

# Van der Waals Coefficients

Michael Liebrecht

February 17, 2014

## Abstract

In this document Van der Waals Coefficients obtained by simple spherically restricted Hartree–Fock calculations are shown alongside with some results calculated by the means of a combination of LiMeReC and the Hartree–Fock code.

## 1 Parameters for the numerical calculations

### 1.1 Pseudopotential

All calculations used the local pseudopotentials from Ref [1].

### 1.2 Spherically restricted Hartree–Fock

All Hartree–Fock calculation were performed on a logarithmic radial grid with 1000 points from  $1 \times 10^{-6} a_0$  to  $1 \times 10^4 a_0$ . The eigenvectors were obtained with an accuracy of  $1 \times 10^{-12}$  and iterated self-consistently until the error in their eigenenergies was  $< 1 \times 10^{-10}$  Ry.

### 1.3 Density functional calculation

All density functional calculation were performed with LiMeReC using the Perdew–Wang exchange–correlation functional [2]. The box size was  $N_x = N_y = N_z = 128$  points and the discretization length was  $0.375 a_0$ . The accuracy settings were  $\epsilon_i = 7.5 \times 10^{-9}$ ,  $\epsilon_r = 1 \times 10^{-8}$  and  $\epsilon_n = 1 \times 10^{-8}$ .

## 2 Long–range dispersion coefficients

The results for the  $C_6$  coefficients are shown in Table 1. We used the spherically restricted Hartree–Fock method to obtain the values from the second column of Table 1. The values from the third column were obtained by means of spherically restricted Hartree–Fock for the first atom and density functional theory for the second atom of the corresponding atom pair. We also show results from a theoretical study using effective valence electron numbers [3, 4], all–electron second order perturbation theory [5] as well as a semi–empirical study, which provides lower and upper bounds for the long–range dispersion coefficients [6].

