

Adsorption of C₆₀ on Au(111) revisited: A van der Waals density functional studyIkutaro Hamada^{1,*} and Masaru Tsukada^{1,2}¹*WPI-Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*²*CREST, Japan Science and Technology Agency, Kawaguchi, Saitama 332-0012, Japan*

(Received 5 April 2011; published 28 June 2011)

We address the dispersion force in a C₆₀/Au(111) interface using the van der Waals density functional with improved exchange [V. R. Cooper, *Phys. Rev. B* **81**, 161104(R) (2010)] and nonlocal correlation [K. Lee, É. D. Murray, L. Kong, B. I. Lundqvist, and D. C. Langreth, *Phys. Rev. B* **82**, 081101(R) (2010)]. We found that the adsorption is solely attributed to the nonlocal correlation, i.e., the van der Waals (vdW) forces, and the correct account of vdW attraction between C₆₀ molecules is also essential to obtain accurate binding energy. The bonding of C₆₀ is, however, covalent-like, which is originated from the hybridization of the lowest unoccupied molecular orbital of C₆₀, in agreement with a previous theoretical study.

DOI: [10.1103/PhysRevB.83.245437](https://doi.org/10.1103/PhysRevB.83.245437)

PACS number(s): 73.20.Hb, 68.35.bp, 71.15.Mb, 71.15.Nc

I. INTRODUCTION

Since its discovery C₆₀ has attracted much attention owing to its interesting properties such as superconductivity, magnetism, and metal-insulator transition. There is renewed interest in using a C₆₀-based nanostructure as a component of molecular electronics devices, e.g., electrical amplifier,¹ single-molecule transistor,² and molecular switch.³ Interaction and geometry of C₆₀ on electrode surface are fundamental to the molecule-metal contact and their correct description is prerequisite for predicting as well as understanding the interfacial electronic properties.

Theoretical studies on C₆₀/metal interfaces is mostly based on density-functional theory within the local density approximation (LDA) or the generalized gradient approximation (GGA), and have been used successfully to describe several C₆₀/metal interfaces.^{5–13} However, given that LDA and GGA describe the van der Waals forces less accurately, which is important in C₆₀-metal and C₆₀-C₆₀ interactions, the successes are likely to be results of error cancellation in exchange and correlation. To understand the mechanism of C₆₀/metal interface correctly, it is of great importance to clarify the role of the van der Waals (vdW) forces.

In this work, we use the van der Waals density functional (vdW-DF) (Ref. 14) which is able to describe covalent and weak bonding in a seamless fashion, to address the van der Waals forces in C₆₀/Au(111) interface, and re-examine the bonding nature of the interface. Because the original vdW-DF is known to overestimate adsorption distances and thus predict wrong interfacial electronic structures,^{15,16} we employed an improved version of vdW-DF which was shown to describe graphene/metal interfaces accurately.¹⁷ We found that the vdW forces are solely responsible for the adsorption of C₆₀, and that the inclusion of vdW attraction is essential to predict accurate binding energy of C₆₀. Our calculated binding energy is in good agreement with experimental data. We also found the covalent-like bonding between the C₆₀ and Au interface, associated with the lowest unoccupied orbitals of C₆₀.

II. METHOD

All the calculations were performed using the STATE (Ref. 18) code. Electron-ion interactions were described by

ultrasoft pseudopotentials,¹⁹ and wave functions and augmented charge density were expanded in terms of a plane wave basis with cutoff energies of 25 Ry and 225 Ry, respectively. Standard GGA calculations were performed using the Perdew-Burke-Ernzerhof (PBE) (Ref. 20) exchange-correlation functional. The Au(111) surface was modeled using a five-layer slab separated by vacuum equivalent to ten-monolayer thickness. The slab was constructed using a theoretical lattice constant of 0.415 nm. C₆₀ was adsorbed on one side of the slab with a (2√3 × 2√3) periodicity, and spurious electrostatic interaction between periodic images in the slab calculations²¹ were eliminated by using the effective screening medium method.²² Brillouin zone sampling was done using a (2 × 2) *k*-point set, and Fermi surface was treated by the Methfessel-Paxton scheme²³ with the smearing width of 0.136 eV.

