# FORCE FIELDS

# MD: interatomic interactions

$$\hat{H} = \hat{T}_{\text{nuc}} + \hat{T}_{\text{ele}} + V(\boldsymbol{R}) + V(|\boldsymbol{R} - \boldsymbol{r}|) + V(\boldsymbol{r})$$

$$= \hat{T}_{\text{nuc}} + E_{\text{pot}}(\boldsymbol{R})$$

Obtaining $E_{\text{pot}}(R)$ via *ab initio*: AIMD

$$\left[\hat{T}_{\text{ele}} + V(|\boldsymbol{R} - \boldsymbol{r}|) + V(\boldsymbol{r})\right]\psi(\boldsymbol{r};\boldsymbol{R}) = E_{\text{pot}}(\boldsymbol{R})\psi(\boldsymbol{r};\boldsymbol{R})$$

$$\boldsymbol{F} = M\boldsymbol{a} = -\left(\frac{\partial E_{\text{pot}}(\boldsymbol{R})}{\partial \boldsymbol{R}}\right)$$

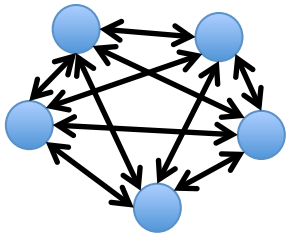
Using model to simulate $E_{\text{pot}}(R)$: force field

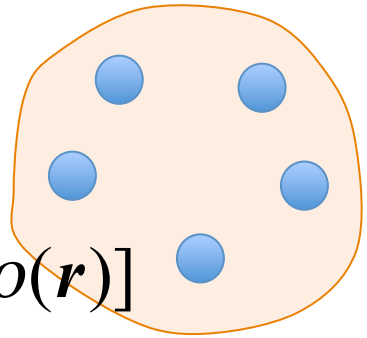
# MD: $H_{\text{ele}}$

Hartree-Fock and post H-F

$$\hat{H}_{\text{ele}} = \hat{T}_{\text{ele}} + V(|\boldsymbol{R} - \boldsymbol{r}|) + V(\boldsymbol{r})$$

$$= -\sum_{i=1}^{N_e} \frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N_e}\sum_{I=1}^{N_n} \frac{Z_I}{|\boldsymbol{R}_I - \boldsymbol{r}_i|} + \sum_{i=1}^{N_e}\sum_{j=i+1}^{N_e} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$$





Density Functional Theory

$$H_{\text{ele}}^{\text{DFT}}[\rho(\boldsymbol{r})] = T_{\text{ele}}[\rho(\boldsymbol{r})] + V_{\text{ext}}[\rho(\boldsymbol{r})] + V_{\text{H}}[\rho(\boldsymbol{r})] + V_{\text{XC}}[\rho(\boldsymbol{r})]$$

$$= T_{\text{ele}}[\rho(\boldsymbol{r})] - \sum_{I=1}^{N_n} \int \frac{Z_I \rho(\boldsymbol{r})}{|\boldsymbol{R}_I - \boldsymbol{r}|} \mathrm{d}^3 r + \int\int \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \mathrm{d}^3 r \mathrm{d}^3 r' + V_{\text{XC}}[\rho(\boldsymbol{r})]$$

# MD: force calculations

$$\boldsymbol{F}_I^{\mathrm{HFT}} = -\nabla_I \left\langle \Psi_0 \middle| \hat{H}_e \middle| \Psi_0 \right\rangle$$

$$= -\left\langle \nabla_I \Psi_0 \middle| \hat{H}_e \middle| \Psi_0 \right\rangle - \left\langle \Psi_0 \middle| \nabla_I \hat{H}_e \middle| \Psi_0 \right\rangle - \left\langle \Psi_0 \middle| \hat{H}_e \middle| \nabla_I \Psi_0 \right\rangle$$

$$= -\left\langle \Psi_0 \middle| \nabla_I \hat{H}_e \middle| \Psi_0 \right\rangle - E_0 \left\langle \nabla_I \Psi_0 \middle| \Psi_0 \right\rangle - E_0 \left\langle \Psi_0 \middle| \nabla_I \Psi_0 \right\rangle$$

$$\nabla^\dagger = -\nabla$$

$$= -\left\langle \Psi_0 \middle| \nabla_I \hat{H}_e \middle| \Psi_0 \right\rangle$$

Hellman-Feynman theorem!
The wave functions here must be the solution of stationary Schrödinger equation.

Problem: must be complete basis, containing *infinite* number of basis functions. Ideal only.

# MD: force calculations

In practice: using Slater determinant, and LCAO.

$$\Psi_0 = \frac{1}{\sqrt{N!}} \det\{\phi_i\}$$

Use basis sets:

$$\phi_i = \sum_v c_{iv} f_v(\boldsymbol{r};\boldsymbol{R})$$

$$\nabla_I \phi_i = \sum_v \left(\nabla_I c_{iv}\right) f_v(\boldsymbol{r};\boldsymbol{R}) + \sum_v c_{iv} \left(\nabla_I f_v(\boldsymbol{r};\boldsymbol{R})\right)$$

So in practices, there will be additional terms appear.

# MD: force calculations

$$\boldsymbol{F}_I^{\mathrm{IBS}} = \sum_{i\nu\mu}\left(\left\langle \nabla_I f_\nu \middle| H_e^{\mathrm{NSC}} - \varepsilon_i \middle| f_\mu \right\rangle + \left\langle f_\nu \middle| H_e^{\mathrm{NSC}} - \varepsilon_i \middle| \nabla_I f_\mu \right\rangle\right)$$

Another name:
Pulay force

IBS: incomplete-basis-set correction
NSC: non-self-consistency correction

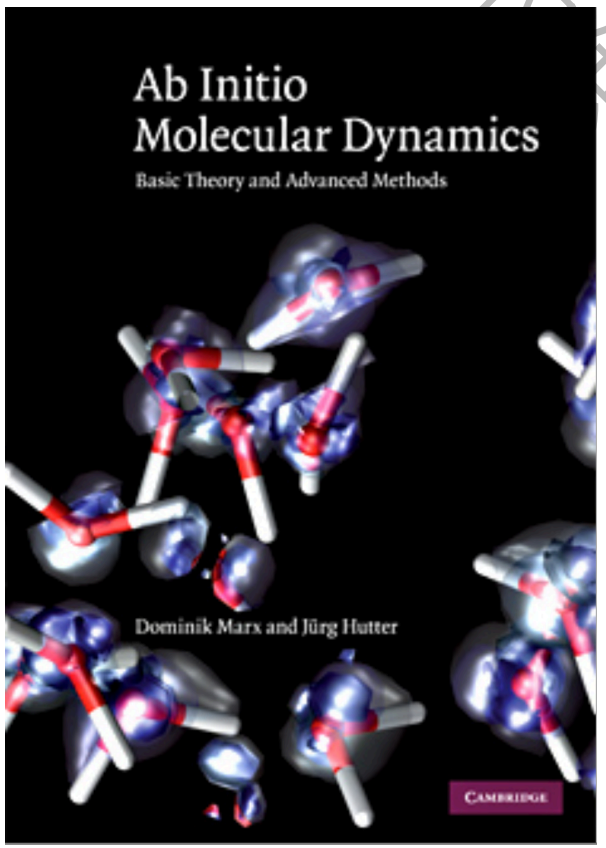
There is no Pulay force in plane wave calculations, but once one uses finite basis, it appears.

$$\boldsymbol{F}_I^{\mathrm{NSC}} = -\int \mathrm{d}^3 r (\nabla_I n(\boldsymbol{r}))\left(V^{\mathrm{SCF}} - V^{\mathrm{NSC}}\right)$$

$$\boldsymbol{F}_I = \boldsymbol{F}_I^{\mathrm{HFT}} + \boldsymbol{F}_I^{\mathrm{IBS}} + \boldsymbol{F}_I^{\mathrm{NSC}}$$

# MD: AIMD

本质上是电子结构计算的问题!




