Supporting Information

First-principles Based Dispersion Augmented Density Functional Theory: from Molecules to Crystals

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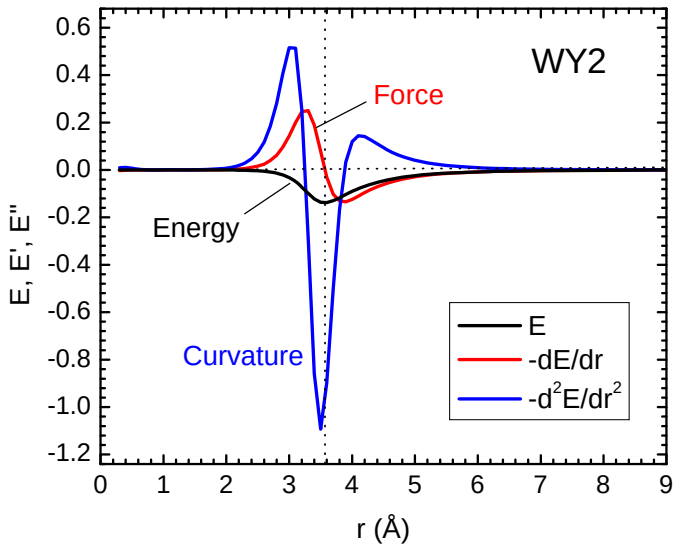
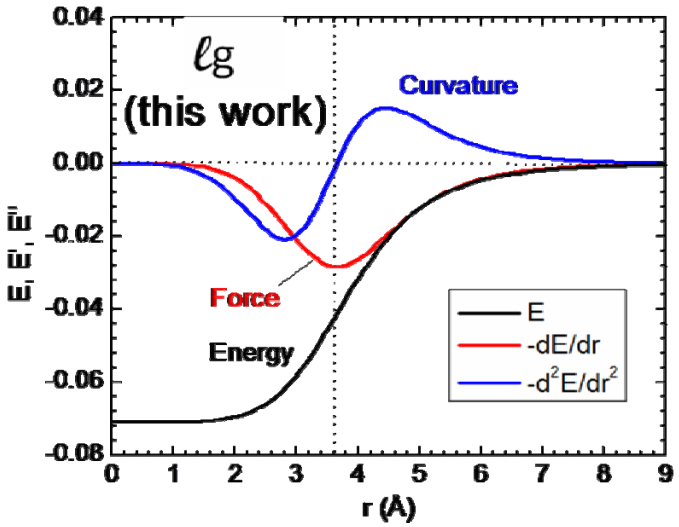


(a)



(b)

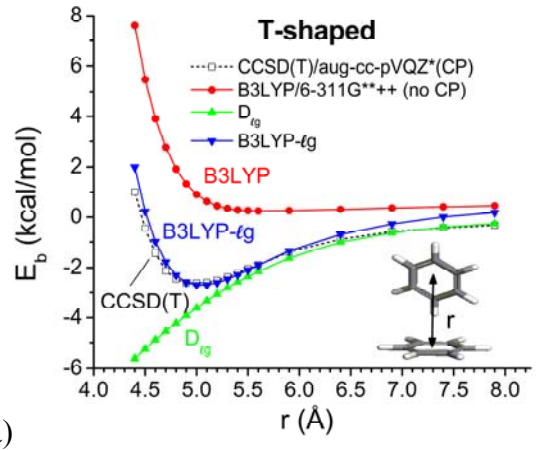
S1 Schematic illustration of energy, force, and curvature of dispersive interactions as a function of distance: (a) WY2[9], (b) ℓg (this work).

S2 Equilibrium distances (R_{min}) and energy minima (E_{min}) of benzene (C_6H_6) dimers calculated using pure B3LYP and PBE as well as the dispersion corrected methods, B3LYP-**ℓ**g and PBE-**ℓ**g. The dispersion parameters ($C_{\ell g}$) are obtained by fitting to the CCSD(T) results[7]. R_{min} and equilibrium distances R_0 have units of Å, E_{min} kcal/mol, $C_{\ell g}$ kcal/mol·Å^6.

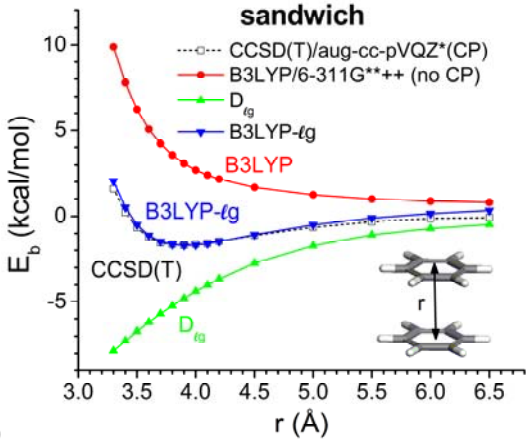
$(C_6H_6)_2$		exact	B3LYP	B3LYP- **ℓ**g	PBE	PBE- **ℓ**g
T-shaped	R_{min}	5.0[a]	5.6	5.0	5.3	5.1
	E_{min}	-2.61[a]	0.248	-2.6911	-1.1000	-2.6886
sandwich	R_{min}	3.9[a]	-	3.9	5.5	4.0
	E_{min}	-1.70[a]	-	-1.7133	0.1290	-1.7815
parallel-displaced	R_{min}	1.6[a]	-	1.8	-	1.8
	E_{min}	-2.63[a]	-	-2.7278	-	-2.6573
$C_{\ell g}$	C-C			833.6259		586.8113
	H-H			84.3735		31.1372
	C-H			27.0301		8.6912
R_0[b]	C			3.851		3.851
	H			2.880		2.880

[a] The CCSD(T) results are taken from reference 7.

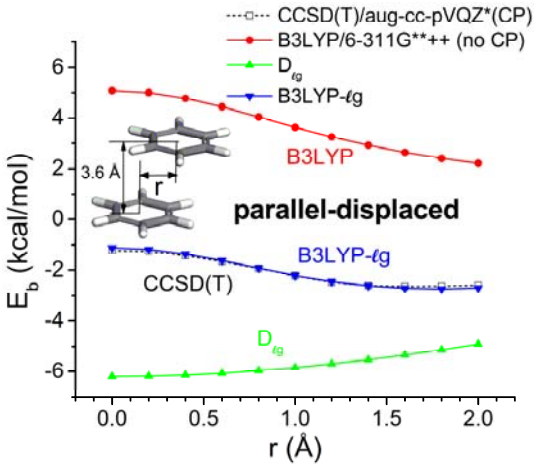
[b] The vdW radii are taken from the UFF force field (reference 8).



(a)



(b)

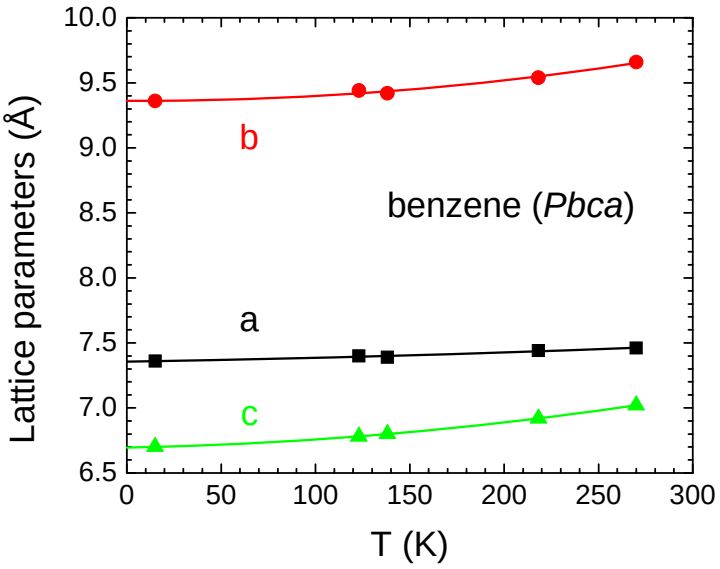


(c)

S3 Binding energy of benzene dimers as a function of distance calculated using the pure B3LYP and the dispersion corrected method (B3LYP-ℓg) for (a) T-shaped, (b) sandwich, (c) parallel-displaced configurations. The CCSD(T) results are taken from reference 7.

