

# User Manual

# CP2K

A program package to perform  
Molecular Dynamics Simulations

The CP2K developers group

CP2K program release 1.0

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## Disclaimer

Please note that this manual is not complete. Basically it refers to the CP2K program release 1.0, but the CP2K program package is continuously improved and extended. Therefore the ultimate reference is always the CP2K source code.

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CP2K: A program package to perform molecular dynamics simulations

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# 1 Introduction

The CP2K project was started in 2000 at the Max-Planck institute for solid state research in Stuttgart. Now it is continued at the ETH Zurich (CSCS) and at the University Zurich. The current members of the CP2K developers group are

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## 2 Installation

You can download the current version of the CP2K code from

`http://developer.berlios.de/project/?group\_id=129`

using CVS or FTP which also allow to update your current CP2K version. Alternatively, you can directly download the full CP2K tarball which you have to uncompress with

```
$ gunzip cp2k.tar.gz
```

Then extract the archive file with

```
$ tar -xvf cp2k.tar
```

In order to generate an executable change to the directory with the makefile

```
$ cd cp2k/makefiles
```

and run GNU make which is on LINUX systems simply make

```
$ make
```

The default make will create a serial optimized (sopt) executable which is equivalent to  
`make sopt`

Other choices are

```
$ make sdbg (serial executable for debugging)
```

```
$ make pdbg (parallel executable for debugging)
```

```
$ make popt (optimized parallel executable)
```

You can remove all the stuff generated by make with

```
$ make distclean
```

If you want to remove only one version completely use e.g.

```
$ make sopt/realclean
```

or

```
$ make sopt/clean
```

to get rid of the object files only. After a successful compilation you may find the corresponding executable in the directory

```
cp2k/exe/⟨architecture name⟩
```

There are some test inputs in the directory

```
cp2k/tests
```

and the next section describes how to run the example inputs.

## 3 Running CP2K

The CP2K program is started with the command

```
$ cp2k.sopt <input file> ><output file>
```

The start command for the parallel CP2K version depends on the parallel execution environment of the underlying architecture, e.g. with LINUX/MPICH you may start 4 processes with

```
$ mpirun -np 4 cp2k.popt <input file> ><output file>
```

whereas on IBMs (AIX) you have to type something like

```
$ poe cp2k.popt <input file> -procs 4 ><output file>
```

### 3.1 Input files

The methods implemented in CP2K may require different additional input files.

#### 3.1.1 Fist

#### 3.1.2 Quickstep

- Potential file (default name: POTENTIAL)
- Basis set file (default name: BASIS\_SET)

The Gaussian basis set format and all the atomic potential formats are explained in the corresponding default database files.

## 4 Input description

### 4.1 General rules

- **Warning:** Do not expect the input to be logic. The programmers logic may be different from yours.
- **Warning:** This input description may not refer to the actual version of the program you are using. Therefore the ultimate and authoritative input guide is the source code.
- The input is free format and is not case sensitive except where especially stated.
- Empty lines and white spaces at the beginning of a line are ignored.
- All characters in a line following the comment character are ignored. The default comment character is #.
- The CP2K input file is divided into input sections which are started and terminated with the section keywords listed below.
- Each section keyword starts with the section character. The default section character is &.
- The order of the keywords inside an input section is arbitrary except where especially stated.
- For some keywords there are one or even more alias names which are given below as a comma-separated list.
- Lists enclosed in { } imply that you have to choose **exactly one** of the items.
- Lists enclosed in [ ] imply that you can choose **any number** of items (optional keywords).
- There are several possibilities to define a floating point number  $\langle \text{real} \rangle$ , e.g. 0.05, 5.0E-2, 5.e-2, 1/20, or 50/1000. Also the specification of an integer number  $\langle \text{integer} \rangle$  is allowed where a floating point number  $\langle \text{real} \rangle$  is requested, but not vice versa.
- Strings  $\langle \text{string} \rangle$  with special characters like blanks have to be delimited by " ".

### 4.2 Section &CP2K ...&END

The global CP2K section.

#### 4.2.1 Required keywords

PROGRAM {FIST, QUICKSTEP}

Defines the methods which is used for the calculation.