*AB INITIO* MOLECULAR DYNAMICS: BASIC THEORY AND ADVANCED METHODS

DOMINIK MARX
*Ruhr-Universität Bochum*
and
JÜRG HUTTER
*University of Zürich*

CAMBRIDGE UNIVERSITY PRESS

# MD: cMD

c: conventional, classical

Use a physical/mathematical model for $E_{\mathrm{pot}}(\boldsymbol{R})$

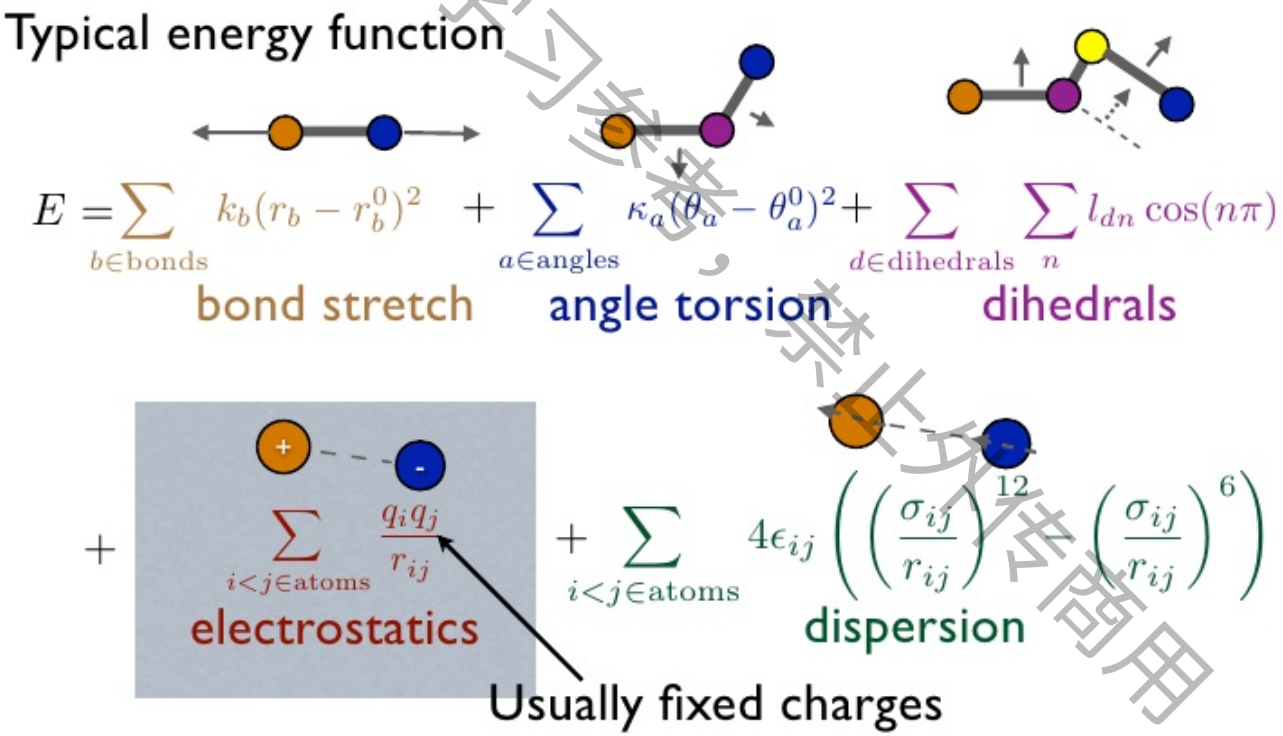
$$E_{\mathrm{pot}} \approx E^{\mathrm{EF}}(\boldsymbol{R}) = \sum_{I=1}^{N_n} \upsilon_1(\boldsymbol{R}_I) + \sum_{I<J}^{N_n} \upsilon_2(\boldsymbol{R}_I, \boldsymbol{R}_J)$$

$$+ \sum_{I<J<K}^{N_n} \upsilon_3(\boldsymbol{R}_I, \boldsymbol{R}_J, \boldsymbol{R}_K) + \cdots$$

# MD: cMD

c: conventional, classical

Use a physical/mathematical model for $E_{\text{pot}}(R)$

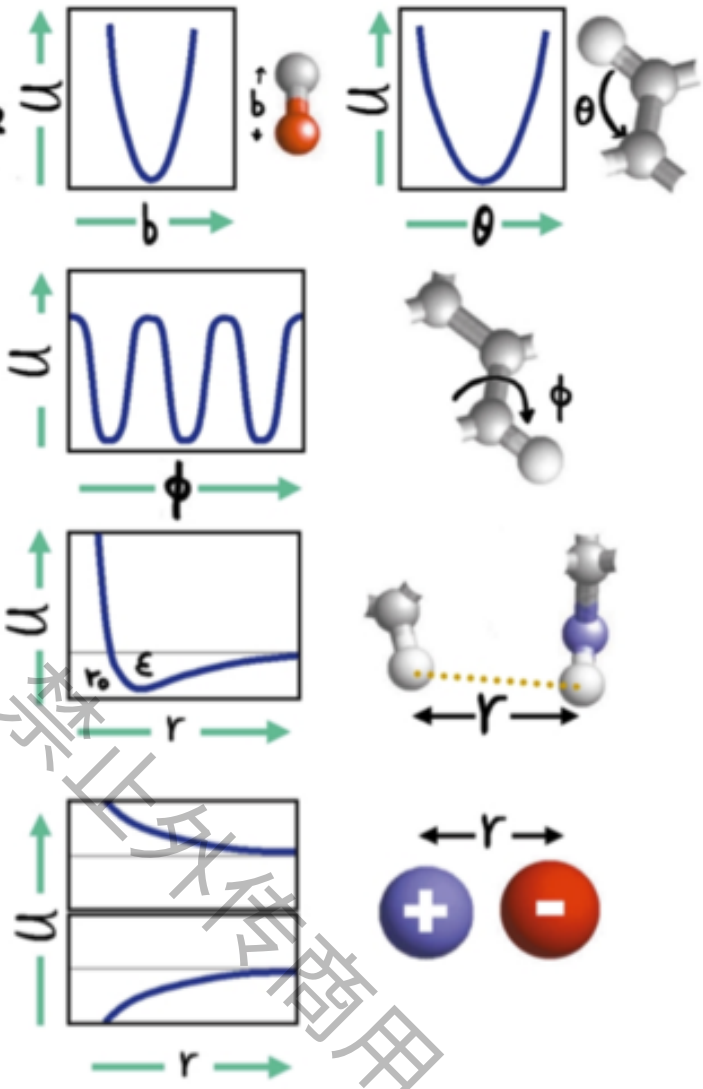


$$U = \sum_{\text{All Bonds}} \tfrac{1}{2} K_b (b - b_0)^2 + \sum_{\text{All Angles}} \tfrac{1}{2} K_\theta (\theta - \theta_0)^2$$

$$+ \sum_{\text{All Torsion Angles}} K_\phi [1 - \cos(n\phi + \delta)]$$

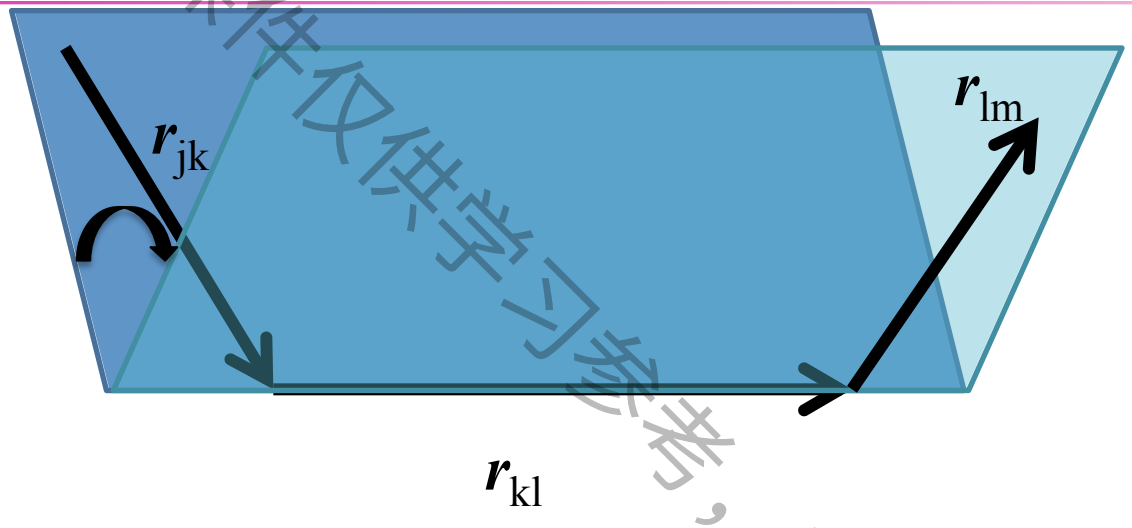
$$+ \sum_{\text{All nonbonded pairs}} \varepsilon \left[ (r_0/r)^{12} - 2(r_0/r)^6 \right]$$

