

CM5PAC

**A package to calculate CM5 and CM5M partial
atomic charges**

Version 2015

User's Manual

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Distribution site: <http://comp.chem.umn.edu>

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Contents

1. User agreement	3
2. Revision history	3
3. Description of CM5PAC	4
4. Installation	4
5. Execution	5
6. Test suite	7
7. Citation	8
8. Notes	9

1. User agreement

CM5PAC is a licensed program, and the use of this program implies acceptance of the terms of the license, which are repeated here for convenience:

A. No user or site will redistribute the source code or executable code to a third party in original or modified form without written permission of the principal investigator (Donald G. Truhlar or Christopher J. Cramer). A license does not entitle the licensee to relicense the code or distribute it in original or modified form to parties not covered by the license. The licensee has no ownership rights in the *CM5PAC* software or in any copyrights for the *CM5PAC* software or documentation through this license. A user license covers the work of a single research group and the code may be shared and disseminated within a group without requiring permission. Site-license inquiries should be directed to the principal investigator.

B. Publications resulting from using this package will cite the corresponding program and the *CM5* journal article. The required references are given in the documentation.

C. No guarantee is made that this program is bug-free or suitable for specific applications, and no liability is accepted for any limitations in the mathematical methods and algorithms used within the program.

D. No consulting or maintenance services are guaranteed or implied.

2. Revision history

Version 2011

Authors: Aleksandr V. Marenich, Christopher J. Cramer, and Donald G. Truhlar.

Version 2011 is the first distributed version.

Version 2013

Authors: Aleksandr V. Marenich, Christopher J. Cramer, and Donald G. Truhlar.

The program was made compatible with Revision D.01 of Gaussian 09.

Version 2015

Authors: Kaining Duanmu, Bo Wang, Aleksandr V. Marenich, Christopher J. Cramer, and Donald G. Truhlar.

1. A new charge model *CM5M* was added.
2. The program can now calculate *CM5* partial atomic charges for periodic systems.

3. Description of CM5PAC

CM5PAC is a package containing a Fortran program along with a shell script to carry out a calculation of CM5 and CM5M partial atomic charges using Hirshfeld atomic charges. The package is based on Charge Model 5 (CM5)¹ and Charge Model 5 for Metals (CM5M)² that yield class IV partial atomic charges by mapping from those obtained by Hirshfeld population analysis of density functional electronic charge distributions.

The CM5 and CM5M models are applicable to any charged or uncharged molecule composed of any element of the periodic table in the gas phase or in solution, and they can be used with any level of electronic structure theory (Hartree–Fock, post-Hartree–Fock and other correlated wave function methods, or density functional theory) as long as an accurate electronic charge distribution and a Hirshfeld population analysis can be computed for that level of theory.

At this time, there is no charge for a *CM5PAC* license, which has no expiration period.

1. Marenich, A. V.; Jerome, S. V.; Cramer, C. J.; Truhlar, D. G. Charge Model 5: An Extension of Hirshfeld Population Analysis for the Accurate Description of Molecular Interactions in Gaseous and Condensed Phases. *J. Chem. Theor. Comput.* **2012**, *8*, 527–541.
2. Duanmu, K.; Truhlar, D. G. Partial Ionic Character beyond the Pauling Paradigm: Metal Nanoparticles. *J. Phys. Chem. C* **2014**, *118*, 28069–28074.

4. Installation

The *CM5PAC* software package comes as a single tar file called `cm5pac.tar`, first it should be untarred by

```
>tar -xvf cm5pac.tar
```

Compile the Fortran code by

```
>gfortran -o cm5pac.exe cm5pac.f
```

The user should define the full path to `cm5pacdir` through the `$PATH` environment variable in `.bashrc` or in `.cshrc` (depending on which shell is used). For example:

```
export PATH=$PATH:$HOME/cm5pacdir
```

or

```
setenv PATH ${PATH} : $HOME/cm5pacdir
```

The user can check if the *CM5PAC* package is properly set up by executing the following command:

```
>which cm5pac.exe cm5pac
```

5. Execution

CM5PAC works with Gaussian output file and periodic systems. If the user is running *Gaussian*, a *Gaussian* calculation of Hirshfeld charges should be done before running *CM5PAC*. Here is an example of *Gaussian 09*'s input file for such a calculation:

```
%nproc=8
%mem=1600mb
# mPW1PW91/6-311+G(2df,2p) pop=Hirshfeld scf=tight
Methanol
0 1
8 -0.046153000 -0.751257000 0.000000000
6 -0.046153000 0.658469000 0.000000000
1 0.857779000 -1.062372000 0.000000000
1 -1.086394000 0.976180000 0.000000000
1 0.437376000 1.072716000 0.889654000
1 0.437376000 1.072716000 -0.889654000
```

Note: The keyword `pop=Hirshfeld` is critical.

