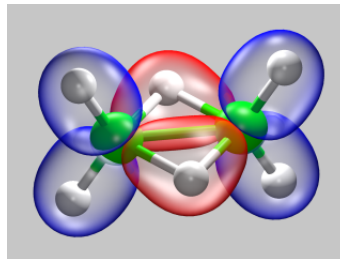


Introduction to the CPMD program

CPMD program

- *ab initio* electronic structure (DFT) and molecular dynamics program
- plane wave basis set (PBC), pseudopotentials
- massively parallelized, linear scaling up to thousands of CPU's
- WF, GEO, CPMD, BOMD, KS-orbitals, response functions, TDDFT, properties
- solids, liquids, gas-phase, materials, chemistry, biology
- <http://www.cpmd.org>, download, manual, mailing list, PP's



Installation and Running

more details in the manual or in the source

Installation

- Distribution of source *via* <http://www.cpmc.org/> for free for non-commercial users.
- `# Configure` to see for which platforms a Makefile can be generated.
- `# Configure platform > Makefile` to obtain Makefile for your platform.
- `# make` to get executable `cpmd.x`.
- frequent problem: libraries and paths are incorrect in Makefile, Makefile needs to be edited manually.
- to change preprocessor flags type `# make clean`.

Running

```
# cpmd.x input pseudopotentialdirectory > output
```

- required files: executable, input, pseudopotentials
- pseudopotentialdirectory is either
 - 1 omitted and instead given by an environment variable called **PP_LIBRARY_PATH**,
 - 2 or explicitly given,
 - 3 or omitted and the pseudopotentials are in the running directory.
- other files: detailed/more condensed output is written to various files depending on the keyword.
- RESTART-files are written upon a proper ending of a run.
- runs can be properly ended by creating a file EXIT in the running directory.

Input

more details in the manual or in the source

Sections

- `&CPMD ... &END`
↔ Control (mandatory)
- `&DFT ... &END`
↔ Functional (mandatory)
- `&SYSTEM ... &END`
↔ Cell (mandatory)
- `&ATOMS ... &END`
↔ Pseudopotentials, Coordinates, Constraints (mandatory)
- `&PIMD ... &END`
↔ Path Integral Molecular Dynamics
- `&RESP ... &END`
↔ Response

- `&TDDFT ... &END`
↔ TDDFT
- `&VDW ... &END`
↔ Empirical van der Waals correction

Keywords

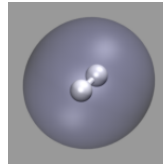
- Manual is incomplete by construction → only source is complete.
- Keywords relate to variables which trigger desired calculations, relations are often found in
`control.F`, `sysin.F`, `pi_cnt1.F`, `ratom.F`, `recpnew.F`, `dftin.F`, `proppt.F`, `respin.F`,
`lr_in.F`
- Order of keywords is arbitrary unless stated otherwise
- Only capital letters
- Choose one item from lists enclosed in {...}
- Choose any number of items from lists enclosed in [...]
- Arguments (for instance numbers) for keywords are given on following lines.

Examples

Wavefunction, Geometry, Car-Parrinello MD



Wavefunction Optimization of H₂: input



- `&INFO`
isolated hydrogen molecule.
single point calculation.
`&END`

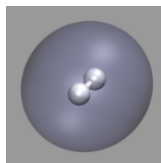
- `&CPMD`
OPTIMIZE WAVEFUNCTION
CONVERGENCE ORBITALS
1.0d-7
CENTER MOLECULE OFF
PRINT FORCES ON
`&END`