$$+ \sum_{\text{All partial charges}} 332 q_i q_j / r$$



```
(base) leap:yongleli$ ls
cmd/     lib/     parm/    pixmaps/ prep/
(base) leap:yongleli$ grep "Mn" * -r
cmd/leaprc.water.spce:    { "Mn2+" "Mn"  "sp3" }
cmd/leaprc.DNA.OL15:    { "Mn2+" "Mn"  "sp3" }
cmd/leaprc.water.opc:    { "Mn2+" "Mn"  "sp3" }
cmd/leaprc.water.tip3p:    { "Mn2+" "Mn"  "sp3" }
cmd/leaprc.water.tip4pew:    { "Mn2+" "Mn"  "sp3" }
cmd/leaprc.water.fb3:    { "Mn2+" "Mn"  "sp3" }
cmd/leaprc.water.fb4:    { "Mn2+" "Mn"  "sp3" }
lib/atomic_ions.log:> i = createAtom MN Mn2+ 2.0
lib/atomic_ions.log:> set i element "Mn"
lib/atomic_ions.lib: "MN" "Mn2+" 0 1 131072 1 25 2.000000
lib/atomic_ions.lib: "MN" "Mn2+" 0 -1 0.0
lib/atomic_ions.cmd:i = createAtom MN Mn2+ 2.0
lib/atomic_ions.cmd:set i element "Mn"
parm/frcmod.ions234lm_hfe_spce:Mn2+ 54.94
parm/frcmod.ions234lm_hfe_spce:Mn2+  1.338  0.00789684    HFE set for SPC\E water from Li et al., JCTC, 2013, 9, 2733
parm/frcmod.ions234lm_iod_spce:Mn2+ 54.94
parm/frcmod.ions234lm_iod_spce:Mn2+  1.467  0.02960343    IOD set from Li et al., JCTC, 2013, 9, 2733
parm/frcmod.ions234lm_iod_tip4pew:Mn2+ 54.94
parm/frcmod.ions234lm_iod_tip4pew:Mn2+  1.467  0.02960343    IOD set from Li et al., JCTC, 2013, 9, 2733
parm/frcmod.ions234lm_126_tip3p:Mn2+ 54.94
parm/frcmod.ions234lm_126_tip3p:Mn2+  1.407  0.01686710    CM set for TIP3P water from Li et al., JCTC, 2013, 9, 2733
parm/frcmod.ions234lm_126_tip4pew:Mn2+ 54.94
parm/frcmod.ions234lm_126_tip4pew:Mn2+  1.401  0.01586934    CM set for TIP4P\EW water from Li et al., JCTC, 2013, 9, 2733
parm/frcmod.ions234lm_1264_tip3p:Mn2+ 54.94
parm/frcmod.ions234lm_1264_tip3p:Mn2+  1.485  0.03450196    12-6-4 set for TIP3P water from Li and Merz, JCTC, 2014, 10, 289
parm/frcmod.ions234lm_iod_tip3p:Mn2+ 54.94
parm/frcmod.ions234lm_iod_tip3p:Mn2+  1.467  0.02960343    IOD set from Li et al., JCTC, 2013, 9, 2733
parm/frcmod.ions234lm_1264_spce:Mn2+ 54.94
parm/frcmod.ions234lm_1264_spce:Mn2+  1.495  0.03745682    12-6-4 set for SPC\E water from Li and Merz, JCTC, 2014, 10, 289
parm/lj_1264_pol.dat:Mn2+  0.534    Caculated from B3LYP/6-311++G(2d,2p) level of theory
parm/frcmod.ions234lm_126_spce:Mn2+ 54.94
parm/frcmod.ions234lm_126_spce:Mn2+  1.406  0.01669760    CM set for SPC\E water from Li et al., JCTC, 2013, 9, 2733
parm/frcmod.ions234lm_1264_tip4pew:Mn2+ 54.94
parm/frcmod.ions234lm_1264_tip4pew:Mn2+  1.485  0.03450196    12-6-4 set for TIP4P\EW water from Li and Merz, JCTC, 2014, 10, 289
parm/frcmod.ions234lm_hfe_tip4pew:Mn2+ 54.94
parm/frcmod.ions234lm_hfe_tip4pew:Mn2+  1.276  0.00354287    HFE set for TIP4P\EW water from Li et al., JCTC, 2013, 9, 2733
parm/frcmod.ions234lm_hfe_tip3p:Mn2+ 54.94
parm/frcmod.ions234lm_hfe_tip3p:Mn2+  1.339  0.00799176    HFE set for TIP3P water from Li et al., JCTC, 2013, 9, 2733
(base) leap:yongleli$
```

# How to calculate dihedral angle



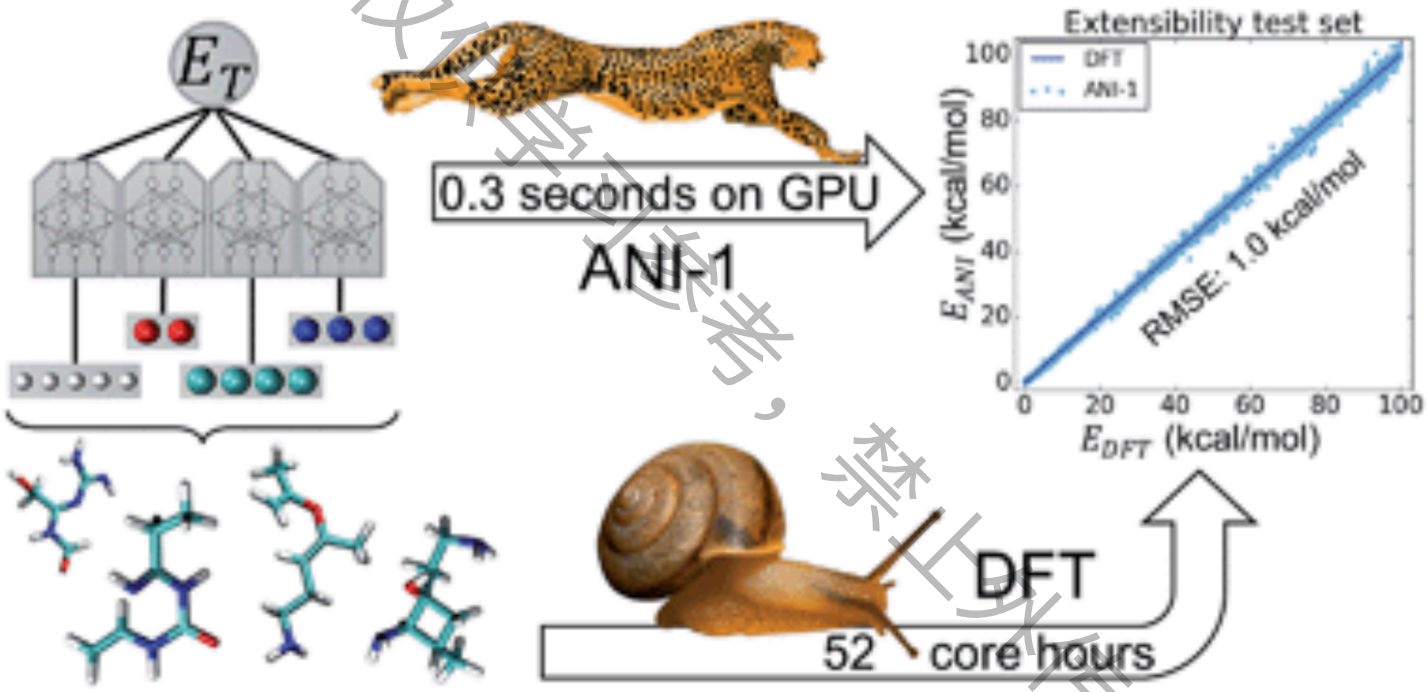

$$\phi_{jklm} = \arccos\left\{u_{jklm}\right\}$$

simplemd/run

$$u_{jklm} = \vec{e}_{jkl} \bullet \vec{e}_{klm}$$

$$\vec{e}_{jkl} = \frac{\vec{r}_{jk} \times \vec{r}_{kl}}{\left|\vec{r}_{jk} \times \vec{r}_{kl}\right|} \quad , \quad \vec{e}_{klm} = \frac{\vec{r}_{kl} \times \vec{r}_{lm}}{\left|\vec{r}_{kl} \times \vec{r}_{lm}\right|}$$