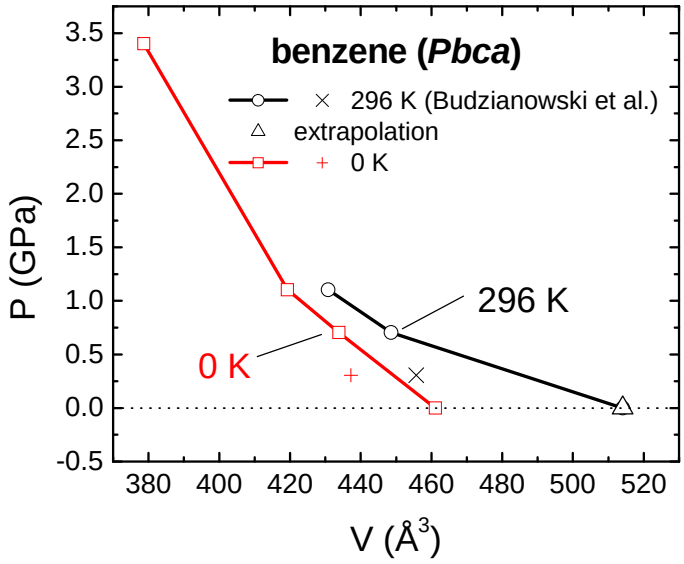
S4 Fitting function $E_b(c) = A\exp[B(c-c_0)] + D/(c-c_0)^F$ and its parameters: *A*, *B*, *D*, and *F*. c_0 is the equilibrium *c* lattice parameter. The functions are used to fit the binding energies, E_b (kcal/mol), as a function of *c* lattice parameter (Å) of graphite crystals with AA and AB stacking in PBE and PBE-ℓg models.

	$E_b(c) = A\exp[B(c-c_0)] + D/(c-c_0)^F$			
	AB, PBE-ℓg	AB, PBE	AA, PBE-ℓg	AA, PBE
A	1.3914	0.2443	0.5165	0.0144
B	-1.5870	-1.8761	-1.8394	-2.2106
D	-2.3957	-0.3558	-1.2912	-0.0903
F	6.0000 (fixed)	9.3446	5.0923	2.8567
c_0	6.5080	7.2560	6.9211	8.1370



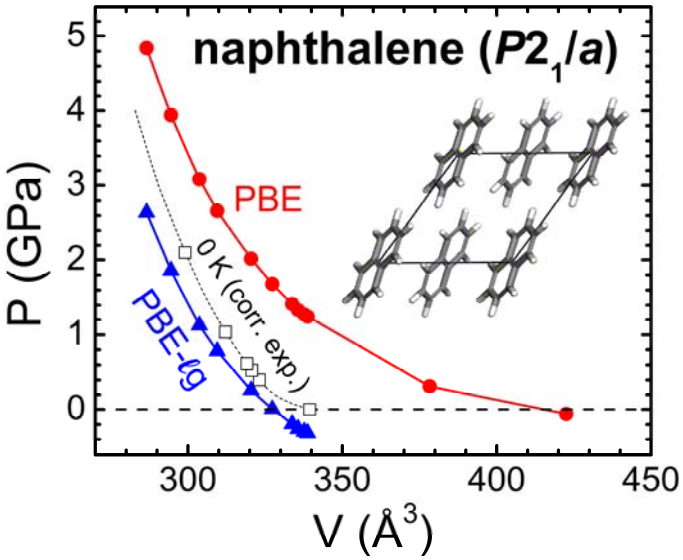
S5 Lattice parameters of benzene (*Pbca*) as a function of temperature. The solid lines are parabolic fits to the experimental data[S5-1].

[S5-1] A. Budzianowski and A. Katrusiak, Acta Cryst. B **62**, 94 (2006) and references therein.



S6 Equation of state (EOS) of benzene crystal (orthorhombic phase I) at 296 K[S6-1] and the corrected EOS at 0 K.

[S6-1]A. Budzianowski and A. Katrusiak, Acta Cryst. B **62**, 94 (2006) and references therein.



S7 Equation of states (EOS) of naphthalene crystal calculated using the PBE and the PBE-ℓg methods, compared with the corrected experimental EOS at 0 K. The inserts show the unit cell of the crystal.

S8 Equilibrium volumes of benzene, naphthalene, and anthracene crystals calculated using the pure PBE and the PBE-***ℓ***g methods. The pressures were calculated at the corrected experimental volumes at 0 K.

	volume (Å^3)				pressure (GPa)	
	exp. (296 K)	corr. exp. (0 K)	PBE	PBE-***ℓ***g	PBE	PBE-***ℓ***g
benzene	514.0608[S8-1]	461.1079(±1%)	622.4956(35.0%)	474.0700(2.8%)	1.43	0.11
naphthalene	361.4397[S8-2]	338.7870(±1%)	422.5207(24.7%)	327.3275(-3.4%)	1.24	-0.31
anthracene	473.1678[S8-3]	451.5852(±1%)	580.8861(28.6%)	441.6709(-2.2%)	1.39	-0.28

[S8-1]A. Budzianowski and A. Katrusiak, Acta Cryst. B **62**, 94 (2006).

[S8-2]C. P. Brock and J. D. Dunitz, Acta Cryst. B **38**, 2218 (1982).

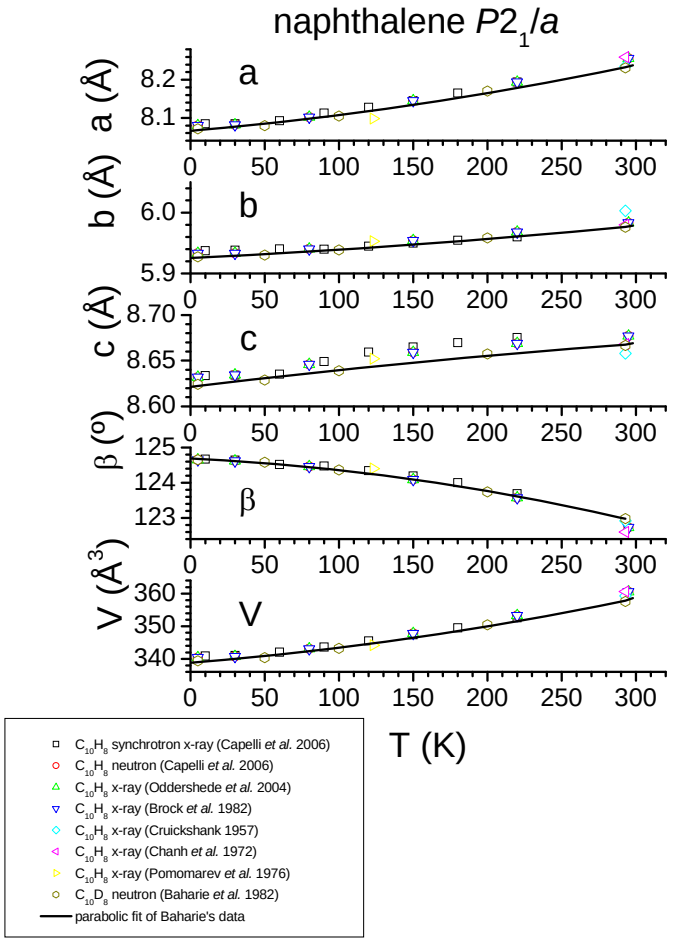
[S8-3]C. P. Brock and J. D. Dunitz, Acta Cryst. B **46**, 795 (1990).

S9 Heat of sublimation, $\Delta_{sub}H$, of benzene, naphthalene and anthracene crystals calculated using the pure PBE and the dispersion corrected PBE-*ℓ*g methods. $\Delta_{sub}H$ has a unit of kcal/mol.

	experiment		PBE	PBE-*ℓ*g
benzene	10.612(183-197 K)[a]	11.295(0 K)[b]	0.913	6.762
naphthalene	17.208± 0.956(300 K)[a]	20.095(0 K)[b]	2.043	11.335
anthracene	23.423± 2.390(300 K)[a]	27.042(0 K)[b]	-0.286	12.329

[a]Experimental data are taken from NIST chemistry WebBook (http://webbook.nist.gov/).

[b]DREIDING force field (reference 27) was used to calculate the corrections of zero point energy and lattice vibrations at experimental temperatures.



S10 Lattice parameters and volume of naphthalene crystal ($P2_1/a$) as functions of temperature. The solid lines are parabolic fits to Baharie's neutron measurement on perdeuturated naphthalene ($C_{10}D_8$)[S10-1]. Other x-ray and neutron experimental data[S10-2-7] are shown for comparison.

[S10-1]E. Baharie and G. S. Pawley, Acta Cryst. A **38**, 803 (1982).