Within vdW-DF, the exchange correlation energy is described as

$$E_{xc} = E_x^{\text{GGA}} + E_c^{\text{LDA}} + E_c^{\text{nl}}, \quad (1)$$

where E_x^{GGA} is the GGA exchange energy and E_c^{LDA} is the correlation energy within LDA. The nonlocal correlation energy E_c^{nl} is given by

$$E_c^{\text{nl}}[n] = \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' n(\mathbf{r}) \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}'), \quad (2)$$

with the vdW kernel $\phi(\mathbf{r}, \mathbf{r}')$ which depends on $|\mathbf{r} - \mathbf{r}'|$, charge density n , and its gradient $|\nabla n|$. In this work, we use the nonlocal correlation functional of the second version of vdW-DF (vdW-DF2) (Ref. 24) with the exchange functional developed by Cooper (C09) (Ref. 25), which is denoted as vdW-DF2^{C09_x}. We also use the original vdW-DF(2) which uses revised PBE (Ref. 26) [revised PW86 (Ref. 27)], and vdW-DF nonlocal correlation with C09 exchange (vdW-DF^{C09_x}) for comparison. The vdW-DF calculations were done as a post-GGA perturbation, i.e., total energies within vdW-DF were calculated non-self-consistently using the charge densities determined by PBE. The effect of self-consistency on calculated binding energy was shown to be negligible.²⁸ For the evaluation of E_c^{nl} for periodic systems, we follow the prescription given in Refs. 29 and 30: the interaction range for \mathbf{r}' in Eq. (2) needs to be cut off at a certain distance, while the

integral over \mathbf{r} is evaluated in a primitive unit cell. we used the cutoff distance of 2.033 nm for the lateral directions, which corresponds to a 2×2 supercell, and that of 2.396 nm for the surface normal direction, to ensure the convergence of binding energy within 10 meV with respect to the cutoff distance.

Binding energy of C_{60} on Au(111) was calculated with different exchange-correlation functionals, which is defined as a sum of interaction energy between C_{60} monolayer and Au substrate, and interaction energy between molecules in the adsorbed C_{60} monolayer. The former is calculated by subtracting total energies of isolated Au substrate and C_{60} monolayer from that of the combined system, and the latter, by the energy difference between the C_{60} monolayer and an isolated C_{60} molecule placed in a larger ($4\sqrt{3} \times 4\sqrt{3}$) unit cell.

III. RESULTS AND DISCUSSION

We first calculated the interaction energy of C_{60} monolayer with Au substrate as a function of C_{60} -Au distance, fixing C_{60} and Au substrate at the respective isolated geometries. No further structural optimization was performed. We considered atop, bridge, fcc-hollow, and hcp-hollow sites as the adsorption site. A hexagonal ring was assumed to face to the surface as shown in Fig. 1, and other configurations (pentagon or C-C bond faced to the surface) and surface reconstruction (e.g., vacancy-adatom and nanopit formation) were not taken into account.

Calculated interaction energy curves of C_{60} on a fcc-hollow site with different exchange-correlation functionals are shown in Fig. 2. We found that PBE predicts significantly small binding energy and large adsorption distance, implying the necessity of vdW forces to describe the adsorption of C_{60} on the Au(111) surface correctly. On the other hand, inclusion