# 机器学习力场

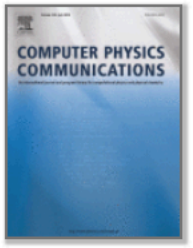



J. S. Smith, O. Isayev and A. E. Roitberg
*Chem. Sci.*, 2017, 8, 3192

ELSEVIER

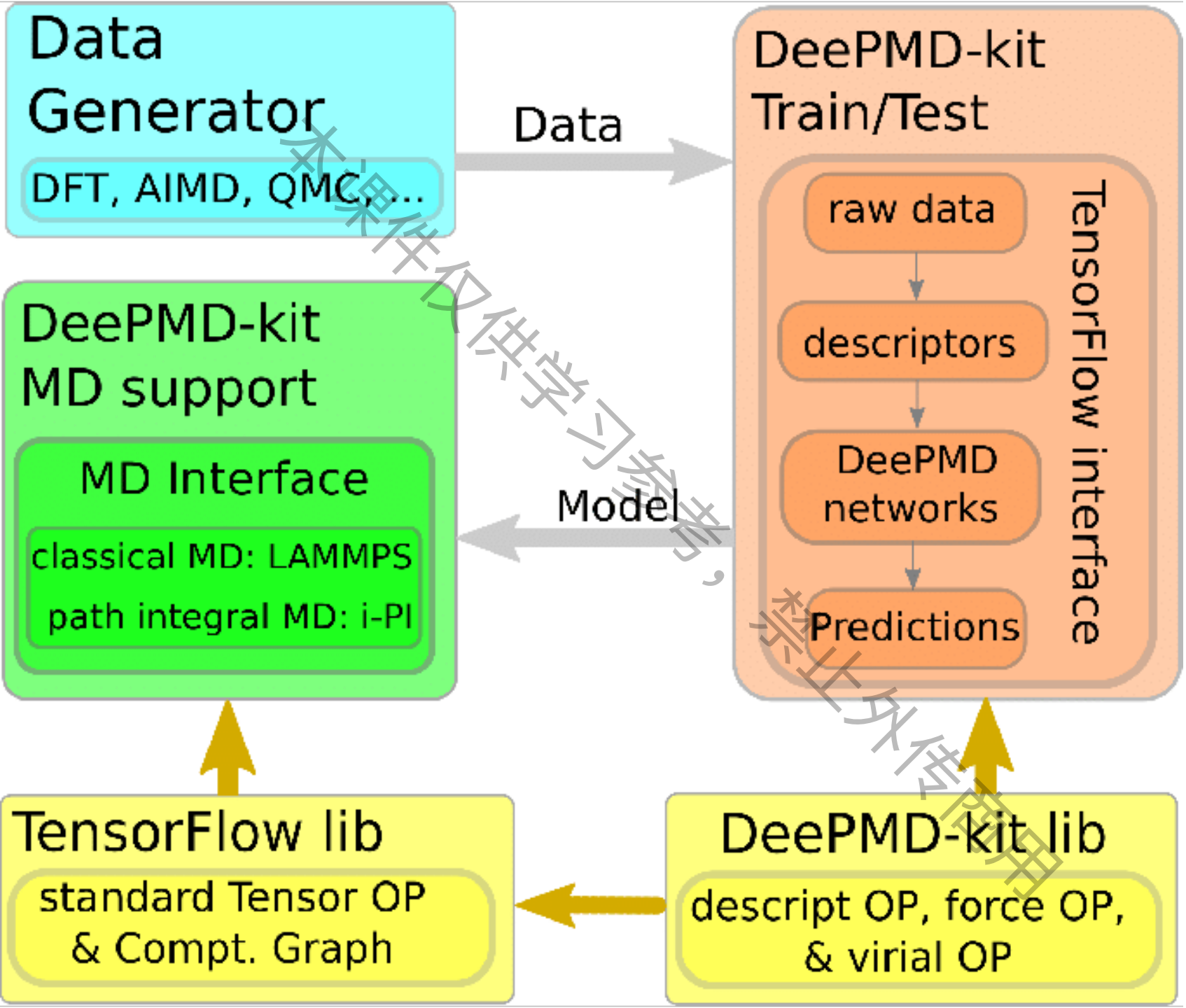
Computer Physics Communications

Volume 228, July 2018, Pages 178-184




# DeePMD-kit: A deep learning package for many-body potential energy representation and molecular dynamics ☆

Han Wang [a, b], Linfeng Zhang [c], Jiequn Han [c], Weinan E [c, d, e]



# Neural Network Potential Software

## ANI/Torchani

- Improved from BP descriptor
- Training using PyTorch, GPU accelerations
- Python interface. Better usability.

$$\hat{H}(\vec{R})|\Psi\rangle = E|\Psi\rangle$$

TORCHANI

## RuNNer/N2P2

- Original / Improved BP descriptor
- Training using RuNNer by Behler , no GPU accelerations
- Lammps interface

## DeePMD-kit

- Other descriptor
- Training using TensorFlow, GPU accelerations
- Lammps interface

Ref 1: Smith J. S., et. Al. Chemical Science, 2017, 8(4): 3192-3203.
Ref 2: Singraber, et al. Journal of chemical theory and computation, 2019.
Ref 3: Wang H., et al. Computer Physics Communications, 2018, 228: 178-184.

Chin. Phys. B Vol. 30, No. 5 (2021) 050706

SPECIAL TOPIC — Machine learning in condensed matter physics

# Accurate Deep Potential model for the Al–Cu–Mg alloy in the full concentration space*

Wanrun Jiang(姜万润)[1,2], Yuzhi Zhang(张与之)[3,4], Linfeng Zhang(张林峰)[5,†], and Han Wang(王涵)[6,‡]

# MD：cMD

1. Hard sphere、Lonnard-Jones、Morse、Hubbard、Heisenberg

Simple physical models, only related to pair interactions.
Used in theoretical physics, gas, etc.

2. FFMM、Compass

Gas, liquids and crystals composed by small molecules

3. CHARMM、AMBER、Gromos

Bio-molecules: proteins、RNA、DNA、membranes，molecular crystals
Used pair-additional assumptions

4. EAM, MEAM, inversion P(Chen-Mobius inversion), Tersoff P…

Inorganic compounds, graphene, alloy, carbon nanotubes, etc.

# Common force fields

| force field | originated by (year) | used for / coverage |
|---|---|---|
| AMBER | Kollman, UCSF (1994) | proteins, nucleic acids, carbohydrates |
| CHARMM | Karplus, Harvard (1983) | proteins, nucleic acids, lipids, organics |
| GROMOS | U. Groningen (1996) | proteins, nucleic acids, sugars, organics |
| OPLS | Jorgensen, Purdue (1988) | many liquids |
| ECEPP | Scheraga, Cornell (1975) | proteins |
| UFF | Rappe et al. (1992) | approximate for full periodic table |
| MM2/3/4 | Allinger, U Georgia (1977) | small molecules and hydrocarbons |

# Assessment of GAFF2 and OPLS-AA General Force Fields in Combination with the Water Models TIP3P, SPCE, and OPC3 for the Solvation Free Energy of Druglike Organic Molecules

Dario Vassetti, Marco Pagliai, and Piero Procacci*

**Cite this:** *J. Chem. Theory Comput.* 2019, 15, 3, 1983−1995
Publication Date: January 29, 2019
https://doi.org/10.1021/acs.jctc.8b01039




# Evaluation of nine condensed-phase force fields of the GROMOS, CHARMM, OPLS, AMBER, and OpenFF families against experimental cross-solvation free energies†



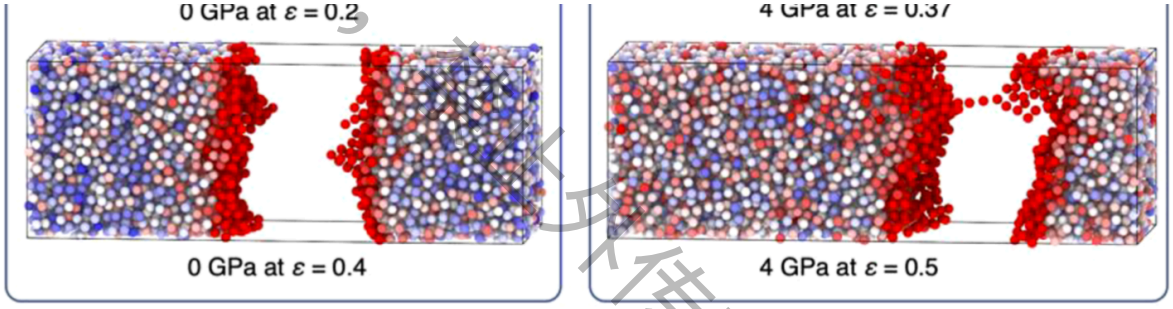
Sadra Kashefolgheta, [a] Shuzhe Wang, [a] William E. Acree, Jr. [b] and Philippe H. Hünenberger*[a]

$$V(r_{ij}) = \frac{q_i q_j}{r_{ij}} - \frac{C_i C_j}{r_{ij}^6} + D(B_i + B_j)\exp\left(\frac{A_i + A_j - r_{ij}}{B_i + B_j}\right)$$

# Predicting Fracture Propensity in Amorphous Alumina from Its Static Structure Using Machine Learning

Tao Du, Han Liu, Longwen Tang, Søren S. Sørensen, Mathieu Bauchy,* and Morten M. Smedskjaer*

Cite This: *ACS Nano* 2021, 15, 17705−17716 Read Online




$$V(r_{ij}) = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} - \frac{C_{OO}}{r_{ij}^6} + A_{OO}\exp\left(-\frac{r_{ij}}{\rho_{OO}}\right) + A_{MO}\exp\left(-\frac{r_{ij}}{\rho_{MO}}\right)$$

Sun, Jizhong, et al. "A simple transferable interatomic potential model for binary oxides applied to bulk α-Al2O3 and the (0001) α-$Al_2O_3$ surface." *Journal of crystal growth* **290** (2006): 235-240.

# MD: interatomic interactions

$$\boldsymbol{F} = M\boldsymbol{a} = -\left(\frac{\partial E_{pot}(\boldsymbol{R})}{\partial \boldsymbol{R}}\right)$$

Gradients:

1. Analytic gradients
   Analytical formula for $\mathrm{d}E_{\mathrm{pot}}(\boldsymbol{R})/\mathrm{d}\boldsymbol{R}$
   AIMD, or Hellman-Feynman theorem, or…
2. Numerical gradients: central difference

$$\left(\frac{\partial E_{\mathrm{pot}}}{\partial R_i}\right) \approx \frac{E_{\mathrm{pot}}(R_i + \delta R_i) - E_{\mathrm{pot}}(R_i - \delta R_i)}{2\delta R_i}$$

# Frontier for force field

1. Key: Accuracy + speed
2. Many-body interactions
   (F. Paesani)
3. Quantum mechanics calculated data
   thousands→tens or hundreds of thousands
   several molecules→database of molecules
4. Machine Learning:
   a. fitting the parameters
   b. Directly learn the *ab initio* results

# MD: polarizable force fields

## Electrostatic functional forms

How detailed does the function need to be in order to describe reality?