[S10-2]S. C. Capelli, A. Albinati, S. A. Mason, and B. T. Willis, J. Phys. Chem. A **110**, 11695 (2006).

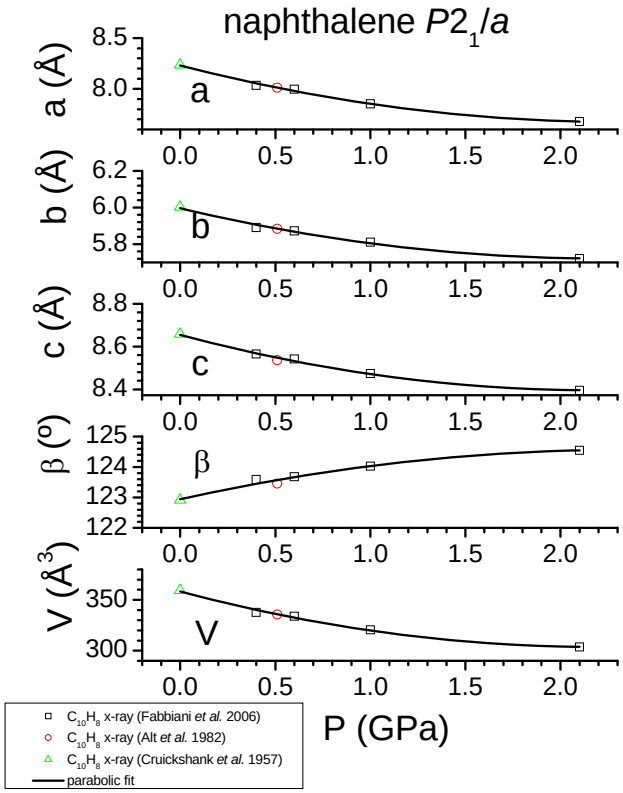
[S10-3]J. Oddershede and S. Larsen, J. Phys. Chem. A **108**, 1057 (2004).

[S10-4]C. P. Brock and J. D. Dunitz, Acta Cryst. B **38**, 2218 (1982).

[S10-5]D. W. J. Cruickshank, Acta Cryst. **10**, 504 (1957).

[S10-6]N. B. Chanh and Y. Haget-Bouillaud, Acta Cryst. B **28**, 3400 (1972).

[S10-7]V. I. Ponomarev, O. S. Filipenko and L. O. Atovmyan, Kristallografiya(Russ.) (Crystallogr. Rep.). **21**, 392 (1976).

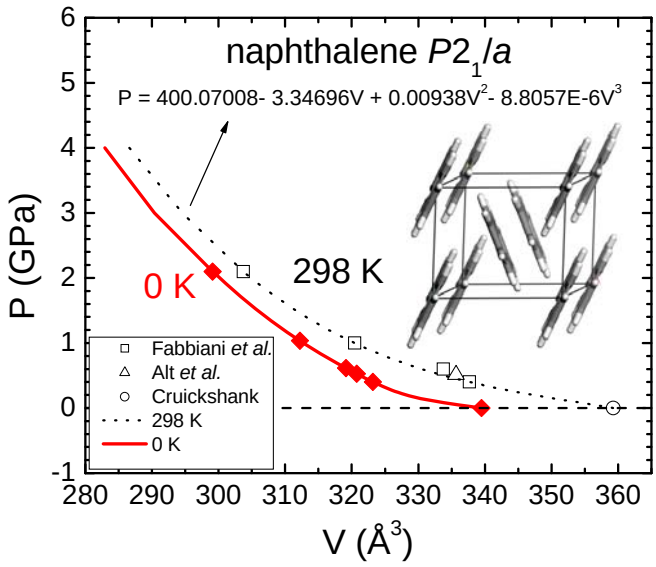


S11 Lattice parameters and volume of naphthalene ($P2_1/a$) as functions of pressure. The solid lines are parabolic fits to the x-ray experimental data[S11-1-3].

[S11-1]F. P. A. Fabbiani, D. R. Allan, S. Parsons and C. R. Pulham, Acta Cryst. B **62**, 826 (2006).

[S11-2]H. C. Alt and J. Kalus, Acta Cryst. B **38**, 2595 (1982).

[S11-3]D. W. J. Cruickshank, Acta Cryst. **10**, 504 (1957).

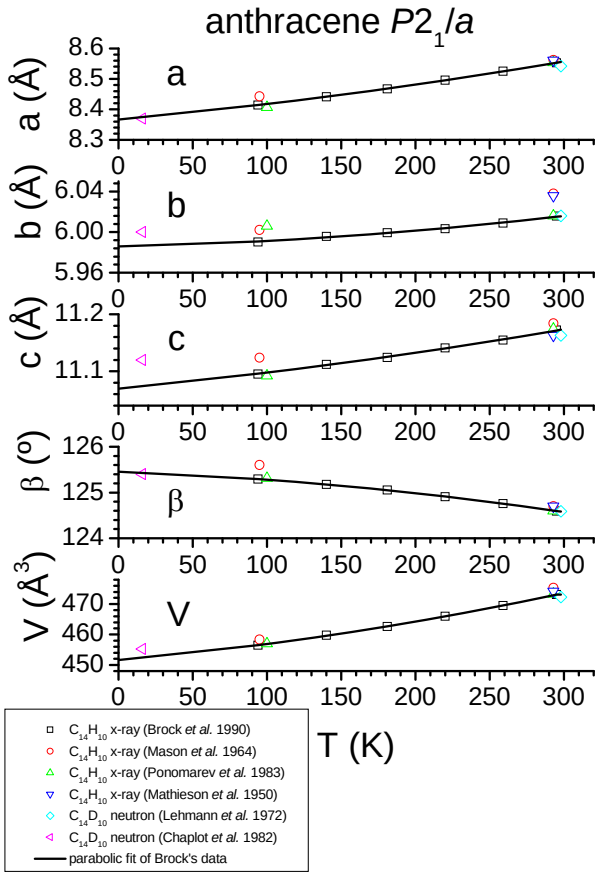


S12 Equation of states (EOS) of naphthalene crystal ($P2_1/a$). The dotted line is a cubic fit (equation shown in the insert) to the experimental data at 298 K (square: Fabbini et al.[S12-1]; triangle: Alt et al.[S12-2]; circle: Cruickshank[S12-3]). The solid line is the corrected EOS at 0 K.

[S12-1]F. P. A. Fabbiani, D. R. Allan, S. Parsons and C. R. Pulham, Acta Cryst. B **62**, 826 (2006).

[S12-2]H. C. Alt and J. Kalus, Acta Cryst. B **38**, 2595 (1982).

[S12-3]D. W. J. Cruickshank, Acta Cryst. **10**, 504 (1957).



S13 Lattice parameters and volume of anthracene ($P2_1/a$) as functions of temperature. The solid lines are parabolic fits to Brock's data[S13-1]. Other x-ray and neutron experimental data[S13-2-6] are shown for comparison.

[S13-1]C. P. Brock and J. D. Dunitz, Acta Cryst. B **46**, 795 (1990).

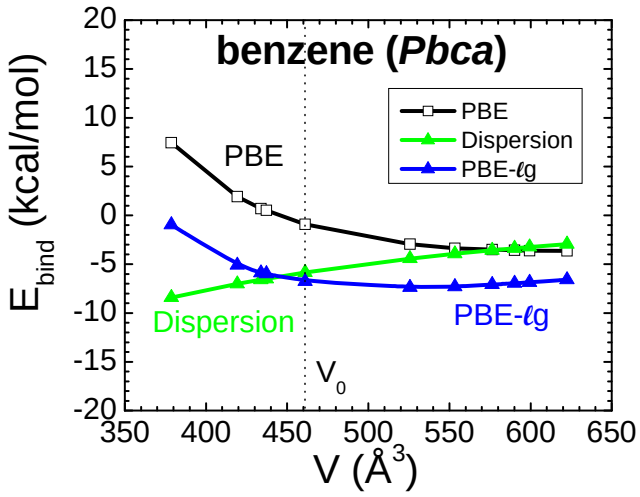
[S13-2]R. Mason, Acta Cryst. **17**, 547 (1964).

[S13-3]V. I. Ponomarev, and G. V. Shilov, Kristallografiya(Russ.) (Crystallogr. Rep.). **28**, 674 (1983).

