TINKERPLUS:

A Module Incorporating Screened Electrostatic Interactions into *TINKER*

Users Manual – Version 2014

Date of finalization of this version of the software: June 5, 2014

Date of most recent change in this document: June 6, 2014

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Distribution site: *http://comp.chem.umn.edu/tinkerplus*

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Abstract

TINKERPLUS is a module that incorporates screened charges for evaluating Coulomb interactions between atoms into TINKER. The screened charge model, which is called the molecular mechanics outer density screening (MMODS) model, uses a combination of point charge and charge distributions to describe the charge densities of atoms in molecules. The program can calculate the Coulomb interactions between the screened charges.

Theory

In the MMODS model,[1] the electron density of an atom is approximated as a point charge representing the nucleus and the electrons closest to the nucleus and a smeared charge representing n_{screen} electrons in the outer region. The smeared charge is in a Slater-type orbital (STO), whose radial function is given by

$$\varphi = Br^{n-1}\exp(-\zeta r) \tag{1}$$

where B normalizes φ^2 to n_{screen}, r is the distance of the electron from the nucleus, n is the highest principal quantum number of the element, and ζ is the exponential parameter of the STO. A comparison between a point charge model and the MMODS screened charge model is shown in Figure 1. The point charge scheme is the unscreened scheme, and it corresponds to the limit as $\zeta \rightarrow \infty$.
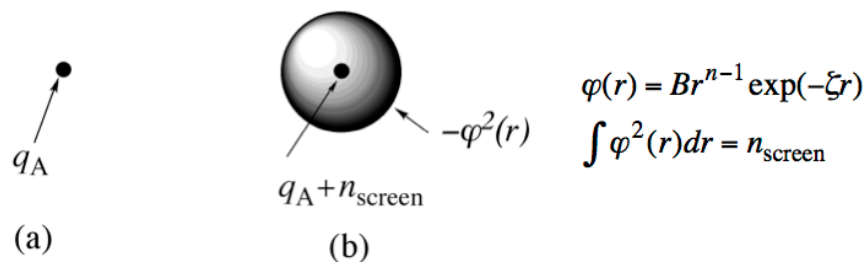
Figure 1. Comparison between (a) a point charge and (b) a screened charge distribution, where the screening is done by the MMODS algorithm.

We have also developed a screened charge model for QM/MM calculations, which is just called ODS,[2] and the QM/MM version is in the QMMM package.[3] The present manual discuses only the MMODS method that is in TINKERPLUS.[4] In the MMODS scheme,[1] the electrostatic energy between two screened atoms A and B is written as

$$E = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \{(q_A + n_{\text{screen,A}})\delta(\mathbf{r}_1 - \mathbf{r}_A) - n_{\text{screen,A}}[B_1 |\mathbf{r}_1 - \mathbf{r}_A|^{n_A - 1} e^{-\zeta_A |\mathbf{r}_1 - \mathbf{r}_A|}]^2\}$$

$$\{(q_B + n_{\text{screen},B})\delta(\mathbf{r}_2 - \mathbf{r}_B) - n_{\text{screen,B}}[B_2 |\mathbf{r}_2 - \mathbf{r}_B|^{n_B - 1} e^{-\zeta_B |\mathbf{r}_2 - \mathbf{r}_B|}]^2\}$$

$$= E(\text{coreA} - \text{coreB}) + E(\text{coreA} - \text{smearB}) + E(\text{smearA} - \text{coreB}) + E(\text{smearA} - \text{smearB}) \tag{2}$$

where B_1 and B_2 are the normalization constants, $\mathbf{r}_i$ denotes the position of electron i, $\mathbf{r}_A$ and $\mathbf{r}_B$ are the postions of the nuclei of atoms A and B, n_A and n_B are the highest principal quantum numbers of atoms A and B, and ζ_A and ζ_B are the exponents for the STOs for atoms A and B.

Citation

Publications including work performed with *TINKERPLUS* should cite the publication of the method[1] and the software package.[2] Two styles in *J. Chem. Phys.* and *J. Amer. Chem. Soc.* are given below.

J. Chem. Phys. style:

[1] B. Wang and D. G. Truhlar, Screened Electrostatic Interactions in Molecular Mechanics, to be published.

[2] B. Wang and D. G. Truhlar, TINKERPLUS (University of Minnesota, Minneapolis, 2014) based on TINKER 6.3 by J. W. Ponder, TINKER –version 6.3 (Washington University, St. Louis, MO, 2014).

J. Amer. Chem. Soc. style:

(1) Wang, B.; Truhlar, D. G. Screened Electrostatic Interactions in Molecular Mechanics, to be published.

(2) Wang, B.; Truhlar, D. G.; TINKERPLUS-version 2014; University of Minnesota: Minneapolis, 2014, based on based on TINKER 6.3 by Ponder, J. W. TINKER –version 6.3, Washington University: St. Louis, MO, 2014.

A preprint of ref. (1) is available on request.

Download and Install

The current version of TINKERPLUS (version 2014) has been developed to work with version 6.3 of TINKER (version 6.3, 2014). To use TINKERPLUS, the user needs to obtain the TINKER package from http://dasher.wustl.edu/tinker/ and TINKERPLUS (version 2014) from University of Minnesota.

Step A. Install the TINKER package.

Obtain the TINKER package from http://dasher.wustl.edu/tinker/ and follow the TINKER compiling instructions in the TINKER User's guide, http://dasher.wustl.edu/tinker/downloads/guide.pdf.