If the *Gaussian* calculation is terminated normally, the user can run a *CM5* or *CM5M* calculation by executing the following command:

```
>cm5pac
```

The user will type in the file name and select the charge model, and the *CM5PAC* program will modify the output file by adding the corresponding output. Here is an example of such an output (*Gaussian 09*, Revision C.01):

Charges (in a.u.) from *CM5PAC* version 2015

Center Number	Atomic Number	CM5 Charge	Hirshfeld Charge
1	8	-0.474015	-0.250109
2	6	-0.157794	-0.031642
3	1	0.338597	0.164045
4	1	0.108245	0.047951
5	1	0.092486	0.034880
6	1	0.092486	0.034880

Dipole moment (in Debye)

	X	Y	Z	Total
CM5	1.3589	0.9442	0.0000	1.6547
Hirshfeld	0.6347	0.5496	0.0000	0.8396

For periodic systems, the user should have an input file like this:

```
MnO2
1.0
-0.0000000000000000 4.0720837535025582 4.0720837535025582
 4.0720837535025582 0.0000000000000000 4.0720837535025582
 4.0720837535025582 4.0720837535025582 0.0000000000000000
Direct
25 0.6250000000000000 0.6250000000000000 0.6250000000000000
25 0.6250000000000000 0.6250000000000000 0.1250000000000000
25 0.1250000000000000 0.6250000000000000 0.6250000000000000
25 0.6250000000000000 0.1250000000000000 0.6250000000000000
8 0.3890246768642103 0.3890246768642103 0.3890246768642103
8 0.3890246768642103 0.3890246768642103 0.8329259694073549
8 0.8329259694073549 0.3890246768642103 0.3890246768642103
8 0.3890246768642103 0.8329259694073549 0.3890246768642103
8 0.8609753231357897 0.8609753231357897 0.8609753231357897
8 0.8609753231357897 0.8609753231357897 0.4170740305926451
8 0.8609753231357897 0.4170740305926451 0.8609753231357897
8 0.4170740305926451 0.8609753231357897 0.8609753231357897
----
0.445
0.445
0.445
0.445
-0.2225
-0.2225
-0.2225
-0.2225
-0.2225
-0.2225
-0.2225
-0.2225
-0.2225
-0.2225
```

The first line is a comment line, the second is a scaling factor, which is used to scale all lattice vectors. The following three lines are lattice vectors defining the unit cell. The sixth line specifies whether the atomic positions are in Cartesian or in Direct coordinates. Each of the

following lines before “----” represents the atomic number and the position of the atom, each of the lines after “----” represents the Hirshfeld charges on the atoms.

The user can run *CM5PAC* by executing:

```
>cm5pac
```

The user will type in the file name and select the charge model, and the *CM5PAC* program will generate .out file.

To run *CM5PAC* on periodic systems, the user needs to calculate the Hirshfeld charges from other programs. The user may find the following programs helpful:

- (1) *BAND* program. Hirshfeld charges are automatically printed out in the output.
<http://www.scm.com/Doc/Doc2013/BAND/BandUsersGuide/page1.html>
- (2) *Chargemol* program. This program needs the charge density from other programs, such as *VASP*. The *Chargemol* program can be used to get DDEC charges (which are not used here), but it also prints out Hirshfeld charges, which are needed here.
<http://sourceforge.net/projects/ddec/files/>

6. Test suite

The *CM5PAC* test suite (directory Tests) contains the following tests:

CM5 for Gaussian output:

In the gas phase

- mPW1PW91/MG3S on methanol (test1.inp)
- HF/6-31G(d) on formamide (test2.inp)
- CCSD/6-311+G(2d,p) on formaldehyde with the density=current keyword (test3.inp)
- TDDFT/M06/MG3S on formaldehyde in the first excited electronic state (test4.inp)
- M06-2X/MG3S on acetone (test5.inp)

In water

- M06-2X/MG3S on acetone in water using a wave function obtained from the SMD SCRF calculation (test6.inp)

CM5M for Gaussian output:

- TPSS/jun-cc-pVTZ-PP on silver trimer (test7.inp)

CM5 for periodic system:

- MnO₂ (test8)

The MG3S basis set used in some of the test runs is the same as the 6-311+G(2df,2p) basis for elements H through Ne.

