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Modeling the physisorption of graphene on metals

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Many processes of technological and fundamental importance occur on surfaces. Adsorption is one of these phenomena that has received the most attention. However, it presents a great challenge to conventional density functional theory. Starting with the Lifshitz-Zaremba-Kohn second-order perturbation theory, here we develop a long-range van der Waals (vdW) correction for physisorption of graphene on metals. The model importantly includes quadrupole-surface interaction and screening effects. The results show that, when the vdW correction is combined with the Perdew-Burke-Enzerhof functional, it yields adsorption energies in good agreement with the random-phase approximation, significantly improving upon other vdW methods. We also find that, compared with the leading-order interaction, the higher-order quadrupole-surface correction accounts for about 25% of the total vdW correction, suggesting the importance of the higher-order term.

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Since the discovery of graphene, it has received considerable attention from scientists and technologists, due to its many remarkable properties and a variety of commercial applications. For example, it can be used in optoelectronic devices and nanoelectronics [1] for high delocalization of surface electrons, gas sensing [2–4], hydrogen and natural gas storage [5], energy conversion [6], etc.

A striking property of graphene is its strong ability to adsorb, due to its large surface area and high polarizability. To fundamentally understand this interface problem, many van der Waals–corrected density functionals have been employed to calculate binding energies and equilibrium distances between graphene and metal surfaces [7–19]. In particular, Ruiz *et al.* proposed a vdW method [20] to model the adsorption of molecules on the surface of a transition metal based on the Zaremba-Kohn theory. But their vdW coefficient C_3 for physisorption was calculated from C_6. To calculate C_3 from C_6, the screening effect of valence electrons of substrate (metal) has to be neglected. Nevertheless, this model can describe the adsorption of molecules on the surface of a transition metal quite well [21].

Adsorption on metals is of broad interest. Metal can be used for the preparation of highly ordered graphene layers of different thickness which are transferred onto an insulating or polymer support. In the latter case, the obtained material can be used to fabricate touch screens. In the application to electronic devices such as transistors, graphene has to contact metals. These facts have made the graphene industry very promising.

In recent years, a large literature on 2D layered materials has appeared [22]. Understanding the interaction between graphene and metal surfaces can provide insights into the properties of other 2D materials, which have presented a major challenge to conventional DFT, due to the dominant interlayer vdW interactions. The random-phase approximation (RPA) calculation [23] of graphene on nickel reveals that there is a double well in the binding energy curve: one well arises from the short-range dominant chemisorption or orbital overlap of surface electrons of graphene and nickel, while the other arises from the long-range vdW interaction. While the RPA may underestimate the strengths of normal chemical bonds [24,25], it is reliable for weak vdW bonds. Recent studies [23,26,27] showed that, while some semilocal DFT methods are able to reproduce this double-well feature, the second well located further away from the surface is not deep enough, indicating the need for the long-range interaction. Recently, it has been shown that the nonlocal functionals vdw-DF-cx [28], optB88-vdW [23,29], and SCAN+rVV10 [30] agree with one another for the physisorption of graphene on nickel (1,1,1), and with the RPA value. For the chemisorption minimum, optB88-vdW agrees with RPA, while vdW-DF-cx and SCAN+rVV10 provide deeper minima that agree between them. While the RPA provides a benchmark for vdW bonds, it typically underbinds covalent bonds. Therefore, its use as a benchmark for the chemisorption minimum is questionable. In addition, its computational cost requires the use of constrained geometries. For graphene at a metal surface, the metal lattice constants are taken from bulk experimental values, and the in-plane graphene lattice constants are stretched or compressed into registry with the surface.