### 4.2.2 Optional keywords

FFTLIB {FFTESSL, FFTSG, FFTSGI, FFTW}

Defines the library which is used for the Fast Fourier Transformations (FFT). The availability of the libraries depends on the architecture and/or installation, but at least the FFTSG library is available which is included in the CP2K distribution.

default: FFTSG

IOLEVEL {<integer>}

Global print level. See also input section &PRINT.

default: 0

PP\_LIBRARY\_PATH {<path name>}

Path to the directory with the pseudo potential database files.

Default: <the current working directory>

PROJECT {<string>}

Name of the actual project.

default: project

## 4.3 Section &IO ...&END

In this section the names of input and/or output files can be modified.

BASIS\_SET\_FILE {<file name>}

Name of the Gaussian basis set database file.

default: BASIS\_SET

POTENTIAL\_FILE {<file name>}

Name of the potential database file.

default: POTENTIAL

RESTART\_FILE {<file name>}

Name of the restart file.

default: RESTART

## 4.4 Section &CELL ...&END

This section is always needed to define the simulation cell.

### 4.4.1 Required keywords

ABC {<real> <real> <real>}

Lengths of the vectors **a**, **b**, and **c** which define the orthorhombic simulation cell. The unit of length is defined by the keyword UNIT.

#### 4.4.2 Optional keywords

UNIT {ANGSTROM, BOHR, SCALED\_ANGSTROM, SCALED\_BOHR}

Defines the unit of length for the simulation cell and it also applies to the definition of the atomic coordinates in the input section &COORD. Moreover, all lengths and distances in the output are printed using this unit.

default: BOHR

### 4.5 Section &COORD ...&END

Each non-empty input line in this section defines an atom of the considered system. The first entry in each line has to correspond to an atomic kind name defined by a &KIND section which can be a  $\langle \text{string} \rangle$  or an  $\langle \text{integer} \rangle$  number. The kind name has to follow a set of three  $\langle \text{real} \rangle$  numbers defining the  $x$ ,  $y$ , and  $z$  coordinates of the atom.

### 4.6 Section &KIND ...&END

This section has to be defined for each atomic kind in a QUICKSTEP run. The name of the kind has to be defined right after the &KIND section keyword on the same input line. The kind name is referenced by the &COORD section. Alternatively, the atomic number of the kind can be defined as an integer number, e.g.

```
&KIND 6
```

for carbon which is equivalent to

```
&KIND C
```

In general, any  $\langle \text{string} \rangle$  can be defined for an atomic kind

```
&KIND  $\langle \text{string} \rangle$ 
```

which allows to define different atomic kinds for the same element e.g. carbon with different orbital basis sets

```
&KIND C-DZVP
```

```
&KIND C-TZVP
```

One or more &KIND sections are required for a QUICKSTEP run.

#### 4.6.1 Required keywords

ORBITAL\_BASIS\_SET, BASIS\_SET, BAS { $\langle \text{string} \rangle$ }

Name of the Gaussian orbital basis set which has to be read from the Gaussian basis set database file (see section &IO).

POTENTIAL, POT { $\langle \text{string} \rangle$ }

Name of the atomic potential which has to be read from the potential database file (see section &IO).

### 4.6.2 Optional keywords

ELEMENT\_SYMBOL, ELEMENT {<string>}

Defines the element to which the atomic kind belongs.

ATOMIC\_MASS, MASS {<real>}

Defines an atomic mass different from the default atomic mass, e.g. for the definition of isotopes.

PAO\_MIN\_BAS {list of <integer>}

Definition of the projected atomic orbital (PAO) basis. Indices of the PAOs with respect to the full basis set.

## 4.7 Section &DFT ... &END

In this section the configuration of a density functional calculation (DFT) can be modified.

EXCHANGE-CORRELATION-FUNCTIONAL, XC-FUNCTIONAL, FUNCTIONAL  
{BLYP, BP86, LDA, PADE, PBE, NONE}

Name of the requested exchange-correlation functional for a density functional calculation.

default: PADE

EXCHANGE-FUNCTIONAL, X-FUNCTIONAL {B88, SLATER, NONE}

Name of the requested exchange functional.

default: NONE

CORRELATION-FUNCTIONAL, C-FUNCTIONAL {LYP, P86, NONE}

Name of the requested correlation functional.

default: PADE

KINETIC-ENERGY-FUNCTIONAL, KE-FUNCTIONAL {NONE}

Name of the requested kinetic energy functional.

default: NONE

DENSITY\_CUTOFF {<real>}

Cutoff for the calculation of the density.

default: 1.0E-10

GRADIENT\_CUTOFF {<real>}

Cutoff for the calculation of the gradients.

default: 1.0E-8

GRID {CUTOFF, MESH, PLANE\_WAVES}

Definition of the integration grid.

