Overview of selected topics in computational catalysis that are helpful

Neeraj Rai

neerajrai@che.msstate.edu

Dave C. Swalm School of Chemical Engineering and Center for Advanced Vehicular Systems, Mississippi State University, USA

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Exchange-correlation functional

- **Write down total kinetic energy functional as the sum of non-interacting particle density (*n*) and the one that represents rest of the kinetic energy functional**

$$T[n] = T_s[n] + T_c[n]$$

where,

$$T_s[n] = -\frac{\hbar^2}{2m} \sum_i^N \int d^3r \, \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r})$$

We rewrite the exact energy functional as:

$$E[n] = T[n] + U[n] + V[n] = T_s[\{\phi_i[n]\}] + U_H[n] + E_{xc}[n] + V[n]$$

Capelle, *Brazilian Journal of Physics*, 36, 1318-1343, 2006

Local density approximation (LDA)

Exchange Functional (based on the exact exchange energy of homogeneous electron system):

$$E_x^{LDA}[n] = -\frac{3q^2}{4}\left(\frac{3}{\pi}\right)^{1/3} \int d^3r\, n(\mathbf{r})^{4/3}$$

The correlation functionals are parameterized against quantum Monte Carlo results for uniform electron gas. The overall exchange-correlation functional is of the form:

$$E_{xc}[n] \approx E_{xc}^{LDA}[n] = \int d^3r\, e_{xc}^{hom}(n)\big|_{n \to n(\mathbf{r})} = \int d^3r\, e_{xc}^{hom}(n(\mathbf{r}))$$

Success of LDA is primarily due to the cancellation of errors (E_X is overestimated while the E_C is underestimated]

Capelle, *Brazilian Journal of Physics*, 36, 1318-1343, 2006

Semilocal functionals

Gradient expansion approximations (GEA, $|\nabla n(r)|$, $|\nabla n(r)|^2$, $\nabla^2(n(r))$)

$$T_s[n] \approx T_s^W[n] = T_s^{LDA}[n] + \frac{\hbar^2}{8m} \int d^3r \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})}$$

$$E_x[n] \approx E_x^{GEA(2)}[n] = E_x^{LDA}[n] - \frac{10q^2}{432\pi(3\pi^2)^{1/3}} \int d^3r \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})^{4/3}}$$

Generalized gradient approximation (GGA)

$$E_{xc}^{GGA}[n] = \int d^3r \, f(n(\mathbf{r}), \nabla n(\mathbf{r}))$$

Different choices for $f(n(r), \nabla n(r))$ lead to different GGA density functionals such as PBE (used extensively in physics community) and LYP (used extensively in chemistry community)

GGA: improved molecular structure and energetics; can not account for weak interactions such as van der Waals.

Capelle, *Brazilian Journal of Physics*, 36, 1318-1343, 2006

Perdew's Jacob's ladder
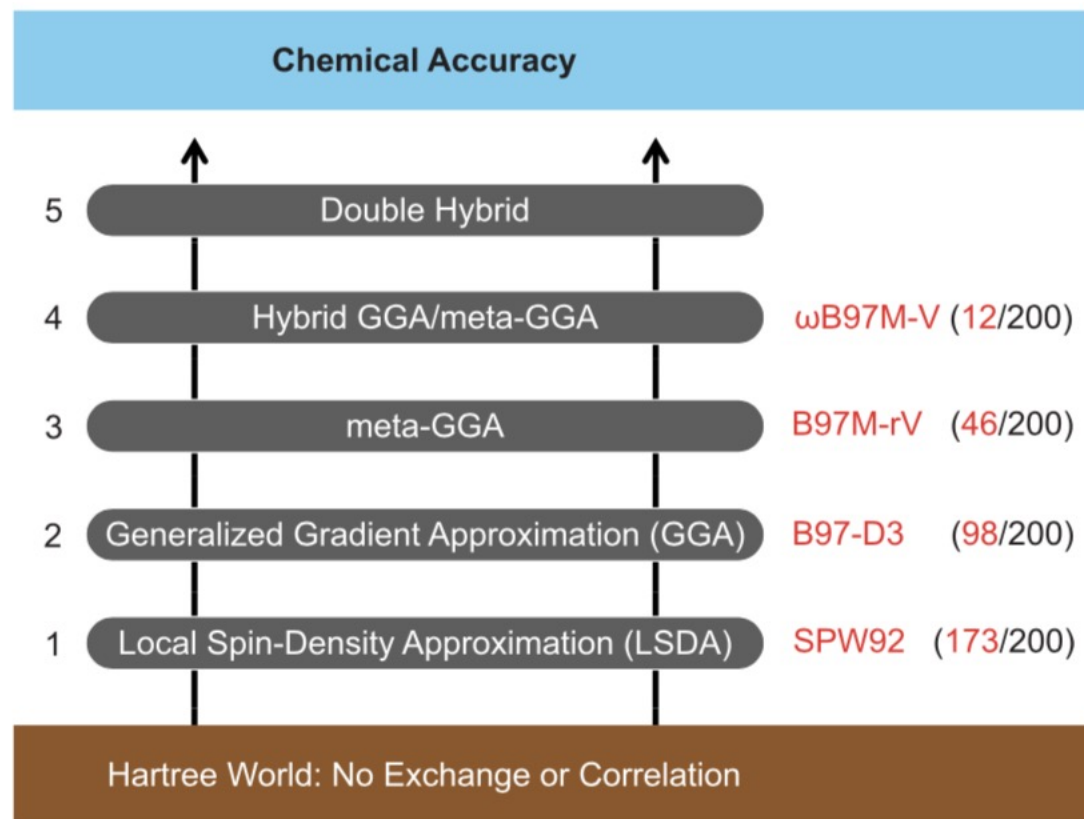
Mardirossian and Head-Gordon, *Mol. Phys.,* **115, 2315-2372, 2017**

Comparison of different LDA and GGA functions

method	-E/a.u.
Thomas-Fermi	625.7
Hartree-Fock	526.818
OEP (exchange only)	526.812
LDA (exchange only)	524.517
LDA (VWN)	525.946
LDA (PW92)	525.940
LDA-SIC(PZ)	528.393
ADA	527.322
WDA	528.957
GGA (B88LYP)	527.551
experiment	527.6

Ground state energy of the argon atom in atomic units (Hartree)

Capelle, *Brazilian Journal of Physics*, **36, 1318-1343, 2006**

Meta-GGA functionals

Exchange-correlation functional depends not only on the density, gradient of the density but also on the Kohn-Sham kinetic energy density

$$\tau(\mathbf{r}) = \frac{\hbar^2}{2m} \sum_i |\nabla \phi_i(\mathbf{r})|^2$$

$$E_{xc}[n(\mathbf{r}), \nabla n(\mathbf{r}), \tau(\mathbf{r})]$$

The additional degree of freedom is used to satisfy:
- self-interaction corrected correlation functional
- recovery of fourth order gradient expansion for the exchange
- finite exchange potential at the nucleus

Capelle, *Brazilian Journal of Physics*, 36, 1318-1343, 2006
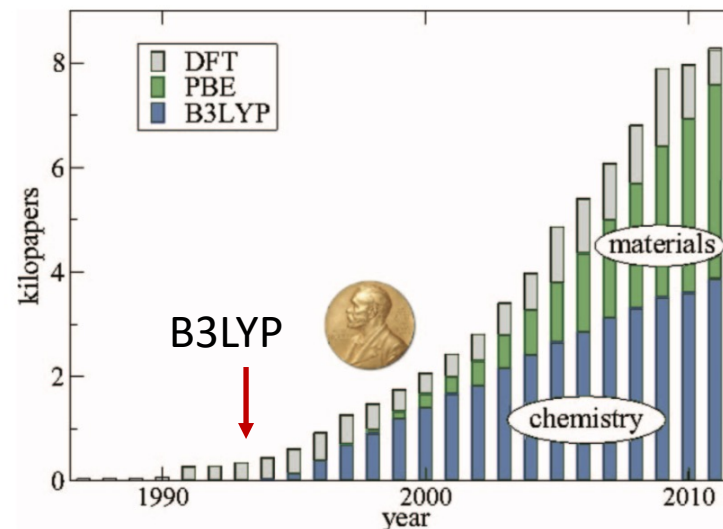
Hybrid GGA, meta GGA

