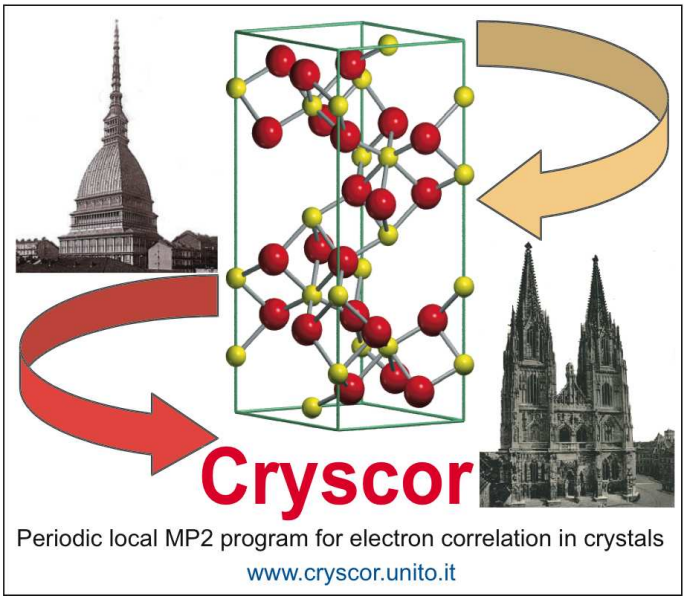

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1.1 Introduction

CRYSCOR is a **post-Hartree-Fock** (HF) **local**-correlation program for periodic systems. Since the reference HF solution is provided by the CRYSTAL code, it can be considered as the post-HF option of it.

The post-HF method currently implemented is a perturbative method, namely Møller-Plesset at the second-order (**MP2**), reformulated within the so-called *local approach*. Well localized, symmetry adapted Wannier Functions (WF) are adopted instead of delocalized Bloch functions for the description of the occupied manifold; this permits the exploitation of the **short-range** nature ($E \propto r^{-6}$) of electron correlation following the general Pulay scheme as implemented in the molecular MOLPRO code. Its generalization to periodic 1-3D systems requires the full exploitation of both point and translational symmetry.

For the time being, the CRYSCOR program can compute the MP2 correction to both the HF energy and HF one-electron Density Matrix of the ground state of the system.

Note that the localization procedure and the MP2 technique are not suitable for conducting systems or for semiconductors with very small band gaps.

This is a Quick Start Manual; for a detailed description of the functionality of the program, please refer to the extended version of the CRYSCOR *User's Manual* and website (www.cryscor.unito.it).

1.2 How to run a CRYSCOR job

To execute a CRYSCOR job, you have to run two preliminary calculations. The first one is a CRYSTAL calculation, performed at HF level which is the default option; from this run, together with the output file (*filename1.out*), you get the unformatted external unit 9 (*fort.9*) which contains information about the geometry, symmetry, computed wavefunction, Fock and Density matrices. As a second step you have to run a PROPERTIES calculation for transforming the canonical Crystalline Orbitals into localized Wannier Functions (WF); in order to do that, you need feeding the *fort.9* unit to PROPERTIES. This second run generates the unformatted external unit 80 (*fort.80*). A CRYSCOR run needs both units 9 and 80. For more details about how to run a CRYSTAL calculation please refer to *Crystal User's Manual* and to CRYSTAL web page: www.crystal.unito.it.

On Unix systems, the CRYSTAL, PROPERTIES and CRYSCOR executables (to be placed in the same directory) can be called via the standard scripts (written for the

Program	input file	output file	unit saved
CRYSTAL	.d12	.out	.f9
PROPERTIES	.d3	.outp	.f80
CRYSCOR	.d4	.outc	

Table 1.1: A summary of the extensions of input/output files and external units.

`csh` shell type): **runcry09**, **runprop09** and **runcryscor09**. A common sequence of commands is schematized in what follows:

A. **runcry09** *filename1*
The input file *filename1.d12* must be there; this script launches the CRYSTAL calculation and automatically saves in your working directory both the output file *filename1.out* and the unit 9 as *filename1.f9*.

B. **runprop09** *filename2 filename1*
Both the PROPERTIES input file (*filename2.d3*, see the **LOCALWF** keyword of the CRYSTAL Manual) and the unit 9 (*filename1.f9*) must be there. This script saves the output file (*filename2.outp*) and the unit 80 as *filename2.f80*; this unit contains information about the localized and symmetrized WFs.