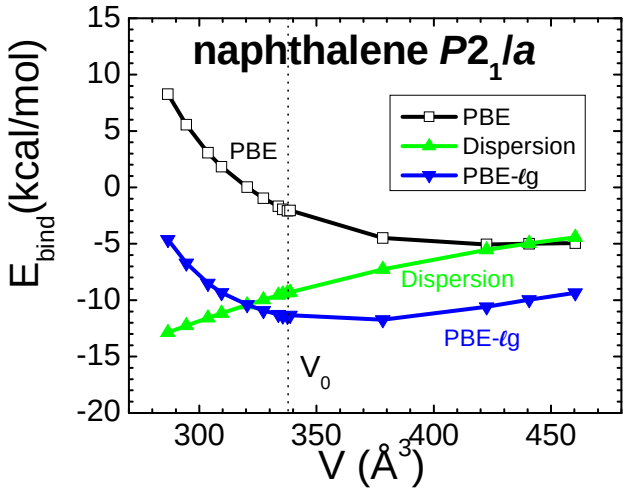
[S13-4]A. M. Mathieson, J. M. Robertson and V. C. Sinclair, Acta Cryst. **3**, 245 (1950).

[S13-5]M. S. Lehmann and G. S. Pawley, Acta Chem. Scand. **26**, 1996 (1972).

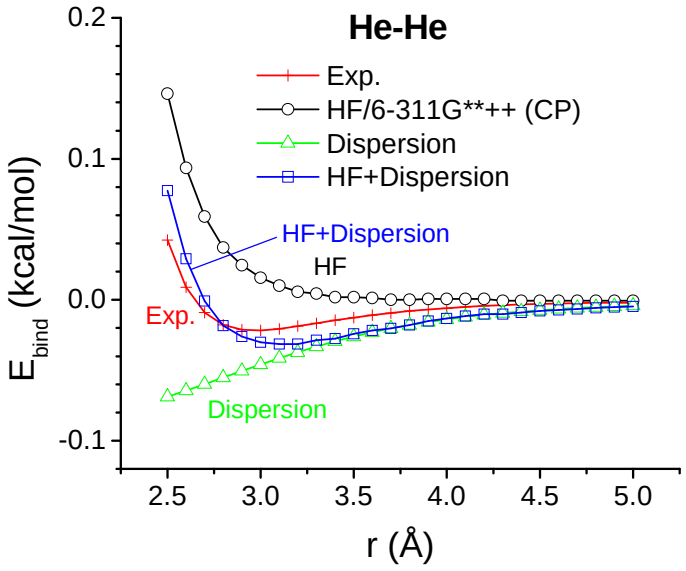
[S13-6]S. L. Chaplot, N. Lehner and G. S. Pawley, Acta Cryst. B **38**, 483 (1982).



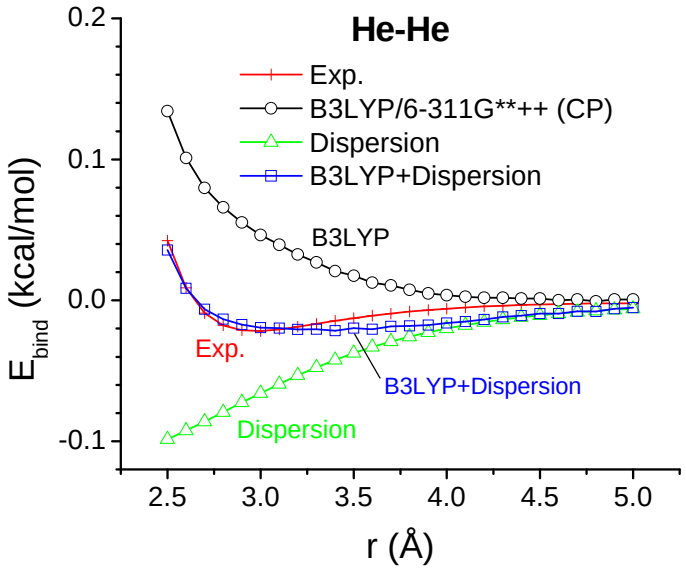
S14 Binding energy as a function of volume for the benzene crystal calculated using the PBE, dispersion and PBE-ℓg methods.



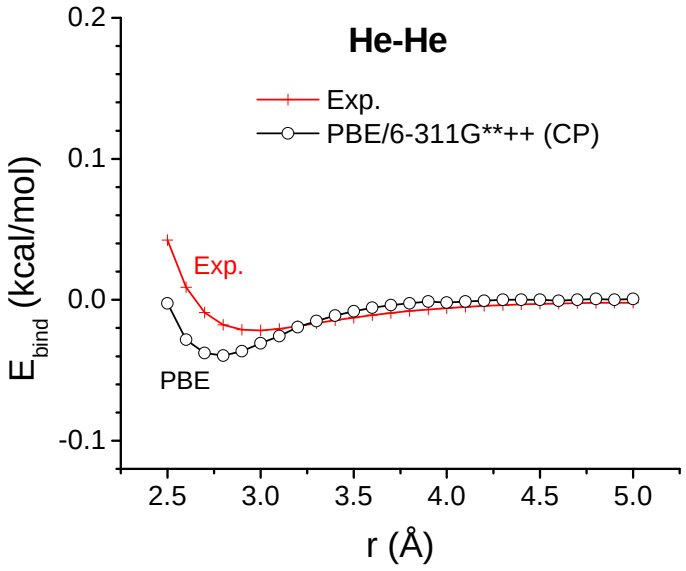
S15 Binding energy as a function of volume for the naphthalene crystal using the PBE, dispersion and PBE-***ℓ***g methods.


He-He
Exp.
HF/6-311G**++ (CP)
Dispersion
HF+Dispersion
HF+Dispersion
HF
Exp.
Dispersion
0.2
0.1
0.0
-0.1
2.5
3.0
3.5
4.0
4.5
5.0
E_bind (kcal/mol)
r (Å)

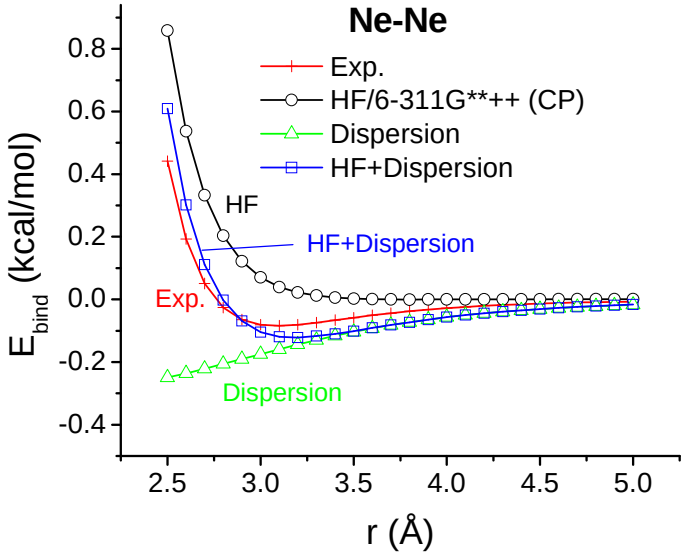
(a)


He-He
Exp.
B3LYP/6-311G**++ (CP)
Dispersion
B3LYP+Dispersion
B3LYP
Exp.
B3LYP+Dispersion
Dispersion
0.2
0.1
0.0
-0.1
2.5
3.0
3.5
4.0
4.5
5.0
E_bind (kcal/mol)
r (Å)

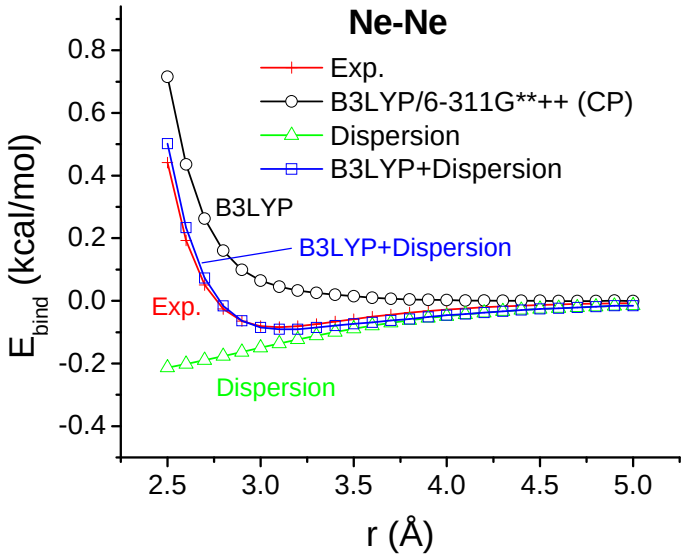
(b)