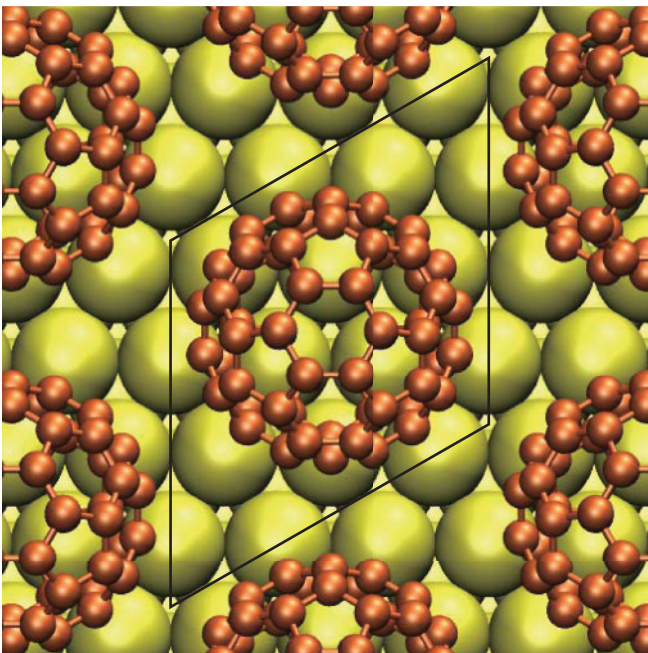


FIG. 1. (Color online) Top view of adsorption geometry of C_{60} at an fcc-hollow site of Au(111). The unit cell used is indicated by the parallelogram.

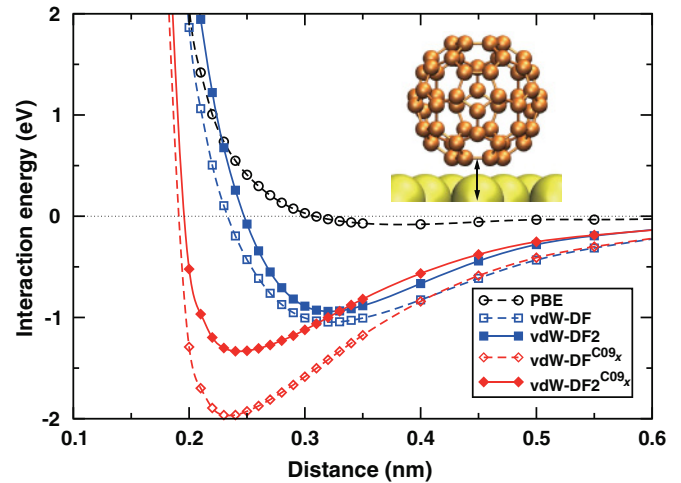


FIG. 2. (Color online) Interaction energy of C_{60} with Au substrate on a fcc-hollow site as a function of C_{60} -Au distance obtained using different exchange-correlation functionals. The distance is indicated by the arrow in the inset. The molecule-molecule interaction energy is not included.

of nonlocal correlation by vdW-DF results in larger binding energy, suggesting that the vdW forces play an important role in C_{60} adsorption. By decomposing interaction energy into contributions from the nonlocal correlation and the remaining part, we found that the nonlocal correlation, i.e., the vdW force is solely responsible for the adsorption of C_{60} . Within vdW-DF, equilibrium distance depends strongly on the choice of exchange and correlation: vdW-DF predicts a large adsorption distance, in line with the fact the original vdW-DF overestimates the binding distance.¹⁵ vdW-DF2 predicts a slightly smaller distance and smaller interaction energy than that with vdW-DF by ~ 0.2 eV. The large distances are results of too repulsive exchange energies used in these functionals to describe adsorption on metal surfaces.¹⁷ On the other hand, vdW-DF(2)^{C09x} predicts smaller distance. Interaction energy with vdW-DF^{C09x} is overestimated because the vdW-DF correlation overestimate the vdW attraction. We consider that vdW-DF2^{C09x} is appropriate to describe C_{60} adsorption on metal surfaces, because the functional describe graphene/metal interfaces accurately¹⁷ and because the calculated “total” binding energy is in good agreement with experiment (shown below).

We then calculated the binding energy by taking into account the interaction energy between C_{60} molecules in the monolayer. Equilibrium binding energies and distances at different adsorption sites are summarized in Table I. With PBE, binding energy is almost independent of the adsorption site. However, the inclusion of the nonlocal correlation has huge impact on the binding energy, and the adsorption on the fcc-hollow site is significantly stabilized, in particular with vdW-DF(2)^{C09x}, suggesting the importance of the vdW forces in determining the site preference of C_{60} on Au(111). This is similar to what was found in Xe adsorption on noble metal surfaces³¹ and flat aromatic molecules on Cu(110).³² Our result is in contradiction to the previous LDA study, which predicted that the hcp-hollow site is the most stable adsorption site.⁶ Calculated intermolecular-interaction