C. **runcryscor09** *filename3 filename1 filename2*
Each CRYSCOR run needs an input file (*filename3.d4*), and the external units 9 and 80 (*filename1.f9* and *filename2.f80*). This script generates the output file *filename3.outc* [and on request some external units that can be useful for later calculations].

1.2.1 The HF reference solution

In order to obtain the HF reference solution, a CRYSTAL calculation has to be performed. The user is addressed to the *Crystal User's Manual* for any detail concerning this preliminary step.

The only thing we want to stress here is that the effect on the quality of the HF solution (wavefunction) of the tolerances (governed by the **TOLINTEG** keyword) which control the computation of the integrals in the HF calculation, was found to be far from negligible also in the case they do not affect very much the HF total energy of the system. For this reason we recommend the use of the **TOLMP2** keyword for an optimal setup of such tolerances.

1.2.2 The localization step

A PROPERTIES input file (with extension *.d3*, see Table 1.1) has to be prepared in order to obtain well localized and symmetry adapted WFs. The definition of WFs is controlled by an input block, opened by the **LOCALWF** keyword and containing a set of keywords, as explained in the *Crystal User's Manual*; a strongly recommended keyword among them is **VALENCE** which activates the localization procedure for valence orbitals only. The subsequent CRYSCOR run will be a valence-electron correlation calculation. As a common practice, the shrinking factor used for the localization is twice the one adopted for the HF calculation.

The *a posteriori* symmetrization procedure, mandatory in the case of a subsequent MP2 calculation with CRYSCOR, is activated by means of the **SYMMWF** keyword. A typical input file for the localization/symmetrization procedure looks like that:

`NEWK`	Diagonalization of the Fock matrix
`8 8 8`	Shrinking factor
`1 0`	Fermi energy is computed
`LOCALWF`	Start of the localization input block
`VALENCE`	Only valence orbitals are localized
`SYMMWF`	Start of the symmetrization input block
`END`	End of the symmetrization input block
`END`	End of the localization input block
`END`	End of the properties input block

Table 1.2: The simplest possible localization input.

1.2.3 The MP2 calculation

The CRYSCOR input consists of a series of keywords (KW) possibly followed by the respective arguments, to be written in separate cards in free format. The order in which the KWs have to be inserted in the input file is practically free, but some conditions must be respected:

1. **KNET** must be the first keyword;
2. **MEMORY** must be the second keyword;
3. One of the KWs aimed at the definition of excitation domains has to be inserted (**DOMPUL/DOMMOL/DOMDEF**);

4. The use of the **DFITTING** keyword which activates the Density Fitting approximation for the computation of the bi-electronic integrals is *strongly recommended*, although not mandatory since in principle one could solve these integrals exactly.

5. **END** must be the last keyword of the input.

The whole set of keyword of CRYSCOR which can be entered in the input file by the user, is reported in the extended version of the Manual (*User's Manual*). The simplest possible CRYSCOR input file looks as follows (Table 1.3):

`KNET`	Construction of the HF Density Matrix
`12`	Shrinking factor
`MEMORY`	Memory required
`2500`	Value in Mbytes
`DOMPUL`	Definition of the excitation domains
`0.98`	T^{BP} parameter
`DFITTING`	Density Fitting input block
`DIRECT`	Direct-space technique
`PG-VTZ`	DF auxiliary basis set
`ENDDF`	End Density Fitting input block
`END`	End of CRYSCOR input

Table 1.3: The simplest possible CRYSCOR input. In this way many default values are used.

The **KNET** keyword defines the shrinking factor that has to be used in the reconstruction of the HF Density Matrix; the **MEMORY** keyword defines the amount of memory available to the program. Through the **DOMPUL** keyword, the excitation domains to be associated to each WF are defined according to a Mulliken population analysis. The **DFITTING** input block switches on the Density Fitting approximation in the computation of some two-electron integrals.

1.3 Possible sources of mistakes

In this section we report a brief list of possible sources of errors or mistakes (a richer list is reported in the reference *User's Manual*):

- The quality of the MP2 correction to the HF energy and density matrix is affected by the quality of the reference HF solution. In this respect, some

truncations introduced at HF level (governed by the **TOLINTEG** keyword) are very important. Please, keep in mind the **TOLMP2** keyword.

- When a binding energy $\Delta E = E(A+B) - [E(A) + E(B)]$ has to be computed, attention must be paid on the consistency of the size and shape of the excitation domains in the different calculations involved.

- The same attention as that of the previous item has to be paid when evaluating the BSSE (Basis Set Superposition Error) through the *counterpoise correction*.

Enjoy CRYSCOR!