He-He
Exp.
PBE/6-311G**++ (CP)
Exp.
PBE
E_{bind} (kcal/mol)
r (Å)
0.2
0.1
0.0
-0.1
2.5
3.0
3.5
4.0
4.5
5.0

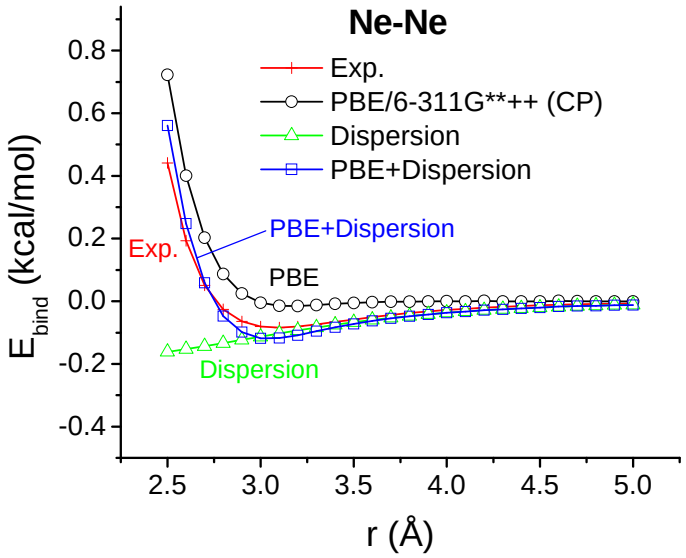
(c)


Ne-Ne
Exp.
HF/6-311G**++ (CP)
Dispersion
HF+Dispersion
HF
HF+Dispersion
Exp.
Dispersion
E_{bind} (kcal/mol)
r (Å)
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
2.5
3.0
3.5
4.0
4.5
5.0

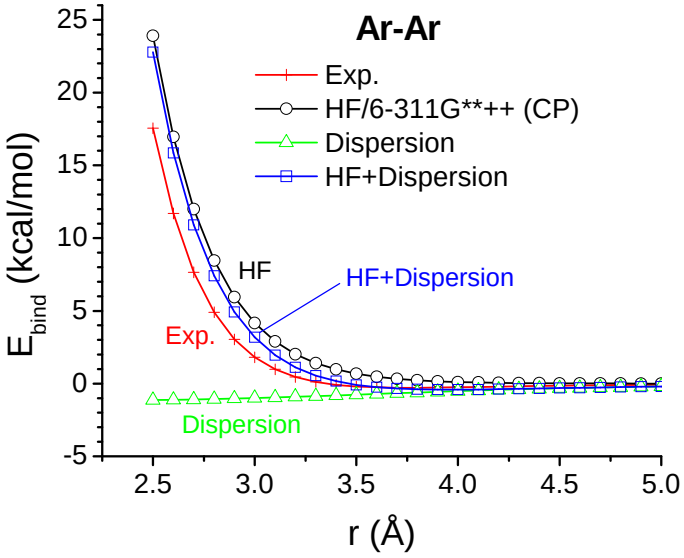
(d)


Ne-Ne
Exp.
B3LYP/6-311G**++ (CP)
Dispersion
B3LYP+Dispersion
B3LYP
B3LYP+Dispersion
Exp.
Dispersion
E_bind (kcal/mol)
r (Å)
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
2.5
3.0
3.5
4.0
4.5
5.0

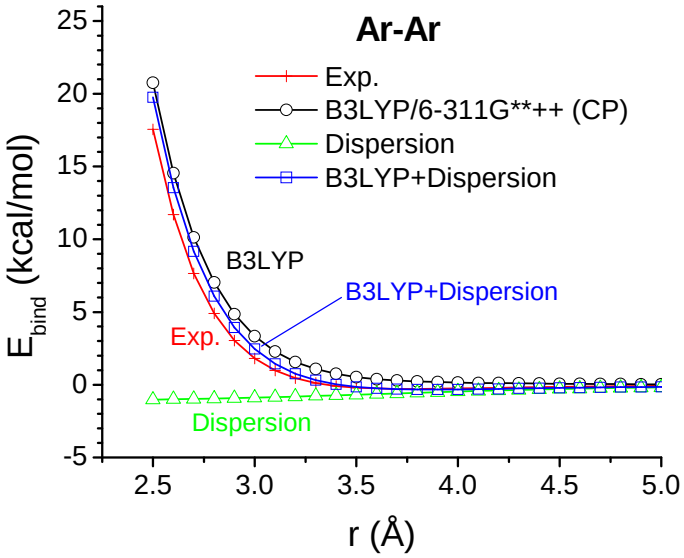
(e)


Ne-Ne
Exp.
PBE/6-311G**++ (CP)
Dispersion
PBE+Dispersion
PBE+Dispersion
Exp.
PBE
Dispersion
E_bind (kcal/mol)
r (Å)
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
2.5
3.0
3.5
4.0
4.5
5.0

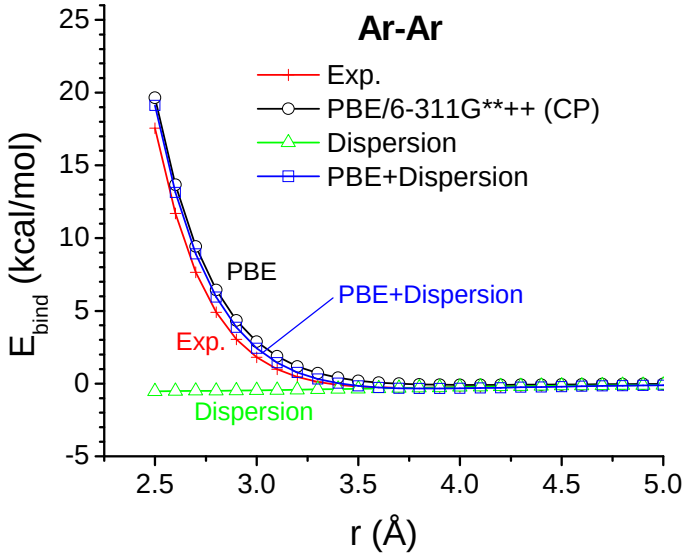
(f)


Ar-Ar
Exp.
HF/6-311G**++ (CP)
Dispersion
HF+Dispersion
HF
HF+Dispersion
Exp.
Dispersion
E_bind (kcal/mol)
r (Å)
25
20
15
10
5
0
-5
2.5
3.0
3.5
4.0
4.5
5.0

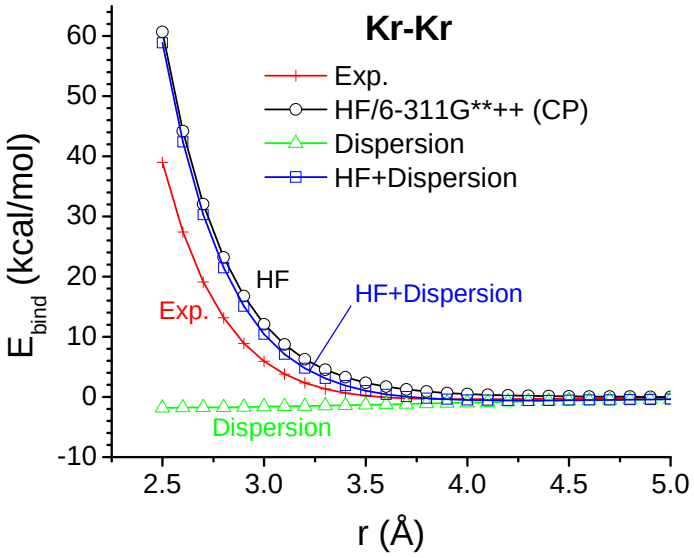
(g)


Ar-Ar
Exp.
B3LYP/6-311G**++ (CP)
Dispersion
B3LYP+Dispersion
B3LYP
B3LYP+Dispersion
Exp.
Dispersion
E_bind (kcal/mol)
r (Å)
25
20
15
10
5
0
-5
2.5
3.0
3.5
4.0
4.5
5.0

