

## Long-range van der Waals attraction and alkali-metal lattice constants

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While the short-range part of the van der Waals (vdW) interaction can be described by semilocal density functionals, the long range cannot. By respecting two uniform electron gas and other exact limits, we construct a nonlocal density functional for the long-range coefficient  $C_6$ .  $C_8$  and  $C_{10}$  may be determined empirically from  $C_6$ . Then we estimate the effect of the core-core vdW attraction upon the lattice constants of the alkali metals, including dynamic valence-electron screening. This attraction is important for the softest metals, shrinking the lattice constant of Cs by 0.1 Å.

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A central task of electronic structure theory is to predict properties of materials and ultimately to control and optimize device functionalities. For example, successful prediction of lattice constants is crucial in the design and fabrication of electronic devices. The most efficient way to calculate these properties is density-functional theory (DFT),<sup>1,2</sup> in which all components are treated exactly except for the exchange-correlation energy which must be approximated as a functional of the electron density. With the rapid development of reliable semilocal density-functional approximations, DFT has become a standard electronic-structure method. However, despite its practical success for normally bonded systems, its accuracy is limited<sup>3</sup> for weakly bound molecules (e.g., rare-gas dimers) and solids (e.g., graphite), due to the omission of the long-range van der Waals (vdW) interaction, which cannot be included in semilocal functionals. Since the bulk moduli of K, Rb, and Cs are as small as those of the rare-gas solids Ar and Kr, Ref. 4 recently proposed that these simple metals are also “soft matter.”

The vdW interaction is an important correlation affecting the properties of molecules, liquids, and solids.<sup>5</sup> Numerical study shows<sup>6</sup> that, while semilocal density functionals can describe the short-range part of the vdW interaction well, they fail to describe the long-range part in inhomogeneous densities. This inadequacy has a direct impact on the performance of these functionals in ground-state electronic-structure calculations. To date, many density functionals<sup>7–14</sup> have been proposed to simulate this interaction. However, no method has been proposed to estimate the effect of this long-range vdW interaction on the lattice constants of the alkali metals; most methods, including Ref. 15, are not intended for metals.

In the simulation of the long-range vdW interaction, nonlocal density functionals are usually developed to achieve good accuracy for molecules<sup>10,11,13</sup> or for systems of slowly varying densities.<sup>7,8</sup> The former approach makes use of molecular information while the latter starts with the second-order perturbative treatment of the interaction between two fragments of slowly varying density. There are *two* uniform-gas long-range vdW interactions: one is for the interaction between nonoverlapped spherical pieces of a uniform electron gas and the other is for the interaction between two nonoverlapped spheres of uniform density in empty space. The former is the standard uniform gas while the latter is

relevant to a Wigner crystal<sup>16</sup> and seems more like and thus more relevant to the atom-atom interaction in empty space. In this work, we present a nonlocal density functional to simulate this long-range vdW interaction. Our functional satisfies the exact zero- and high-frequency limits of the dynamic polarizability imposed by Lima and Caldas<sup>12</sup> but in addition it is constrained to be exact for  $C_6$  in the latter uniform-gas limit. [Note that the uniform-gas limit we impose here differs from that which has been imposed on the semilocal meta-generalized gradient approximation (meta-GGA) of Tao, Perdew, Staroverov, and Scuseria (TPSS) (Ref. 17) and its revised version (revTPSS).<sup>4</sup>] Then we derive a simple formula for the effect of the long-range vdW interaction on the DFT lattice constants of metals. In evaluating the vdW coefficient for the ion pair  $M^+, \dots, M^+$  in metals, the screening effect from the valence electrons is calculated via second-order time-dependent perturbation theory.<sup>18</sup> Finally we illustrate our approach with the revTPSS functional, without losing generality. Our calculations show that, with the vdW correction, the maximum error (Cs) of the revTPSS lattice constants of the alkali metals drops significantly from 0.151 to 0.056 Å.

