Physical Adsorption: Theory of van der Waals Interactions between Particles and Clean Surfaces

Jianmin Tao[*] and Andrew M. Rappe
Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323, USA

(Received 22 July 2013; revised manuscript received 26 December 2013; published 10 March 2014)

van der Waals (vdW) interactions between particles and surfaces are critical for the study of physical adsorption. In this work, we develop a method to calculate the leading- and higher-order coefficients, describing the dependence of vdW interaction on height above the surface. We find that the proposed method can produce the vdW coefficients for atoms on surfaces of metals and semiconductors, with a mean absolute relative deviation of about 5%. As an important application, we study the adsorption energies for rare-gas atoms on noble-metal surfaces by combining the present method, which accounts for the long-range part, with semilocal density functional theory (DFT), which accounts for the short-range part. This combined DFT + vdW approach yields adsorption energies in excellent agreement (5%) with experiments. This suggests that the present method may serve as a useful dispersion correction to density functional approximations.

DOI: 10.1103/PhysRevLett.112.106101 PACS numbers: 68.43.-h, 31.15.E-, 34.35.+a

Many processes of technological and fundamental importance occur on solid surfaces. Physical adsorption is one of them that has received the most attention [1]. Making use of the reversible nature of physical adsorption, various techniques have been developed for catalyst preparation, hydrogen storage, and purification. To probe the electronic structure of surfaces, many experiments have been designed to study electronic and chemical properties of surfaces and their influence on the interaction of particles with surfaces. For example, atomic beam scattering and diffraction can yield information about the particle-surface potential.

Physical adsorption is a ubiquitous phenomenon arising from the van der Waals (vdW) interaction. However, description of this phenomenon presents computational challenges to physicists and chemists. Although density functional theory (DFT) has achieved practical success for normally bonded systems, it can only describe the short-range part [2] of the vdW interaction, leaving the long-range part missing. For example, semilocal DFT may yield correct on-top site preference of adsorption, due to error cancellation, but it significantly underestimates the adsorption energy. (This error cancellation does not apply to chemisorption [3,4], for which the short-range part is dominantly important.) This has been confirmed by many DFT calculations (e.g., rare-gas atoms on metal surfaces [5–9]). Recent calculations [10,11] show that this difficulty can be reduced with the nonlocal vdW-DF functional [12], and the accuracy of this functional can be improved by a proper choice of its exchange part [13,14]. In recent years, it was found that the performance of DFT can be significantly improved by adding a long-range vdW correction [15].

This combined DFT + vdW approach greatly expands the scope of DFT applicability. It has been used to study molecules [16] and solids [17,18]. In particular, Chen *et al.* [11] used the DFT-D method, with the dispersion corrections proposed by Grimme *et al.* [19], to study the adsorption of rare-gas atoms on metal surfaces. It was shown that DFT-D tends to overestimate the adsorption energy. Interestingly, it was also found in a recent study [20] that DFT-D strongly overestimates the sublimation energy of ice. However, the reasons for these two overestimates are quite different. In the first case, the vdW coefficients that are used in DFT-D, such as C_6 and C_8, are valid only for particle-particle pair interactions, but not for particles on a surface, while in the latter, the dispersion correction in DFT-D contains a global scaling parameter, which may not be transferable to solids, because in solids one needs to consider the dielectric screening. Here, we develop a method for calculating the leading- and higher-order vdW coefficients between particles and surfaces, which may provide a more realistic dispersion correction for physical adsorption.