CUTOFF {<real>}

Definition of the plane waves cutoff.

MESH {⟨integer⟩ ⟨integer⟩ ⟨integer⟩}  
 Explicit definition of the grid size.

PLANE\_WAVES , PW  
 default

FORCES  
 The calculation of the forces is requested.  
 default: no force calculation

CHARGE {⟨integer⟩}  
 The total charge of the system.  
 default: 0

## 4.8 Section &QS ...&END

Program parameters QUICKSTEP

CUTOFF {⟨real⟩}  
 Plane waves cutoff of the largest grid in Rydberg.  
 default: 320

EPS\_DEFAULT {⟨real⟩}  
 Defines a default threshold value. All threshold values of QUICKSTEP are set to this value.

EPS\_CORE\_CHARGE {⟨real⟩}  
 Threshold value for the interaction range of the atomic core charge distributions.  
 default: 1.0E-12

EPS\_GVG\_RSPACE , EPS\_GVG {⟨real⟩}  
 Threshold value for the integration of the Hartree potential on the real space grid.  
 default: 1.0E-6

EPS\_PGF\_ORB {⟨real⟩}  
 Threshold value for interaction range of the primitive Gaussian-type orbital functions.  
 default: 1.0E-6

EPS\_PPL {⟨real⟩}  
 Threshold value for the interaction range of the local part of the GTH pseudo potential.  
 default: 1.0E-12

EPS\_PPNL {⟨real⟩}  
 Threshold value for the interaction range of the non-local part of the GTH pseudo potential.  
 default: 1.0E-12

EPS\_RHO {⟨real⟩}  
 Threshold values for EPS\_RHO\_GSPACE and EPS\_RHO\_GSPACE.  
 default: 1.0E-8

EPS\_RHO\_GSPACE {<real>}

Threshold value for the calculation of the electronic charge density in Fourier space.  
default: 1.0E-8

EPS\_RHO\_RSPACE {<real>}

Threshold value for the calculation of the electronic charge density in real space.  
default: 1.0E-8

PROGRESSION\_FACTOR, PROFAC {<real>}

Progression factor for the generation of the multi-grid levels.  
default: 2.0

RELATIVE\_CUTOFF, REL\_CUTOFF {<real>}

Relative plane waves cutoff for each multi-grid level. Values less than 20.0 give inaccurate results and values greater than 30.0 are used for reference calculations (save).  
default: 25.0

METHOD {GPW}

Method used by QUICKSTEP. GAPW is not available yet.  
default: GPW

MULTI\_GRID {list of <integer>}

The plane waves cutoffs for each multi grid level in Rydberg. The number of grid levels is defined by the keyword NGRID\_LEVEL.

NGRID\_LEVEL, NGRID {<integer>}

Number of the multi-grid levels.  
default: 4

PAO

Use the projected atomic orbital (PAO) method.  
default: no PAO

## 4.9 Section &SCF...&END

This section defines the parameters for the configuration of the self consistent field (SCF) procedure which is used for the wavefunction optimization.

ARPACK\_ON

The ARPACK eigensolver is used in a parallel run which requires a proper installation of the ARPACK library.  
default: no ARPACK usage

CHOLESKY\_ON, CHOLESKY\_OFF

Decides whether the Cholesky decomposition is used in the eigensolver or not.  
default: CHOLESKY\_ON

DENSITY\_GUESS, SCF\_GUESS, GUESS {ATOMIC, CORE, RESTART}

Defines the type of guess which is employed to generate the first density matrix. For RESTART a valid restart has to be supplied.

default: ATOMIC

OT

An orbital transformation approach instead of a diagonalization is used for the wavefunction optimization during the SCF iteration procedure.