TABLE I. Binding energy (E_b) and equilibrium distance (Z_C) of C₆₀ on Au(111) with different exchange-correlation functionals. Interaction energy of the C₆₀ layer with the substrate is also shown in parenthesis. Units of distance and energy are in nm and eV, respectively.

| | PBE | | vdW-DF | | vdW-DF2 | | vdW-DF ^{C09x} | | vdW-DF2 ^{C09x} | |
|--------|--------------------|-------|--------------------|-------|--------------------|-------|------------------------|-------|-------------------------|-------|
| | E_b | Z_C | E_b | Z_C | E_b | Z_C | E_b | Z_C | E_b | Z_C |
| Atop | -0.009 (-0.074) | 0.397 | -1.910 (-1.013) | 0.329 | -1.677 (-0.904) | 0.325 | -2.604 (-1.605) | 0.266 | -1.664 (-1.071) | 0.277 |
| Bridge | -0.014 (-0.080) | 0.387 | -1.937 (-1.040) | 0.324 | -1.707 (-0.934) | 0.322 | -2.844 (-1.845) | 0.248 | -1.847 (-1.254) | 0.257 |
| fcc | -0.017 (-0.082) | 0.384 | -1.943 (-1.046) | 0.322 | -1.714 (-0.941) | 0.321 | -2.968 (-1.970) | 0.235 | -1.929 (-1.335) | 0.243 |
| hcp | -0.013 (-0.079) | 0.388 | -1.936 (-1.039) | 0.323 | -1.705 (-0.932) | 0.322 | -2.874 (-1.876) | 0.242 | -1.863 (-1.269) | 0.252 |

energies are 0.066 eV, -0.897 eV, -0.773 eV, -0.998 eV, and -0.594 eV with PBE, vdW-DF, vdW-DF2, vdW-DF^{C09x}, and vdW-DF2^{C09x}, respectively. Note that the interaction is repulsive within PBE. The binding energy calculated using vdW-DF2^{C09x} is in good agreement with the experimental desorption energy of 1.9 eV.³³ Because an experimental value for C₆₀/Au(111) is unavailable, we compare the experimental vertical distance of C₆₀ on Ag(111) of 0.2 ± 0.01 nm (Ref. 9) and found that the equilibrium distance with vdW-DF2^{C09x} is in reasonable agreement with it, although we do not consider the reconstruction of the surface. Calculated work-function changes ($\Delta\Phi$) with vdW-DF2^{C09x} for atop, bridge, hcp-hollow, and hcp-hollow sites are -0.405 eV, -0.417 eV, -0.460 eV, and -0.364 eV, respectively. $\Delta\Phi$ for the fcc-hollow site is in reasonable agreement with the experimental value of -0.6 eV.³³ The slight underestimation is presumably because of the insufficient k -point sampling for the work-function calculation: $\Delta\Phi$ for fcc-hollow site becomes -0.509 eV when a denser 4×4 k -point set is used. We solved the Schrödinger equation based on the interaction energy curve for the fcc-hollow site with vdW-DF2^{C09x}, and obtained the vibrational eigenvalues of center of motion for adsorbed C₆₀. Calculated zero-point energy is 2.1 meV, and the difference between first-excited state and ground state (second- and first-excited states) is 4.2 meV and 4.1 meV, in reasonable agreement with an experimental estimate of vibrational quantum of 5 meV.² From the comparison above, we conclude that vdW-DF2^{C09x} is the most accurate functional to describe C₆₀/metal interfaces, among those used in the present work. We note that the binding energy with vdW-DF is similar in magnitude with that with vdW-DF2^{C09x}, because of the error cancellation in interaction energies, i.e., underestimation of molecule-substrate interaction energy and overestimation of vdW attraction in molecule-molecule interaction energy.

In the present vdW-DF calculations, self-consistent potential, hence Hellmann-Feynman forces are not implemented, and no further structural relaxations are allowed. To examine the effect of the relaxation upon adsorption on the relative study of C₆₀, we employed a semiempirical dispersion correction proposed by Grimme^{34,35} and compare equilibrium distance obtained from fitting of interaction energy curves and that from full structural optimization. We obtained adsorption distances of 0.220 nm and 0.232 nm for fcc-hollow and hcp-hollow

sites, respectively, from curve fitting. On the other hand, those from full relaxation are 0.200 nm (fcc) and 0.206 nm (hcp), accompanied with average Au displacements of 0.021 nm and 0.026 nm, respectively. Although the difference in distance is fairly large, adsorption on the fcc-hollow site is more stable than that on hcp-hollow site by 0.132 eV, and the relative stability is unchanged upon inclusion of structural relaxation by the vdW forces.