The long-range vdW interaction between particles and a surface takes the general form [21] $V(Z) = -C_3/Z^3 - C_4/Z^4 - C_5/Z^5 - \cdots$. Here, C_3 and C_5 are the vdW coefficients that describe the dielectric response of the bulk solid to the instantaneous dipole and quadrupole of particles. Z is the normal distance of a particle from surface. In this expression, there are additional terms that describe the lateral interaction between particles on the surface, but they are small [8] and vanish exponentially with the distance between particles. Here we only consider the lateral average $V(Z) = \int dXdY\, V(X,Y,Z)/A$, with A being the surface area. With an appropriate choice of the reference plane position Z_0, the Z^{-4} term may be eliminated [22], leading to

$$V(Z) = -C_3/(Z-Z_0)^3 - C_5'/(Z-Z_0)^5 - \cdots, \quad (1)$$

where C_5' is the effective higher-order coefficient related to C_5 via $C_5' = C_5 + 6C_3Z_0^2$. It measures the strength of vdW interaction between the quadrupole and surface, with the reference plane position at Z_0.

According to second-order perturbation theory, the vdW coefficients for particles on a clean surface can be expressed as [23]

$$C_{2l+1} = \frac{1}{4\pi}\int_0^\infty du\,\alpha_l(iu)\frac{\epsilon_1(iu)-1}{\epsilon_1(iu)+1}, \tag{2}$$

where $\alpha_l(iu)$ is the dynamic multipole polarizability of the particle, with $l = 1$ (dipole), 2 (quadrupole), 3 (octupole), etc.; $\epsilon_1(iu)$ is the bulk dielectric function. Many methods [21,24,25] have been proposed for C_3, and good accuracy has been achieved [26]. However, work on higher-order coefficients such as C_5 is scarce [22]. Because of the energy gap in semiconductors and d electrons in noble metals, the dielectric functions of these two materials are very different. In the following, we will first present our calculations of C_3 and C_5 for particles on simple and noble-metal surfaces and then on surfaces of semiconductors.

Jellium.—Jellium is a realistic model for simple metals. Particles on a jellium surface is the simplest example of physical adsorption that still allows analysis of higher-order fluctuations. The dynamic multipole polarizability of a particle may be modeled accurately by [27]

$$\alpha_l(iu) = \frac{2l+1}{4\pi d_l}\int_0^{R_l} dr\,4\pi r^2\frac{r^{2l-2}d_l^4\omega_l^2}{d_l^4\omega_l^2+u^2}, \tag{3}$$

where R_l is the effective vdW radius, and d_l is a parameter introduced to satisfy the exact zero- and high-frequency limits. In the uniform-gas limit, $\alpha_l(iu)$ reduces to the exact dynamic multipole polarizability of the classical conducting sphere. Numerical calculation shows that the model can generate vdW coefficients for diverse atom pairs in excellent agreement with accurate reference values, with a mean absolute relative error of only 3%, suggesting high accuracy of the model. This model may be regarded as an interpolation of $\alpha_l(iu)$ between zero and high frequencies. The two parameters R_l and d_l are determined by $R_l = [d_l\alpha_l(0)]^{1/(2l+1)}$ and $d_l = [\int_0^\infty dr 4\pi r^2 r^{2l-2} n(r)/\int_0^{R_l} dr 4\pi r^2 r^{2l-2} n(r)]^{1/3}$. In Eq. (3), $\omega_l = \omega_p\sqrt{l/(2l+1)}$ is the sphere plasmon vibrational frequency, with $\omega_p = \sqrt{4\pi n}$ being the plasmon frequency of the extended uniform electron gas. (hartree atomic units are used.) For atoms and molecules, we generalize ω_l and call it the local sphere plasmon frequency $\omega_l(\mathbf{r})$ calculated with the local electron density $n(\mathbf{r})$.

The bulk dielectric function of jellium at infinite wavelength is given by $\epsilon_1(iu) = 1 + \bar{\omega}_p^2/u^2$. Substituting Eq. (3) into Eq. (2) leads to the expression

$$C_{2l+1} = \frac{2l+1}{32\pi d_l}\int_0^{R_l} dr\,4\pi r^2 r^{2l-2}\frac{d_l^2\omega_l\sqrt{\bar{\omega}_p^2/2}}{d_l^2\omega_l+\sqrt{\bar{\omega}_p^2/2}}, \tag{4}$$

where $\sqrt{\bar{\omega}_p^2/2}$ is the surface plasmon frequency of jellium.