General form of global hybrid functionals is:

$$E_{xc}^{GH} = c_x E_x^{HF} + (1 - c_x) E_x^{DFT} + E_c^{DFT}$$

$$E_{xc}^{B3PW91} = c_x E_x^{HF} + (1 - c_x - a_x) E_x^S + a_x E_x^{B88}$$
$$+ (1 - a_c) E_c^{PW92} + a_c E_c^{PW91}$$

B3LYP

Burke, *J. Chem. Phys.*, **136**, 150901, 2018

where $c_x = 0.20, a_x = 0.72, and\ a_c = 0.81$

Other common hybrid functionals are B3LYP, PBE0, etc.

Mardirossian and Head-Gordon, *Mol. Phys.*, **115**, 2315-2372, 2017

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Range separated functionals

Range separated functionals attempt to address self-interaction error and are given by the following form:

$$E_{xc}^{\text{RSH}} = c_{x,\text{sr}} E_{x,\text{sr}}^{\text{HF}} + c_{x,lr} E_{x,\text{lr}}^{\text{HF}} + \left(1 - c_{x,\text{sr}}\right) E_{x,sr}^{\text{DFT}}$$
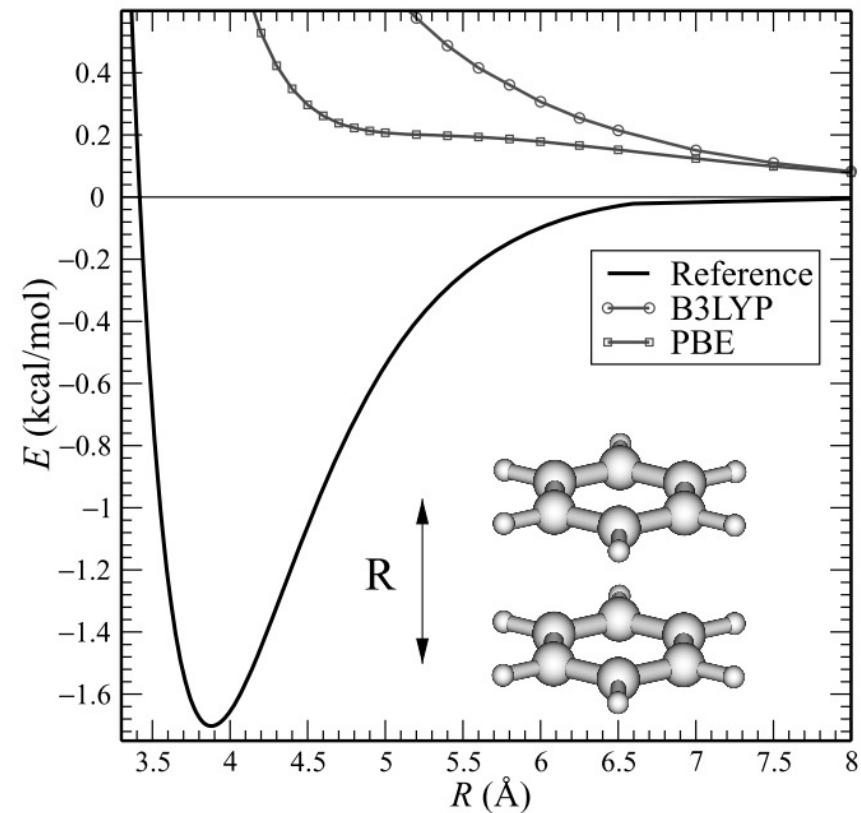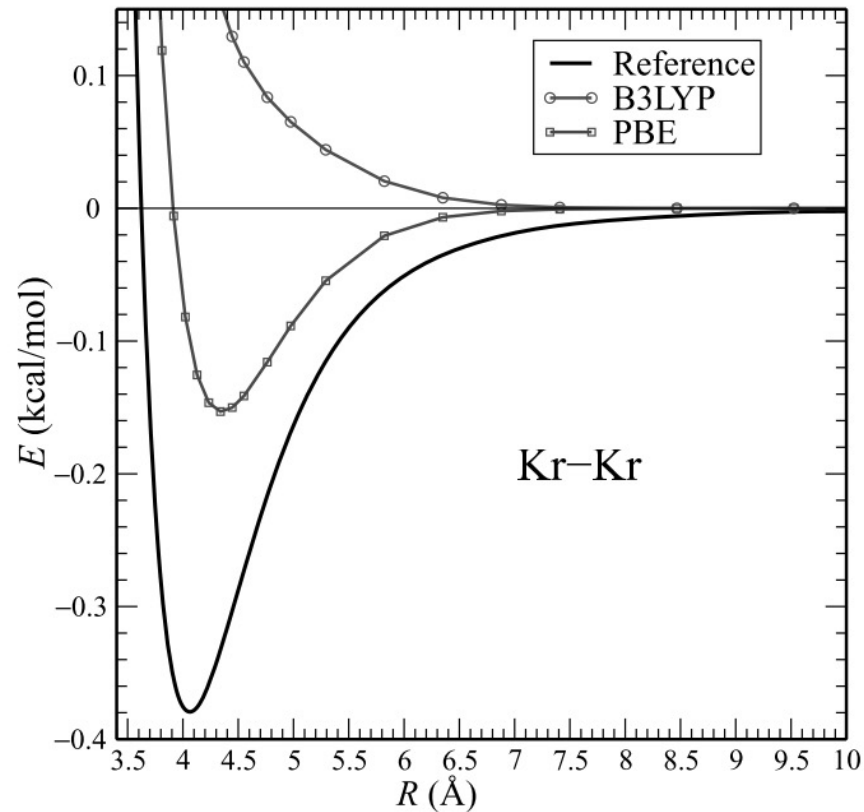$$+ \left(1 - c_{x,\text{lr}}\right) E_{x,\text{lr}}^{\text{DFT}} + E_c^{\text{DFT}}$$

Common examples include: ωB97, ωB97X, LRC-ωPBE, etc.