To investigate the bonding nature of C₆₀ with the Au(111) surface, we calculated the differential charge of the interface ($\Delta\rho$). $\Delta\rho$ is defined by $\Delta\rho = \Delta\rho_{\text{tot}} - \rho_{\text{C}_{60}} - \rho_{\text{Au}}$, where ρ_{tot} is the total charge density, and $\rho_{\text{C}_{60}}$ and ρ_{Au} are charge densities of C₆₀ and Au substrate, respectively, fixed at the adsorption geometries. We found the charge accumulation at the interface [Fig. 3(a)], suggesting the covalent-like bonding at the C₆₀/Au(111) interface. Each C atom forms a bond with the closest Au atom, thereby maximizing the number of C-Au bonds (two bonds per Au atom). This corroborates the stability of fcc-hollow site adsorption. Our finding is in line with the previous LDA study.⁶ In order to gain insight into the interfacial electronic structures we calculated the projected densities of states (PDOSs) onto the molecular orbitals of C₆₀ and the crystal orbital overlap populations (COOP) (Refs. 36 and 37) in which positive value indicates bonding interaction of the molecular orbital with the substrate, whereas negative value indicates their antibonding interaction. PDOSs for the highest molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of C₆₀ are shown in Fig. 3(b), and corresponding COOPs are shown in Fig. 3(c). Sharp peaks originated from HOMOs are located at 1.35–1.13 eV below the Fermi level (E_F) and those from LUMOs are at $(0.29-0.55) + E_F$ eV. The HOMO and LUMO levels are in reasonable agreement with the experimental peak positions of -1.7 eV (Refs. 5 and 33) for HOMO and 1.0 eV for LUMO,⁵ despite the fact that GGA underestimates HOMO-LUMO gap because of the self-interaction error. This is because of error cancellation between the self-interaction and the lack of image charge effect.³⁸⁻⁴⁰ Both bonding (positive) and antibonding (negative) components of COOPs for HOMOs are fully occupied, indicating the Pauli repulsion, hence the repulsive interaction of HOMOs with the substrate. On the other hand, LUMO derived PDOSs are partially occupied, suggesting that they are involved in the bonding with the

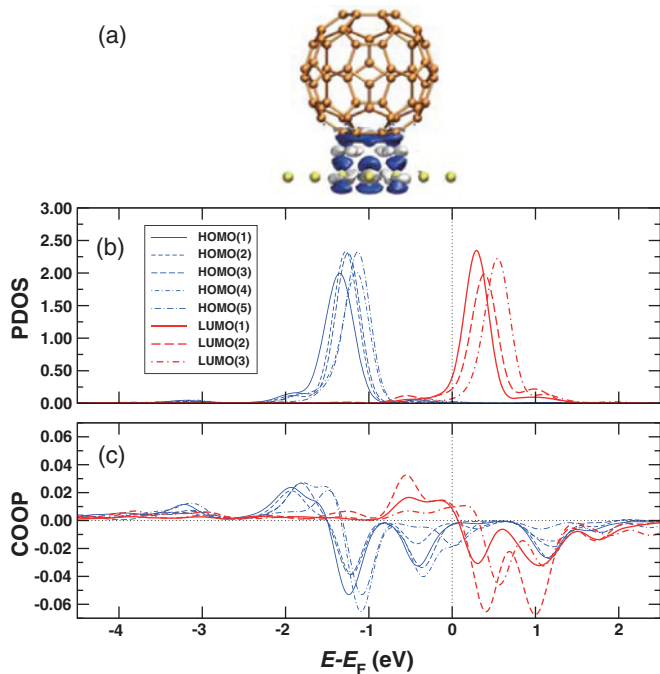


FIG. 3. (Color online) (a) Isosurface of the differential charge between C₆₀ and Au substrate. White (light) surfaces indicate accumulated charge, while blue (dark) surfaces indicate depleted charge. The isovalue is 1.350 e/nm^3 . (b) PDOSs onto HOMOs and LUMOs, and (c) corresponding COOPs.