Next, we calculate the reference plane position Z_0 with respect to which the position of the particle is determined. According to Zaremba and Kohn [21], for a flat surface

$$Z_0 = \frac{1}{4\pi C_3}\int_0^\infty du\,\alpha_1(iu)\frac{\epsilon_1(iu)-1}{\epsilon_1(iu)+1}d_{\mathrm{IP}}(iu), \tag{5}$$

where d_{IP} is the frequency-dependent image plane [28] given by $d_{\mathrm{IP}} = [d_\parallel + \epsilon_1(iu)d_\perp(iu)]/[\epsilon_1(iu)+1]$, with $d_\perp(iu)$ being the center of gravity of the density induced on the jellium surface and $d_\parallel$ being the spatial distribution of the currents parallel to the surface induced by a uniform tangential electric field. Because of translational invariance of the surface, $d_\parallel = Z_B$ [29], the edge of the jellium background. Choosing the origin of coordinates to coincide with Z_B leads to

$$d_{\mathrm{IP}}(iu) = \epsilon_1(iu)d_\perp(iu)/[\epsilon_1(iu)+1]. \tag{6}$$

Persson and Zaremba [29] proposed a simple approximation, $d_\perp(iu) = d_\perp(0)/[1+\eta(u/\bar{\omega})^2/2]$, which is consistent with the sum rule [30]. Here, $\eta = d_\perp(0)/\lambda$, $\bar{\omega} = \sqrt{\bar{\omega}_p^2/2}$, and $d_\perp(0)$ is the static centroid position. Both λ and $d_\perp(0)$ for $r_s = 2, 3, 4$ are given by Ref. [29]. For $2 \le r_s \le 6$, they can be obtained from the simple analytic parametrizations $\lambda = -0.0105r_s^2 + 0.1285r_s + 0.248$ and $d_\perp(0) = 0.02r_s^2 - 0.27r_s + 2.06$.

Noble metals.—Because of the remarkable properties of noble metals, adsorption on metal surfaces has been widely studied. A major difference between noble metals and jellium is the participation of d electrons. The dielectric function of noble metals can be split into two parts [21,29], i.e., $\epsilon_1(iu) = 1 + \bar{\omega}_{pf}^2/u^2 + \Omega^2/(u^2+\omega_0^2)$, where the second term is due to the free-electron intraband transition, whereas the third accounts for the bound-electron interband transition. Here, $\bar{\omega}_{pf}^2 = (1/m_{\mathrm{opt}})\bar{\omega}_p^2$ is the corrected bulk plasmon frequency, with m_{opt} being the ratio of the optical mass [31] to m_e. All three parameters m_{opt}, Ω, and ω_0 for Cu, Ag, and Au were determined [29] by a fit to experiments. However, they are not available in the literature for Pt and Pd. Considering that Pt is a neighbor of Au, that Pd is a neighbor of Pt, and that C_{2l+1} are not sensitive to these three parameters, here we determine them by the interpolation of these parameters as a function of r_s based on the data for Cu, Ag, and Au (Table I). Inserting $\alpha_l(iu)$ and $\epsilon_1(iu)$ for noble metals into Eq. (2) leads to

$$C_{2l+1} = \frac{(2l+1)A_1}{16\pi^2 d_l}\int_0^{R_l} dr\,r^{2l-2}d_l^4\omega_l^2 I, \tag{7}$$

TABLE I. Input data (in a.u.) for noble metals (Ref. [29] for Cu, Ag, and Au. See text for Pt and Pd).