Mardirossian and Head-Gordon, *Mol. Phys.*, 115, 2315-2372, 2017

neerajrai@che.msstate.edu
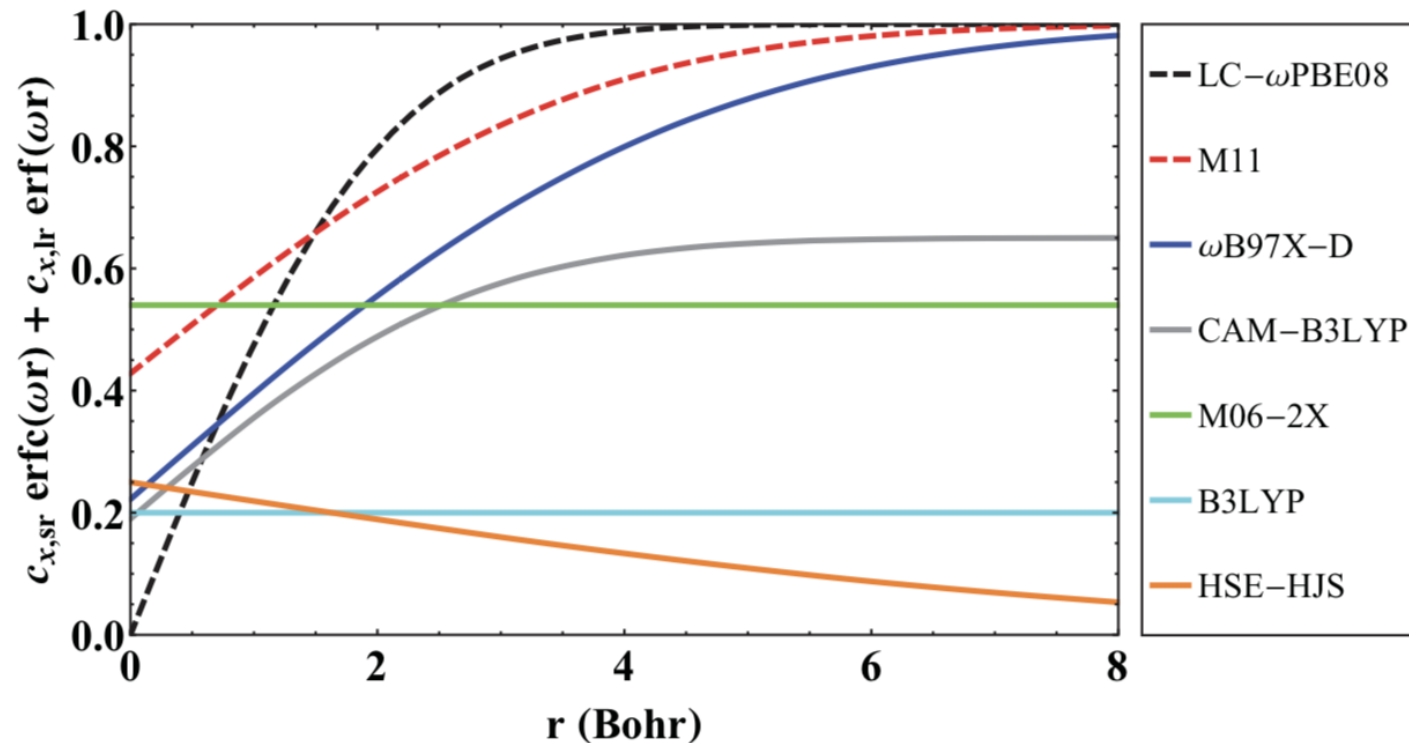
Another short coming of DFT functionals is the inability to capture vdW interactions

Kr–Kr

R

Grimme, *Comput. Mol. Sci.*, 1, 211-228, 2011

Dispersion-corrected/nonlocal density functionals

Grimme's dispersion correction model:

$$E_{\text{disp}}^{\text{DFT}-D} = -\sum_{A<B} \sum_{n=6,8,\dots} s_n \frac{C_n^{AB}}{R_{AB}^n} f_{\text{damp},n}(R_{AB})$$

Nonlocal density functionals

$$E_{\text{disp}}^{\text{VV10}} = \int d\mathbf{r} \rho(\mathbf{r}) \left[\frac{1}{32} \left(\frac{3}{b^2} \right)^{\frac{3}{4}} + \frac{1}{2} \int d\mathbf{r}' \rho(\mathbf{r}') \Phi(\mathbf{r}, \mathbf{r}') \right]$$

Mardirossian and Head-Gordon, *Mol. Phys.*, 115, 2315-2372, 2017

Accuracy of different dispersion correction models

Mardirossian and Head-Gordon, *Mol. Phys.*, **115, 2315-2372, 2017**

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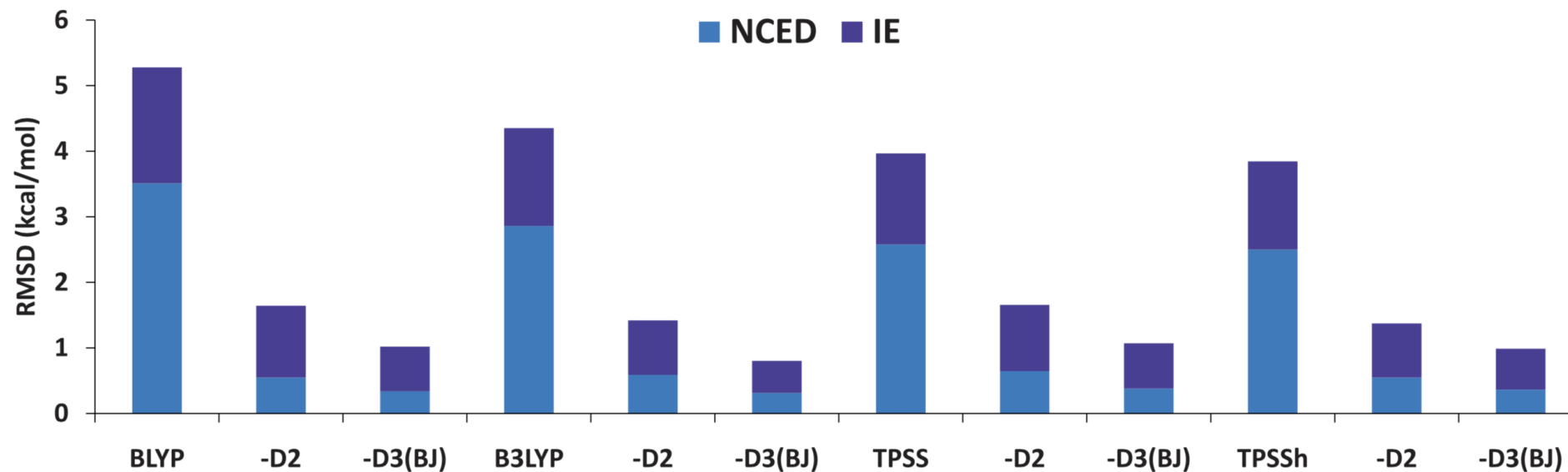
General accuracy for selected MN functionals for atomization energies bond dissociation

