

## Density-functional calculation of the dynamic image plane at a metal surface: Reference-plane position of He- and H<sub>2</sub>-metal van der Waals interaction

Ansgar Liebsch

*Institut für Festkörperforschung, Kernforschungsanlage Jülich, D-5170 Jülich, West Germany*

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The time-dependent density-functional approach is used to calculate the dynamic image-plane position of a metal surface for external fields that vary exponentially in time and slowly in space. This image plane determines the reference plane of the atom-metal van der Waals interaction which is evaluated for He and H<sub>2</sub> interacting with several simple- and noble-metal surfaces.

The van der Waals interaction between an atom and a metal surface (in the absence of retardation effects) was shown by Zaremba and Kohn (ZK)<sup>1</sup> to be asymptotically of the form

$$E_{\text{vdw}}(z) = -C/(z - z_0)^3 + O(z^{-5}) ,$$

where the van der Waals constant is defined as

$$C = \frac{1}{4\pi} \int_0^\infty du \alpha(iu) \frac{\epsilon(iu) - 1}{\epsilon(iu) + 1} ,$$

and the van der Waals reference-plane position is

$$z_0 = \frac{1}{4\pi C} \int_0^\infty du \alpha(iu) \frac{\epsilon(iu) - 1}{\epsilon(iu) + 1} d_{\text{IP}}(iu) .$$

Here,  $\alpha(iu)$  is the dynamic dipole polarizability of the atom and  $\epsilon(iu)$  the bulk dielectric function of the metal which is assumed to occupy the half-space  $z \leq 0$ . Thus, while  $C$  is determined solely by bulk dielectric properties of the metal,  $z_0$  depends sensitively, via the dynamic image-plane position,  $d_{\text{IP}}(iu)$ , on the microscopic screening properties of the metal surface. For jellium surfaces (edge of positive background at  $z=0$ ), Feibelman<sup>2</sup> has shown that  $d_{\text{IP}}(iu)$  may be expressed as  $d_{\text{IP}}(iu) = d(iu)\epsilon(iu)/[\epsilon(iu) + 1]$ , where

$$d(iu) = \int dz z \delta n(z, iu) / \int dz \delta n(z, iu)$$

is the centroid of the surface charge induced by a uniform external electric field oriented perpendicular to the surface and varying in time like  $\exp(iut)$ . In the case of real metals,  $d_{\text{IP}}(iu)$  involves an additional term characterizing the response to a uniform tangential electric field.<sup>2</sup>

The purpose of this paper is to present results, obtained within the time-dependent density-functional approach,<sup>3</sup> for the induced charge centroid  $d(iu)$  and for the He and H<sub>2</sub> van der Waals reference-plane position,  $z_0$ . Numerical values of  $z_0$  are given for several simple (jelliumlike) and noble-metal surfaces. These calculations represent the first consistent determination of the dynamic-induced charge at imaginary frequencies in the long-wavelength limit; in particular,  $d(iu)$  satisfies all the known sum rules.<sup>4-7</sup>

In the work of ZK,  $d(iu)$  was approximated by the simple form<sup>1</sup>

$$d(iu) = d(0)/(1 + \bar{u}^2) , \quad (1)$$

where  $\bar{u} = u/\omega_p$  and  $\omega_p$  is the plasma frequency.  $d(0)$  is the static image-plane position as calculated by Lang and Kohn.<sup>8</sup> Recently, Persson and co-workers<sup>4,5</sup> showed that, at

high frequencies,  $d(iu)$  behaves as  $d(iu) \rightarrow \lambda/\bar{u}^2$ , where  $\lambda$  is determined by the ground-state electronic density  $n_0(z)$  of the jellium surface:  $\lambda = \int_0^\infty dz n_0(z)/\bar{n}$  ( $\bar{n}$  is the bulk density). An approximate expression for  $d(iu)$  consistent with the static limit and the high-frequency behavior is<sup>5</sup>

$$d(iu) = d(0)/(1 + \eta \bar{u}^2) , \quad (2)$$

where  $\eta = d(0)/\lambda$ .

In order to achieve a better description of  $d(iu)$  at intermediate imaginary frequencies, Persson and Zaremba<sup>5</sup> made use of the known low-frequency behavior,<sup>4,9</sup>  $\text{Im}d(\omega) \approx \xi\omega/k_F\omega_p$ , where  $k_F$  is the Fermi wave vector. The coefficient  $\xi$  was calculated using the golden rule and assuming that the surface contribution to the self-consistent potential can be approximated by its static limit. They also extrapolated Feibelman's<sup>2</sup> results for  $\text{Im}d(\omega)$  into the low- and high-frequency regions and then calculated  $d(iu)$  from the relation

$$d(iu) = \frac{2}{\pi} \int_0^\infty d\omega \omega \text{Im}d(\omega)/(\omega^2 + u^2) .$$