Noble metal	r_s	$m_{\rm opt}$	ω_0	Ω	λ	$d_\perp(0)$
Cu	2.67	1.5	0.3458	0.7481	0.516	1.421
Ag	3.02	0.96	0.5443	1.001	0.540	1.433
Au	3.01	0.99	0.3863	1.051	0.540	1.430
Pt	2.90	1.17	0.355	1.07	0.532	1.422
Pd	2.87	1.22	0.350	1.05	0.530	1.420

$$I=\frac{\pi}{2}\frac{B+A_2[f(a_l,b_l;a_M,b_M)+f(a_M,b_M;a_l,b_l)]}{D_1D_2(a_l+a_M)(b_l+a_M)(a_l+b_M)(b_l+b_M)}, \tag{8}$$

with $A_1=[(1/m_{\rm opt})\bar{\omega}_p^2+\Omega^2]/2$, $B=a_lb_la_Mb_M[D_1+D_2+(d_l^4\tilde{\omega}_l^2+A_2)(a_l+b_l+a_M+b_M)]$, $A_2=d_l^4\tilde{\omega}_l^2(1/m_{\rm opt})\bar{\omega}_p^2\omega_0^2/2A_1$. $D_1=a_lb_l(a_M+b_M)$, $D_2=a_Mb_M(a_l+b_l)$, $f(p,q;s,t)=(p+q)(pq+2st+s^2+t^2)$, $a_l=d_l^2\tilde{\omega}_l$, $b_l=d_l^2\omega_l$. $a_M^2=\{[(1/m_{\rm opt})\bar{\omega}_p^2+\Omega^2+2\omega_0^2]/2-\sqrt{Y}\}/2$, $b_M^2=\{[(1/m_{\rm opt})\bar{\omega}_p^2+\Omega^2+2\omega_0^2]/2+\sqrt{Y}\}/2$, and $Y=[(1/m_{\rm opt})\bar{\omega}_p^2+\Omega^2+2\omega_0^2]^2/4-(2/m_{\rm opt})(\bar{\omega}_p\omega_0)^2$.

Now we turn to Z_0. For noble metals, $d_\perp(iu)$ can be written as a sum of two contributions [21,29] weighted by the dielectric function, i.e., $d_\perp(iu)=[\epsilon_f(iu)d_\perp^f(iu)+\epsilon_b(iu)d_\perp^b(iu)]/[\epsilon_f(iu)+\epsilon_b(iu)]$. Here, $d_\perp^f(iu)$ is assumed to take the same form as for the jellium, but with r_s replaced by the corrected [29] density parameter $r_s^f=(1/m_{\rm opt})^{1/3}r_s$. For real metals, $d_\parallel$ is close to Z_B. To a good approximation, we assume that $d_\perp^b(iu)=d_\parallel\approx Z_B$. Similar to jellium, we choose the origin of coordinates to coincide with Z_B. This yields $d_\perp(iu)=\epsilon_f(iu)d_\perp^f(iu)/[\epsilon_f(iu)+\epsilon_b(iu)]$. Z_0 can be calculated by combining $d_\perp(iu)$ with Eqs. (5) and (6).

Semiconductors.—Since many properties of materials are related to their dielectric response, the dielectric functions of semiconductors have been widely studied [32–37]. Among these studies, the model dielectric function proposed by Penn [33] is of particular interest. This model was derived from the isotropic nearly free electron gas and has been used to study semiconductors [38]. However, a drawback of this model is that it violates the Kramers-Kronig relation. To fix this problem, Breckenridge *et al.* [39] proposed a modification of the Penn model, in which the imaginary part for $\omega_g\le\omega\le 4\epsilon_F\sqrt{1+\Delta^2}$ is given by $\epsilon_2(\omega)=\pi\bar{\omega}_p^2[\omega_g-\Delta(\omega^2-\omega_g^2)^{1/2}]^2/[2\omega^3(\omega^2-\omega_g^2)^{1/2}]$, where ω_g is the effective energy gap determined by recovering the exact $\epsilon_1(0)$. $\Delta=\omega_g/4\epsilon_F$ and $\epsilon_F=\bar{k}_F^2/2$ is the Fermi energy, with $\bar{k}_F=(3\pi^2\bar{n})^{1/3}$ being the Fermi wave vector and $\bar{n}$ the average valence electron density. Assuming that this expression is valid for the whole range of frequency, Vidali and Cole [40] calculated the real part using the Kramers-Kronig relation. In their calculations, all Δ^2 terms are neglected. Here, we include all the Δ^2-term contributions. The result is