DENSITY\_MIXING, MIXING {<real>}

Factor for the mixing of the old and new density matrix during the wavefunction optimization.

default: 0.4 (i.e. 40% of the new and 60% of the old density are used)

EPS\_DIIS {<real>}

The DIIS procedure is switched on, if the maximum DIIS error vector element is below this threshold value.

default: 0.1

EPS\_EIGVAL {<real>}

Threshold value for eigenvector quenching when  $S^{-1/2}$  is used as the orthogonalization matrix in the eigensolver.

default: 1.0E-5

EPS\_SCF {<real>}

SCF convergence criterion, i.e. the maximum difference between the corresponding density matrix elements of two consecutive SCF iteration steps.

default: 1.0E-5

LEVEL\_SHIFT {<real>}

Shift value for the unoccupied (virtual) molecular orbitals (MOs) in atomic units.

default: 0.0

MAX\_DIIS {<integer>}

Maximum size of the SCF DIIS buffer.

default: 0

MAX\_SCF {<integer>}

Maximum number of SCF iteration steps.

default: 30

NREBUILD {<integer>}

Number of SCF steps between two full calculations of the electronic charge density.

default: 1

SMEAR {<real>}

Window size in atomic units with respect to the eigenvalue of the highest occupied molecular orbital (HOMO) for the smearing of the occupation numbers.

default: 0.0

WORK\_SYEVX {<real>}

Defines the amount of additional work space for the PDSYEVX routine from the SCALAPACK library. A value between 0.0 and 1.0 is accepted. (only for parallel runs using SCALAPACK and an eigensolver with diagonalization.

default: 0.0

## 4.10 Section &PRINT ... &END

This sections allows for detailed output control when running QUICKSTEP. There are 5 predefined print levels: 0, 1, 2, 3, and 4 which correspond to the keywords NO, LOW, MEDIUM, HIGH, and DEBUG or FULL. The print level has to be defined right after the &PRINT section keyword on the same input line, e.g.

&PRINT LOW

which is equivalent to

&PRINT 1

The following keywords may be used based on the selected print level to requested an additional output or to suppress an output selectively by using the prefix NO\_ for the keyword, e.g. at print level LOW the atomic coordinates are listed in the output which may be inconvenient for large sytems, thus simply request NO\_COORDINATES in the &PRINT section. The default print level is LOW.

ANGLES

Print the angles between all atom triples in the simulation cell.

**Warning:** That is much output for large systems.

ATOMIC\_COORDINATES , COORDINATES , COORD

Print all atomic coordinates together with the some atomic kind information.

BASIC\_DATA\_TYPES

Print informations about the basic data types like REAL, INTEGER, or LOGICAL.

BASIS\_SETS , BASIS\_SET , BASIS

Print the Gaussian basis set information, i.e. all Gaussian function exponents and the corresponding contraction coefficients as read from the Gaussian basis set database file. Furthermore, the normalized contraction coefficients are printed.

BLACS\_INFO

Print the process grid information of BLACS (Basic linear algebra subprograms)

CARTESIAN\_MATRICES

Print all operator matrices in the Cartesian instead of the spherical representation.

CELL\_PARAMETERS , CELL

Print the simulation cell data like the cell vectors, cell volume etc.

CORE\_HAMILTONIAN\_MATRIX , H\_MATRIX

Print the core Hamiltonian matrix.

CORE\_CHARGE\_RADII , CORE\_RADII

Print the radius of the core charge distribution for each atomic kind.

DENSITY\_MATRIX , P\_MATRIX

Print the density matrix.

DERIVATIVES

Print the first derivatives of the operator matrices.

DFT\_CONTROL\_PARAMETERS

Print the DFT control parameters as defined in the &DFT section.

DIIS\_INFORMATION

Print information about the SCF DIIS procedure.

DISTRIBUTION

Print the distribution and the sparsity of the overlap matrix (only parallel version).

EACH\_SCF\_STEP

Print the requested energies, densities, or matrices for each SCF iteration step.

E\_DENSITY\_CUBE

Print the electronic charge density as a cube file.

FORCES

Print the atomic force contributions for all atoms.

HOMO

Print the highest occupied molecular orbital (HOMO) as a cube file.