Although the numerical values of  $d(iu)$  and the van der Waals reference plane  $z_0$  determined by this procedure are more accurate than those obtained from Eqs. (1) or (2), they are still not correct for two reasons. (a) The parameter  $\xi$  that characterizes the important low-frequency region is so far known only approximately, and (b) Feibelman employed the random-phase approximation (RPA) to determine the response (at real frequencies) of a semi-infinite jellium surface whose ground-state electronic properties were described<sup>8</sup> within the local density approximation (LDA) of the exchange-correlation functional. As has been shown recently,<sup>5,6</sup> this type of LDA-based RPA response treatment violates the force sum rule<sup>7</sup> (valid for static uniform fields) and the surface  $f$ -sum rule<sup>5</sup> (obtained from a high-frequency expansion of the induced charge). These violations lead to incorrect results for the first and first-inverse frequency moment of  $\text{Im}d(\omega)$ , i.e., to distortions of the spectral distribution of the induced density.<sup>10</sup> In order to achieve a consistent response description which satisfies the known sum rules, it is essential<sup>6</sup> to include exchange-correlation contributions to the induced potential on the same level of approximation as in the ground-state calculation.

Within the time-dependent density-functional approach,<sup>3,11</sup> the density induced by a weak uniform external potential  $\phi_{\text{ext}}(z, iu)$  at the surface of a semi-infinite (jel-

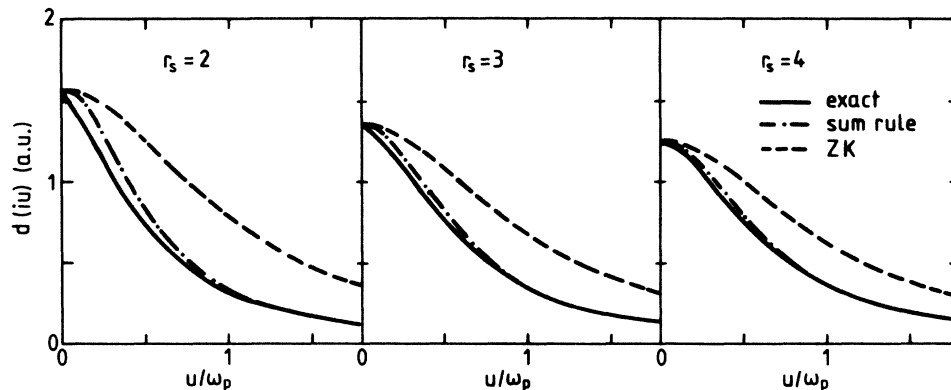


FIG. 1. Centroid of induced charge for several jellium surfaces. The exact results are the solutions of Eqs. (3)–(6). The other two curves are obtained from Eqs. (1) and (2).

lium-) metal is given by

$$\delta n(z, iu) = \int dz' \chi_0(z, z', iu) \phi_{\text{SCF}}(z', iu), \quad (3)$$

$$\phi_{\text{SCF}} = \phi_{\text{ext}} + \delta\phi + \delta V_{\text{xc}}, \quad (4)$$

where  $\chi_0$  is the independent-particle susceptibility and  $\delta\phi$ ,  $\delta V_{\text{xc}}$  represent the Coulomb and exchange-correlation contributions to the induced potential:

$$\delta\phi(z, iu) = \int dz' e^{-\kappa|z-z'|} \times \left[ \frac{2\pi}{\kappa} \delta n(z', iu) + \frac{\kappa}{2} \delta\phi(z', iu) \right], \quad (5)$$

$$\delta V_{\text{xc}}(z, iu) = \partial V_{\text{xc}}[n] / \partial n |_{n=n_0(z)} \delta n(z, iu). \quad (6)$$

$\phi_{\text{SCF}}$  is the total, self-consistent-field potential. Equation (5) implies  $\delta\phi''(z, iu) = -4\pi\delta n(z, iu)$  independently of the value of the parameter  $\kappa$  which is conveniently chosen as  $\kappa \approx k_F$ .<sup>12</sup> The functional  $V_{\text{xc}}[n]$  in Eq. (6) is the same as in the calculation of the ground-state energies and wave functions that enter  $\chi_0$ . Equations (3)–(6) form a self-consistent system of equations which we have solved as a function of  $u$  for several values of the density parameter  $r_s = (3/4\pi\bar{n})^{1/3}$ . Since the external potential is of the form  $\phi_{\text{ext}} \sim z$ , special care must be taken of the long-range (bulk) behavior of  $\phi_{\text{SCF}}$ . Also, the Friedel oscillations of  $\phi_{\text{SCF}}$  and  $\delta n$  must be described accurately in order to be able to determine the centroid of the induced charge,  $d(iu)$ . The details of these calculations will be given elsewhere.