atom pairs	HF	DFT	Ref [3, 4]	Ref [5]	Ref [7]	Ref [6] <sup>1</sup>	Ref [6] <sup>2</sup>
H-H	6.50(0)		6.50(0)		6.51(0)	6.50(0)	6.47(0)
H-He	2.76(0)		2.81(0)		2.82(0)	2.80(0)	2.83(0)
H-Li	4.83(1)	5.05(1)	6.56(1)	6.65(1)		6.58(1)	6.68(1)
H-Be	2.99(1)	3.13(1)	3.40(1)	3.48(1)		3.55(1)	3.58(1)
H-Na	6.52(1)	6.77(1)	7.30(1)	7.42(1)		7.02(1)	1.75(2)
H-Mg	6.47(1)	6.57(1)	5.66(1)	5.76(1)		5.74(1)	5.84(1)
H-K	9.69(1)	9.94(1)	1.03(2)	1.12(2)		1.11(2)	1.16(2)
H-Ca	1.04(2)	1.04(2)	9.28(1)	1.00(2)		1.19(2)	1.23(2)
H-Rb	1.07(2)	1.10(2)	1.14(2)	1.25(2)		1.18(2)	1.26(2)
H-Cs	1.23(2)	1.25(2)	1.45(2)			1.34(2)	1.39(2)
He-He	1.45(0)		1.46(0)		1.46(0)	1.44(0)	1.47(0)
He-Li	1.62(1)	1.70(1)	2.19(1)	2.25(1)		2.21(1)	2.28(1)
He-Be	1.21(1)	1.26(1)	1.36(1)	1.32(1)		1.36(1)	1.39(1)
He-Na	2.13(1)	2.22(1)	2.46(1)	2.58(1)		2.37(1)	6.87(1)
He-Mg	2.40(1)	2.43(1)	2.07(1)	2.15(1)		2.11(1)	2.21(1)
He-K	3.08(1)	3.17(1)	3.41(1)	3.95(1)		3.78(1)	4.18(1)
He-Ca	3.69(1)	3.68(1)	3.32(1)	3.66(1)		4.51(1)	4.85(1)
He-Rb	3.38(1)	3.48(1)	3.77(1)	4.47(1)		4.01(1)	4.63(1)
He-Cs	3.84(1)	3.94(1)	4.48(1)			4.43(1)	4.92(1)
Li-Li	5.58(2)	5.86(2)	1.39(3)			1.38(3)	1.39(3)
Li-Be	2.41(2)	2.62(2)	4.73(2)			4.78(2)	4.82(2)
Li-Na	8.07(2)	8.39(2)	1.48(3)			1.43(3)	2.16(3)
Li-Mg	6.01(2)	6.31(2)	8.48(2)			8.52(2)	8.57(2)
Li-K	1.31(3)	1.34(3)	2.30(3)			2.34(3)	2.36(3)
Li-Ca	1.06(3)	1.09(3)	1.62(3)			1.83(3)	1.85(3)
Li-Rb	1.47(3)	1.50(3)	2.52(3)			2.53(3)	2.55(3)
Li-Cs	1.73(3)	1.76(3)	3.20(3)			3.01(3)	3.03(3)
Be-Be	1.40(2)	1.49(2)	2.08(2)			2.19(2)	2.21(2)
Be-Na	3.29(2)	3.42(2)	5.18(2)			5.06(2)	1.05(3)
Be-Mg	3.12(2)	3.21(2)	3.57(2)			3.69(2)	3.74(2)
Be-K	4.96(2)	5.08(2)	7.55(2)			8.01(2)	8.18(2)
Be-Ca	5.09(2)	5.15(2)	6.23(2)			7.62(2)	7.77(2)
Be-Rb	5.49(2)	5.62(2)	8.31(2)			8.60(2)	8.86(2)
Be-Cs	6.31(2)	6.44(2)	1.06(3)			9.91(2)	1.01(3)
Na-Na	1.19(3)	1.24(3)	1.58(3)			1.47(3)	5.00(3)
Na-Mg	8.39(2)	8.83(2)	9.24(2)			8.97(2)	1.75(3)
Na-K	1.96(3)	2.01(3)	2.43(3)			2.41(3)	3.67(3)
Na-Ca	1.50(3)	1.55(3)				1.92(3)	3.61(3)
Na-Rb	2.22(3)	2.27(3)	2.67(3)			2.60(3)	3.97(3)
Na-Cs	2.63(3)	2.67(3)	3.39(3)			3.08(3)	4.50(3)
Mg-Mg	7.26(2)	7.52(2)	6.18(2)			6.30(2)	6.38(2)
Mg-K	1.29(3)	1.33(3)	1.36(3)			1.43(3)	1.45(3)
Mg-Ca	1.22(3)	1.24(3)	1.10(3)			1.30(3)	1.33(3)
Mg-Rb	1.44(3)	1.48(3)	1.50(3)			1.53(3)	1.57(3)
Mg-Cs	1.67(3)	1.70(3)	1.90(3)			1.78(3)	1.81(3)

Table 1: (continues on next page)

atom pairs	HF	DFT	Ref [3, 4]	Ref [5]	Ref [7]	Ref [6] <sup>1</sup>	Ref [6] <sup>2</sup>
K–K	3.35(3)	3.41(3)	3.82(3)			3.97(3)	4.03(3)
K–Ca	2.36(3)	2.45(3)	2.63(3)			3.08(3)	3.16(3)
K–Rb	3.82(3)	3.89(3)	4.19(3)			4.29(3)	4.37(3)
K–Cs	4.57(3)	4.63(3)	5.31(3)			5.12(3)	5.18(3)
Ca–Ca	2.09(3)	2.14(3)	2.01(3)			2.74(3)	2.83(3)
Ca–Rb	2.64(3)	2.69(3)	2.90(3)			3.32(3)	3.43(3)
Ca–Cs	3.07(3)	3.13(3)	3.67(3)			3.86(3)	3.95(3)
Rb–Rb	4.36(3)	4.44(3)	4.60(3)			4.64(3)	4.74(3)
Rb–Cs	5.23(3)	5.30(3)	5.83(3)			5.53(3)	5.62(3)
Cs–Cs	6.30(3)	6.37(3)	7.38(3)			6.63(3)	6.70(3)

Table 1: Results for  $C_6$  [ $\text{H a}_0^6$ ]. The spherically restricted Hartree–Fock method was used to obtain the values for the second columns. The values for the third column were calculated by by means of spherically restricted Hartree–Fock for the first atom and density functional theory for the second atom of the corresponding atom pair. Note use of parentheses: 1.38(5) means  $1.38 \times 10^5$

In a more recent publication [8] concerning the pseudopotentials [1], the parameters for sodium were revised. The parameters of the original pseudopotentials were fitted to a perturbative calculation, the revised parameters were fitted to a variational calculation. In at least one other publication of Perdew it is recommended to use the revised parameters.