- &SYSTEM
SYMMETRY
CUBIC
ANGSTROM
CELL
8.00 1.0 1.0 0.0 0.0 0.0
CUTOFF
70.0
&END

- &DFT
FUNCTIONAL LDA
&END

- &ATOMS
*H_MT_LDA.psp
LMAX=S
2
4.371 4.000 4.000
3.629 4.000 4.000
&END

Wavefunction Optimization of H₂: output



PROGRAM CPMD STARTED AT: Tue Jul 19 15:47:26 2005

```
*****  *****  *****  *****  *****
*****  *****  *****  *****  *****
***      **  ***  **  *****  **  **  ***
**      **  ***  **  **  **  **  **  **
**      *****  **  **  **  **  **
***      *****  **  **  **  **  ***
*****  **      **  **  *****
*****  **      **  **  *****
```

VERSION 3.9.2

COPYRIGHT
IBM RESEARCH DIVISION
MPI FESTKOERPERFORSCHUNG STUTTGART

The CPMD consortium
WWW: <http://www.cpmc.org>
Mailinglist: cpmd-list@cpmd.org
E-mail: cpmd@cpmd.org

*** Jul 10 2005 -- 20:54:03 ***

THE INPUT FILE IS: h2-wave.inp
THIS JOB RUNS ON: Server1.must.org
THE CURRENT DIRECTORY IS:
/home/cpmd/CPMD/work/h2
THE TEMPORARY DIRECTORY IS:
/home/cpmd/CPMD/work/h2
THE PROCESS ID IS: 14621

* INFO - INFO - INFO - INFO - INFO - INFO - INFO - INFO - INFO - INFO - INFO - INFO *

* isolated hydrogen molecule. *
* single point calculation. *

CPMD section

SINGLE POINT DENSITY OPTIMIZATION

```
PATH TO THE RESTART FILES:                ./
GRAM-SCHMIDT ORTHOGONALIZATION
MAXIMUM NUMBER OF STEPS:                   10000 STEPS
PRINT INTERMEDIATE RESULTS EVERY           10001 STEPS
STORE INTERMEDIATE RESULTS EVERY           10001 STEPS
NUMBER OF DISTINCT RESTART FILES:          1
TEMPERATURE IS CALCULATED ASSUMING EXTENDED BULK BEHAVIOR
FICTITIOUS ELECTRON MASS:                   400.0000
TIME STEP FOR ELECTRONS:                    5.0000
TIME STEP FOR IONS:                         5.0000
CONVERGENCE CRITERIA FOR WAVEFUNCTION OPTIMIZATION: 1.0000E-07
WAVEFUNCTION OPTIMIZATION BY PRECONDITIONED DIIS
THRESHOLD FOR THE WF-HESSIAN IS             0.5000
MAXIMUM NUMBER OF VECTORS RETAINED FOR DIIS: 10
STEPS UNTIL DIIS RESET ON POOR PROGRESS:    10
FULL ELECTRONIC GRADIENT IS USED
SPLINE INTERPOLATION IN G-SPACE FOR PSEUDOPOTENTIAL FUNCTIONS
  NUMBER OF SPLINE POINTS:                   5000
```

DFT section, atoms, and electrons

EXCHANGE CORRELATION FUNCTIONALS

LDA EXCHANGE:

NONE

LDA XC THROUGH PADE APPROXIMATION

S.GOEDECKER, J.HUTTER, M.TETER PRB 54 1703 (1996)

*** DETSP| THE NEW SIZE OF THE PROGRAM IS 1528/ 43068 kBYTES ***

***** ATOMS *****

NR	TYPE	X(bohr)	Y(bohr)	Z(bohr)	MBL
1	H	8.259992	7.558904	7.558904	3
2	H	6.857816	7.558904	7.558904	3

NUMBER OF STATES: 1

NUMBER OF ELECTRONS: 2.00000

CHARGE: 0.00000

ELECTRON TEMPERATURE(KELVIN): 0.00000

OCCUPATION

2.0

[...]


```
*****  
*  ATOM      MASS  RAGGIO NLCC          PSEUDOPOTENTIAL *  
*    H      1.0080  1.2000  NO          S      LOCAL *  
*****
```