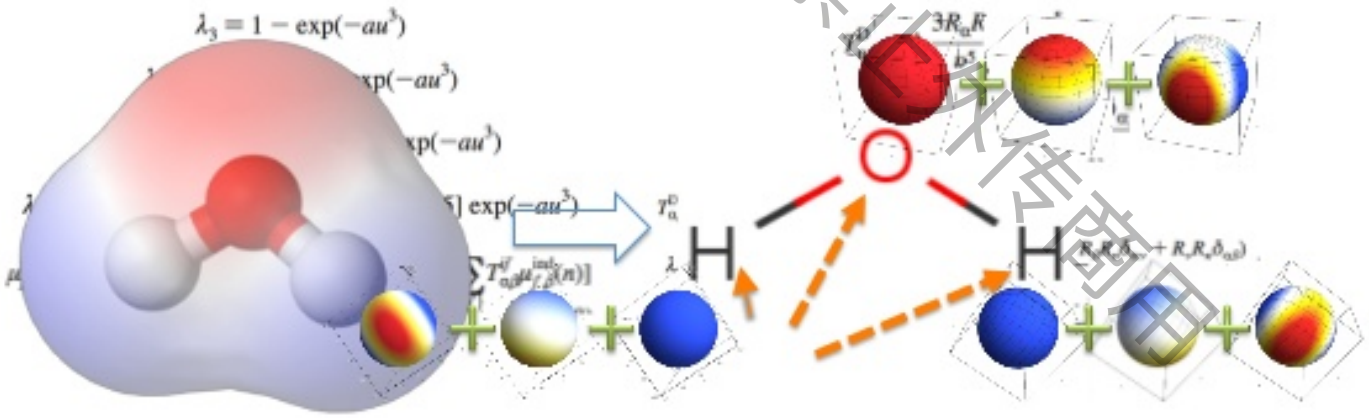
**AMBER fixed-charge force field:**

- Point charge on each atom

$$\sum_{i<j} \frac{q_i q_j}{r_{ij}}$$

**AMOEBA polarizable force field:**

- Point charge, dipole, and quadrupole on each atom
- Polarizable point dipole on each atom with short-range damping

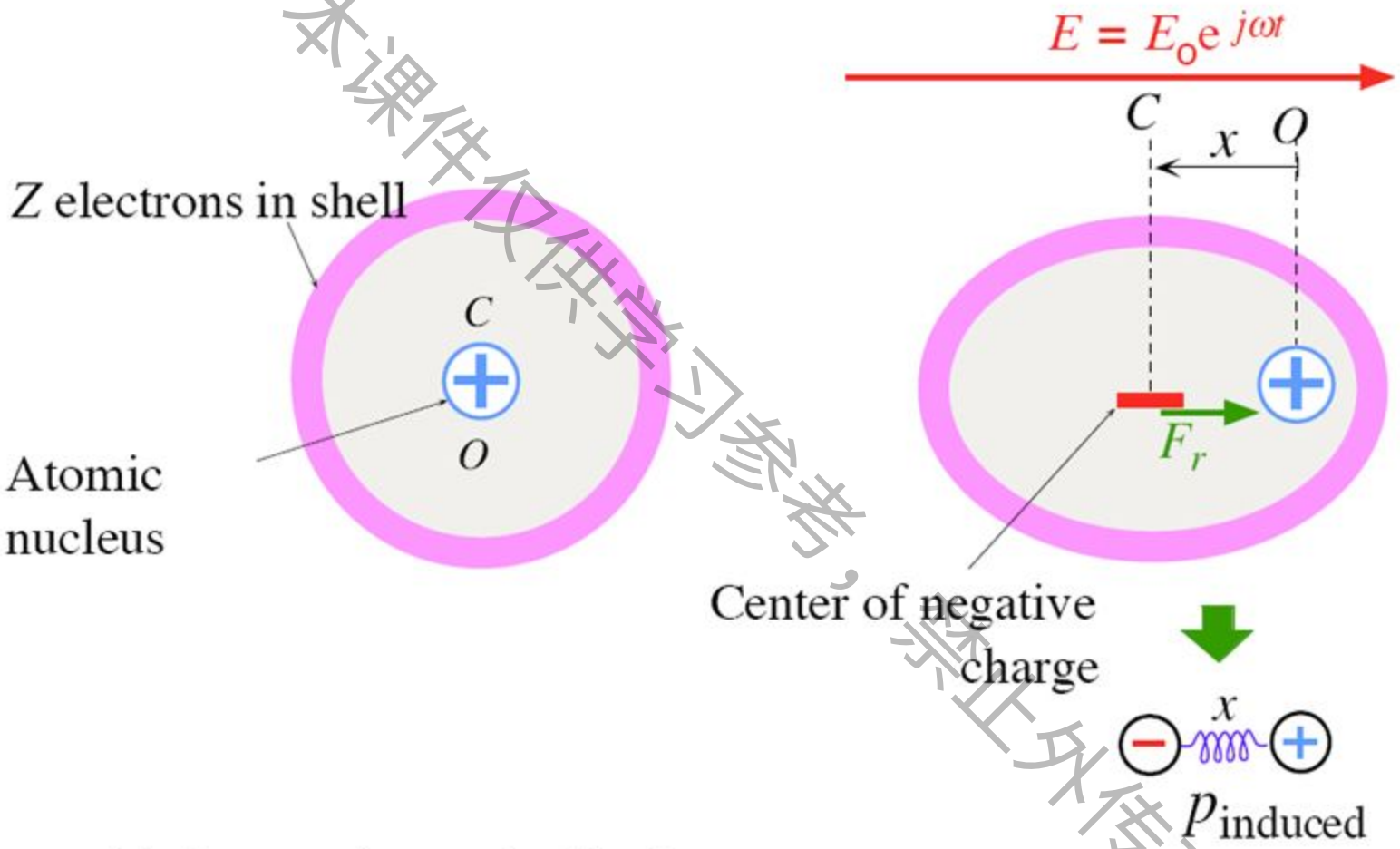


# Evaluation of the AMOEBA force field for simulating metal halide perovskites in the solid state and in solution

J. Chem. Phys. **152**, 024117 (2020); https://doi.org/10.1063/1.5131790

P. V. G. M. Rathnayake[1], Stefano Bernardi[1], *and* Asaph Widmer-Cooper[1,2,a)]

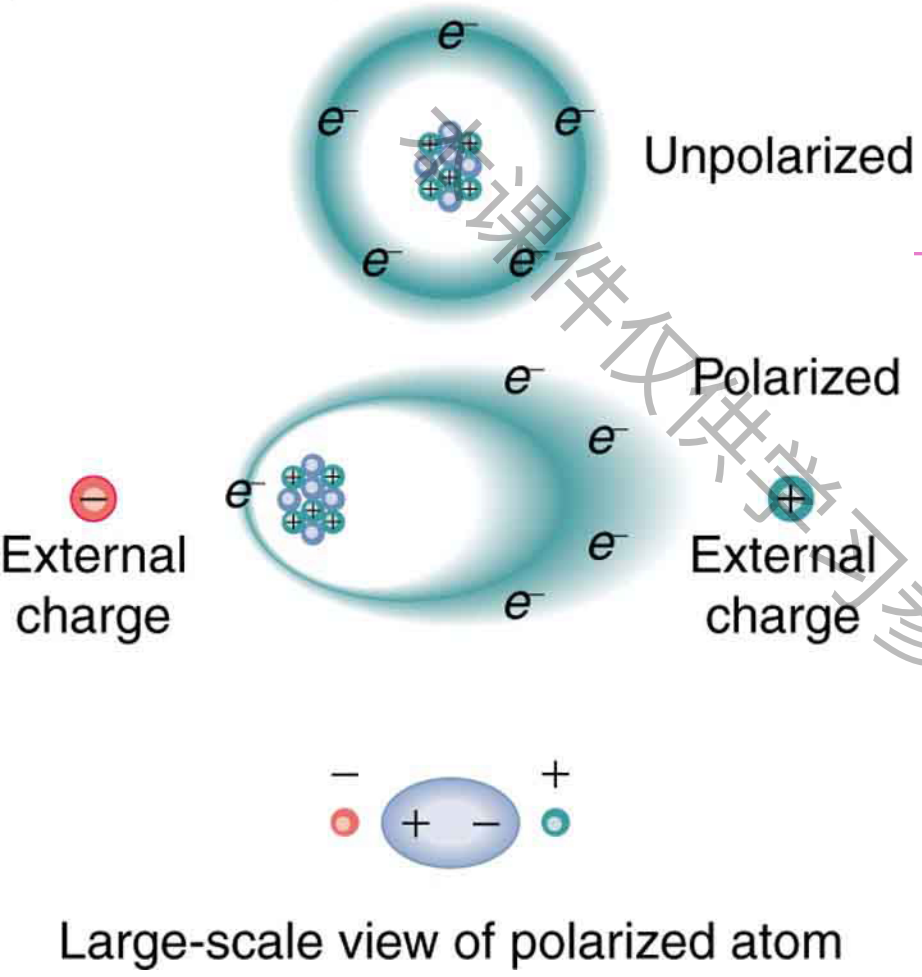
# Electronic Polarization, $\varepsilon_r$ and $n$