INTERATOMIC\_DISTANCES , DISTANCES

Print a matrix with the interatomic distances.

**Warning:** That is much output for large systems.

KIND\_RADII

Print the maximum interaction radius of each atomic kind.

KINETIC\_ENERGY\_MATRIX , T\_MATRIX

Print the kinetic energy integral matrix.

KOHN\_SHAM\_MATRIX

Print the Kohn-Sham matrix.

LUMO

Print the lowest unoccupied molecular orbital (LUMO) as a cube file.

MEMORY

Print informations about the memory usage of the CP2K program.

MO\_EIGENVALUES

Print the eigenvalues of the molecular orbitals (MOs).



MO\_EIGENVECTORS , MOS

Print the eigenvectors, eigenvalues, and the occupation numbers of the molecular orbitals (MOs).

MO\_OCCUPATION\_NUMBERS

Print the occupation numbers and the eigenvalues of the molecular orbitals (MOs).

NEIGHBOR\_LISTS

Print all neighbor lists.

**Warning:** That is much output for large systems.

ORTHO\_MATRIX

Print the orthogonalisation matrix used to transform the Kohn-Sham matrix.

OVERLAP\_MATRIX

Print the overlap matrix.

PGF\_RADII

Print the interaction radii of all primitive Gaussian-type functions.

PHYSICAL\_CONSTANTS , PHYSCON

Print the values of all physical constants used in the program.

POTENTIALS

Print a detailed atomic potential information for each atomic kind.

PPL\_RADII

Print the interaction radii of the local part of the Goedecker-Teter-Hutter (GTH) pseudo potential [1, 2].

PPNL\_RADII

Print the interaction radii of the non-local projector functions of the Goedecker-Teter-Hutter (GTH) pseudo potential [1, 2].

PROGRAM\_BANNER

Print a program banner.

PROGRAM\_RUN\_INFORMATION

Print informations about the current program run.

PW\_GRID\_INFORMATION

Print detailed informations about the used plane waves grid.

RADII

Print all interaction radii for each atomic kinds.

SCF

Print the SCF iteration.

**SCF\_ENERGIES**

Print all contributions to the total SCF energy.

**SET\_RADII**

Print the interaction radii of all Gaussian orbital sets.

**SPHERICAL\_HARMONICS**

Print the transformation matrices between Cartesian and spherical function.

**TIMING\_INFORMATION**

Print timing information depending on the IOLEVEL defined in the &CP2K section.

**TITLE**

Print the title.

**TOTAL\_DENSITIES**

Print

**TOTAL\_NUMBERS**

Print the total number of atoms, shell sets, basis functions, projectors etc.

**V\_HARTREE\_CUBE**

Print the Hartree potential as a cube file.

**W\_MATRIX**

Print the energy weighted density matrix used for the force calculation.

## 5 Input examples

### 5.1 Argon atom

```

&CP2K
  PROGRAM      Quickstep
  IOLEVEL      10
  FFTLIB       FFTSG
&END

&DFT
  FUNCTIONAL    PADE
&END

&QS
  CUTOFF        300
  EPS_DEFAULT   1.0E-12
  EPS_RHO       1.0E-8
  EPS_GVG       1.0E-6
  REL_CUTOFF    30
&END

&SCF
  GUESS         ATOMIC
  EPS_DIIS      0.1
  MAX_DIIS      4
  EPS_SCF       1.0E-6
  MAX_SCF       30
  MIXING        0.4
&END

&PRINT medium
NO_BLACS_INFO
&END

&KIND Ar
  BASIS_SET     DZVP-GTH-PADE
  POTENTIAL     GTH
&END

&CELL
  UNIT          ANGSTROM
  ABC           12.0  12.0  12.0
&END

&COORD
  18           0.000000  0.000000  0.000000
&END

```

## 5.2 Water molecule

```
&CP2K
  PROGRAM      Quickstep
  IOLEVEL      10
  FFTLIB       FFTSG
&END

&DFT
  FUNCTIONAL    Pade
  FORCES
&END

&QS
  CUTOFF       200
&END

&SCF
  GUESS         ATOMIC
  MIXING        0.4
  EPS_SCF       1.0E-5
&END

&PRINT medium
&END

&KIND H
  BASIS_SET     DZV-GTH-PADE
  POTENTIAL     GTH
&END

&KIND O
  BASIS_SET     DZVP-GTH-PADE
  POTENTIAL     GTH
&END

&CELL
  UNIT          ANGSTROM
  ABC           10.0  10.0  10.0
&END

&COORD
  H   0.000000   -0.757136    0.520545
  O   0.000000    0.000000   -0.065587
  H   0.000000    0.757136    0.520545
&END
```