The original CM5 model was parametrized using Hirshfeld charges computed by Gaussian 09 (Revision A.02). Hirshfeld charges obtained using more recent versions of Gaussian 09 (for example, Revision C.01 or D.01) may differ by a few percent, which should not be an issue in terms of the overall accuracy of the CM5 model. The directory Tests contains output files with CM5 and Hirshfeld charges obtained using Revision A.02, Revision C.01, and Revision D.01.

Note that CM5 charges can be computed along with Hirshfeld charges using Revision D.01 of Gaussian 09 without *CM5PAC* but such calculations may produce wrong CM5 charges in certain cases due to a bug which will be fixed in the next revision of Gaussian. In the meantime, we strongly recommend to use *CM5PAC* to calculate CM5 charges because *CM5PAC* does not experience such a problem.

7. Citation

Publications including work performed with *CM5PAC* should cite the following:

Duanmu, K.; Wang, B.; Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *CM5PAC* version 2015, University of Minnesota, Minneapolis, 2015. <http://comp.chem.umn.edu/cm5pac/>

Marenich, A. V.; Jerome, S. V.; Cramer, C. J.; Truhlar, D. G. Charge Model 5: An Extension of Hirshfeld Population Analysis for the Accurate Description of Molecular Interactions in Gaseous and Condensed Phases. *J. Chem. Theor. Comput.* **2012**, *8*, 527–541.

Duanmu, K.; Truhlar, D. G. Partial Ionic Character beyond the Pauling Paradigm: Metal Nanoparticles. *J. Phys. Chem. C* **2014**, *118*, 28069–28074.

Depending on the calculations, the users may need to cite *Gaussian*, *VASP* or *BAND* programs, and Hirshfeld population analysis:

Hirshfeld, F. L. Bonded-Atom Fragments for Describing Molecular Charge Densities. *Theor. Chem. Acc.* **1977**, *44*, 129–138.

Ritchie, J. P. Electron Density Distribution Analysis for Nitromethane, Nitromethide, and Nitramide. *J. Am. Chem. Soc.* **1985**, *107*, 1829–1837.

Ritchie J. P.; Bachrach, S. M. Some Methods and Applications of Electron Density Distribution Analysis. *J. Comp. Chem.* **1987**, *8*, 499–509.

8. Notes

1. CM5 parameters are available for the entire periodic table, but at the present time CM5M parameters are only available for silver clusters.
2. CM5 charges can be used for a variety of applications such as molecular mechanics, solvation models, and electrostatic modeling. Some examples are:

Solvation and liquid-phase simulations:

“Generalized Born Solvation Model SM12,” A. Marenich, C. J. Cramer, and D. G. Truhlar, *Journal of Chemical Theory and Computation* **9**, 609-620 (2013).
[dx.doi.org/10.1021/ct300900e](https://doi.org/10.1021/ct300900e)

Vilseck JZ, Tirado-Rives J, Jorgensen WL. Evaluation of CM5 charges for condensed-phase modeling. *Journal of Chemical Theory and Computation*. 2014; 10(7):2802-12.

Electrostatically embedded fragment methods:

“Tuned and Balanced Redistributed Charge Scheme for Combined Quantum Mechanical and Molecular Mechanical (QM/MM) Methods and Fragment Methods: Tuning Based on the CM5 Charge Model,” B. Wang and D. G. Truhlar, *Journal of Chemical Theory and Computation* **9**, 1036-1042 (2013). [dx.doi.org/10.1021/ct300935m](https://doi.org/10.1021/ct300935m)

“Electrostatically Embedded Molecular Tailoring Approach and Validation for Peptides,” M. Isegawa, B. Wang, and D. G. Truhlar, *Journal of Chemical Theory and Computation* **9**, 1381-1393 (2013). [dx.doi.org/10.1021/ct300845q](https://doi.org/10.1021/ct300845q)

“Quantum Mechanical Fragment Methods Based on Partitioning Atoms or Partitioning Coordinates,” B. Wang, K. R. Yang, X. Xu, M. Isegawa, H. R. Leverentz, and D. G. Truhlar, *Accounts of Chemical Research* **47**, 2731-2738 (2014). (Special Issue: Beyond QM/MM: Fragment Quantum Mechanical Methods) [dx.doi.org/10.1021/ar500068a](https://doi.org/10.1021/ar500068a)

Partial atomic charges for solids

“Modeling the Partial Atomic Charges in Inorganometallic Molecules and Solids and Charge Redistribution in Lithium-Ion Cathodes,” B. Wang, S. L. Li, and D. G. Truhlar, *Journal of Chemical Theory and Computation* **10**, 5640-5650 (2014).
[dx.doi.org/10.1021/ct500790p](https://doi.org/10.1021/ct500790p)