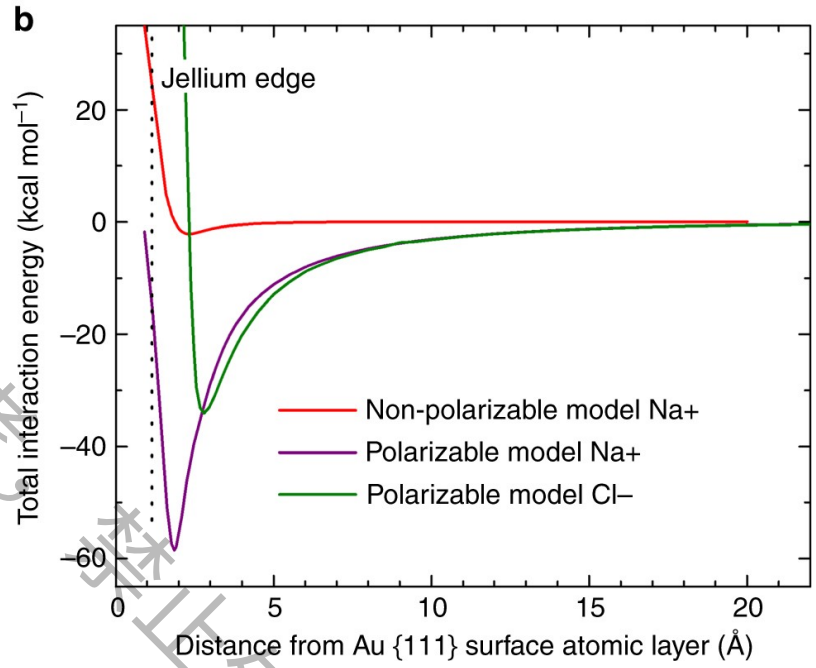



(a) A neutral atom in $E = 0$. (b) Induced dipole moment in a field

Electronic polarization of an atom. In the presence of a field in the $+x$ direction, the electrons Are displaced in the $-x$ direction (from O), and the restoring force is in the $+x$ direction.

Fig 9.4

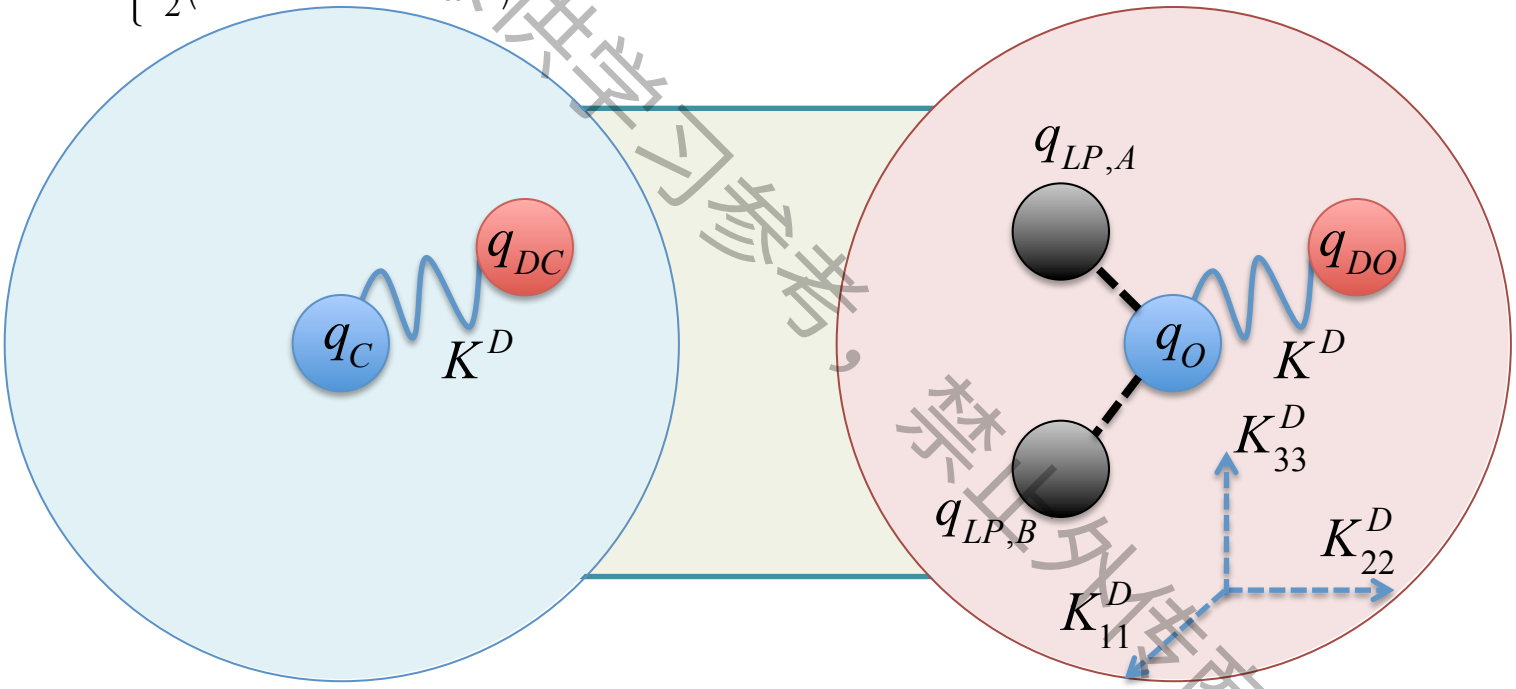



I. L. Geada, et al. *Nat. Commun.* **2018**, *9*, 716.

$$E_{\text{elec,Coulomb}} = \frac{1}{4\pi D}\left(\sum_{i\neq j}\frac{q_i q_j}{\|\boldsymbol{r}_i-\boldsymbol{r}_j\|}+\sum_{i\neq j}\frac{q_{D,i} q_j}{\|\boldsymbol{r}_{D,i}-\boldsymbol{r}_j\|}+\sum_{i\neq j}\frac{q_{D,i} q_{D,j}}{\|\boldsymbol{r}_{D,i}-\boldsymbol{r}_{D,j}\|}\right)$$

$$U_{\text{self}} = \begin{cases} K^D d^2, & \text{homogeneous} \\ \frac{1}{2}\left(K_{11}^D d^2 + K_{22}^D d^2 + K_{33}^D d^2\right), & \text{inhomogeneous} \end{cases}$$




Polarizability $\alpha = \frac{q_D^2}{K^D}$ dipole $d = \frac{q_D E}{K^D}$ induced dipole $\mu = \frac{q_D^2 E}{K^D}$

**Table 1**
**The scope of available polarizable force fields**

| Force fields | Polarizable models | Scope of biomolecules |
|---|---|---|
| AMBER ff02 | Induced dipole | Proteins [99, 100]<br>Nucleic acids [99]<br>Atomic ions [96, 98] |
| AMOEBA | Induced dipole | Proteins [112, 127]<br>Nucleic acids[a]<br>Small molecules [128, 129]<br>Atomic ions [130, 131] |
| CHARMM-FQ | Fluctuating charge | Proteins [92, 93]<br>Lipids [132]<br>Carbohydrates [133]<br>Atomic ions [134] |
| CHARMM Drude | Classical Drude Oscillator | Proteins [135]<br>Nucleic acids [136–139]<br>Lipids [124, 140]<br>Carbohydrates [141–144]<br>Small molecules [119, 145–157]<br>Atomic ions [47] |

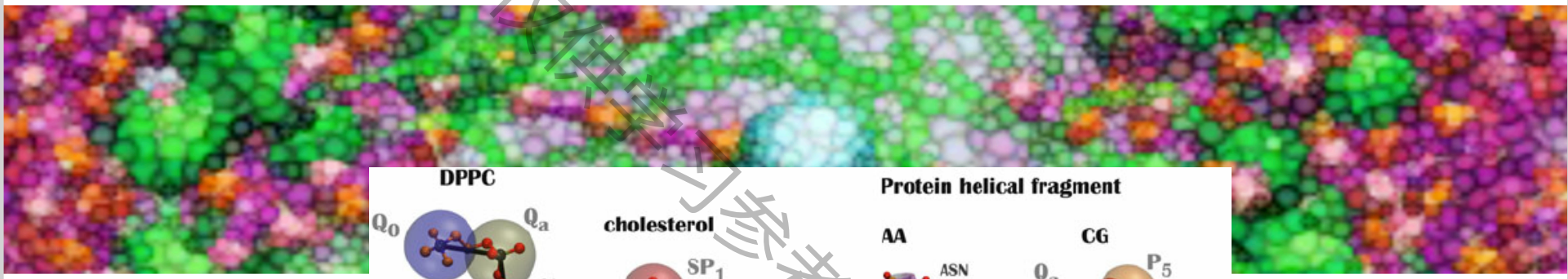
[a]Parameters have not been reported in the literature, but they are available through the website http://dasher.wustl.edu