The vdW interaction arises from density fluctuations. In the large separation ( $R=|\mathbf{r}_2-\mathbf{r}_1|\rightarrow\infty$ ) limit, the leading term of the long-range part of the interaction between two fragments of nonoverlapped densities  $n(\mathbf{r}_1)$  and  $n(\mathbf{r}_2)$  can be written as  $E_{\text{vdW}}^{\text{LR}}=-C_6/R^6$ , where

$$C_6 = \int_{V_1} d\mathbf{r}_1 \int_{V_2} d\mathbf{r}_2 \phi(\mathbf{r}_1, \mathbf{r}_2) n(\mathbf{r}_1) n(\mathbf{r}_2) \quad (1)$$

with  $n=n_1+n_2$  and  $\phi$  being the pair interaction. Based on the second-order perturbation theory, Rapcewicz and Ashcroft<sup>7</sup> proposed the uniform-gas equivalent effective interaction  $\phi = (3/4)\hbar(e^2/m)^2/[\omega_p(\mathbf{r}_1, \mathbf{r}_2)]^3$ , where  $\omega_p = \sqrt{4\pi n_{\text{eff}}(e^2/m)}$  is the average plasmon frequency, and  $n_{\text{eff}} = \sqrt{n(\mathbf{r}_1)n(\mathbf{r}_2)}$  is the effective density. Because the fluctuating interaction is carried out by plasmons, which become Landau damped when  $q \geq \omega_p/v_F$ , where  $q$  is the local wave vector characterizing the spatial variation in the density ( $q \sim |\nabla n|/6n$ ),<sup>19,20</sup> and  $v_F$  is the local Fermi velocity, a cutoff  $\Theta(\omega_p/v_F - q)$  must be imposed on each integral of Eq. (1). To take into account the limit of separated atoms, Andersson, Langreth, and

Lundqvist<sup>8</sup> found a better choice for  $n_{\text{eff}}(\mathbf{r}_1, \mathbf{r}_2)$ .

In order to make our nonlocal functional for the long-range vdW interaction accurate for both molecules and solids, we respect the paradigm densities in condensed matter physics (slowly varying densities) and quantum chemistry (one- or two-electron densities). For this purpose, we start with the exact expression<sup>5</sup>

$$C_6 = \frac{3\hbar}{\pi} \int_0^\infty du \alpha_1(iu) \alpha_2(iu), \quad (2)$$

where  $\alpha_j(\omega)$  is the atomic dynamical polarizability. While the exact frequency dependence of the dynamical polarizability remains unknown, several exact properties have been discovered. For example, in the high-frequency ( $u \rightarrow \infty$ ) limit,  $\alpha_j(\omega)$  has the asymptotic form<sup>5</sup>  $\alpha_j(\omega) \rightarrow \int d\mathbf{r} n(\mathbf{r})/u^2$ . In the low-frequency limit,  $\alpha_j(\omega)$  reduces to the static polarizability  $\alpha_j(0)$ . For the interaction between two nonoverlapped spheres of uniform density, the pair interaction is given by<sup>16</sup>

$$\tilde{\phi}_{\text{unif}} = (3b^2/4) \sqrt{4\pi n/b} / (4\pi n)^2. \quad (3)$$

(Atomic units  $e^2 = \hbar = m = 1$  are used from now on unless otherwise explicitly stated.)  $b=1$  if the sphere belongs to part of the uniform electron gas and 3 if it is an isolated sphere. The pair potential  $\tilde{\phi}_{\text{unif}}$  for  $b=3$  is larger than that for  $b=1$  by a factor of 5.2. (The size of this factor strongly suggests that a valence-valence  $C_6$  in a metal would be seriously overestimated by the free-atom value.)

To satisfy the above conditions, we assume

$$\alpha_j(iu) = \frac{3}{4\pi a_j} \int d\mathbf{r} \frac{f_j^2(\tilde{\omega}_p)}{u^2 + f_j^2(\tilde{\omega}_p)} \Theta(\mathbf{r}_{cj} - \mathbf{r}), \quad (4)$$

where  $\tilde{\omega}_p = \sqrt{4\pi n/3}$  is the vibrational frequency of an isolated uniform sphere,<sup>16</sup>  $\Theta$  is the step function,  $a_j$  is a constant to be fixed below, and  $\mathbf{r}_{cj}$  is the cut-off radius determined by requiring that the static polarizability be reproduced

$$\alpha_j(0) = \frac{3}{4\pi a_j} \int d\mathbf{r} \Theta(\mathbf{r}_{cj} - \mathbf{r}). \quad (5)$$