Mardirossian and Head-Gordon, *Mol. Phys.*, 115, 2315-2372, 2017

Number of parameters in different density functionals

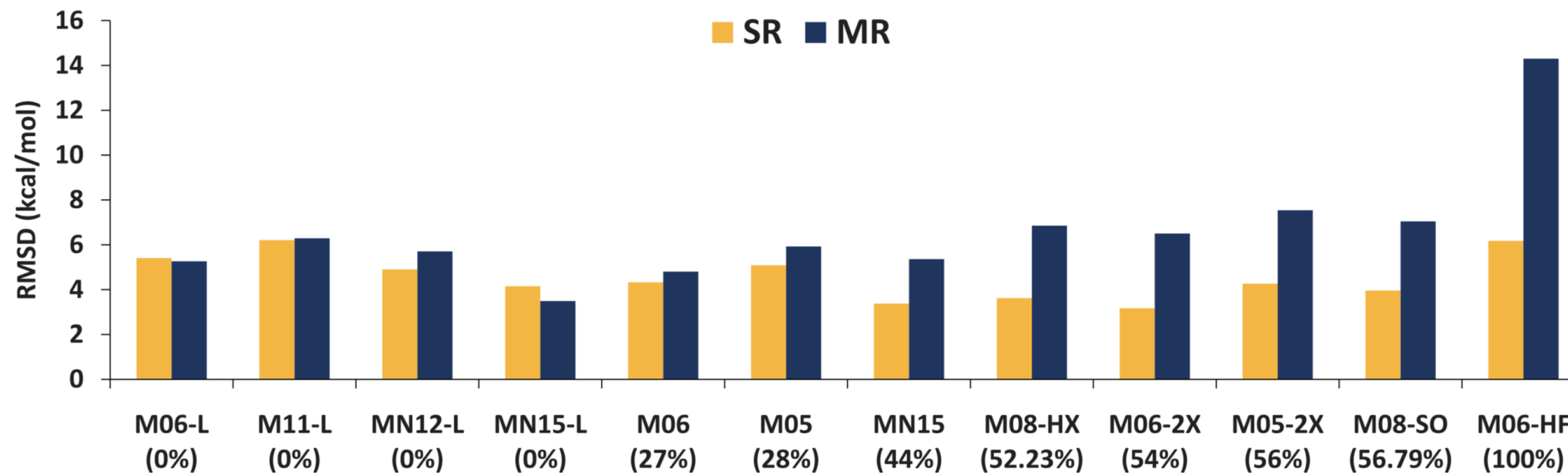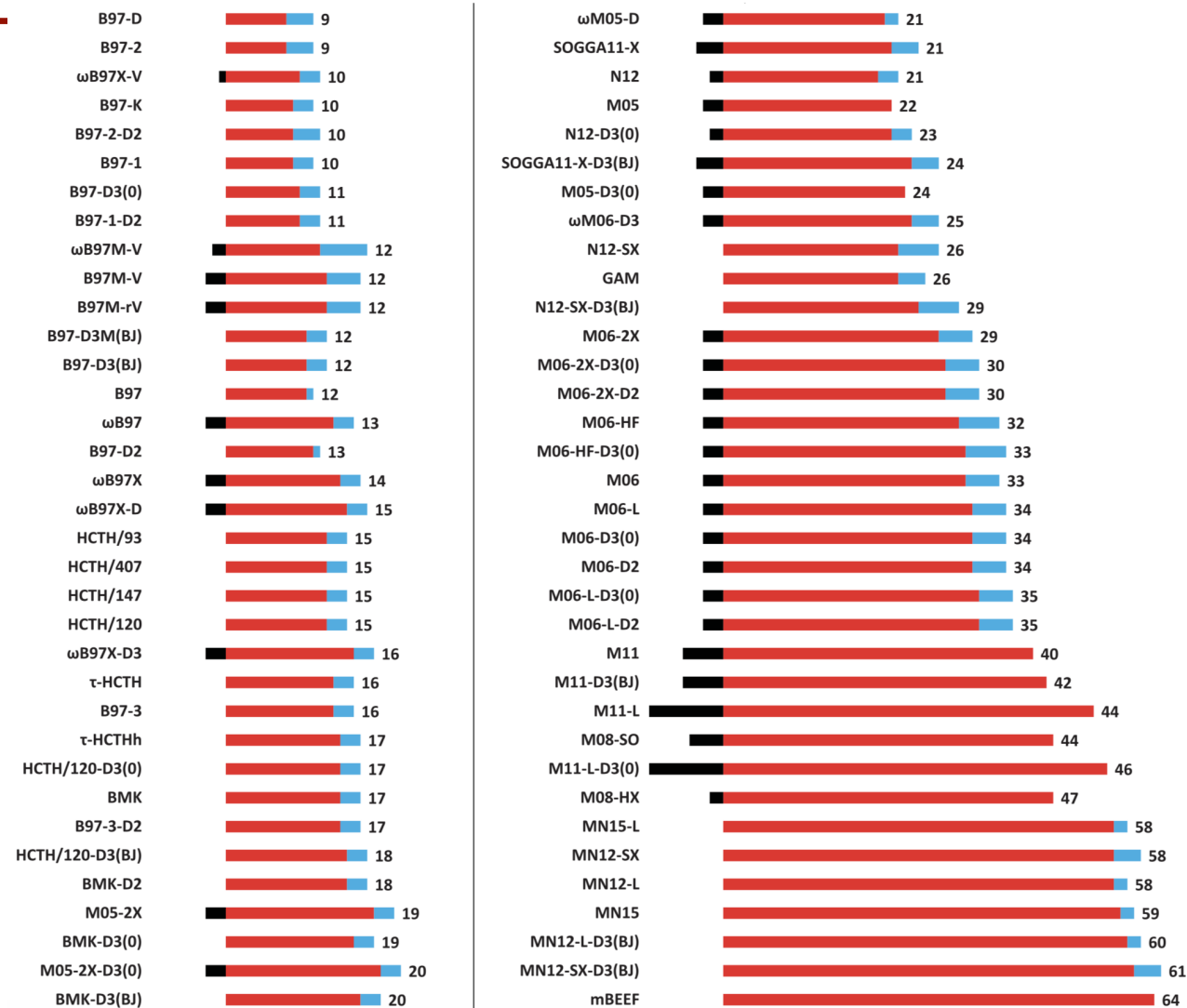| Functional	Parameters
B97-D	9
B97-2	9
ωB97X-V	10
B97-K	10
B97-2-D2	10
B97-1	10
B97-D3(0)	11
B97-1-D2	11
ωB97M-V	12
B97M-V	12
B97M-rV	12
B97-D3M(BJ)	12
B97-D3(BJ)	12
B97	12
ωB97	13
B97-D2	13
ωB97X	14
ωB97X-D	15
HCTH/93	15
HCTH/407	15
HCTH/147	15
HCTH/120	15
ωB97X-D3	16
τ-HCTH	16
B97-3	16
τ-HCTHh	17
HCTH/120-D3(0)	17
BMK	17
B97-3-D2	17
HCTH/120-D3(BJ)	18
BMK-D2	18
M05-2X	19
BMK-D3(0)	19
M05-2X-D3(0)	20
BMK-D3(BJ)	20

Functional	Parameters
ωM05-D	21
SOGGA11-X	21
N12	21
M05	22
N12-D3(0)	23
SOGGA11-X-D3(BJ)	24
M05-D3(0)	24
ωM06-D3	25
N12-SX	26
GAM	26
N12-SX-D3(BJ)	29
M06-2X	29
M06-2X-D3(0)	30
M06-2X-D2	30
M06-HF	32
M06-HF-D3(0)	33
M06	33
M06-L	34
M06-D3(0)	34
M06-D2	34
M06-L-D3(0)	35
M06-L-D2	35
M11	40
M11-D3(BJ)	42
M11-L	44
M08-SO	44
M11-L-D3(0)	46
M08-HX	47
MN15-L	58
MN12-SX	58
MN12-L	58
MN15	59
MN12-L-D3(BJ)	60
MN12-SX-D3(BJ)	61
mBEEF	64