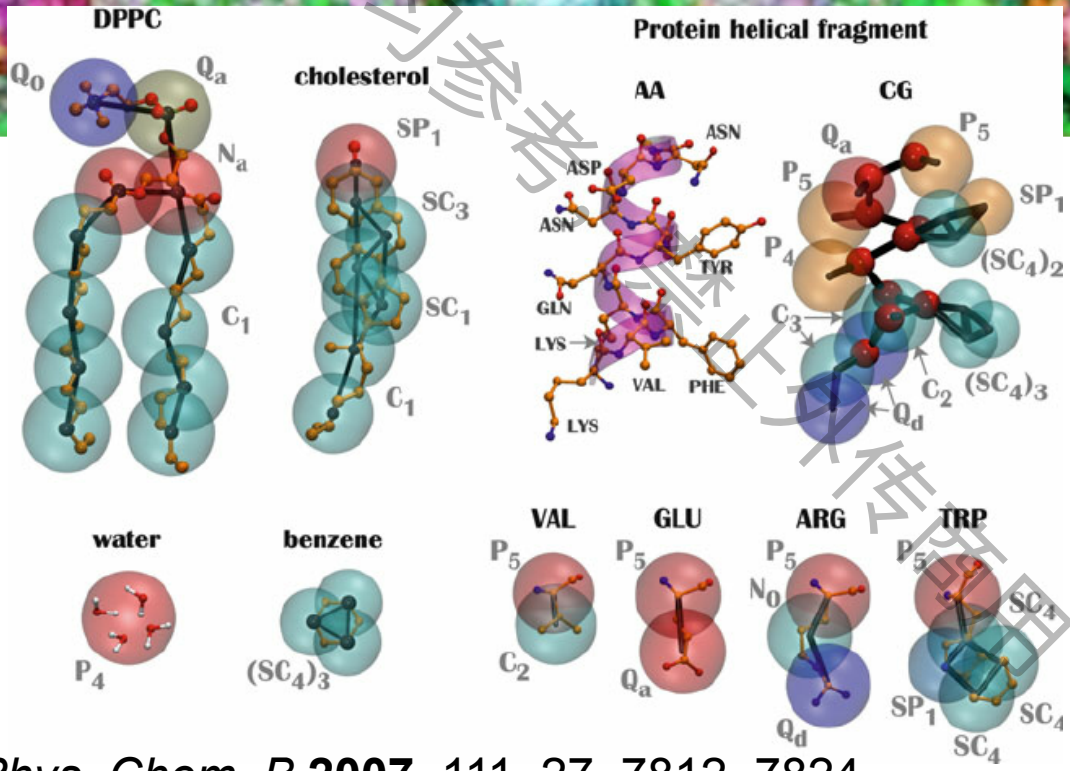
M. Bonomi, C. Camilloni, *Biomolecular Simulations*, Springer, 2019, Chapter 2

# FF: Coarse Grained

**Martini**

Coarse Grain Forcefield for Biomolecules






Marrink, et. al. *J. Phys. Chem. B* **2007**, 111, 27, 7812–7824

# On-the-fly updated polarized charge MD

THE JOURNAL OF PHYSICAL CHEMISTRY B

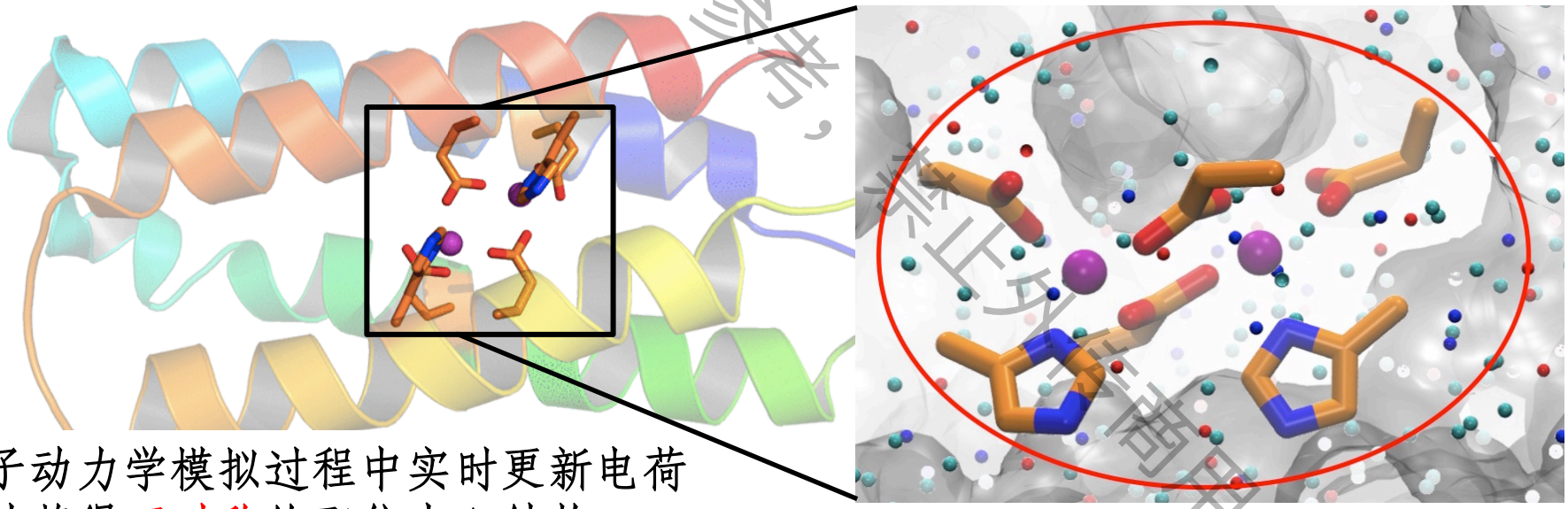
ARTICLE

pubs.acs.org/JPCB



## Structure and Dynamics of a Dizinc Metalloprotein: Effect of Charge Transfer and Polarization

Yong L. Li,[†] Ye Mei,[*,†,§] Da W. Zhang,[∥] Dai Q. Xie,[⊥] and John Z. H. Zhang[*,†,§,#]



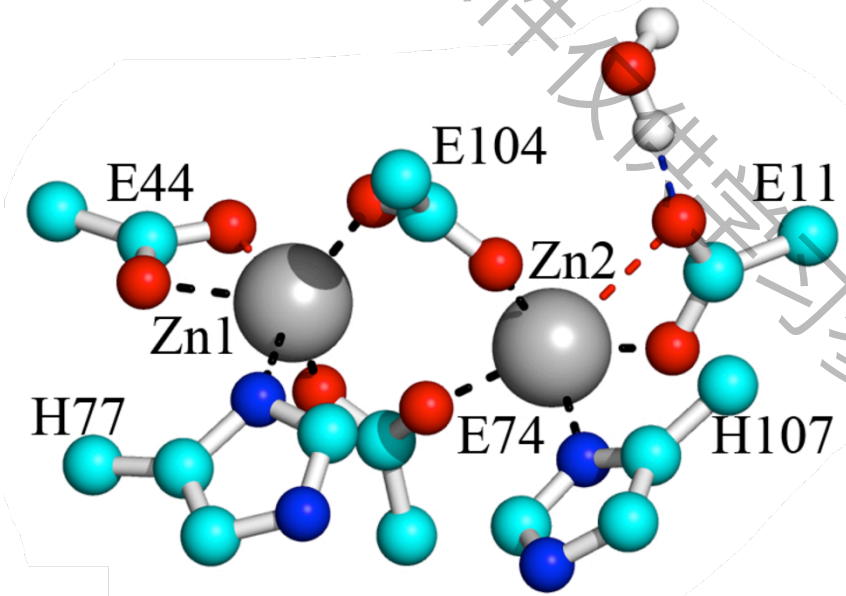
分子动力学模拟过程中实时更新电荷
成功获得不对称的配位中心结构

研究体系：双锌蛋白DFsc，作用：金属离子缓冲、胆固醇代谢、DNA合成

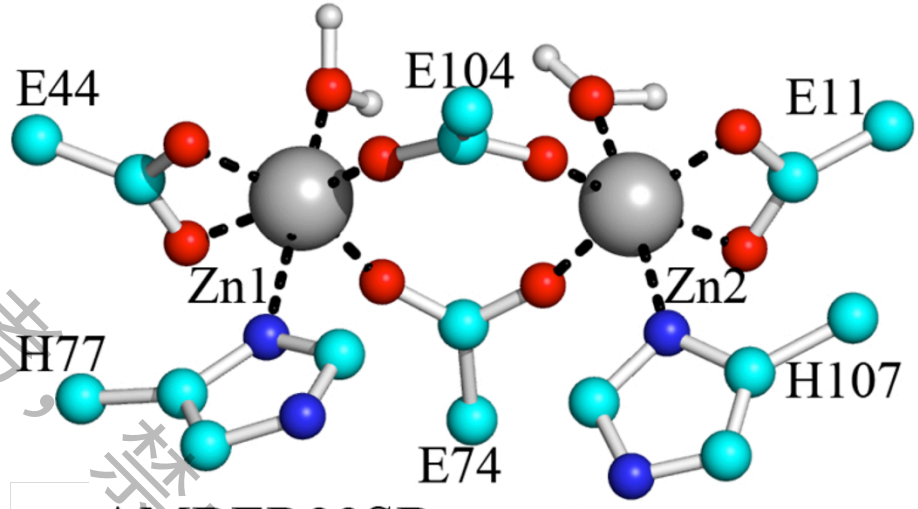
J. R. Calhoun, F. Nastri, O. Maglio, *et al. Structure.* 2008, 16, 210-215