$$\epsilon_1(iu)=1+\frac{\omega_p^2}{u^2}\left[\frac{(1-\Delta^2)y}{P}-\frac{\omega_g^2-(\omega_g^2+u^2)\Delta^2}{2u\sqrt{\omega_g^2+u^2}}\ln\frac{I_+}{I_-}\right]+\frac{2\omega_p^2\Delta}{u^2}\left\{\frac{\omega_g}{u}\left[\tan^{-1}\left(\frac{\omega_pP}{u}\right)-\tan^{-1}\left(\frac{\omega_p}{u}\right)\right]+\frac{1}{P}-1\right\}, \tag{9}$$

where $I_\pm=\sqrt{(1+y^2)(1+u^2/\omega_g^2)}\pm uy/\omega_g$, $y=1/\Delta$, and $P=\sqrt{1+y^2}$. Our calculations show that, while these Δ^2 terms have little effect on C_3, as found by Vidali and Cole [40], they have a noticeable effect on C_5. For Si, Ge, and GaAs, ω_g is taken from the literature, whereas for C (diamond), LiF, NaF, and MgO it is calculated from the Penn model,

$$\epsilon_1(0)=1+(\omega_p^2/\omega_g^2)(1-\Delta). \tag{10}$$

All the inputs including those obtained here are listed in Table II.

Figure 1 shows comparison of the model dielectric function for some of the materials considered. By comparing the two curves for jellium, we see that the ratio $[\epsilon_1(iu)-1]/[\epsilon_1(iu)+1]$ increases with the decrease of r_s. We also see that, if the density is the same, the ratio for jellium is larger than that for semiconductors. However, except in the low-frequency region, the ratio for noble metal decays with u more slowly than those for jellium and semiconductor, due to the d-electron contribution. Thus, we may conclude that, for materials with the same density, the physical adsorption is strongest on noble-metal surfaces, followed by simple metals, and then semiconductors.

TABLE II. Average density, effective energy gap (eV), plasmon frequency (eV), Fermi energy (eV), and static dielectric function of semiconductors studied here.

	r_s	ω_g	$\bar{\omega}_p$	ϵ_F	$\epsilon_1(0)$
Si	2.0	4.8[a]	17[b]	12.9[c]	12.0[a]
Ge	2.0	4.3[a]	17[b]	12.9[c]	16.0[a]
GaAs	2.1	4.3[d]	15.6[e]	11.5[c]	11.3[a]
C(diamond)	1.3	13.0[f]	31.2[e]	28.9[c]	5.9[g]
LiF	1.5	23.3[f]	26.1[h]	22.8[c]	1.96[j]
NaF	1.7	20.5[f]	21.1[h]	17.2[c]	1.74[j]
MgO	1.6	15.5[f]	24.3[h]	20.7[c]	3.0[a]

[a] From Ref. [38].
[b] From Ref. [32].
[c] Obtained from $\epsilon_F=k_F^2/2$.
[d] From Ref. [39].
[e] From Ref. [34].
[f] Obtained from Eq. (10).
[g] From Ref. [35].
[h] Obtained from the average valence electron density.
[i] From Ref. [36].
[j] From Ref. [37].

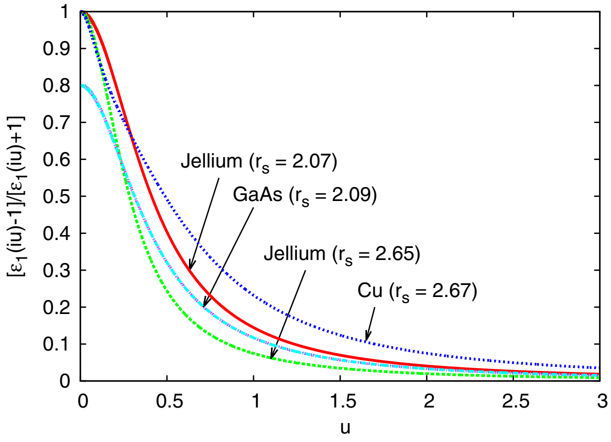

FIG. 1 (color online). Plot of $[\epsilon_1(iu) - 1]/[\epsilon_1(iu) + 1]$ as a function of u for jellium ($r_s = 2.07$, 2.65, which correspond to Al and Mg, respectively), Cu ($r_s = 2.67$), and GaAs ($r_s = 2.09$).