In Fig. 1,  $d(iu)$  is shown as a function of  $u$  for  $r_s = 2, 3$ , and 4. These results are exact in the sense that they represent a complete solution of Eqs. (3)–(6). The only approximation lies in the use of a local, frequency-independent exchange-correlation functional (the same functional was used as in the work by Lang and Kohn<sup>8</sup>). Also shown are the functions given by expressions (1) and (2). The exact results for  $d(iu)$  are seen to join excellently with the static and the large- $u$  limits which are solely determined by the ground-state parameters  $d(0)$  and  $\lambda$ . For the densities shown, the exact  $d(iu)$  lies always below that derived from the sum-rule expression, in contrast to the approximate  $d(iu)$  determined in Ref. 5. In part, this is the result of the incorrect shape of the RPA spectral distribution of  $\text{Im}d(\omega)$  used in Ref. 5. In addition, we have found that

the parameter  $\xi$ , which also enters the calculation of  $d(iu)$  in Ref. 5 and which has been determined (approximately) in Refs. 5 and 6, does not give a sufficiently accurate representation of the low-frequency behavior of  $\text{Im}d(\omega)$  and  $d(iu)$ . In general, however, the differences between the exact results for  $d(iu)$  and those obtained from Eq. (2) are remarkably small and both functions lead to rather similar van der Waals reference-plane positions.

The numerical values of  $z_0$  for He and H<sub>2</sub> interacting with several jelliumlike and noble-metal surfaces are given in Table I. The parameters specifying the polarizabilities and the method used to treat the dielectric properties of the noble metals are the same as those in the work of Persson and Zaremba.<sup>5</sup> However, we have used slightly more accurate values for the static image plane  $d(0)$  and the parameter  $\lambda$ .<sup>6,13</sup> The reference-plane positions obtained from Eqs. (1) and (2) are also given in Table I. Both curves labeled “sum rule” and “ZK” in Fig. 1, as well as the corresponding entries in Table I, are based on the new values of  $d(0)$  and  $\lambda$  given in Ref. 13 and therefore differ slightly from those in Refs. 1 and 5. The exact positions lie typically 20% closer to the surface than those obtained by ZK using Eq. (1). The sum rule expression, Eq. (2), leads to values of  $z_0$  that are too large by about 8% (at  $r_s = 2$ ) to 2% (at  $r_s = 4$ ). It would be interesting to investigate why this simple expression does so well, in particular in the case of low-density substrates. We point out here that a LDA-based RPA response treatment [i.e., neglecting the term  $\delta V_{\text{xc}}$  in Eq. (4)] would give quite different reference-plane positions since the frequency

TABLE I. van der Waals reference-plane positions  $z_0$  (a.u.) for He and H<sub>2</sub> interacting with jellium and noble-metal surfaces (see text).

$r_s$	He			H <sub>2</sub>	
	Exact	Sum rule	ZK	Exact	Sum rule
2	0.736	0.806	1.018	0.846	0.926
3	0.638	0.665	0.803	0.709	0.740
4	0.592	0.603	0.708	0.643	0.656
Cu	0.324	0.340	0.398	0.409	0.430
Ag	0.286	0.298	0.352	0.376	0.392
Au	0.228	0.238	0.277	0.304	0.317

dependence of  $d(iu)$  is in this case significantly different from that shown in Fig. 1.<sup>14</sup>

In the case of the He-Cu interaction, the inward shift of the reference-plane position leads to a weakening of the van der Waals interaction energy near the physisorption well minimum (5.7 a.u.) by about 5% or 0.5 meV compared with the ZK potential. This potential had been used by Harris and co-workers<sup>15</sup> to analyze the observed He-Cu bound state energies. To fit these levels with the new van der Waals interaction would require a weakening of the repulsive part of the He-surface potential by about 10% which is well within the present limits of accuracy of the calculated repulsive interaction.

In summary, the dynamic image plane of a metal surface has been calculated consistently within the time-dependent density-functional approach, satisfying all the known sum rules. The calculations have been carried out in the long-wavelength limit and at imaginary frequencies with the aim of determining the reference-plane position of the atom-surface van der Waals interaction. For the specified ground-state exchange-correlation functional and with the assumption of using this functional also at finite frequencies, the results for the dynamic image plane are exact. The calculated numerical values of  $z_0$  for He and H<sub>2</sub> interacting with jellium and noble-metal surfaces can therefore be regarded as accurate.

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<sup>10</sup>In Ref. 5, this was partially compensated for by the rescaling the

results of Feibelman to ensure that they satisfy the surface  $f$ -sum rule. However, since the first and first-inverse moments are affected rather differently by the sum-rule violations, it is not possible to reconcile both by a simple rescaling procedure.

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<sup>13</sup>For  $r_s = 2, 3, 4$ , these values are  $d(0) = 1.57, 1.35, 1.25$  a.u. and  $\lambda = 0.44, 0.50, 0.54$  a.u., respectively.

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