Mardirossian and Head-Gordon, *Mol. Phys.*, **115, 2315-2372, 2017**

neerajrai@che.msstate.edu

Accuracy of functionals for bond lengths and binding energies

Functional	NCED	NCEC	NCD	IE	ID	TCE	TCD	BH	EBL	EBE
SPW92	2.14	37.77	7.60	2.22	6.76	42.23	65.35	19.55	0.195	2.81
PBE	1.96	4.08	3.26	1.15	6.53	9.22	15.58	9.17	0.327	2.16
TPSS	2.58	8.90	2.63	1.39	8.44	5.94	10.45	8.03	0.398	2.80
B3LYP	2.86	8.91	1.77	1.49	11.10	5.24	11.97	5.96	0.643	3.04
PBE-D3(BJ)	0.46	5.78	3.67	0.71	5.19	9.67	17.20	9.99	0.049	0.42
revPBE-D3(BJ)	0.49	6.60	2.54	0.77	5.21	6.60	9.91	8.30	0.053	0.44
BLYP-D3(BJ)	0.34	2.18	2.82	0.68	11.40	6.63	11.11	9.91	0.031	0.25
B97-D3(BJ)	0.47	4.82	2.52	0.78	9.15	4.66	7.92	8.32	0.045	0.42
TPSS-D3(BJ)	0.38	2.28	3.06	0.69	6.47	5.88	8.86	8.72	0.070	0.33
SCAN-D3(BJ)	0.54	9.18	3.41	0.55	4.46	5.25	6.39	7.83	0.037	0.60
M06-L	0.55	2.20	1.87	0.71	10.16	5.44	12.97	6.85	0.043	0.60
B97M-rV	0.22	0.67	2.04	0.28	6.45	3.57	4.78	4.36	0.025	0.17
PBE0-D3(BJ)	0.44	4.45	2.28	0.58	3.47	4.76	8.72	4.91	0.043	0.46
B3LYP-D3(BJ)	0.31	3.02	1.88	0.49	8.51	3.72	5.97	5.65	0.022	0.37
ωB97X-D	0.37	1.01	1.46	0.67	3.11	3.44	5.79	2.34	0.038	0.42
ωB97X-V	0.24	0.64	1.23	0.27	2.72	3.41	5.01	2.44	0.042	0.15
TPSSh-D3(BJ)	0.36	1.73	2.49	0.62	5.29	5.55	5.92	6.63	0.068	0.33
M06-2X	0.43	2.52	0.99	0.50	5.56	3.29	7.23	2.57	0.077	0.33
MN15	0.47	1.83	0.96	0.71	4.06	3.76	6.44	1.98	0.042	0.60
ωB97M-V	0.18	0.48	1.13	0.28	2.05	2.48	4.30	1.68	0.014	0.15
Minimum	0.18	0.48	0.91	0.27	2.05	2.48	4.30	1.68	0.014	0.15
Best	ωB97M-V	ωB97M-V	M08-SO	B97M-V	ωB97M-V	ωB97M-V	ωB97M-V	ωB97M-V	ωB97M-V	ωB97X-V

Mardirossian and Head-Gordon, *Mol. Phys.*, 115, 2315-2372, 2017

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Open-shell non-covalent or dimers characterized by significant electron delocalization

Functional	TA13	XB18	Bauza30	CT20	XB51
SPW92	11.49	4.47	9.63	1.32	5.34
PBE	6.22	0.80	3.59	0.42	1.88
TPSS	5.06	0.80	2.76	0.64	1.65
B3LYP	3.37	1.26	1.66	0.70	1.28
PBE-D3(BJ)	6.54	1.36	4.20	0.49	2.43
revPBE-D3(BJ)	5.06	0.45	2.55	0.39	1.63
BLYP-D3(BJ)	6.10	0.87	2.32	0.43	1.86
B97-D3(BJ)	5.31	0.38	2.31	0.43	1.50
TPSS-D3(BJ)	5.46	1.02	3.49	0.34	2.13
SCAN-D3(BJ)	4.89	1.57	4.57	0.41	2.25
M06-L	3.78	0.39	1.95	0.40	0.89
B97M-rV	4.15	0.63	2.12	0.32	0.91
PBE0-D3(BJ)	3.31	0.38	3.19	0.25	1.12
B3LYP-D3(BJ)	3.85	0.37	1.87	0.28	1.04
ωB97X-D	2.91	0.98	1.34	0.50	0.89
ωB97X-V	2.88	0.51	0.81	0.11	0.63
TPSSh-D3(BJ)	4.20	0.62	3.06	0.28	1.59
M06-2X	1.38	0.58	1.30	0.23	0.69
MN15	2.12	0.28	0.81	0.19	0.52
ωB97M-V	2.75	0.42	0.60	0.11	0.54
Minimum	1.38	0.09	0.60	0.10	0.44
Best	M06-2X	ωB97X	ωB97M-V	PW6B95-D3(0)	M05-D3(0)

Mardirossian and Head-Gordon, *Mol. Phys.*, **115, 2315-2372, 2017**

neerajrai@che.msstate.edu

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Barrier heights

Functional	BHPERI26	CRBH20	DBH24	CR20	HTBH38	NHTBH38	PX13	WCPT27
SPW92	13.24	3.45	16.63	14.26	18.59	15.81	42.96	24.79
PBE	4.38	7.97	9.99	3.13	10.08	10.30	13.56	9.98
TPSS	2.88	10.14	9.21	5.69	8.38	10.06	8.37	5.75
B3LYP	5.10	8.49	4.79	10.83	4.89	5.52	3.38	1.78
PBE-D3(BJ)	6.87	7.91	10.36	1.83	10.63	10.62	15.77	11.56
revPBE-D3(BJ)	6.54	10.95	8.74	4.09	8.63	9.14	7.31	8.19
BLYP-D3(BJ)	4.29	16.62	9.56	9.77	9.42	10.61	9.12	7.20
B97-D3(BJ)	4.24	14.16	7.63	9.53	8.28	7.58	6.46	6.72
TPSS-D3(BJ)	5.70	10.08	9.67	2.68	8.99	10.46	10.95	7.70
SCAN-D3(BJ)	5.74	6.21	8.00	1.97	7.98	8.61	12.64	8.75
M06-L	2.18	13.73	5.24	12.70	4.66	4.86	1.66	2.24
B97M-rV	1.44	7.55	4.97	2.03	4.62	5.33	1.50	2.19
PBE0-D3(BJ)	3.49	1.29	4.68	2.53	5.03	4.68	9.00	6.42
B3LYP-D3(BJ)	1.55	8.29	5.39	6.48	5.62	6.00	6.40	4.29
ωB97X-D	2.40	1.66	2.03	3.68	2.69	1.86	1.62	2.05
ωB97X-V	2.75	3.16	1.75	2.90	2.36	1.69	3.38	2.12
TPSSh-D3(BJ)	4.21	6.44	7.60	1.90	7.21	8.11	8.42	5.82
M06-2X	1.81	1.58	1.08	2.07	1.29	1.67	6.94	3.42
MN15	1.77	1.09	1.82	1.72	1.38	2.55	2.87	2.24
ωB97M-V	1.44	1.23	1.46	0.56	1.72	1.98	2.55	1.82
Minimum	1.21	0.80	1.08	0.56	1.25	1.48	1.04	1.39
Best	PW6B95-D3(0)	ωM05-D	M06-2X	ωB97M-V	M08-HX	M11-D3(BJ)	M06-L-D2	M08-SO

Mardirossian and Head-Gordon, *Mol. Phys.*, 115, 2315-2372, 2017

neerajrai@che.msstate.edu

Molecular Dynamics, Born-Oppenheimer MD, Metadynamics

Reference books

Understanding Molecular Simulations, Smit and Frenkel

Computer Simulation of Liquids, Allen and Tildesley

Ab initio Molecular Dynamics, Marx and Hutter

Statistical Mechanics: Theory and Molecular Simulation, Tuckerman

Particle based simulations (molecular simulations)

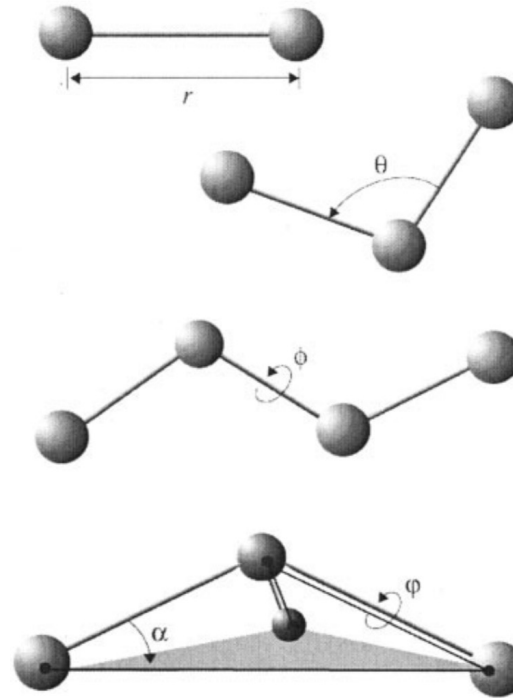| Molecular motion (Microscopic) | → Statistical Mechanics → | Thermodynamic and transport properties (Macroscopic) |