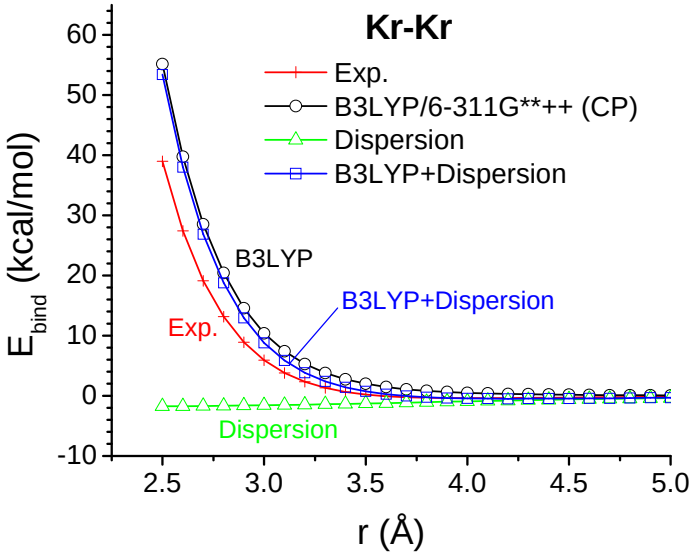
(h)


Ar-Ar
Exp.
PBE/6-311G**++ (CP)
Dispersion
PBE+Dispersion
PBE
PBE+Dispersion
Exp.
Dispersion
E_bind (kcal/mol)
r (Å)
25
20
15
10
5
0
-5
2.5
3.0
3.5
4.0
4.5
5.0

(i)


Kr-Kr
Exp.
HF/6-311G**++ (CP)
Dispersion
HF+Dispersion
HF
HF+Dispersion
Exp.
Dispersion
E_bind (kcal/mol)
r (Å)
60
50
40
30
20
10
0
-10
2.5
3.0
3.5
4.0
4.5
5.0

(j)


Kr-Kr
Exp.
B3LYP/6-311G**++ (CP)
Dispersion
B3LYP+Dispersion
B3LYP
B3LYP+Dispersion
Exp.
Dispersion
E_bind (kcal/mol)
r (Å)
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50
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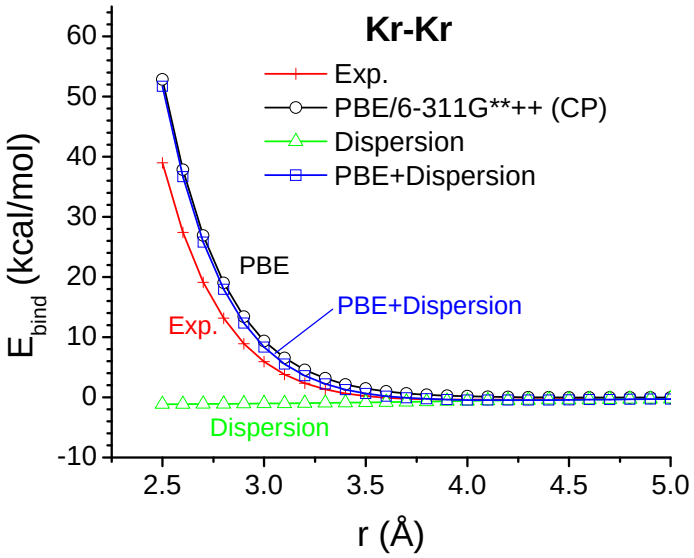
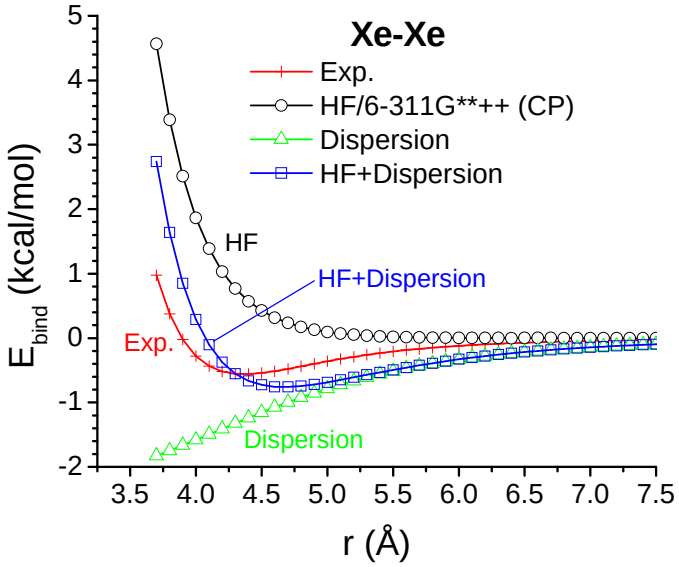
30
20
10
0
-10
2.5
3.0
3.5
4.0
4.5
5.0

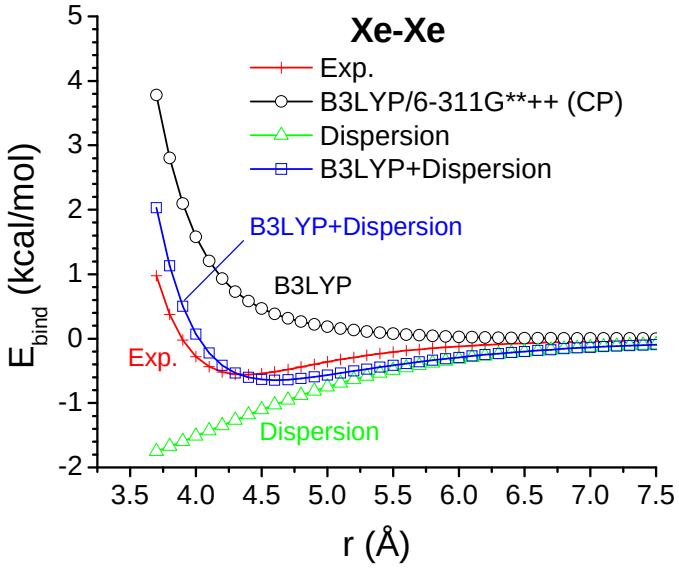
(k)


Kr-Kr
Exp.
PBE/6-311G**++ (CP)
Dispersion
PBE+Dispersion
PBE
PBE+Dispersion
Exp.
Dispersion
E_bind (kcal/mol)
r (Å)
60
50
40
30
20
10
0
-10
2.5
3.0
3.5
4.0
4.5
5.0

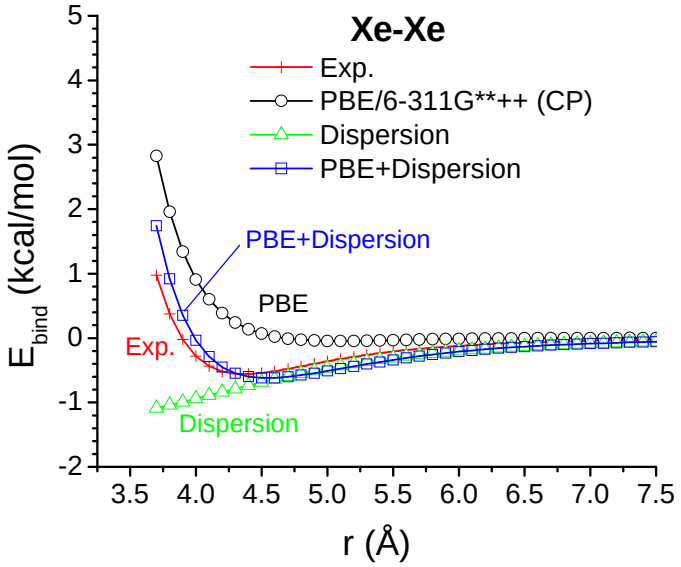
(l)


Xe-Xe
Exp.
HF/6-311G**++ (CP)
Dispersion
HF+Dispersion
HF
HF+Dispersion
Exp.
Dispersion
E_bind (kcal/mol)
r (Å)
5
4
3
2
1
0
-1
-2
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5

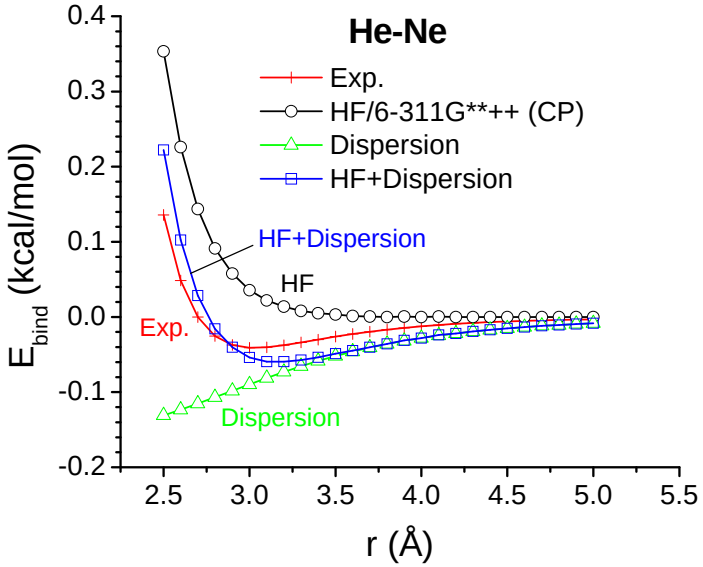
(m)