In order to recover the uniform-gas and separate-atom limits, we choose  $f_j = a_j^2 \tilde{\omega}_p$ . Substituting Eq. (4) into Eq. (2) and performing the integration over the frequency  $u$  yields the desired result

$$C_6 = \frac{27a_1 a_2}{32\pi^2} \int d\mathbf{r}_1 \Theta_1 \int d\mathbf{r}_2 \Theta_2 \frac{\tilde{\omega}_p(\mathbf{r}_1) \tilde{\omega}_p(\mathbf{r}_2)}{a_1^2 \tilde{\omega}_p(\mathbf{r}_1) + a_2^2 \tilde{\omega}_p(\mathbf{r}_2)}, \quad (6)$$

where  $\Theta_j = \Theta(\mathbf{r}_{cj} - \mathbf{r}_j)$ . For spherical systems, the radial cutoff is  $r_{cj} = [a_j \alpha_j(0)]^{1/3}$ . The parameter  $a_j$  may be found by requiring that the exact high-frequency limit of the dynamical polarizability be reproduced. Thus, from the spherical density of system  $j$

$$a_j = \left[ \int_0^\infty dr 4\pi r^2 n(r) / \int_0^{r_{cj}} dr 4\pi r^2 n(r) \right]^{1/3} \geq 1. \quad (7)$$

To better understand Eqs. (4)–(7) with Eqs. (1) and (3), consider two uniform-gas limits: (a) for a sphere of uniform density with radius  $R$  in empty space,  $\alpha(0) = R^3$ .<sup>16</sup> Then  $a$

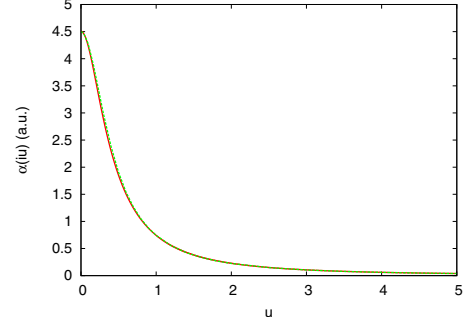


FIG. 1. (Color online) Dynamical polarizability  $\alpha(iu)$  (in atomic units) of the H atom: Exact (solid red line), and Eq. (4) with  $a = 1.143$  and  $r_c = 1.726$  (dashed green line).

$= 1$ ,  $f = \sqrt{4\pi n}/3$ , and  $\tilde{\phi}_{\text{unif}}$  is given by Eq. (3) with  $b=3$ . (b) For a sphere of uniform density with radius  $R$ , which is part of a uniform electron gas,  $\alpha(0) = R^3/3$ .<sup>16</sup> Then  $a = 3^{1/4}$ ,  $f = \sqrt{4\pi n}$ , and  $\tilde{\phi}_{\text{unif}}$  is given by Eq. (3) with  $b=1$ . Thus the characteristic frequency  $f$  and the pair interaction  $\tilde{\phi}_{\text{unif}}$  are right in both uniform-gas limits. For the other paradigm density, Fig. 1 shows that the proposed  $\alpha_j(iu)$  of Eq. (4) almost reproduces the exact one<sup>21</sup> for the H atom.

As a simple test, we apply our nonlocal functional of Eq. (6) to evaluate  $C_6$  for diverse atom pairs. The results are shown in Table I. In our calculations, spin-restricted Hartree-Fock densities<sup>22</sup> are used. The static polarizabilities  $\alpha(0)$  are taken, respectively, from Ref. 23 for H, Mg, and Ca, Ref. 24 for He, Ne, Ar, and Kr, Ref. 25 for Xe, Ref. 26 for Li, Na, and K, and Ref. 27 for Be. From Table I we can see that the present nonlocal functional is remarkably accurate with a mean absolute relative error of only 6.2%. Note that, while the Lima-Caldas ansatz for the form of  $\alpha_j(iu)$  [their Eqs. (1)–(6)] differs from ours in its form and in its avoidance of a sharp cutoff, we find that it is also exact in *both* uniform-gas limits. Thus we have found an important reason why both functionals are accurate. Generalization to nonspherical densities, as in Ref. 30, is possible.