Force fields

Bonded interactions   **Nonbond interactions**

$$U_{\text{total}} = U_{\text{bond}} + U_{\text{angle}} + U_{\text{dihedral}} + U_{\text{vdW}} + U_{\text{Coulomb}}$$

$$U_{\text{bond}} = \sum_{\text{bonds } i} k_i^{\text{bond}}(r_i - r_{0i})^2,$$

$$U_{\text{angle}} = \sum_{\text{angles } i} k_i^{\text{angle}}(\theta_i - \theta_{0i})^2,$$

$$U_{\text{dihedral}} = \sum_{\text{dihedral } i} \begin{cases} k_i^{\text{dihe}}[1 + \cos(n_i\phi_i - \gamma_i)], n_i \neq 0 \\ k_i^{\text{dihe}}(0_i - \gamma_i)^2 \ n = 0, \end{cases}$$

Phillips et al., *J. Comp. Chem*. **26**, 1781--1802, 2005

Force fields

Bonded interactions

Nonbond interactions

$$U_{\text{total}} = U_{\text{bond}} + U_{\text{angle}} + U_{\text{dihedral}} + U_{\text{vdW}} + U_{\text{Coulomb}}$$

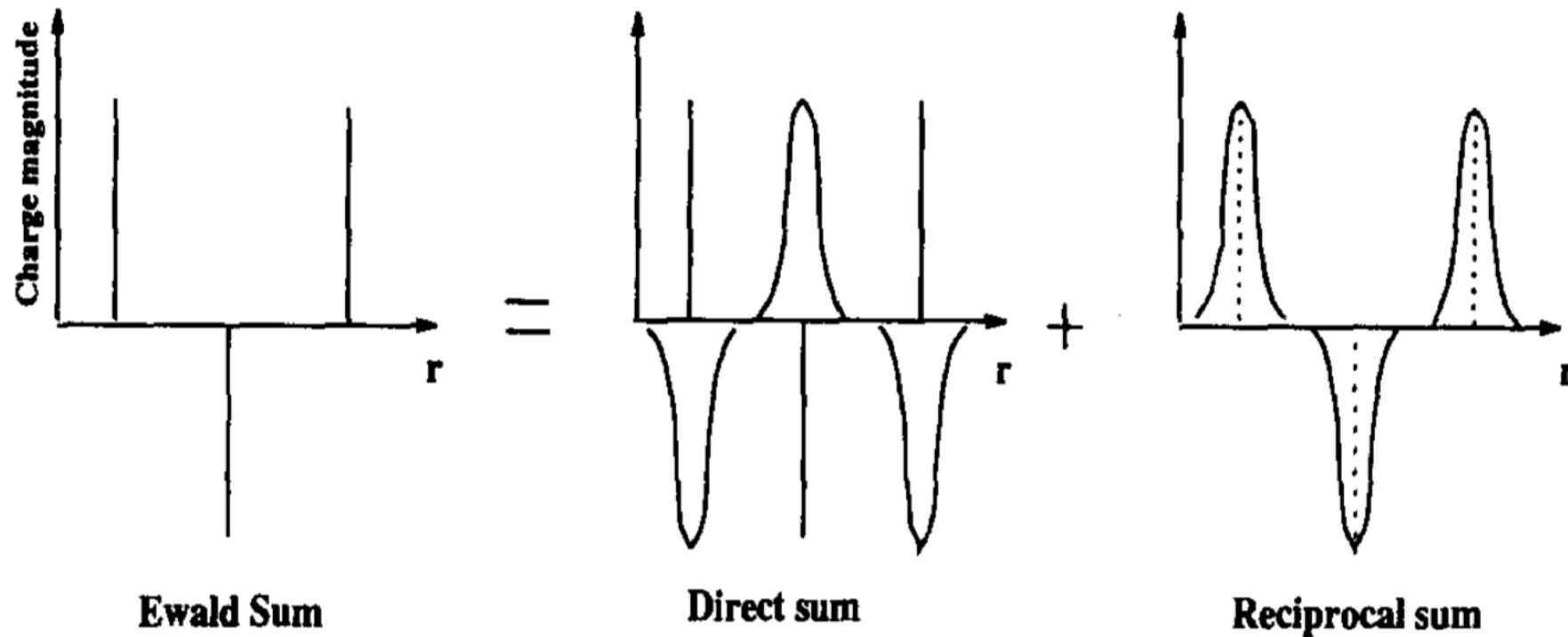$$U_{\text{vdW}} = \sum_i \sum_{j>i} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right],$$

$$U_{\text{Coulomb}} = \sum_i \sum_{j>i} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}},$$
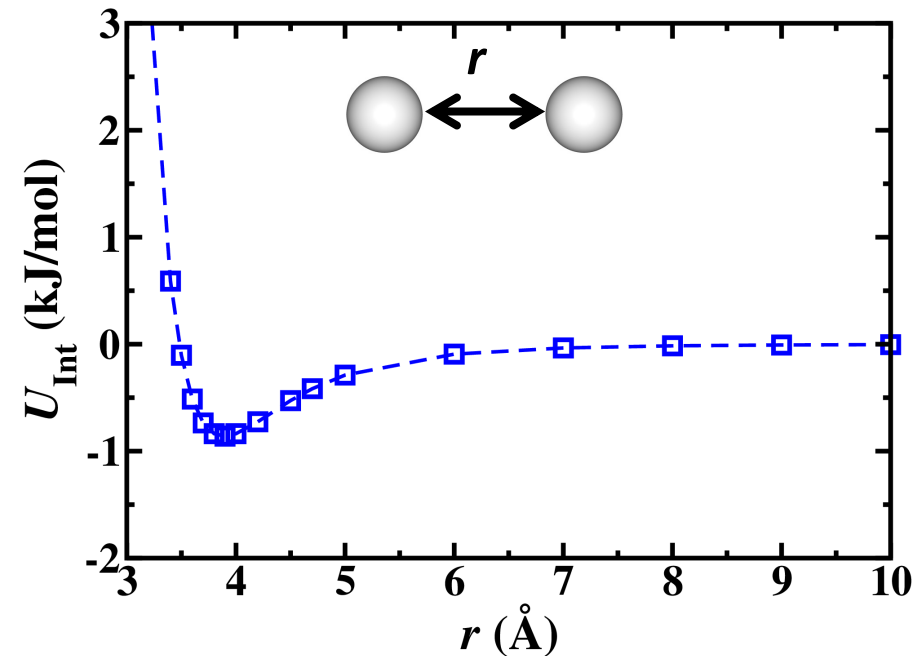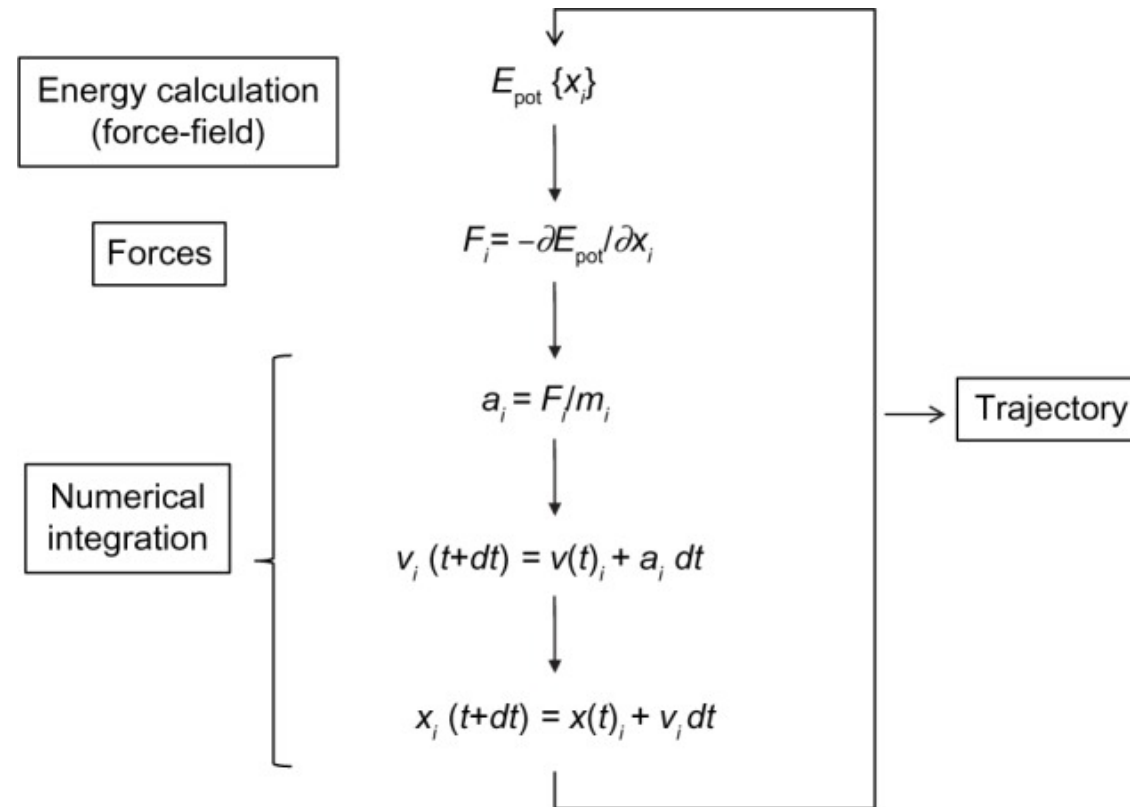