According to the distance d between graphene and metals (see explicit definition for d below), adsorption of graphene can be classified into two types. One is chemisorption, occurring at about 2–2.5 Å, while another is a relatively weak physisorption, which occurs at a longer range of $\geqslant 3.0$ Å. The former involves a dramatic electron density redistribution and stronger bonding between electrons of graphene and surfaces, while the latter involves little electron redistribution. Here we aim to address the physisorption problem. For this purpose, we develop a vdW correction to model the physisorption of graphene on metals. Then, in the same spirit as our work on lattice constants and cohesive energies of ionic and transition-metal solids [31], we combine it with DFT-GGA to study the physisorption

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of graphene on metals. Our calculation shows that, with the vdW correction, the DFT-GGA can reproduce the adsorption energies with a mean absolute error of 6 meV, improving upon many other vdW-corrected DFT methods. We find that the higher-order term can contribute as much as about 25% of physisorption energy.

Theory. The vdW interaction for physisorption arises from instantaneous charge fluctuations of particles and induced multipole moments on the surface of a substrate. In the large-separation limit, the vdW interaction between particles and a clean surface is given by the asymptotic expansion [32,33]

$$E_{\text{vdW}} = -\frac{C_3}{(Z-Z_0)^3} - \frac{C_5}{(Z-Z_0)^5}, \tag{1}$$

where Z is the distance between the centers of the particles and the planar surface of the outermost metal slab (or background edge for a jellium surface) and Z_0 is the distance between a vdW reference plane and that planar surface. In this formula, we have eliminated the need for an explicit C_4/Z^4 term by the appropriate choice of Z_0. The reference position Z_0 is usually small, compared to the equilibrium distance Z_{eq}. The vdW coefficient C_3 describes the dielectric response of the bulk solid to the instantaneous dipole moment of particles. $C_5 = C_5^{\text{q}} + C_5^{\text{nl}} + C_5^{\text{d}}$ represents the fluctuating quadrupole, nonlocal, and diffuse contributions of particles. Since the diffuse part is small [33] in comparison with the quadrupole and nonlocal parts, we neglect it in this work. In the above formula, there are additional terms that describe the lateral interaction between particles on the surface, but they are also small [34] and vanish exponentially with the distance between particles. Here we only consider the lateral average $V(Z) = \int dX\,dY\,V(X,Y,Z)/A$, with A being the surface area.

From Eq. (1), we can see that the long-range vdW interaction beween particles and surfaces is quite different from the vdW interaction between particles, whose asymptotic expansion is given by $-C_6/R^6 - C_8/R^8 - \cdots$. The difference between the correct C_3 and that predicted by summation of pairwise interactions is largely due to the strong screening effect of the substrate [35]. However, when the distance between particles and surface approaches the lattice constant, their interactions can be approximated as pair interactions.

For a clean surface, the vdW coefficients C_3 and C_5^{q} arising from the fluctuating dipole and quadrupole moments can be calculated from second-order perturbation theory [36,37] by

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

where iu is the imaginary frequency. $\alpha_l(iu)$ is the mean dynamic multipole polarizability of the adsorbate particle defined in terms of the dynamic multipole polarizability tensor, $\alpha_l(iu) = [\alpha_{l,xx}(iu) + \alpha_{l,yy}(iu) + \alpha_{l,zz}(iu)]/3$. $\epsilon_1(iu)$ is the isotropic dielectric function of the substrate [38]. The nonlocal part of C_5 can be evaluated by [33]

$$C_5^{\text{nl}} = \frac{3}{4\pi}\int_0^\infty du\,\alpha_1(iu)\frac{\epsilon_1(iu)[\epsilon_1(iu)-1]^2\xi^2}{[\epsilon_1(iu)+1]^3}, \tag{3}$$

where $\xi = \beta/\sqrt{\omega_p^2+u^2}$ and $\beta^2 = 3k_F^2/5$ [39]. Note that, in this expression, the dipole polarizability rather than the quadrupole polarizability of graphene appears.