## 6 Methods

### 6.1 GPW method

The electronic energy functional for a molecular or crystalline system in the framework of the Gaussian Plane Waves (GPW) method is defined as [3]

$$\begin{aligned}
 E^{\text{el}}[n] &= E^{\text{T}}[n] + E^{\text{V}}[n] + E^{\text{H}}[n] + E^{\text{XC}}[n] \\
 &= \sum_{\mu\nu} P_{\mu\nu} \langle \phi_{\mu}(\mathbf{r}) | -\frac{1}{2} \nabla^2 | \phi_{\nu}(\mathbf{r}) \rangle + \\
 &\quad \sum_{\mu\nu} P_{\mu\nu} \langle \phi_{\mu}(\mathbf{r}) | V_{\text{loc}}^{\text{PP}}(r) | \phi_{\nu}(\mathbf{r}) \rangle - \\
 &\quad \sum_{\mu\nu} P_{\mu\nu} \langle \phi_{\mu}(\mathbf{r}) | V_{\text{nl}}^{\text{PP}}(\mathbf{r}, \mathbf{r}') | \phi_{\nu}(\mathbf{r}') \rangle +
 \end{aligned} \tag{1}$$

$$\begin{aligned}
 &4\pi\Omega \sum_{|\mathbf{G}| < G_{\text{C}}} \frac{\tilde{n}^*(\mathbf{G}) \tilde{n}(\mathbf{G})}{G^2} + \\
 &\int \tilde{n}(\mathbf{r}) \varepsilon_{\text{XC}}[\tilde{n}] d\mathbf{r}
 \end{aligned} \tag{2}$$

where  $E^{\text{T}}[n]$  is the kinetic energy,  $E^{\text{V}}[n]$  is the electronic interaction with the ionic cores,  $E^{\text{H}}[n]$  is the electronic Hartree (Coulomb) energy and  $E^{\text{XC}}[n]$  is the exchange-correlation energy.

The electronic density

$$n(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu} \phi_{\mu}(\mathbf{r}) \phi_{\nu}(\mathbf{r})$$

is expanded in a set of contracted Gaussian functions

$$\phi_{\mu}(\mathbf{r}) = \sum_i C_{i\mu} g_i(\mathbf{r})$$

$P_{\mu\nu}$  is a density matrix element,  $g_i(\mathbf{r})$  is a primitive Gaussian function and  $C_{i\mu}$  is the corresponding contraction coefficient.

An auxiliary basis set of plane waves is used as an intermediate basis set to describe the electronic charge density

$$\tilde{n}(\mathbf{r}) = \frac{1}{\Omega} \sum_{|\mathbf{G}| < G_{\text{C}}} n(\mathbf{G}) e^{i\mathbf{G}\mathbf{r}}$$

which is used for the calculation of the density dependent contributions  $E^{\text{H}}[n]$  and  $E^{\text{XC}}[n]$ .  $\Omega$  is the volume of the periodic cell. The plane wave expansion is truncated by the specification of a cutoff value for the kinetic energy

$$E_{\text{C}} = \frac{1}{2} G_{\text{C}}^2$$

of the plane waves. Since the  $G = 0$  term of the Hartree energy is treated with the Ewald method, the nuclear charges are represented by a Gaussian charge distribution and not by point charges.

The GPW method works like pure plane waves methods with atomic pseudo potentials, since an expansion of Gaussian functions with large exponents is numerically not efficient or even not feasible. The current implementation of the GPW method uses only the pseudo potentials of Goedecker, Teter and Hutter (GTH) [1, 2] which consist of a local part  $V_{\text{loc}}^{\text{PP}}(r)$  and a non-local part  $V_{\text{nl}}^{\text{PP}}(\mathbf{r}, \mathbf{r}')$  as shown in Eq. 1.

## References

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