substrate. Small peaks of PDOSs and positive COOPs for LUMOs are discernible at -0.55 eV which associate the

covalent-like bonding charge between C₆₀ and Au substrate. We also inspected the wave functions responsible for these peaks (not shown) and found these LUMOs are hybridized with substrate states. We thus concluded that the covalent-like bonding is originated from the LUMOs of C₆₀. The result is in line with the experimental observation of peaks at $E_F - 0.1$ eV, which is suggested to be derived from C₆₀ LUMOs.³³

IV. SUMMARY

To summarize, we have re-examined a C₆₀/Au(111) interface using vdW-DF with appropriate exchange and correlation functionals. We show that the vdW attraction plays an essential role in the C₆₀-Au, as well as C₆₀-C₆₀ interactions, and is crucial to describe the adsorption of C₆₀ on metal surfaces accurately. The bonding between C₆₀ and Au are found to be covalent-like, which is associated with LUMOs of C₆₀. This study also demonstrates the accuracy of the proposed exchange and correlation in vdW-DF to describe adsorption of carbon based materials on metal surfaces, and further applications of the functional to adsorption systems are highly anticipated.

ACKNOWLEDGMENTS

The work of I.H. was partly supported by Grant-in-Aid for Scientific Research (A) from Japan Society for the Promotion of Science under Contract No. 22241026. Numerical calculations were performed at the Supercomputer Center, Institute for Solid State Physics, University of Tokyo, and at the Information Technology Center, University of Tokyo.

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- ¹C. Joachim and J. K. Gimzewski, *Chem. Phys. Lett.* **265**, 335 (1997).
- ²H. Park, J. Park, A. K. L. Lim, E. H. Anderson, A. P. Allvisatos, and P. L. McEuen, *Nature (London)* **407**, 57 (2000).
- ³M. Nakaya, S. Tsukamoto, Y. Kuwahara, M. Aono, and T. Nakayama, *Adv. Mater.* **22**, 1622 (2010).
- ⁴M. Stengel, A. De Vita, and A. Baldereschi, *Phys. Rev. Lett.* **91**, 166101 (2003).
- ⁵X. Lu, M. Grobis, K. H. Khoo, S. G. Louie, and M. F. Crommie, *Phys. Rev. B* **70**, 115418 (2004).
- ⁶L.-L. Wang and H.-P. Cheng, *Phys. Rev. B* **69**, 165417 (2004).
- ⁷A. Tamai, A. P. Seitsonen, F. Baumberger, M. Hengsberger, Z.-X. Shen, T. Greber, and J. Osterwalder, *Phys. Rev. B* **77**, 075134 (2008).
- ⁸M. Hinterstein, X. Torrelles, R. Felici, J. Rius, M. Huang, S. Fabris, H. Fuess, and M. Pedio, *Phys. Rev. B* **77**, 153412 (2008).
- ⁹H. I. Li, K. Pussi, K. J. Hanna, L.-L. Wang, D. D. Johnson, H.-P. Cheng, H. Shin, S. Curtarolo, W. Moritz, J. A. Smerdon *et al.*, *Phys. Rev. Lett.* **103**, 056101 (2009).
- ¹⁰J. Schiessling, A. Grigoriev, M. Stener, L. Kjeldgaard, T. Balasubramanian, P. Decleva, R. Ahuja, J. Nordgren, and P. A. Brühwiler, *J. Phys. Chem. C* **114**, 18686 (2010).
- ¹¹W. W. Pai, H. T. Jeng, C.-M. Cheng, C.-H. Lin, X. Xiao, A. Zhao, X. Zhang, G. Xu, X. Q. Shi, M. A. Van Hove *et al.*, *Phys. Rev. Lett.* **104**, 036103 (2010).