For a clean surface, the reference plane position is given by

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

where d_{IP} is the dynamic image plane given by $d_{\text{IP}} = [d_\parallel + \epsilon_1(iu)d_\perp(iu)]/[\epsilon_1(iu)+1]$. Here $d_\perp(iu)$ is the gravity center of the density induced on the surface and $d_\parallel$ reflects the spatial distribution of the currents parallel to the surface induced by a uniform tangential electric field [40]. Because of translational invariance of the surface, $d_\parallel = Z_{\text{B}}$ [40], the edge of the positive background.

Dynamic multipole polarizability per atom of graphene. It has been shown [41,42] that the hollow-sphere or solid-sphere [43] model within the single-frequency approximation (SFA) for the dynamic multipole polarizability can yield accurate vdW coefficients for fullerenes, clusters, and molecules. The nonsphericity of the density can enter the formula by the input static polarizability, which can be obtained from *ab initio* many-body calculations. Therefore, the model polarizability can also be useful for nonspherical densities. Since the surface electron density of graphene is quite uniform, the hollow-sphere or solid-sphere model within the SFA should be suitable to graphene. As such, the model dynamic multipole polarizability per atom of graphene can be written as

$$\alpha_l(iu) = \alpha_l(0)\frac{\omega_l^2}{\omega_l^2+u^2}, \tag{5}$$

where $\omega_l = \omega_p\sqrt{l/(2l+1)}$ is the plasmon frequency of a sphere and $\omega_p = \sqrt{4\pi n}$ is the plasmon frequency of the extended electron gas, with n being the electron density of graphene. In this expression, $\alpha_l(0)$ is the input static multipole polarizability per atom of graphene, from the next paragraph.

For nanostructures, the input static higher-order polarizability can be estimated from the static dipole polarizability via $\alpha_l(0) = [\alpha_1(0)]^{(2l+1)/3}$. Therefore, we only need the static dipole polarizability as input in this model. The average valence electron density of graphene can be obtained by $n = N_{\text{valence}}/V_{\text{cell}}$, with $N_{\text{valence}} = 4$ being the number of valence electrons of carbon atoms in the outermost subshell (two carbon atoms in the unit cell). For hcp unit cell, the cell volume is $V_{\text{cell}} = abc$, with $b = a\sin(\pi/3)$ and c being the vdW thickness of graphene, which we set to be 3.4 bohr. This is a value used to confine the relatively constant and size-independent charge density of fullerene [44,45]. Considering the similarity of graphene to the large-size limit of fullerene, we take the same c to confine the electron density of graphene. The lattice constant $a = 2.46$ Å, which is calculated from the DFT-LDA [46]. Thus $\bar{n} = 4/[(2.46/0.529)((2.46\times\sqrt{3}/2)/0.529)\times 3.4]$ (atomic units $e = m_e = \hbar = 1$ are used). The static dipole polarizability per atom of graphene is taken to be $11.7 \times 0.85 = 9.945$ [47], as estimated from the Hirshfeld partitioning scheme [48,49].

Adsorption on jellium. Jellium is a simplified yet realistic model for simple metals. In this model, the valence electrons are evenly distributed over the positive background with ion cores smeared. Study of physisorption of graphene on jellium is quite indicative for graphene on transition metals. The real part of the dielectric function of bulk jellium in the long-wavelength

TABLE I. Electron density parameter $r_s = [3/(4\pi\bar{n})]^{1/3}$, vdW coefficients, and Z_0 for graphene on simple metals, all in atomic units. Al has $r_s = 2.07$.

r_s	C_3	C_5^{q}	C_5^{nl}	C_5	Z_0
2.0	0.291	1.406	0.773	2.179	0.965
2.07	0.284	1.365	0.768	2.133	0.949
3.0	0.201	0.955	0.689	1.644	0.795
4.0	0.147	0.692	0.615	1.306	0.695

TABLE II. Electron density parameter r_s, vdW coefficients, and Z_0 for graphene on the (1,1,1) transition metals Ni, Pd, Pt, Cu, Ag, and Au, and on the (0,0,0,1) surface of Co, all in atomic units.