Phillips et al., *J. Comp. Chem*. **26**, 1781--1802, 2005

Computing electrostatic interactions

Ewald Sum = Direct sum + Reciprocal sum

Toukmaji and Board Jr., *Comput. Phys. Commun.* **95**, 73--92, 1996

Molecular dynamics (MD)

Phillips et al., *J. Comp. Chem*. **26**, 1781--1802, 2005

Different ensembles

Microcanonical (NVE)

Canonical (NVT)

Grand canonical (μVT)

Isothermal isobaric (NPT)

Constant stress (NST)

Constant enthalpy (NPH)

Lagrangian and Hamiltonian equations of motion (EOM)

Kinetic (K) and potential energy (U) of an N particle system is given by:

$$K(\dot{\mathbf{r}}_1, ..., \dot{\mathbf{r}}_N) = \frac{1}{2} \sum_{i=1}^{N} m_i \dot{\mathbf{r}}_i^2 \qquad U(\mathbf{r}_1, ..., \mathbf{r}_N)$$

then the Lagrangian and Lagrangian EOM are:

$$\mathcal{L}(\mathbf{r}_1, ..., \mathbf{r}_N, \dot{\mathbf{r}}_1, ..., \dot{\mathbf{r}}_N) = K(\dot{\mathbf{r}}_1, ..., \dot{\mathbf{r}}_N) - U(\mathbf{r}_1, ..., \mathbf{r}_N)$$

$$\frac{\mathrm{d}}{\mathrm{d}t} \left(\frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_i} \right) - \frac{\partial \mathcal{L}}{\partial \mathbf{r}_i} = 0$$

and the Hamiltonian and Hamiltonian EOM are:

$$\mathcal{H}(\mathbf{r}_1, ..., \mathbf{r}_N, \mathbf{p}_1, ..., \mathbf{p}_N) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}_1, ..., \mathbf{r}_N)$$

$$\dot{q}_\alpha = \frac{\partial \mathcal{H}}{\partial p_\alpha}, \qquad \dot{p}_\alpha = -\frac{\partial \mathcal{H}}{\partial q_\alpha}$$

Statistical Mechanics: Theory and Molecular Simulation, Tuckerman

Integrating EOM: velocity Verlet

$$\mathbf{r}_i(t + \Delta t) \approx \mathbf{r}_i(t) + \Delta t \mathbf{v}_i(t) + \frac{\Delta t^2}{2m_i}\mathbf{F}_i(t)$$
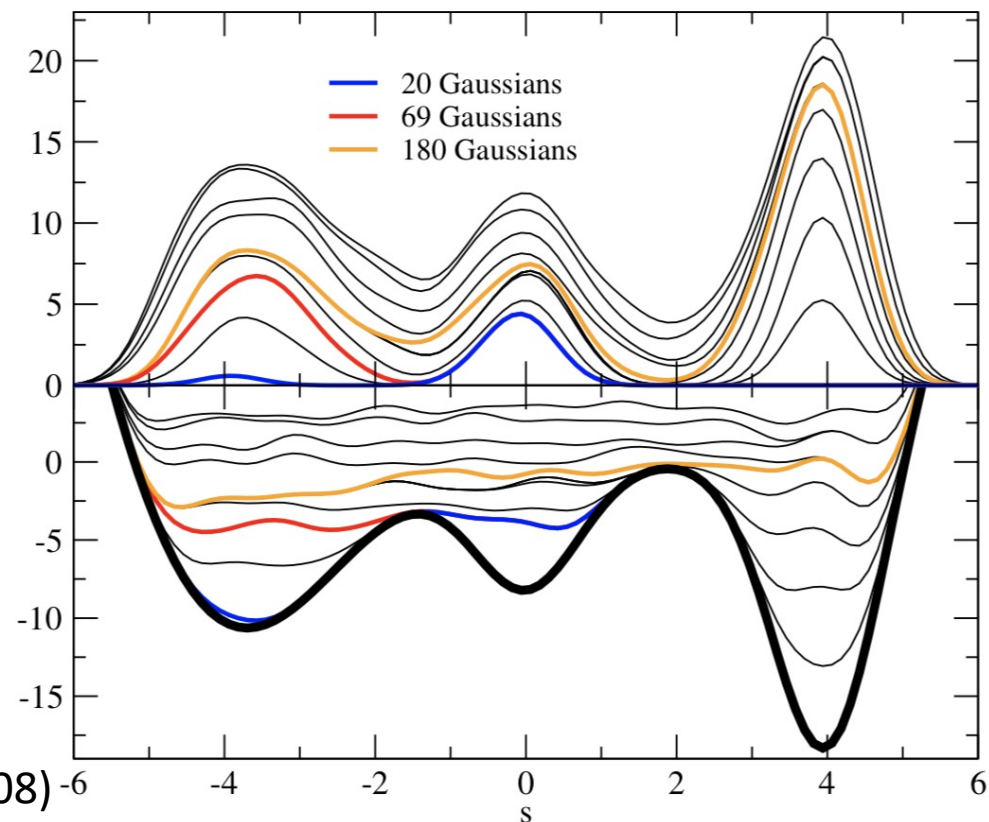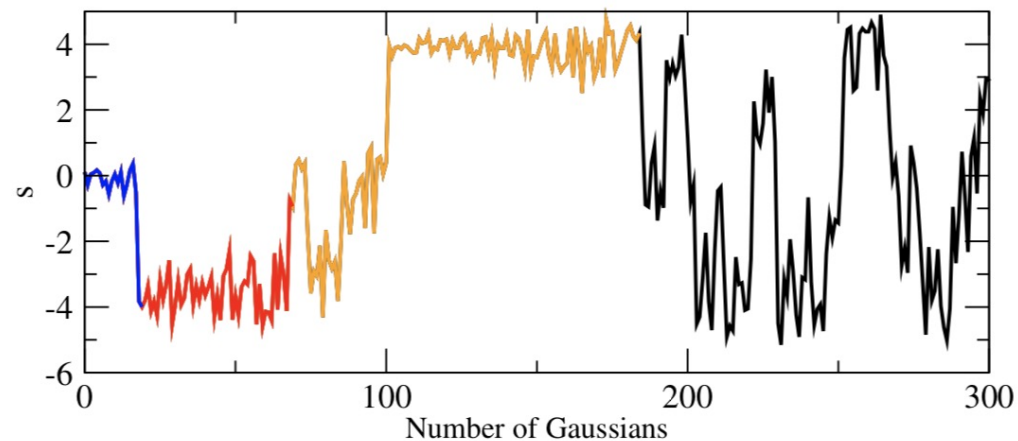
$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + \frac{\Delta t}{2m_i}\left[\mathbf{F}_i(t) + \mathbf{F}_i(t + \Delta t)\right]$$