- ¹²M. Sogo, Y. Sakamoto, M. Aoki, S. Masuda, S. Yanagisawa, and Y. Morikawa, *J. Phys. Chem. C* **114**, 3504 (2010).
- ¹³L. Tang, X. Zhang, Q. Guo, Y.-N. Wu, L.-L. Wang, and H.-P. Cheng, *Phys. Rev. B* **82**, 125414 (2010).
- ¹⁴M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, and B. I. Lundqvist, *Phys. Rev. Lett.* **92**, 246401 (2004).
- ¹⁵D. C. Langreth, B. I. Lundqvist, S. D. Chakarova-Käck, V. R. Cooper, M. Dion, P. Hyldgaard, A. Kelkkanen, J. Kleis, L. Kong, S. Li *et al.*, *J. Phys. Condens. Matter* **21**, 084203 (2009).
- ¹⁶K. Toyoda, I. Hamada, K. Lee, S. Yanagisawa, and Y. Morikawa, *J. Chem. Phys.* **132**, 134703 (2010), and reference therein.
- ¹⁷I. Hamada and M. Otani, *Phys. Rev. B* **82**, 153412 (2010).
- ¹⁸Y. Morikawa, H. Ishii, and K. Seki, *Phys. Rev. B* **69**, 041403(R) (2004).
- ¹⁹D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
- ²⁰J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ²¹I. Hamada, M. Otani, O. Sugino, and Y. Morikawa, *Phys. Rev. B* **80**, 165411 (2009).
- ²²M. Otani and O. Sugino, *Phys. Rev. B* **73**, 115407 (2006).
- ²³M. Methfessel and A. T. Paxton, *Phys. Rev. B* **40**, 3616 (1989).
- ²⁴K. Lee, É. D. Murray, L. Kong, B. I. Lundqvist, and D. C. Langreth, *Phys. Rev. B* **82**, 081101(R) (2010).
- ²⁵V. R. Cooper, *Phys. Rev. B* **81**, 161104(R) (2010).

- ²⁶Y. Zhang and W. Yang, *Phys. Rev. Lett.* **80**, 890 (1998).
- ²⁷É. D. Murray, K. Lee, and D. C. Langreth, *J. Chem. Theory Comput.* **5**, 2754 (2009).
- ²⁸T. Thonhauser, V. R. Cooper, S. Li, A. Puzder, P. Hyldgaard, and D. C. Langreth, *Phys. Rev. B* **76**, 125112 (2007).
- ²⁹S. D. Chakarova-Käck, E. Schröder, B. I. Lundqvist, and D. C. Langreth, *Phys. Rev. Lett.* **96**, 146107 (2006).
- ³⁰E. Ziambaras, J. Kleis, E. Schröder, and P. Hyldgaard, *Phys. Rev. B* **76**, 155425 (2007).
- ³¹P. Lazić, Ž. Črljen, R. Brako, and B. Gumhalter, *Phys. Rev. B* **72**, 245407 (2005).
- ³²N. Atodiresei, V. Caciuc, P. Lazić, and S. Blügel, *Phys. Rev. Lett.* **102**, 136809 (2009).
- ³³C.-T. Tzeng, W.-S. Lo, J.-Y. Yuh, R.-Y. Chu, and K.-D. Tsuei, *Phys. Rev. B* **61**, 2263 (2000).
- ³⁴S. Grimme, *J. Comput. Chem.* **27**, 1787 (2006).
- ³⁵We used C_6 coefficient and vdW radius for Au determined by Toyoda *et al.* (Ref. 16) as they are unavailable in the literature, and those for C were adopted from Ref. 34.
- ³⁶R. Hoffmann, *Rev. Mod. Phys.* **60**, 601 (1988).
- ³⁷H. Aizawa and S. Tsuneyuki, *Surf. Sci.* **399**, L364 (1998).
- ³⁸J. B. Neaton, M. S. Hybertsen, and S. G. Louie, *Phys. Rev. Lett.* **97**, 216405 (2006).
- ³⁹K. S. Thygesen and A. Rubio, *Phys. Rev. Lett.* **102**, 046802 (2009).
- ⁴⁰J. M. Garcia-Lastra, C. Rostgaard, A. Rubio, and K. S. Thygesen, *Phys. Rev. B* **80**, 245427 (2009).