	r_s	C_3	C_5^{q}	C_5^{nl}	C_5	Z_0
Ni	2.60	0.298	1.442	0.869	2.311	0.600
Co	2.61	0.300	1.452	0.875	2.327	0.588
Pd	2.90	0.353	1.721	1.047	2.768	0.358
Pt	2.87	0.354	1.730	1.053	2.783	0.349
Cu	2.67	0.312	1.514	0.912	2.426	0.525
Ag	3.02	0.316	1.537	0.908	2.445	0.424
Au	3.01	0.345	1.684	1.026	2.710	0.346

limit is

$$\epsilon_1(iu) = 1 + \frac{\bar{\omega}_p^2}{u^2}, \tag{6}$$

where $\bar{\omega}_p = \sqrt{4\pi\bar{n}}$ is the plasmon frequency of the extended uniform electron gas and $\bar{n}$ is the average valence electron density of the jellium substrate. From Eq. (2), the vdW coefficients arising from the dipole and quadrupole moments of particles for graphene and the jellium surface can be analytically evaluated as

$$C_{2l+1} = \frac{1}{4\pi}\int_0^\infty du\left(\alpha_l(0)\frac{\omega_l^2}{\omega_l^2+u^2}\right)\left(\frac{\bar{\omega}_p^2/2}{\bar{\omega}_p^2/2+u^2}\right)$$

$$= \frac{\alpha_l(0)}{8}\frac{\omega_l\omega^{\mathrm{sur}}}{\omega_l+\omega^{\mathrm{sur}}}, \tag{7}$$

where $\alpha_l(0)$ is the static multipole polarizability per atom of graphene and $\omega^{\mathrm{sur}} = \bar{\omega}_p/\sqrt{2}$ is the surface plasmon frequency of the jellium substrate. Note that ω_l is the plasmon frequency of graphene defined below Eq. (5).

The dynamic image plane d_{IP} of Eq. (4) for jellium can be calculated as follows. Choosing the origin of coordinates to coincide with the jellium edge of the background Z_{B}, we have $d_{\parallel} = Z_{\mathrm{B}} = 0$. Thus we obtain

$$d_{\mathrm{IP}}(iu) = \epsilon_1(iu)d_{\perp}(iu)/[\epsilon_1(iu)+1]. \tag{8}$$

Persson and Zaremba [40] proposed a simple approximation for $d_{\perp}(iu)$, which assumes

$$d_{\perp}(iu) = \frac{d_{\perp}(0)}{1+\eta[u/\omega^{\mathrm{sur}}]^2/2}. \tag{9}$$

The form is consistent with the sum rule [40]. Here $\eta = d_{\perp}(0)/\lambda$ and $d_{\perp}(0)$ is the static centroid position. For simple metals, λ and $d_{\perp}(0)$ for $r_s = 2,3,4$ are given by the Lang-Kohn self-consistent surface calculation [50]. Tao and Rappe [51] have parametrized λ and $d_{\perp}(0)$ for $2 \leqslant r_s \leqslant 6$. They are given by the simple analytic formulas $\lambda = -0.0105r_s^2 + 0.1285r_s + 0.248$ and $d_{\perp}(0) = 0.02r_s^2 - 0.27r_s + 2.06$. The reference position Z_0 of jellium can be evaluated with Eq. (4). Summarized in Table I are the vdW coefficients and Z_0 of graphene on jellium. From Table I, we see that both vdW coefficients and Z_0 decrease slightly with increasing electron density parameter r_s, as expected.