Xe-Xe
Exp.
B3LYP/6-311G**++ (CP)
Dispersion
B3LYP+Dispersion
B3LYP+Dispersion
B3LYP
Exp.
Dispersion
E_bind (kcal/mol)
r (Å)
5
4
3
2
1
0
-1
-2
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5

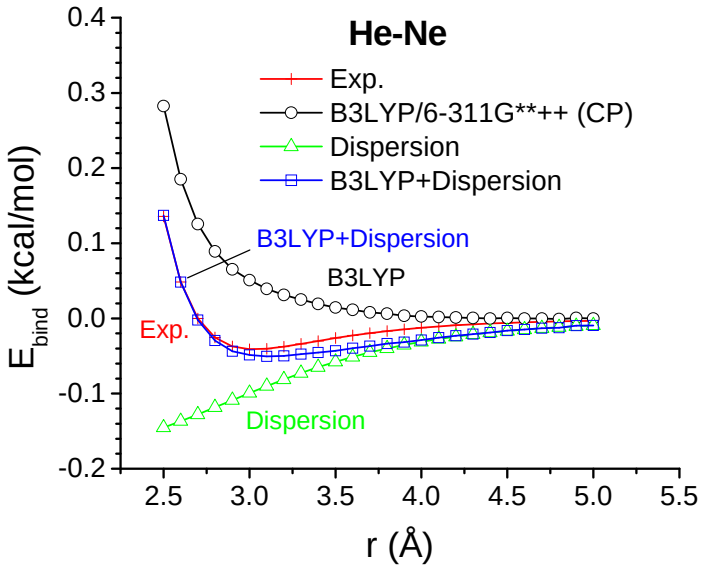
(n)


Xe-Xe
Exp.
PBE/6-311G**++ (CP)
Dispersion
PBE+Dispersion
PBE+Dispersion
PBE
Exp.
Dispersion
E_bind (kcal/mol)
r (Å)
5
4
3
2
1
0
-1
-2
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5

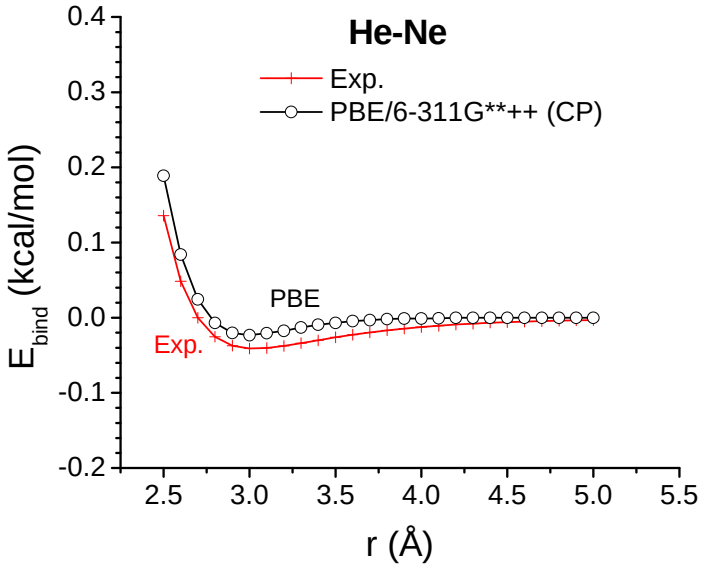
(o)


He-Ne
Exp.
HF/6-311G**++ (CP)
Dispersion
HF+Dispersion
HF+Dispersion
HF
Exp.
Dispersion
E_bind (kcal/mol)
r (Å)
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
2.5
3.0
3.5
4.0
4.5
5.0
5.5

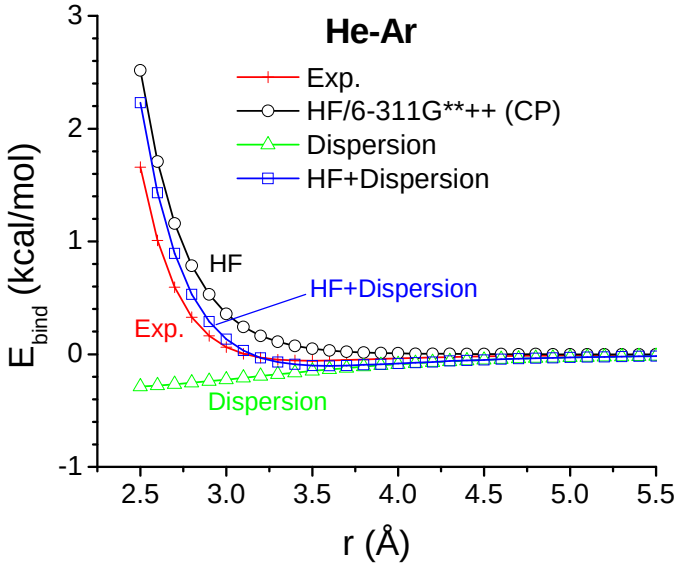
(p)


He-Ne
Exp.
B3LYP/6-311G**++ (CP)
Dispersion
B3LYP+Dispersion
B3LYP+Dispersion
B3LYP
Exp.
Dispersion
E_bind (kcal/mol)
r (Å)
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
2.5
3.0
3.5
4.0
4.5
5.0
5.5

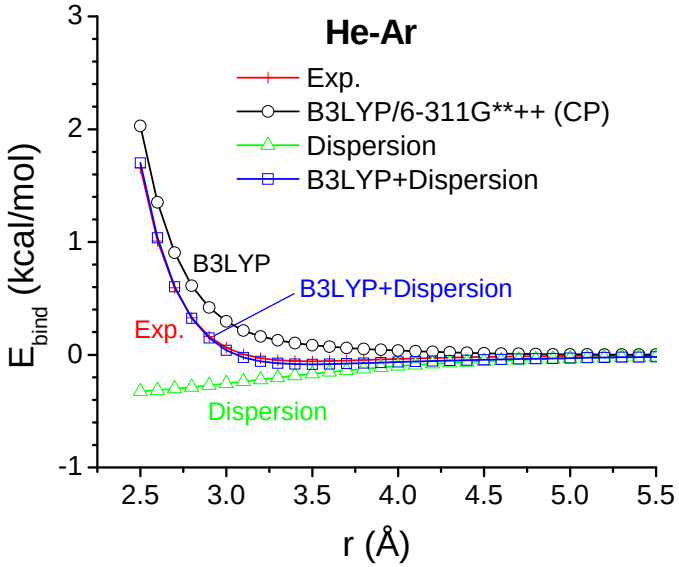
(q)


He-Ne
Exp.
PBE/6-311G**++ (CP)
PBE
Exp.
E_bind (kcal/mol)
r (Å)
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
2.5
3.0
3.5
4.0
4.5
5.0
5.5

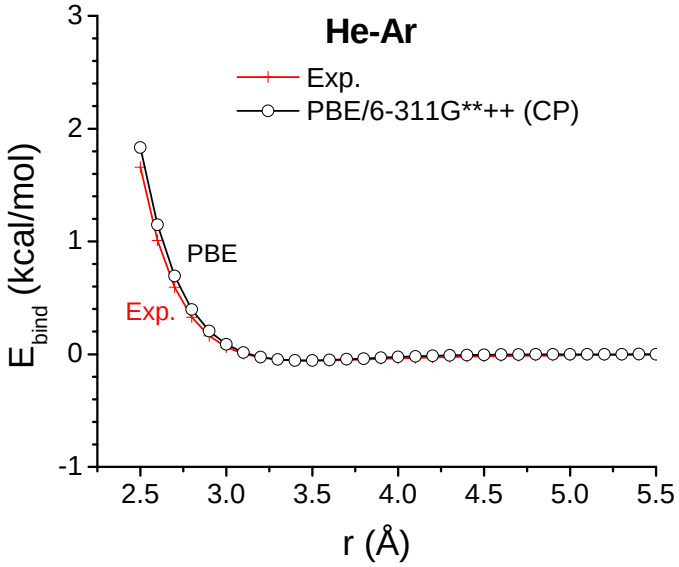
(r)