Near equilibrium, the higher-order contributions  $-C_8/R^8$  and  $-C_{10}/R^{10}$  can also be important. They can be estimated from the empirical formulas

$$C_8 = 10C_6^{1.25}, \quad C_{10} = 121C_6^{1.50}, \quad (8)$$

which fit the reference many-body-perturbation-theory values of Ref. 13 within about 15%.

To estimate the effect of the long-range vdW attraction on the revTPSS lattice constants of the alkali metals, we start with the revTPSS equation of state for the energy per atom as a function of the volume per atom,  $E(v)$ . Then around the equilibrium volume  $v_0$ , we have

$$E(v) = E(v_0) + E'(v_0)\Delta v + \frac{1}{2}E''(v_0)(\Delta v)^2, \quad (9)$$

where  $\Delta v \equiv v - v_0$  is the volume shift per atom. At equilibrium, the revTPSS energy minimizes so that  $E'(v_0) = 0$ . The second derivative of the energy at equilibrium is related to

TABLE I. The vdW coefficients  $C_6$  (in atomic units) calculated with Eq. (6) using spin-restricted Hartree-Fock densities (Ref. 22). The mean absolute relative error is 6.2%.

	Reference	Present		Reference	Present
He-He	1.46 <sup>c</sup>	1.44	Ar-H	20.5 <sup>d</sup>	19.8
Ne-Ne	6.38 <sup>c</sup>	7.35	Ar-Li	171 <sup>d</sup>	180
Ar-Ar	64.3 <sup>c</sup>	67.8	Ar-Na	189 <sup>d</sup>	198
Kr-Kr	130 <sup>c</sup>	132	Ar-K	269 <sup>d</sup>	317
Xe-Xe	286 <sup>c</sup>	295	Kr-H	28.0 <sup>d</sup>	28.0
He-Ne	3.03 <sup>c</sup>	3.22	Kr-Li	255 <sup>d</sup>	265
He-Ar	9.54 <sup>c</sup>	9.81	Kr-Na	282 <sup>d</sup>	289
He-Kr	13.4 <sup>c</sup>	13.6	Kr-K	403 <sup>d</sup>	462
He-Xe	19.5 <sup>c</sup>	20.0	Xe-H	40.7 <sup>d</sup>	42.4
Ne-Ar	19.5 <sup>c</sup>	21.5	Xe-Li	404 <sup>d</sup>	422
Ne-Kr	27.3 <sup>c</sup>	29.6	Xe-Na	448 <sup>d</sup>	456
Ne-Xe	39.7 <sup>c</sup>	43.3	Xe-K	642 <sup>d</sup>	729
Ar-Kr	91.1 <sup>c</sup>	94.4	He-Be	13.0 <sup>a</sup>	13.6
Ar-Xe	135 <sup>c</sup>	140	He-Mg	21.1 <sup>a</sup>	21.2
Kr-Xe	192 <sup>c</sup>	197	He-Ca	32.5 <sup>a</sup>	36.7
H-H	6.50 <sup>a</sup>	6.28	Ne-Be	27.5 <sup>c</sup>	27.7
Li-Li	1389 <sup>a</sup>	1334	Ne-Mg	42.9 <sup>c</sup>	43.3
Na-Na	1540 <sup>a</sup>	1363	Ne-Ca	94.1 <sup>c</sup>	74.8
K-K	3945 <sup>a</sup>	3701	Ar-Be	102 <sup>c</sup>	101
H-Li	65.9 <sup>a</sup>	67.2	Ar-Mg	162 <sup>c</sup>	158
H-Na	72.1 <sup>a</sup>	71.7	Ar-Ca	346 <sup>c</sup>	276
H-K	105 <sup>a</sup>	114	Kr-Be	149 <sup>c</sup>	146
Li-Na	1460 <sup>a</sup>	1346	Kr-Mg	238 <sup>c</sup>	228
Li-K	2334 <sup>a</sup>	2214	Kr-Ca	503 <sup>c</sup>	400
Na-K	2443 <sup>a</sup>	2238	Xe-Be	228 <sup>c</sup>	226
Be-Be	213 <sup>b</sup>	213	Xe-Mg	367 <sup>c</sup>	355
Mg-Mg	618 <sup>a</sup>	569	Xe-Ca	775 <sup>c</sup>	624
Ca-Ca	2005 <sup>a</sup>	1971	H-Be	34.4 <sup>a</sup>	34.7
Be-Mg	362 <sup>a</sup>	346	H-Mg	57.8 <sup>a</sup>	54.8
Be-Ca	619 <sup>a</sup>	630	H-Ca	93.0 <sup>a</sup>	96.9
Mg-Ca	1112 <sup>a</sup>	1051	Li-Be	467 <sup>a</sup>	473
He-H	2.81 <sup>a</sup>	2.75	Li-Mg	854 <sup>a</sup>	811
He-Li	22.0 <sup>a</sup>	23.3	Li-Ca	1615 <sup>a</sup>	1570
He-Na	24.2 <sup>a</sup>	26.0	Na-Be	505 <sup>a</sup>	491
He-K	34.4 <sup>a</sup>	41.7	Na-Mg	920 <sup>a</sup>	837
Ne-H	5.60 <sup>d</sup>	5.79	Na-Ca	1723 <sup>a</sup>	1608
Ne-Li	42.6 <sup>d</sup>	46.4	K-Be	755 <sup>a</sup>	786
Ne-Na	47.0 <sup>d</sup>	52.4	K-Mg	1390 <sup>a</sup>	1347
Ne-K	66.3 <sup>d</sup>	84.2	K-Ca	2663 <sup>a</sup>	2608