Adsorption on transition metals. The dielectric function of transition metals is more complicated, due to the d-electron participation. It can be split into two contributions. One is from the s valence electrons of transition metals (ϵ_f) and the other is the contribution from d-electron participation (ϵ_b). Then the real part of the dielectric function can be written as [40]

$$\epsilon_1(iu) = 1 + \epsilon_f + \epsilon_b, \tag{10}$$

where $\epsilon_f = \bar{\omega}_{pf}^2/u^2$ and $\epsilon_b = \Omega^2/(\omega_0^2+u^2)$. $\bar{\omega}_{pf}^2 = (1/m_{\mathrm{opt}})\bar{\omega}_p^2$ is the plasmon frequency of the uniform gas, but with the density parameter r_s replaced by the corrected density parameter $r_s^f = (1/m_{\mathrm{opt}})^{1/3}r_s$, where m_{opt} is the optical mass [40]. The parameters m_{opt}, Ω, and ω_0 can be obtained from optical experimental data. For convenience, all the parameters r_s, m_{opt}, Ω, and ω_0 for several commonly used transition metals are listed in the Supplemental Material (Table S1). From the dielectric function, we can evaluate vdW coefficients C_3 and C_5 from Eqs. (2) and (3) for physisorption on transition metals.

The reference position Z_0 for transition metals can be calculated as follows. First, we split $d_{\perp}(iu)$ as a sum of two contributions [40] 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 jellium, but with r_s replaced by the corrected density parameter, as discussed above. We also listed λ and $d_{\perp}^f(0)$ in Table S1. Second, we choose the origin to coincide with the planar surface of the outermost metal slab. This leads to $d_{\perp}^b(iu) \approx Z_B = 0$. Then we obtain

$$d_{\perp}(iu) = \epsilon_f(iu)d_{\perp}^f(iu)/[\epsilon_f(iu)+\epsilon_b(iu)]. \tag{11}$$

Then we can calculate Z_0 by combining $d_{\perp}(iu)$ of Eq. (11) with Eqs. (4) and (8). The results for C_3, C_5, and Z_0 of some common metals are listed in Table II.

Now we turn to the vdW part of the adsorption energy. This part can be evaluated with Eq. (1). The equilibrium distance between graphene and metal substrate can be reliably taken from the RPA calculation [25]. However, the reported RPA value is not really the distance from the background edge of metals Z_{eq}, but the distance d from the plane of graphene nuclei to the outermost plane of metal nuclei, as shown by Fig. 1 of Ref. [26]. According to Zaremba and Kohn [36], the background edge of a metal is located at $c/2$ from the outermost plane of metal nuclei, as shown by Fig. 2 of Ref. [52], where c is related to the lattice constant a via $c = a/\sqrt{h^2+k^2+l^2}$, with k,k,l being Miller indices for Al, Ni, Pd, Pt, Cu, Ag, and Au. For Co, with the hexagonal close-packed structure, c is half the lattice constant (4.07 Å) along the z axis. The reported RPA distances d need to be subtracted by $c/2$. The value $c/2$

TABLE III. Physisorption energies (in meV/atom) of graphene on (1,1,1) surfaces of Al, Ni, Pd, Pt, Cu, Ag, Au and (0,0,0,1) surface of Co. d is the RPA equilibrium separation [25] between the plane of graphene nuclei and the outermost plane of metal nuclei and c is the distance between neighboring planes of metal nuclei, both in Å. All calculations employ the constrained geometries that were used in the RPA reference calculation, and all except our PBE+vdW use a relaxed d or are estimated from a binding energy curve.

	d	$d - c/2$	PBE+vdW	RPA	LDA	PBE	vdW-DF	vdW-DF2	vdW-DF2-C09	B86bPBE-XDM
Al	3.51[a]	2.34	67	52[a]	29[a]	2[a]	35[b]			34[c]
Ni	3.26[d]	2.24	70	70[a]	50[a]	2[a]	45[d]	44[d]	75[d]	81[c]
Co	3.25[a]	2.23	70	66[a]		2[a]	30[e]			
Pd	3.34[a]	2.22	83	90[a]	43[a]	4[a]	49[d]	52[d]	72[d]	66[c]
Pt	3.42[a]	2.29	82	84[a]	36[a]	5[a]	52[d]	54[d]	68[d]	71[c]
Cu	3.09[a]	2.05	78	68[a]	40[a]	2[a]	44[d]	46[d]	62[d]	73[c]
Ag	3.31[a]	2.13	75	78[a]	30[a]	2[a]	42[d]	42[d]	53[d]	72[c]
Au	3.22[a]	2.04	83	95[a]	34[a]	2[a]	47[d]	49[d]	59[d]	66[c]
ME			0		−39	−74	−33	−30	−16	−9
MAE			6		39	74	33	30	19	17