While C_3 can be measured directly by experiment [41], C_5 can be only accessed indirectly (e.g., by the binding energy curve measurement). As a simple test, we apply the present method to calculate C_3, C_5, and Z_0 for alkali metal (H, Li, Na, K), alkaline-earth metal (Be, Mg, Ca), and rare-gas (He, Ne, Ar, Kr, Xe) atoms on the surface of jellium with $r_s = 2.07$ (Al), 2, 3, and 4. Then we repeat the calculation for the same set of atoms on the surface of noble metals (Cu, Ag, Au, Pt, and Pd), with the input data in Table I. The results show that, for atoms on metal surfaces (both Al and noble metals), the mean absolute relative deviation (MARD) from the best literature values [25] is 5% for C_3 and 4% for Z_0, but the discrepancy becomes larger (11%) for C_5. This is because the literature values for C_5 may not be as accurate as those for C_3, but our C_5 should be as accurate as C_3, due to the consistent accuracy of $\alpha_l(iu)$ [27].

For the adsorption of particles on the surface of semiconductors, Z_0 is close to $d/2$, where d is the interplane spacing. By inserting Eqs. (9) and (3) into Eq. (2), we calculate C_3 and C_5 for rare-gas atoms (He, Ne, Ar, Kr, and Xe) on the surface of various common semiconductors (Si, Ge, GaAs, C(diamond), LiF, NaF, and MgO). The input data employed in our calculations are given in Table II. The results show that our C_3 agrees well with the best reference values [25], with a MARD of 4%. (No comparison is made with C_5, because it has not been reported in the literature.) All our results, including metal atoms on Al and noble-metal surfaces, are tabulated in the Supplemental Material [42].

Finally, we apply the DFT + vdW approach to study the adsorption energies of Ar, Kr, and Xe on noble-metal surfaces. Although there are extensive discussions on the adsorption of rare-gas atoms on metal surfaces, there is a long-standing issue of adsorption energy that has not been successfully addressed. In this work, we calculate the long-range contribution using Eq. (1), with our C_3 and C'_5. The equilibrium distance of atoms from the surface $Z_{\rm eq}$ is taken from the DFT-LSDA. This choice is due to the fact that LSDA gives good structure, while GGA is more accurate for short-range interactions. The use of the LSDA $Z_{\rm eq}$, which is too-short by about 2%, may yield a change in vdW energy by about 6%. For convenience, all the inputs are listed in Table III. Since $V(Z)$ of Eq. (1) is divergent at $Z = Z_0$, this singularity can be removed by multiplying each term with a damping function, as in the binding energy curve simulation. But here we are interested in the binding energy at $Z_{\rm eq}$, i.e., adsorption energy. It should be sufficient to employ Eq. (1) directly, because $Z_{\rm eq}$ equals approximately the sum of the conventional vdW radius of a rare-gas atom defined by $R = [\alpha(0)]^{1/3}$ (2.23, 2.56, 3.01 bohr for Ar, Kr, and Xe, respectively) and the radius of a metal atom defined as the half distance between the first nearest neighbors of the metal (2.41, 2.60, and 2.62 bohr for Cu, Pt, and Pd), which is much larger than Z_0. By evaluating the long-range vdW interaction this way, the adsorption energy can be found by adding it to the DFT-GGA calculation. The results are displayed in Table III.