# APPC模拟结果反映出体系的不对称性






APPC structure



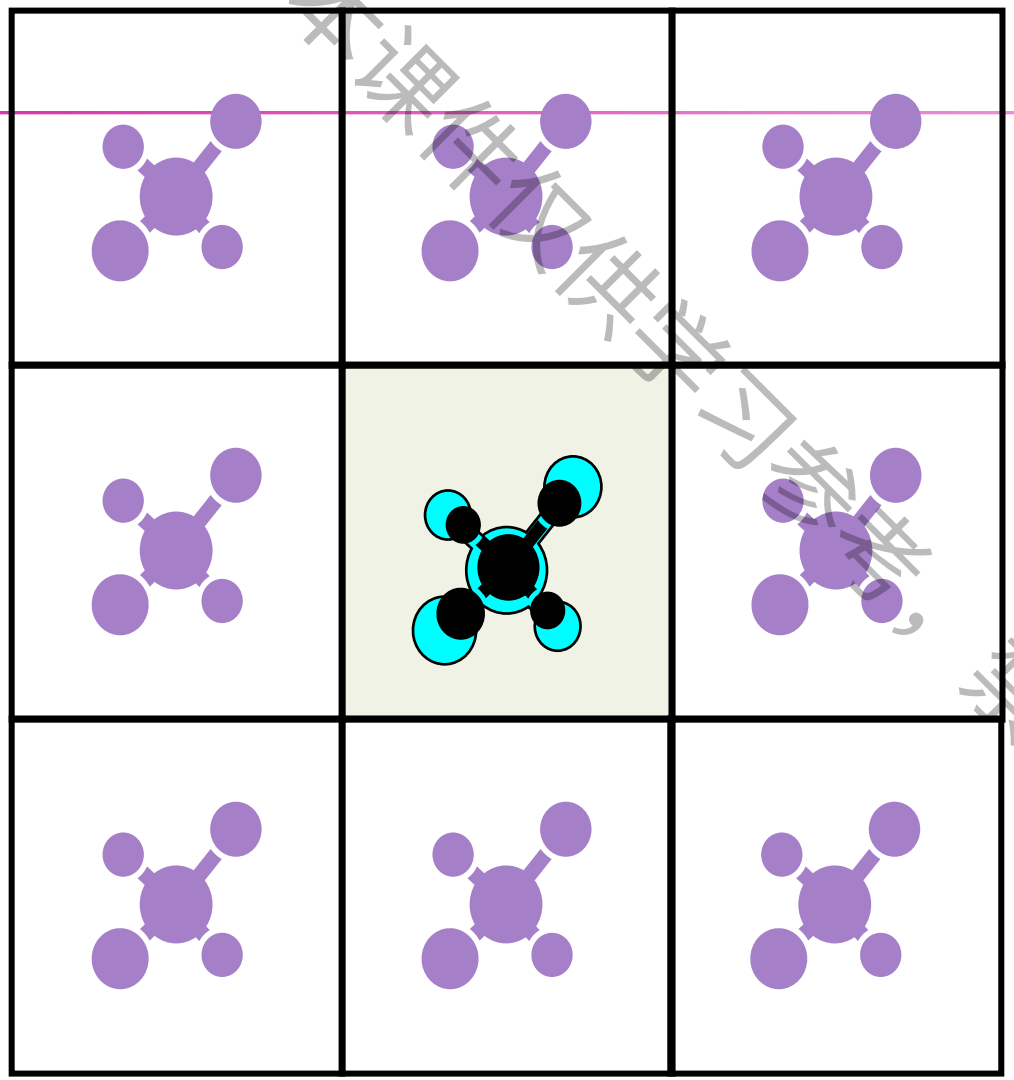

AMBER99SB structure

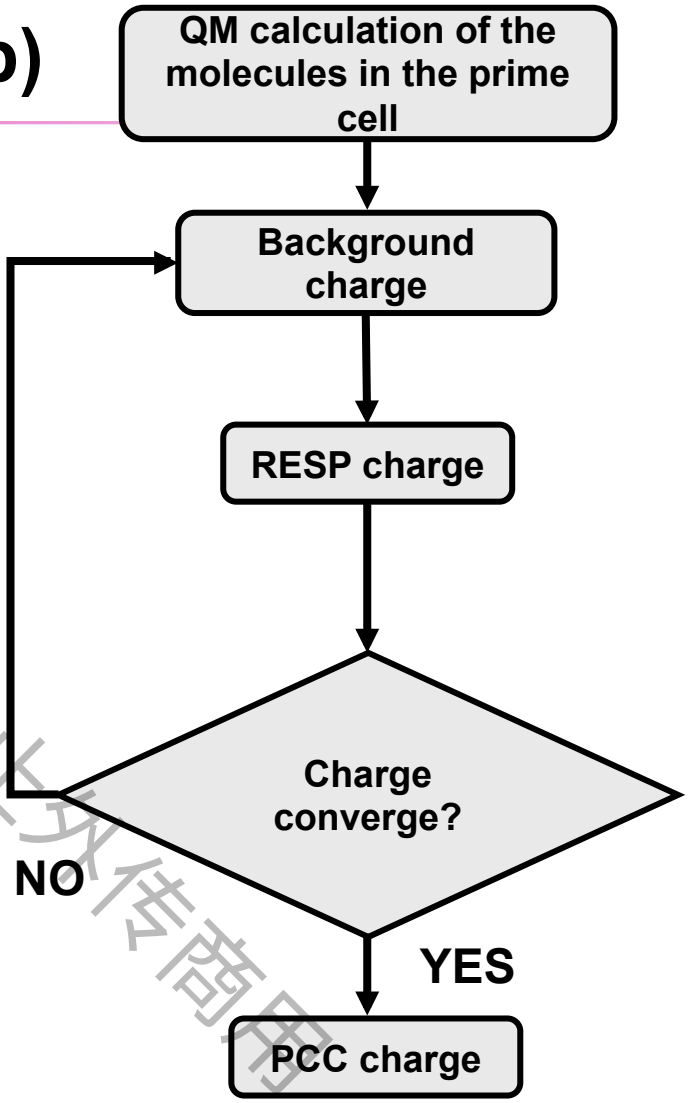
锌离子电荷： 1.19*e* 1.36*e* 2.0*e* 2.0*e*

两锌离子不对称，配位数为5/4，不与水配位

两锌离子对称，配位数为6/6，与水配位

**Li, Y. L.**; Mei, Y.; Zhang, D. W.; Xie, D. Q.; Zhang, J. Z. H. *J. Phys. Chem. B* **2011**, *115* (33), 10154-10162.





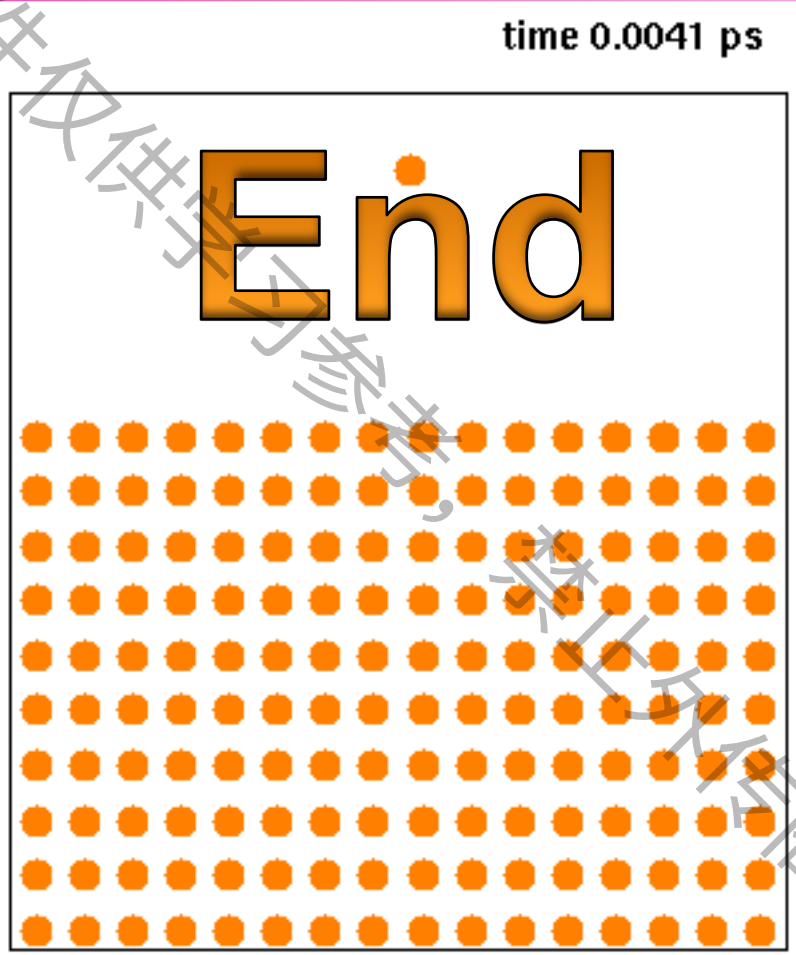

X. He et al. *Acc. Chem. Res.* **2014,** *47* (9), 2748-2757.
Y. Li et al. *J. Phys. Chem. B* **2011**, *115* (33), 10154-10162.

Polarized Crystal Charge (PCC)

# Mechanisms of Molecular Ferroelectrics Made Simple

Xiaoqing Zhu, Wenbin Fan, Wei Ren, and Yongle Li*

**Cite this:** *J. Phys. Chem. C* 2021, 125, 22, 12461−12467
Publication Date: June 2, 2021
https://doi.org/10.1021/acs.jpcc.1c03291




办公室：E楼121，电话：021-66136131；邮箱：yongleli@shu.edu.cn