[a] From Ref. [25].
[b] From Ref. [55].
[c] From Ref. [56].
[d] From Ref. [26].

just defines the background edge of metals. Then we can find the vdW energy from

$$E_{\mathrm{vdW}} = \left[-\frac{C_3}{(Z - Z_0)^3} - \frac{C_5}{(Z - Z_0)^5} \right] f_d. \qquad (12)$$

At equilibrium, $Z_{\mathrm{eq}} = d - c/2$ corresponds to the Zaremba-Kohn equilibrium distance from graphene to the (1,1,1) metal surface [36], and the vdW energy at $Z_{\mathrm{eq}} = d - c/2$ corresponds to the binding energy. In this formula, we need to add a damping function to avoid double counting, due to the long-range part. f_d is the damping function given by

$$f_d = x^5/\sqrt{1 + gx^2 + hx^4 + x^{10}}, \qquad (13)$$

where $x = (Z - Z_0)/b > 0$. The parameters $g = 2b^2C_3/C_5$ and $h = 10b^4C_3^2/C_5^2$ are chosen to zero out the x^2 and x^4 terms of the Taylor expansion of Eq. (12) so that the damped vdW interaction is a monotonically nondecreasing function of Z. Both parameters are safely positive for any combination of C_3, C_5, and b. The parameter $b = 3.35$ bohr is determined by a fit to the RPA values of the binding energy and is interestingly close to our vdW thickness of graphene (3.4 bohr). Figure S1 of the Supplemental Material [53] shows the damping functions for graphene on the (1,1,1) surfaces of Al, Ni, and Au. From Fig. S1, we see that the damping is significantly important at equilibrium.

Finally, taking the lattice constants of metals from Ref. [54] and the RPA values d, we obtain $Z_{\mathrm{eq}} = d - c/2$, as listed in Table III. Based on Z_{eq}, we calculate the vdW binding energies of graphene on metals. Then we combine the vdW part with the PBE (Perdew-Burke-Ernzerhof) GGA value [25], which is almost free of vdW contributions [31]. The results are displayed in Table III, where they are compared with the results of other methods. As a comparison, we have also calculated the undamped vdW energy at the RPA geometry, finding that the undamped vdW energy is about three times bigger than the damped vdW energy, suggesting the significance of damping.

From Table III, we can see that if we take the RPA values to be the standard, our PBE+vdW yields the most accurate results, with a mean absolute error (MAE) of only 6 meV. Our study also shows that the C_3 term contributes only about 75% of the absorption energy, while the higher-order term contributes much of the rest.

In conclusion, we have developed a physically motivated vdW method for physisorption of graphene on metals. The theory is based on the Lifshitz-Zaremba-Kohn second-order perturbation theory, in which metal surfaces must be clean. Then we have calculated the vdW coefficients C_3, C_5, and Z_0, the reference plane position with respect to which the position of the particle is determined, from the dynamic dielectric functions of metals. Using the predetermined RPA distance d between the plane of graphene nuclei and the outermost plane of metal nuclei, we calculate the adsorption energies for the PBE+vdW method. The results are quite close to the RPA values for physisorption, suggesting the promise of the model. Extension of this work to other molecular adsorption is under study. Our model can be also adapted to recent meta-GGAs such as SCAN [57] and TM [58] by scaling up b by a constant fit factor greater than 1.

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