Estimating Free energy landscape: Metadynamics

Metadynamics: the concept

Laio et al., *Rep. Prog. Phys.,* 71, 12601 (2008)

Metadynamics

The external potential added to the system at any given time:

$$V_G(S(x), t) = w \sum_{\substack{t' = \tau_G, 2\tau_G, \dots \\ t' < t}} \exp\left(-\frac{(S(x) - s(t'))^2}{2\delta s^2}\right)$$

$S(x)$ is the collective variable. There are three parameters that governs the external potential:

    1. Gaussian height (w)
    2. Gaussian width (δs)
    3. Frequency (τ_G) at which Gaussians are added

The underlying free energy is given by:

$$\lim_{t \to \infty} V_G(s, t) \sim -F(s)$$

Laio et al., *Rep. Prog. Phys.,* 71, 12601 (2008)

Different flavors of
molecular dynamics

The nomenclature

Type	intermolecular Potential	nuclear coordinate time evolution
MD	analytic form (FF)	classical (Newton's EOM)
AIMD	DFT/WFT	classical
CPMD	DFT	classical, wave function (WFN) evolves along with nuclear coordinates
BOMD	DFT/WFT	classical, SCF cycle for the WFN at new nuclear coordinates
PIMD	DFT/WFT/FF	quantum

Born-Oppenheimer Molecular Dynamics

BOMD

The concept: solve the static electronic structure problem for each MD step

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \min_{\Psi_0} \left\{ \langle \Psi_0 \left| \mathcal{H}_e \right| \Psi_0 \rangle \right\}$$

$$E_0 \Psi_0 = \mathcal{H}_e \Psi_0$$

Ab initio Molecular Dynamics, Marx and Hutter

Relevant sections in CP2K for molecular dynamics

Questions?

How to keep temperature constant in *NVT* ensemble?

Thermostats attempt to mimic the effect of coupling system to thermal reservoir or bath

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How to keep temperature constant in *NVT* ensemble?

Extended Hamiltonian approach due to Nosé introduces a new variable s that controls the temperature

$$\mathcal{H}_N = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i s^2} + U(\mathbf{r}_1, ..., \mathbf{r}_N) + \frac{p_s^2}{2Q} + gkT \ln s$$

Nosé-Hoover formulation is used extensively in molecular dynamics

$$\mathbf{p}_i' = \frac{\mathbf{p}_i}{s}, \qquad dt' = \frac{dt}{s}, \qquad \frac{1}{s}\frac{ds}{dt'} = \frac{d\eta}{dt'}, \qquad p_s = p_\eta$$

Statistical Mechanics: Theory and Molecular Simulation, Tuckerman

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$$\mathbf{p}_i' = \frac{\mathbf{p}_i}{s}, \qquad \mathrm{d}t' = \frac{\mathrm{d}t}{s}, \qquad \frac{1}{s}\frac{\mathrm{d}s}{\mathrm{d}t'} = \frac{\mathrm{d}\eta}{\mathrm{d}t'}, \qquad p_s = p_\eta$$

New EOM are:

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \frac{p_\eta}{Q}\mathbf{p}_i$$

$$\dot{\eta} = \frac{p_\eta}{Q}$$

$$\dot{p}_\eta = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m_i} - dNkT$$

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How to keep pressure constant in *NPT* ensemble?

We can use pressure bath (piston) to maintain and use scaled coordinates:

$$\mathbf{s}_i = V^{-1/3}\mathbf{r}_i, \qquad\qquad \boldsymbol{\pi}_i = V^{1/3}\mathbf{p}_i$$

The Hamiltonian:

$$\mathcal{H} = \sum_i \frac{V^{-2/3}\boldsymbol{\pi}_i^2}{2m_i} + U(V^{1/3}\mathbf{s}_1, ..., V^{1/3}\mathbf{s}_N) + \frac{p_V^2}{2W} + PV \;\; ; \;\; W = (3N+1)kT\tau_b^2$$

New EOM are:

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \frac{1}{3}\frac{\dot{V}}{V}\mathbf{r}_i$$

$$\dot{\mathbf{p}}_i = -\frac{\partial U}{\partial \mathbf{r}_i} - \frac{1}{3}\frac{\dot{V}}{V}\mathbf{p}_i$$

$$\dot{V} = \frac{p_V}{W}$$

$$\dot{p}_V = \frac{1}{3V}\sum_i \left[\frac{\mathbf{p}_i^2}{m_i} - \frac{\partial U}{\partial \mathbf{r}_i}\cdot\mathbf{r}_i\right] - P$$

Statistical Mechanics: Theory and Molecular Simulation, Tuckerman

Computing electrostatic interactions

$$E_{\text{Ewald}} = E_{\text{dir}} + E_{\text{rec}} + E_{\text{self}} + E_{\text{surface}},$$

$$E_{\text{dir}} = \frac{1}{2} \sum_{i,j=1}^{N} q_i q_j \sideset{}{'}\sum_{\vec{n}_r} \frac{\text{erfc}(\beta|\vec{r}_i - \vec{r}_j + \vec{n}_r|)}{|\vec{r}_i - \vec{r}_j + \vec{n}_r|}$$

$$- \sum_{(i,j)\in\text{Excluded}} \frac{q_i q_j}{|\vec{r}_i - \vec{r}_j + \vec{v}_{ij}|},$$

$$E_{\text{rec}} = \frac{1}{2\pi V} \sum_{\vec{m}\neq 0} \frac{\exp(-\pi^2|\vec{m}|^2/\beta^2)}{|\vec{m}|^2} \left| \sum_{i=1}^{N} q_i \exp(2\pi \mathrm{i}\vec{m}\cdot\vec{r}_i) \right|^2,$$

$$E_{\text{self}} = -\frac{\beta}{\sqrt{\pi}} \sum_{i=1}^{N} q_i^2,$$

$$E_{\text{surface}} = \frac{2\pi}{(2\varepsilon_s + 1)V} \left| \sum_{i=1}^{N} q_i\vec{r}_i \right|^2.$$

Phillips et al., *J. Comp. Chem*. **26**, 1781--1802, 2005

Questions?