Three files initial.f, kcharge.f, and echarge3.f in your TINKER source directory will be replaced in Step C, so back up the old version.

Step B. Extract files and verify content.

Obtain TINKERPLUS (version 2014) from http://comp.chem.umn.edu/tinkerplus, and run the following command to extract the files.

tar –xvf tinkerplus.tar

Verify that the files have been placed in the following directory. In TINKERPLUS home directory:

dampchg.i	echarge3.f	initial.f	kcharge.f
input/	output/.		

In the input directory:

test1/	test2/

In the input/test1 directory:

t41.xyz	t41.prm	t41.key

...

In the output directory:

test1/	test2/

In the output/test1 directory:

t41.out

...

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Step C. Compile the program.

   Copy dampchg.i, echarge3.f, initial.f, and kcharge.f from the TINKERPLUS package into the folder called /source in your TINKER program. This will substitute your old echarge3.f, initial.f, kcharge.f in TINKER source code, and add new file dampchg.i. To build the code, use the original TINKER makefile and follow the TINKER compiling instructions in the TINKER User's guide, http://dasher.wustl.edu/tinker/downloads/guide.pdf. The modified executable will be in the /bin folder of your TINKER program.

Step D. Run the test runs.

   The TINKERPLUS sample inputs and outputs are in the input/ and output/ folders. Each test contains a set of TINKERPLUS input files: the coordinate file *.xyz, the keyword parameter file *.key, and the potential energy parameter file *.prm. In the test folder, one runs the modified tinker executable:

       ~/tinker/bin/analyze t41.xyz E > t41.out

New Keywords

In order to do screened electrostatic calculations, one needs to turn on the following keyword in the TINKER keyword file, *.key. (Other files originally used for TINKER, such as the coordinate file and potential energy parameter file, are unchanged)

MMODS

This keyword turns on the usage of the molecular mechanics outer density screening model with the MMODS parameters to calculate the Coulomb interactions in molecular mechanics. The MMODS parameters are from ref. 1. If this keyword is not added, then the conventional point charge model is used. The default numbers of electrons in the screening region are

$$n_{screen} = 1 - q \qquad \text{for H}$$
$$2 \qquad \text{for elements in Table 1 except H}$$
$$0 \quad \text{(point charge)} \qquad \text{for other elements}$$

and the ζ values for parametrized elements are shown in Table 1.

Table 1. Default ζ values used in the Slater-type orbital of the screening region

H	C	N	O	F	Si	P	S	Cl
1.32	1.45	1.15	1.36	1.33	1.21	0.91	1.27	1.21

Currently only the elements in the above table have parameters. For all other elements, the point charge model is used as a temporary measure until parameters become available. Only the energies between screened charges are implemented, while the gradients and hessians are currently unavailable.

There are two new keywords for experts to adjust the parameters used for screened atoms.

DAMPING3 [1 integer & 2 reals]

This keyword set provides an option to change the ζ value and the number of screened electrons in the screening region of the screened atom. The first number is the atom number of the screened atom in the coordinate file, the second number is the ζ value, the third number is the number of valence electrons; the number of electrons in the screening region n_{screen} will be the third number minus q, where q is the partial atomic charge on the atom.

DAMPING4 [1 integer & 3 reals]

This keyword set provides another possible way to change the ζ value and the number of screened electrons in the screening region of the screened atom. The first number is the atom number of the screened atom in the coordinate file, the second number is the ζ value, the third number is the number of valence electrons, and the last number is the extra charge included in the screening region. The number of electrons in the screening region n_{screen} will be the third number minus the fourth number. If one wants to turn off the screening of a screened atom, use 0.0 and 0.0 for the third and fourth numbers (no electrons in the screening region).

The default method is the same as the following:

damping3 atom_number 1.32 1.0 for H atoms

damping4 atom_number ζ 2.0 0.0 for elements in Table 1 except H

damping4 atom_number ζ 0.0 0.0 for other elements

Test Cases

Currently there are two test cases. The inputs and outputs of these test cases are in the input/ and output/ folders in the package.

TEST1: H_2O dimer

This test case calculates the electrostatic interactions between two H_2O molecules using CHELPG screened charges. The CHELPG charges[5] are derived from the monomers using HF/aug-cc-pVTZ.

TEST2: MOF and ethane

This test case calculates the electrostatic interactions between an 88-atom model of Fe-MOF and ethane molecules using CM5 screened charges. The CM5 charges[6] are derived from the separated MOF and ethane molecules using M06-L/def2-TZVP.

References

[1] Wang, B.; Truhlar, D. G., Screened Electrostatic Interactions in Molecular Mechanics, to be published.

[2] Wang, B.; Truhlar, D. G. Including Charge Penetration Effects in Molecular Modeling*, J. Chem. Theory Comput.* **2010**, *6*, 3330-3342.

[3] QMMM-version 2013-beta by H. Lin, Y. Zhang, S. Pezeshki, B. Wang and D. G. Truhlar, University of Minnesota, Minneapolis, 2013.

[4] TINKERPLUS by B. Wang and D. G. Truhlar, University of Minnesota, Minneapolis, 2014. https://t1.chem.umn.edu/truhlar/index.htm#software

[5] Breneman, C. M.; Wiberg, K. B. *J. Comput. Chem.* **1990**, *11*, 361-373.

[6] Marenich, A. V.; Jerome, S. V.; Cramer, C. J.; Truhlar, D. G. *J. Chem. Theory Comput.* **2012,** *8*, 527-541.