atom pairs	HF	DFT	Ref [3, 4]	Ref [5]	Ref [7]	Ref [6] <sup>1</sup>	Ref [6] <sup>2</sup>
H–Na	6.98(1)	7.14(1)	7.30(1)	7.42(1)		7.02(1)	1.75(2)
He–Na	2.27(1)	2.33(1)	2.46(1)	2.58(1)		2.37(1)	6.87(1)
Li–Na	8.78(2)	8.95(2)	1.48(3)			1.43(3)	2.16(3)
Be–Na	3.54(2)	3.62(2)	5.18(2)			5.06(2)	1.05(3)
Na–Na	1.42(3)	1.44(3)	1.58(3)			1.47(3)	5.00(3)
Na–Mg	9.05(2)	8.83(2)	9.24(2)			8.97(2)	1.75(3)
Na–K	2.16(3)	2.01(3)	2.43(3)			2.41(3)	3.67(3)
Na–Ca	1.62(3)	1.68(3)				1.92(3)	3.61(3)
Na–Rb	2.45(3)	2.27(3)	2.67(3)			2.60(3)	3.97(3)
Na–Cs	2.90(3)	2.94(3)	3.39(3)			3.08(3)	4.50(3)

Table 2: same as Table 1, but with revised pseudopotentials [8]

<sup>1</sup>Lower bound in [6]

<sup>2</sup>Upper bound in [6]

### 3 Polarizabilities

The results for the static polarizabilities  $\alpha(0)$  are shown in Table 3. If we use the revised pseudopotentials for Na, the Hartree–Fock calculation results in  $\alpha(0) = 154.0 a_0^3$  and the DFT calculation gives  $\alpha(0) = 151.2 a_0^3$ .

### References

- [1] Carlos Fiolhais, John P. Perdew, Sean Q. Armster, James M. MacLaren, and Maria Brzeczewska. Dominant density parameters and local pseudopotentials for simple metals. *Phys. Rev. B*, 51(20):14001–14011, 1995.
- [2] J. P. Perdew and Y. Wang. Accurate and simple analytic representation of the electron-gas correlation energy. *Phys. Rev. B*, 45(23):13244–13249, 1992.
- [3] N. C. Pyper. Relativistic ab initio calculations of the properties of ionic solids. *Phil. Trans. R. Soc. Lond. A*, 320(1553):107–158, November 1986.
- [4] R. J.-M. Pellenq and D. Nichol森. A simple method for calculating dispersion coefficients for isolated and condensed-phase species. *Mol. Phys.*, 95(3):549–570, 1998.
- [5] J. Mitroy and M. W. J. Bromley. Dispersion coefficients for h and he interactions with alkali-metal and alkaline-earth-metal atoms. *Phys. Rev. A*, 68(6):062710, September 2003.
- [6] J. M. Standard and P. R. Certain. Bounds to 2-body and 3-body long-range interaction coefficients for S-state atoms. *J. Chem. Phys.*, 83(6):3002–3008, 1985.
- [7] Sabyasachi Kar and Y. K. Ho. Effect of debye plasmas on the dispersion coefficients {C6} for interactions among h and he atoms. *Chem. Phys. Lett.*, 449(1-3):246–248, 2007.
- [8] Fernando Nogueira, Carlos Fiolhais, Jingsong He, John P Perdew, and Angel Rubio. Transferability of a local pseudopotential based on solid-state electron density. *Journal of Physics: Condensed Matter*, 8(3):287, 1996.
- [9] T. M. Miller. Atomic and molecular polarizabilities. In D. R. Lide, editor, *Handbook of Chemistry and Physics*, volume 73, pages 10–193, 1990.

	H	He	Li	Be	Na	Mg	K	Ca	Rb	Cs
HF	4.500	1.322	82.72	23.93	136.6	67.91	272.2	132.5	324.7	414.4
DFT			86.53	25.12	139.7	68.12	266.8	129.6	317.0	400.0
Ref [9]	4.500	1.385	164.1	37.83	162.6	71.60	293.2	154.0	319.5	402.6

Table 3: This table shows the static polarizabilities  $\alpha(0)$  [ $a_0^3$ ] obtained by the spherically restricted Hartree–Fock method and by LiMeReC as well as values found in the literature [9] for comparison.