<sup>a</sup>From Ref. 23.

<sup>b</sup>From Ref. 27.

<sup>c</sup>From Ref. 28.

<sup>d</sup>From Ref. 29.

the bulk modulus by  $B_0 = v_0 E''(v_0)$ . Since the lattice of the alkali metals is bcc, we have  $v = a^3/2$ , where  $a$  is the lattice constant. Thus Eq. (9) can be rewritten as

$$E(v) - E(v_0) = (9/4)B_0 a_0 (\Delta a)^2, \quad (10)$$

where  $\Delta a \equiv a - a_0$  is the lattice constant shift relative to the original revTPSS lattice constant  $a_0$ . The vdW interaction of *one* ion core with all others is

$$E_{\text{vdW}} = -b_6 C_6^+ / a^6 - b_8 C_8^+ / a^8 - b_{10} C_{10}^+ / a^{10}, \quad (11)$$

where  $b_n = (1/2) \sum_{i=1}^n (a/R_{i0})^n$  ( $b_6 = 14.52$ ,  $b_8 = 16.36$ , and  $b_{10} = 20.15$ ) and  $C_n^+$  is the  $C_n$  coefficient for the interaction between two singly positive ion cores in the metal, as screened by the valence electrons.  $R_{i0}$  is the distance from atom 0 to any other atom  $i$ . Expansion of  $E_{\text{vdW}}$  around  $a_0$  to second order in  $\Delta a$ , and minimization of the sum of Eqs. (10) and (11), leads straightforwardly to a linear equation for the correction<sup>31</sup>  $\Delta a$  to the revTPSS equilibrium lattice constant. The quantity that determines the importance of  $C_n^+$  is  $x_n = b_n C_n^+ / (B_0 a_0^{n+3})$ .

To evaluate  $C_6^+$ , we let the valence electrons screen the interaction between two cores, according to the simple formula of Rehr, Zaremba, and Kohn,<sup>18,31</sup> who showed that one could use the long-wavelength limit of the dynamic dielectric function of the uniform valence-electron density [with plasma frequency  $\Omega_p = (4\pi n_{\text{valence}})^{1/2}$ ]. For like-pair ionic interactions, we find

$$C_6^+ = \frac{27}{32\pi^2} \int d\mathbf{r}_1 \Theta_1 \int d\mathbf{r}_2 \Theta_2 \frac{\tilde{\omega}_p(\mathbf{r}_1) \tilde{\omega}_p(\mathbf{r}_2)}{\tilde{\omega}_p(\mathbf{r}_1) + \tilde{\omega}_p(\mathbf{r}_2)} S(\mathbf{r}_1, \mathbf{r}_2),$$