TABLE III. Adsorption energies (in meV) of rare-gas atoms on a surface of noble metals (Cu, Pt, and Pd). C_3, C'_5, $Z_{\rm eq}$, and Z_0 are in a.u. Except for Ar/Cu and Kr/Cu, all other reference values are taken from experiments.

		Ar	Kr	Xe
Cu(111)	C_3/C'_5	0.395/2.291	0.558/3.963	0.836/7.930
	$Z_{\rm eq}/Z_0$	^{a}5.95/0.37	^{a}5.99/0.39	^{b}6.16/0.42
	GGA	13.0^{a}	20.3^{a}	40^{b}
	GGA-D2			283^{c}
	vdW-DF		136	283^{c}
	vdW-DF2			270^{c}
	GGA + vdW	86	126	195
	Reference	85^{a}	119^{a}	183 ± 10^{d}, 190^{b}
Pt(111)	C_3/C'_5	0.480/2.605	0.671/4.485	0.996/8.932
	$Z_{\rm eq}/Z_0$	^{c}6.05/0.26	^{c}5.97/0.28	^{b}5.80/0.30
	GGA	15^{c}	24^{c}	82^{b}
	GGA-D2	248^{c}	390^{c}	607^{c}
	vdW-DF	205^{c}	238^{c}	329^{c}
	vdW-DF2	171^{c}	197^{c}	305^{c}
	GGA + vdW	93	143	293
	Reference		161 ± 7^{e}	311 ± 16^{f}
Pd(111)	C_3/C'_5	0.476/2.584	0.666/4.454	0.988/8.873
	$Z_{\rm eq}/Z_0$	^{g}5.59/0.26	^{g}5.55/0.28	^{b}5.39/0.31
	GGA	14.9^{g}	14.3^{g}	55.3^{b}
	GGA-D2	181^{c}	260^{c}	420^{c}
	vdW-DF	203^{c}	235^{c}	330^{c}
	vdW-DF2	171^{c}	200^{c}	309^{c}
	GGA + vdW	117	168	332
	Reference	110^{g}	177^{g}	320 ± 10^{g}

[a] From Ref. [10].
[b] From Ref. [9].
[c] From Ref. [11].
[d] From Ref. [25].
[e] From Ref. [43].
[f] From Ref. [44].
[g] From Ref. [5].

From Table III, we see that our DFT + vdW yields the most accurate adsorption energies for rare-gas atoms on the surface of noble metals, with a mean absolute relative error of only 5%. We also observe from Table III that the long-range part makes the most important contribution to the adsorption energy. This suggests that the adsorption of rare-gas atoms on the surface of noble metals largely arises from the vdW interaction. Our calculation shows that the quadrupole or C_5 term can make a contribution of about 20% to the long-range part (as found for Xe on noble metal surfaces).

In conclusion, we have developed a method to calculate C_3 and C_5 for the physical adsorption of particles on surfaces. Our tests show that this method can yield results that consistently agree well with reference values for atoms on surfaces. Furthermore, we find that DFT + vdW can give an excellent description of atoms on surfaces of noble metals. The inputs for $\epsilon_1(iu)$ are the average valence electron density (jellium) or the parameters in Tables I (noble metals) or 2 (semiconductors), whereas the inputs of $\alpha_l(iu)$ are $n(\mathbf{r})$ and $\alpha_l(0)$, which can be obtained from time-dependent DFT or even from ground-state DFT. Since the nonspherical effect of $n(\mathbf{r})$ enters the formula via $\alpha_l(0)$, this DFT + vdW method should be applicable to adsorption of molecules and clusters as well.

J. T. was supported by the NSF under Grant No. DMR-1305135 and by the Air Force Office of Scientific Research, Air Force Materiel Command, USAF, under Grant No. FA9550-10-1-0248. A. M. R. was supported by the Department of Energy Office of Basic Energy Sciences, under Grant No. DE-FG02-07ER15920. Computational support was provided by the HPCMO and the NERSC.

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[*] jianmint@sas.upenn.edu

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