SYSTEM section

```
***** SUPERCELL *****
SYMMETRY:                               SIMPLE CUBIC
LATTICE CONSTANT(a.u.):                 15.11781
CELL DIMENSION:  15.1178  1.0000  1.0000  0.0000  0.0000  0.0000
VOLUME(OMEGA IN BOHR^3):                3455.14651
LATTICE VECTOR A1(BOHR):                 15.1178    0.0000    0.0000
LATTICE VECTOR A2(BOHR):                 0.0000    15.1178    0.0000
LATTICE VECTOR A3(BOHR):                 0.0000    0.0000    15.1178
RECIP. LAT. VEC. B1(2Pi/BOHR):          0.0661    0.0000    0.0000
RECIP. LAT. VEC. B2(2Pi/BOHR):          0.0000    0.0661    0.0000
RECIP. LAT. VEC. B3(2Pi/BOHR):          0.0000    0.0000    0.0661
REAL SPACE MESH:                         90          90          90
WAVEFUNCTION CUTOFF(RYDBERG):            70.00000
DENSITY CUTOFF(RYDBERG):                 (DUAL= 4.00)  280.00000
NUMBER OF PLANE WAVES FOR WAVEFUNCTION CUTOFF: 17133
NUMBER OF PLANE WAVES FOR DENSITY CUTOFF: 136605
*****
```

After some setup report: initial energy

[...]

(K+E1+L+N+X)	TOTAL ENERGY =	-1.09689769 A.U.
(K)	KINETIC ENERGY =	0.81247073 A.U.
(E1=A-S+R)	ELECTROSTATIC ENERGY =	-0.48640049 A.U.
(S)	ESELF =	0.66490380 A.U.
(R)	ESR =	0.17302596 A.U.
(L)	LOCAL PSEUDOPOTENTIAL ENERGY =	-0.84879443 A.U.
(N)	N-L PSEUDOPOTENTIAL ENERGY =	0.00000000 A.U.
(X)	EXCHANGE-CORRELATION ENERGY =	-0.57417350 A.U.

Optimization

NFI	GEMAX	CNORM	ETOT	DETOT	TCPU
1	3.816E-02	2.886E-03	-1.096898	0.000E+00	1.61
2	8.628E-03	1.041E-03	-1.130803	-3.391E-02	1.64
3	2.736E-03	2.293E-04	-1.132376	-1.572E-03	1.63
4	6.115E-04	4.235E-05	-1.132456	-8.056E-05	1.65
5	1.532E-04	7.007E-06	-1.132459	-3.315E-06	1.66
6	3.895E-05	1.396E-06	-1.132460	-1.338E-07	1.65
7	6.271E-06	4.451E-07	-1.132460	-7.716E-09	1.64
8	7.764E-07	1.274E-07	-1.132460	-4.268E-10	1.69
9	1.317E-07	2.819E-08	-1.132460	-1.993E-11	1.65
10	1.871E-08	5.247E-09	-1.132460	-8.300E-13	1.67

NFI: Step number (number of finite iterations)

GEMAX: largest off-diagonal component

CNORM: average of the off-diagonal components

ETOT: total energy

DETOT: change in total energy to the previous step

TCPU: (CPU) time for this step.

Results in a.u.

```
*****  
*                                                                 *  
*                   FINAL RESULTS                               *  
*                                                                 *  
*****
```

ATOM		COORDINATES			GRADIENTS (-FORCES)		
1	H	8.2600	7.5589	7.5589	1.780E-02	-1.327E-16	-9.739E-17
2	H	6.8578	7.5589	7.5589	-1.780E-02	-2.065E-16	-1.807E-16

```
*****
```

ELECTRONIC GRADIENT:

MAX. COMPONENT = 9.23124E-09 NORM = 1.05089E-09

NUCLEAR GRADIENT:

MAX. COMPONENT = 1.77986E-02 NORM = 1.02760E-02

TOTAL INTEGRATED ELECTRONIC DENSITY

IN G-SPACE = 2.000000

IN R-SPACE = 2.000000

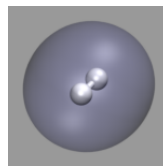
(K+E1+L+N+X)	TOTAL ENERGY =	-1.13245953 A.U.
(K)	KINETIC ENERGY =	1.09007154 A.U.
(E1=A-S+R)	ELECTROSTATIC ENERGY =	-0.47319172 A.U.
(S)	ESELF =	0.66490380 A.U.
(R)	ESR =	0.17302596 A.U.
(L)	LOCAL PSEUDOPOTENTIAL ENERGY =	-1.09902235 A.U.
(N)	N-L PSEUDOPOTENTIAL ENERGY =	0.00000000 A.U.
(X)	EXCHANGE-CORRELATION ENERGY =	-0.65031700 A.U.

Performance at the end

```
=====
                        BIG MEMORY ALLOCATIONS
XF          1507142          PSI          1507142
YF          1507142          SCR          1026981
RHOE        753571          GK           409815
SCG         273210          INYH          204908
PME         171410          RHOPS         136605
-----
[PEAK NUMBER  78]      PEAK MEMORY      8512086 =  68.1 MBytes
=====
```

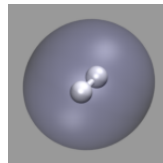
```
*****
*
*
*
*
*****
SUBROUTINE      CALLS      CPU TIME      ELAPSED TIME
S_INVFFT        26         2.82         2.84
  INVFFT        14         2.77         2.76
    FWFFT       13         2.56         2.58
      FFT-G/S   80         2.50         2.53
```


Wavefunction Optimization of H₂: more output



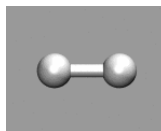
Apart from the console output, a CPMD run creates a few other files. Most importantly the restart file `RESTART.1` and its companion file `LATEST`. The restart file contains the final state of the system when the program terminated. This is needed to start other calculations, which need a converged wavefunction as a starting point. The file `GEOMETRY.xyz` contains cartesian coordinates in Å - a format that can be read in by molecular visualization programs.

Geometry Optimization of H₂: input



```
&CPMD  
OPTIMIZE GEOMETRY XYZ  
CONVERGENCE ORBITALS  
  1.0d-7  
CONVERGENCE GEOMETRY  
  1.0d-4  
&END
```

Geometry Optimization of H₂: output



```
=====
=                               GEOMETRY OPTIMIZATION                               =
=====
NFI      GEMAX      CNORM      ETOT      DETOT      TCPU
EWALD| SUM IN REAL SPACE OVER      1* 1* 1 CELLS
  1  3.816E-02  2.886E-03  -1.096898  -1.097E+00  1.28
  2  8.628E-03  1.041E-03  -1.130803  -3.391E-02  1.33

[...]

 10  1.871E-08  5.247E-09  -1.132460  -8.509E-13  1.43

RESTART INFORMATION WRITTEN ON FILE                               ./RESTART.1

  ATOM      COORDINATES      GRADIENTS (-FORCES)
  1  H  8.2600  7.5589  7.5589  -1.780E-02  9.179E-17  7.909E-17
  2  H  6.8578  7.5589  7.5589   1.780E-02  1.596E-16  1.396E-16
*****
```

```

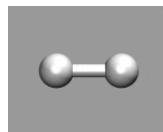
*** TOTAL STEP NR.      10          GEOMETRY STEP NR.      1  ***
*** GNMAX=  1.779864E-02          ETOT=      -1.132460  ***
*** GNORM=  1.027605E-02          DETOT=      0.000E+00  ***
*** CNSTR=  0.000000E+00          TCPU=      13.63  ***
*****
  1  5.012E-03  9.718E-04  -1.131471  9.887E-04  1.34
  2  4.287E-04  1.613E-04  -1.132846  -1.375E-03  1.35
  3  1.489E-04  3.429E-05  -1.132883  -3.659E-05  1.33