$$S = a^6 \tilde{\omega}_p(\mathbf{r}_1) \tilde{\omega}_p(\mathbf{r}_2) \{ \Omega_p [\tilde{\omega}_p(\mathbf{r}_1) + \tilde{\omega}_p(\mathbf{r}_2)] / 2 + a^2 \tilde{\omega}_p(\mathbf{r}_1) \times \tilde{\omega}_p(\mathbf{r}_2) \} \{ [\Omega_p + a^2 \tilde{\omega}_p(\mathbf{r}_1)]^2 [\Omega_p + a^2 \tilde{\omega}_p(\mathbf{r}_2)]^2 \}^{-1}, \quad (12)$$

where  $a$  is given by Eq. (7) and  $S$  accounts for the screening of valence electrons. The accuracy of our  $C_6^+$  is tested for free ion pairs, for which  $S=1$ , using the static polarizabilities<sup>32,33</sup> of the free ions. The results are <10% higher than those estimated<sup>33</sup> with the time-dependent local density approximation. See Ref. 31 for  $a_1 \neq a_2$ .

The alkali metals are well-suited to this proposed correction because their valence densities are nearly uniform outside nearly nonoverlapping cores.<sup>34</sup> The full valence-valence vdW interaction is already included in the revTPSS energy, which is exact for any uniform density. We calculate the vdW-corrected lattice constants of the alkali metals using the expressions in Ref. 31. The  $C_6^+$  are calculated from Eq. (12) using the Hartree-Fock densities<sup>22</sup> of the ion cores (in the corresponding free atoms) and the polarizabilities of these cores in a uniform electron gas.<sup>32</sup> Only the low frequency ( $u < \sim 2\Omega_p$ ) contribution to  $C_6^+$  (about 30% of the unscreened value) gets screened out by Eq. (12).  $C_8^+$  and  $C_{10}^+$  are estimated from Eq. (8), and increase the long-range vdW effect by about 50%. The results are summarized in Table II. The revTPSS lattice constants and bulk moduli are calculated with the all-electron BAND code,<sup>35</sup> as in Ref. 4. We observe that the long-range vdW attraction systematically shrinks the revTPSS lattice constants. The vdW effect grows when we pass from Li (harder) to Cs (softer) due largely to the increase of  $x_6 = b_6 C_6^+ / (B_0 a_0^9)$ . As a result, the vdW-corrected revTPSS lattice constants are considerably closer to experiment than the original revTPSS lattice constants.

TABLE II. Alkali-metal lattice constants calculated with the revTPSS meta-GGA and their core-core vdW-corrected values. Experimental lattice constants from Ref. 2. The last columns show the long-range vdW corrections to the cohesive energy per atom and to the bulk modulus. 1 bohr=0.5292 Å, 1 hartree/bohr<sup>3</sup>=2.9424×10<sup>4</sup> GPa, 1 hartree=27.2 eV.

Solid	$C_6^+$ (a.u.)	$B_0$ (revTPSS) (GPa)	$a_0$ (revTPSS) (Å)	$a_0$ (correc) (Å)	$a_0$ (expt.) (Å)	$\Delta\epsilon_{\text{cohesive}}$ (eV)	$\Delta B/B_0$ (revTPSS)
Li	0.072	12.63	3.425	3.424	3.449	0.000	-0.002
Na	1.69	7.43	4.213	4.207	4.210	0.003	-0.015
K	19.5	3.11	5.312	5.285	5.212	0.010	-0.039
Rb	43.5	2.64	5.689	5.646	5.576	0.015	-0.056
Cs	104.	1.59	6.190	6.095	6.039	0.022	-0.108
Mean error			0.069	0.034			
Mean absolute error			0.078	0.045			

In summary, we use constraint satisfaction to construct a well-motivated nonlocal density functional for the long-range vdW interaction, showing the power of two uniform-gas limits. Then we derive a simple formula to evaluate the core-core vdW correction to the lattice constants of the alkali metals calculated with a semilocal density functional. We

find that the vdW-corrected revTPSS meta-GGA lattice constants of the alkali metals agree better with experiment, showing errors like those of revTPSS for other solids.<sup>4</sup>

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<sup>1</sup>W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).

<sup>2</sup>G. I. Csonka *et al.*, *Phys. Rev. B* **79**, 155107 (2009).

<sup>3</sup>P. Haas *et al.*, *Phys. Rev. B* **79**, 085104 (2009).