He-Ar
Exp.
HF/6-311G**++ (CP)
Dispersion
HF+Dispersion
HF
HF+Dispersion
Exp.
Dispersion
E_bind (kcal/mol)
r (Å)
3
2
1
0
-1
2.5
3.0
3.5
4.0
4.5
5.0
5.5

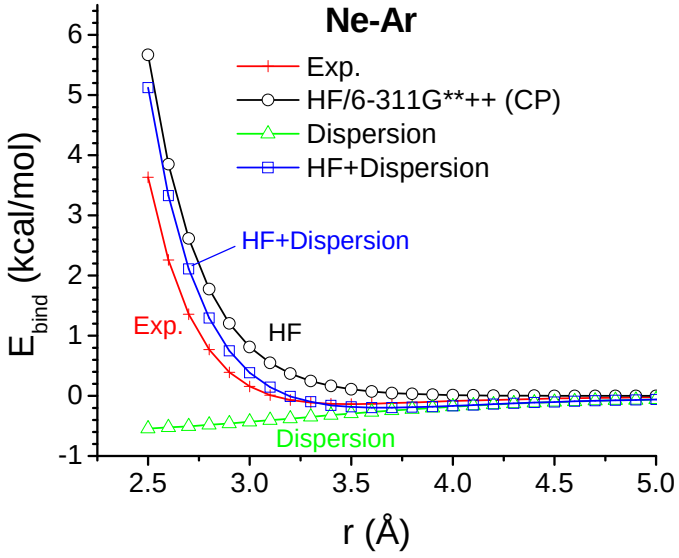
(s)


He-Ar
Exp.
B3LYP/6-311G**++ (CP)
Dispersion
B3LYP+Dispersion
B3LYP
B3LYP+Dispersion
Exp.
Dispersion
E_bind (kcal/mol)
r (Å)
3
2
1
0
-1
2.5
3.0
3.5
4.0
4.5
5.0
5.5

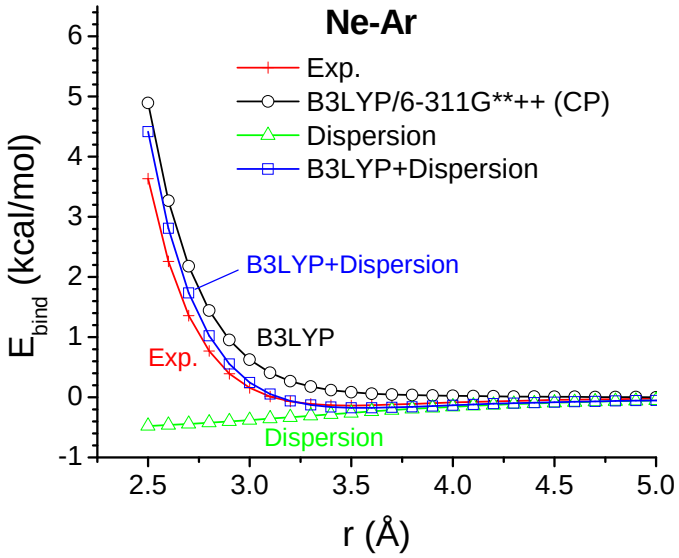
(t)


He-Ar
Exp.
PBE/6-311G**++ (CP)
PBE
Exp.
E_bind (kcal/mol)
r (Å)
3
2
1
0
-1
2.5
3.0
3.5
4.0
4.5
5.0
5.5

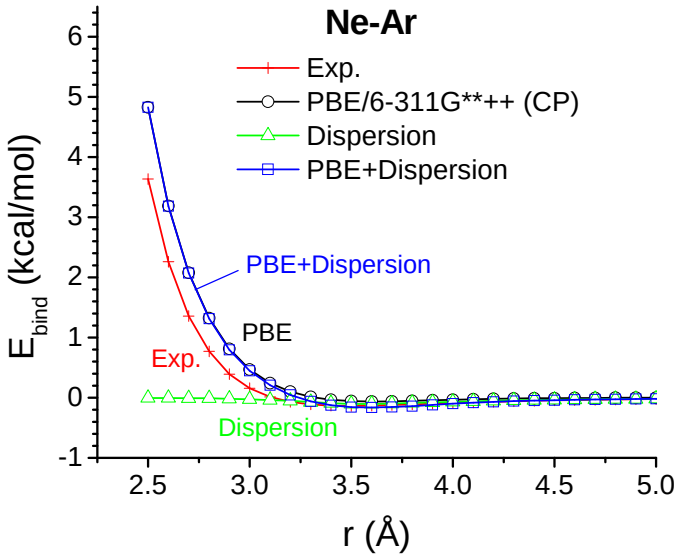
(u)


Ne-Ar
Exp.
HF/6-311G**++ (CP)
Dispersion
HF+Dispersion
HF+Dispersion
Exp.
HF
Dispersion
E_bind (kcal/mol)
r (Å)
6
5
4
3
2
1
0
-1
2.5
3.0
3.5
4.0
4.5
5.0

(v)



(w)



(x)

S16 Binding energy of diatomic rare gas molecules as a function of distance calculated using HF, B3LYP, and PBE as well as their dispersion corrections (HF-*ℓ*g, B3LYP-*ℓ*g and PBE-*ℓ*g): (a)-(c) He-He, (d)-(f) Ne-Ne, (g)-(i) Ar-Ar, (j)-(l) Kr-Kr, (m)-(o) Xe-Xe, (p)-(r) He-Ne, (s)-(u) He-Ar, (v)-(x) Ne-Ar. The experimental data are from references S13-1 and S13-2.

[S16-1] J. F. Ogilvie and F. Y. H. Wang, J. Mol. Stru. **273**, 277 (1992).
[S16-2] J. F. Ogilvie and F. Y. H. Wang, J. Mol. Stru. **291**, 313 (1993).

S17 Equilibrium distances (R_{min}), energy minima (E_{min}), and dispersion parameters (C_{lg}) of diatomic rare gas molecules calculated using pure HF, B3LYP and PBE as well as their dispersion corrections (HF-***ℓ***g, B3LYP-***ℓ***g, and PBE-***ℓ***g). The experimental R_{min} are used as R_0 in the dispersion terms. R_{min} and R_0 have units of Å, E_{min} kcal/mol, C_{lg} kcal/mol Å^6. The experimental data are from references S16-1 and S16-2.

		exp.	HF	HF-***ℓ***g	B3LYP	B3LYP- ***ℓ***g	PBE	PBE- ***ℓ***g
He-He	R_{min}	3.0	-	3.2	-	3.2	2.8	-
	E_{min}	-0.0217	-	-0.0315	-	-0.0206	-0.0395	-
	C_{lg}			66.8860		95.9750		-
Ne-Ne	R_{min}	3.1	-	3.2	-	3.1	3.2	3.0
	E_{min}	-0.0839	-	-0.1219	-	-0.0909	-0.0151	-0.1182
	C_{lg}			282.1128		241.5956		182.9048
Ar-Ar	R_{min}	3.8	-	4.0	-	3.8	4.1	3.9
	E_{min}	-0.2832	-	-0.4107	-	-0.3244	-0.0885	-0.3417
	C_{lg}			3690.5135		3306.0123		1710.9773
Kr-Kr	R_{min}	4.0	-	4.3	-	4.2	4.7	4.2
	E_{min}	-0.3998	-	-0.5856	-	-0.4904	-0.0326	-0.4829
	C_{lg}			7885.1791		7593.0897		4989.4689
Xe-Xe	R_{min}	4.4	-	4.7	-	4.6	5.1	4.5
	E_{min}	-0.5594	-	-0.7583	-	-0.6433	-0.0458	-0.6173
	C_{lg}			17931.1717		17167.2797		10679.4616
He-Ne	R_{min}	3.0	-	3.2	-	3.1	3.0	-
	E_{min}	-0.0409	-	-0.0593	-	-0.0505	-0.0232	-
He-Ar	R_{min}	3.5	-	3.6	-	3.5	3.5	-
	E_{min}	-0.0574	-	-0.1026	-	-0.0850	-0.0546	-
Ne-Ar	R_{min}	3.5	-	3.7	-	3.6	3.6	3.6
	E_{min}	-0.1343	-	-0.1940	-	-0.1742	-0.0621	-0.1636