```

Results

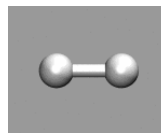
```
ATOM          COORDINATES          GRADIENTS (-FORCES)
 1  H  8.2854  7.5589  7.5589   9.965E-05  1.105E-16  9.709E-17
 2  H  6.8324  7.5589  7.5589  -9.965E-05  1.835E-16  1.392E-16
*****
*** TOTAL STEP NR.    36          GEOMETRY STEP NR.    5  ***
*** GNMAX=  9.965023E-05 [5.98E-05]    ETOT=    -1.132896  ***
*** GNORM=  5.753309E-05          DETOT=    -1.423E-08  ***
*** CNSTR=  0.000000E+00          TCPU=      6.76    ***
*****
=====
=                END OF GEOMETRY OPTIMIZATION                =
=====
```

Car-Parrinello MD of H₂: input



```
&CPMD  
MOLECULAR DYNAMICS CP  
RESTART WAVEFUNCTION COORDINATES LATEST  
TRAJECTORY XYZ  
TEMPERATURE  
  50.000  
MAXSTEP  
  200  
TIMESTEP  
  4.0  
&END
```

Car-Parrinello MD of H₂: output

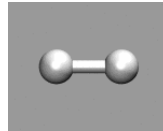


restart

CAR-PARRINELLO MOLECULAR DYNAMICS

```
PATH TO THE RESTART FILES:                ./
RESTART WITH OLD ORBITALS
RESTART WITH OLD ION POSITIONS
RESTART WITH LATEST RESTART FILE
ITERATIVE ORTHOGONALIZATION
  MAXIT:                                    30
  EPS:                                       1.00E-06
MAXIMUM NUMBER OF STEPS:                    200 STEPS
```

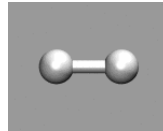
Car-Parrinello MD of H₂: output



timestep, no T control → microcanonical (NVE) ensemble

```
TIME STEP FOR ELECTRONS:          4.0000
TIME STEP FOR IONS:              4.0000
TRAJECTORIES ARE SAVED ON FILE
TRAJEC.xyz IS SAVED ON FILE
ELECTRON DYNAMICS: THE TEMPERATURE IS NOT CONTROLLED
ION DYNAMICS:      THE TEMPERATURE IS NOT CONTROLLED
```


Car-Parrinello MD of H₂: output



No WF velocities found

```
RV30| WARNING! NO WAVEFUNCTION VELOCITIES
```

```
RESTART INFORMATION READ ON FILE
```

```
./RESTART.1
```

NFI	EKINC	TEMPP	EKS	ECLASSIC	EHAM	DIS	TCPU
1	0.00000	49.4	-1.13289	-1.13266	-1.13266	0.207E-05	1.37
2	0.00000	47.7	-1.13289	-1.13266	-1.13266	0.817E-05	1.36
3	0.00001	45.7	-1.13288	-1.13267	-1.13266	0.181E-04	1.37
4	0.00001	43.5	-1.13288	-1.13267	-1.13266	0.314E-04	1.37
5	0.00002	41.5	-1.13287	-1.13268	-1.13266	0.481E-04	1.37
...							
199	0.00001	27.2	-1.13280	-1.13267	-1.13266	0.393E-01	1.36
200	0.00001	28.0	-1.13280	-1.13267	-1.13266	0.397E-01	1.38

The columns mean:

NFI: Step number (number of finite iterations)

EKINC: (fictitious) kinetic energy of the electronic (sub-)system

TEMPP: Temperature (= kinetic energy / degrees of freedom) for atoms (ions)

EKS: Kohn-Sham Energy, equivalent to the potential energy in classical MD

ECLASSIC: Equivalent to the total energy in a classical MD (ECLASSIC = EHAM - EKINC)