<sup>4</sup>J. P. Perdew *et al.*, *Phys. Rev. Lett.* **103**, 026403 (2009).

<sup>5</sup>H. Margenau and N. R. Kestner, *Theory of Interatomic Forces*, 2nd ed. (Pergamon Press, Oxford, 1969).

<sup>6</sup>J. Tao and J. P. Perdew, *J. Chem. Phys.* **122**, 114102 (2005).

<sup>7</sup>K. Rapcewicz and N. W. Ashcroft, *Phys. Rev. B* **44**, 4032 (1991).

<sup>8</sup>Y. Andersson *et al.*, *Phys. Rev. Lett.* **76**, 102 (1996).

<sup>9</sup>J. F. Dobson and B. P. Dinte, *Phys. Rev. Lett.* **76**, 1780 (1996).

<sup>10</sup>Q. Wu and W. Yang, *J. Chem. Phys.* **116**, 515 (2002).

<sup>11</sup>S. Grimme, *J. Comput. Chem.* **25**, 1463 (2004).

<sup>12</sup>N. A. Lima and M. J. Caldas, *Phys. Rev. B* **72**, 033109 (2005).

<sup>13</sup>A. D. Becke and E. R. Johnson, *J. Chem. Phys.* **127**, 154108 (2007); **127**, 124108 (2007).

<sup>14</sup>A. Tkatchenko and M. Scheffler, *Phys. Rev. Lett.* **102**, 073005 (2009).

<sup>15</sup>M. Dion *et al.*, *Phys. Rev. Lett.* **92**, 246401 (2004).

<sup>16</sup>R. E. Goldstein *et al.*, *J. Chem. Phys.* **91**, 1843 (1989).

<sup>17</sup>J. Tao *et al.*, *Phys. Rev. Lett.* **91**, 146401 (2003).

<sup>18</sup>J. J. Rehr *et al.*, *Phys. Rev. B* **12**, 2062 (1975).

<sup>19</sup>D. C. Langreth and M. J. Mehl, *Phys. Rev. Lett.* **47**, 446 (1981).

<sup>20</sup>M. van Faassen *et al.*, *Phys. Rev. Lett.* **88**, 186401 (2002).

<sup>21</sup>D. M. Bishop and J. Pipin, *J. Chem. Phys.* **97**, 3375 (1992).

<sup>22</sup>E. Clementi and C. Roetti, *At. Data Nucl. Data Tables* **14**, 177 (1974).

<sup>23</sup>F. Maeder and W. Kutzelnigg, *Chem. Phys.* **42**, 95 (1979).

<sup>24</sup>P. J. Leonard, *At. Data Nucl. Data Tables* **14**, 21 (1974).

<sup>25</sup>K. T. Tang and J. P. Toennis, *Z. Phys. D* **1**, 91 (1986).

<sup>26</sup>R. W. Molof *et al.*, *Phys. Rev. A* **10**, 1131 (1974).

<sup>27</sup>H. Koch and R. J. Harrison, *J. Chem. Phys.* **95**, 7479 (1991).

<sup>28</sup>A. Kumar and W. J. Meath, *Mol. Phys.* **54**, 823 (1985); T. R. Proctor and W. C. Stwalley, *J. Chem. Phys.* **66**, 2063 (1977).

<sup>29</sup>J. M. Standard and P. R. Certain, *J. Chem. Phys.* **83**, 3002 (1985); R. J. Bell and A. E. Kingston, *Proc. Phys. Soc. London* **88**, 901 (1966).

<sup>30</sup>E. Hult *et al.*, *Phys. Rev. B* **59**, 4708 (1999).

<sup>31</sup>See supplementary material at <http://link.aps.org/supplemental/10.1103/PhysRevB.81.233102> for equations and explanations.

<sup>32</sup>R. M. Nieminen and M. J. Puska, *Phys. Scr.* **25**, 952 (1982).

<sup>33</sup>G. D. Mahan, *J. Chem. Phys.* **76**, 493 (1982).

<sup>34</sup>The core-core vdW effect can also be important in the alkaline earths but in them the valence electron density outside the cores is substantially more nonuniform due to band overlap (Ref. 31).

<sup>35</sup>G. te Velde and E. J. Baerends, *Phys. Rev. B* **44**, 7888 (1991).