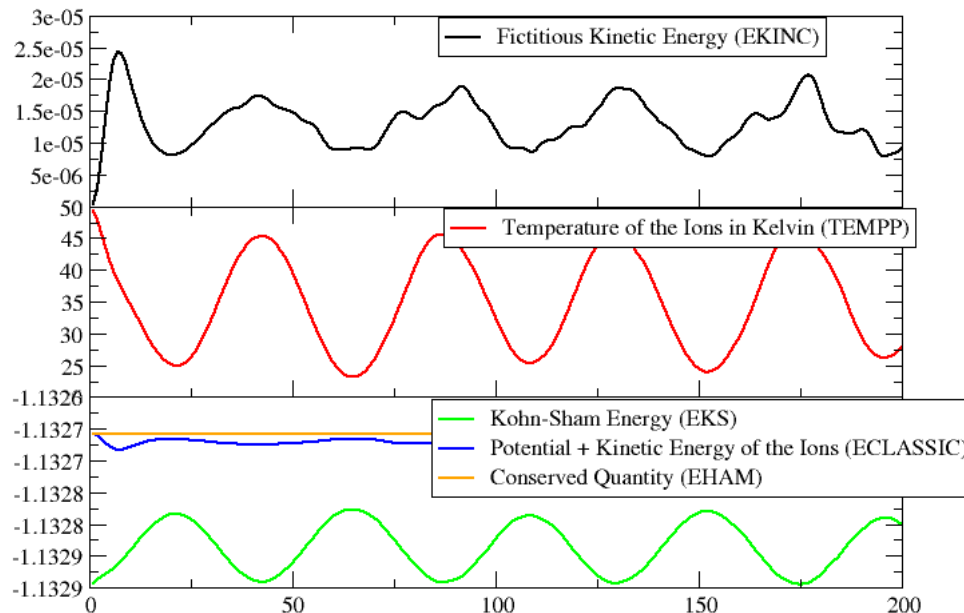
EHAM: total energy, should be conserved

DIS: mean squared displacement of the atoms from the initial coordinates.

TCPU: (CPU) time needed for this step.

Car-Parrinello MD of H₂: analysis

Evolution of various energies. Some energy from ionic system is transferred to fictitious electron dynamics (since the temperature never reaches the initial 50K again). The difference between the orange (EHAM) and the blue (ECLASSIC) graphs is EKINC, and the difference to the potential energy (EKS) is the kinetic energy in the ionic system.



After the geometry optimization the hydrogen molecule is in the minimum of its potential. Upon start of the MD, the initial kinetic energy added to the system is slowly converted into potential energy (cf. EKS) as the bond is elongated. After a while the molecule reaches maximal elongation and the potential energy is converted back into kinetic energy (i.e. the temperature rises again). So we have a regular oscillation of the hydrogen molecule. Also, some energy is transferred into the fictitious dynamic of the electronic degrees of freedom. For a meaningful Car-Parrinello MD this value has to be (and stay) very small (although for larger systems with more electrons, the absolute value of EKINC will be larger).

Car-Parrinello MD of H₂: analysis

```
*****
*                               AVERAGED QUANTITIES                               *
*****
                                MEAN VALUE      +/-  RMS DEVIATION
                                [-^2]**(1/2)
ELECTRON KINETIC ENERGY    0.130119E-04      0.380704E-05
IONIC TEMPERATURE           34.76              7.57
DENSITY FUNCTIONAL ENERGY  -1.132836      0.388578E-04
CLASSICAL ENERGY           -1.132671      0.384979E-05
CONSERVED ENERGY           -1.132658      0.583016E-07
NOSE ENERGY ELECTRONS      0.000000      0.00000
NOSE ENERGY IONS           0.000000      0.00000
CONSTRAINTS ENERGY         0.000000      0.00000
ION DISPLACEMENT            0.135129E-01      0.119249E-01
CPU TIME                     1.3665
```

Summary of averages and root mean squared deviations for some quantities. Quite useful to detect unwanted energy drifts or too large fluctuations in the simulation.