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# Theory of Physisorption: He on Metals

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The attractive and repulsive contributions to the physisorption interaction energy are derived from the assumption of weak coupling between an atom and a metal surface. Results for the physical adsorption of He atoms indicate that an accurate determination of the dynamic polarizability is essential in calculations of the attractive interaction energy using a local-dielectric-function formalism. The major contribution to the physisorption interaction is the van der Waals energy, so that the physisorption energy curve is largely temperature independent. The repulsive energy is evaluated via the density-functional method. The equilibrium distances of the atom are a monotonically increasing function of the metallic-electron density. For high electron densities the binding energy increases monotonically. Values for the adsorption energies of He on various metals are in good agreement with available experimental results.

## I. INTRODUCTION

Recent experimental and theoretical advances in the understanding of physical phenomena characteristic to metal-surface systems have triggered a revived interest in theoretical microscopic approaches. Following the development of surface-sensitive probes and the ability to routinely maintain stable, controlled, ultrahigh-vacuum environment during the experiments, coupled with the construction of theoretical models, quantitative determination of surface geometrical and electronic structure parameters have been attempted for several clean surfaces and adsorption systems.[1–15] Understanding the nature of the interactions between particles and the surface net is a basic component in the construction of theoretical models of surface processes. The adsorption of gases on metal surfaces is one of the most relevant and intriguing problems in surface science, in view of its intimate relation with chemical processes such as oxidation and catalysis[16] occurring on some of these surfaces. Fundamental to an analysis of adsorption mechanisms is the understanding of the adsorption of a single atom (or molecule) on a metal surface. Besides its relevance to surface chemical reactions, and ultimately, to the solution of practical problems, it is of great scientific interest because the atom-metal-surface system is a prototype system for theoretical models.

Customarily in the literature[16–18] a distinction is drawn between physical and chemical adsorption, the distinction often being on the basis of binding-energy magnitudes (of the order of $10^{-2}$ eV and several eV for the former and latter, respectively). Chemisorption can be roughly defined as the state of chemical binding between an adsorbed atom (or molecule) and a surface. A great deal of theoretical work has recently been done on the problem of the fundamental chemisorption interaction (e.g., Refs. 16–21), whereas relatively little effort has been spent on the important theoretical problem of determining the interaction energy between a metal surface and a physisorbed atom. Aside from its intrinsic appeal as a fundamental interaction, the importance of physisorption lies in its suggested[16] role as a precursor stage to chemisorption. Hence, physisorption is of interest in the evaluation of the adsorption mechanism. In particular, the magnitude of the potential barrier for chemisorption is determined by the shape of the interaction energy curves for both "types" of adsorption and by the relative equilibrium distances of the atom from the surface.[16,17] In addition, an important aspect of the physisorption state of a molecule may be the part it plays in geometrically "aligning" the molecule[21] relative to the metal surface. This "alignment" may be critical in enhancing the probability of chemical interaction.

In the case of noble-gas atoms adsorbed on metals, physisorption is the main form of interaction (due to the inert electronic configuration of the gas atoms) rendering these systems particularly attractive for the study of physisorption processes.[22] Physical adsorption is usually considered to arise from the presence of van der Waals forces.[18] Considerable effort has been applied to the problem of understanding the nature of these forces[23–35] resulting in several formulations of the interactions. Nevertheless, detailed systematic studies of the physical parameters describing the interaction of single atoms or molecules with metal surfaces have not been usually performed. A number of quantum mechanical and semiclassical methods for calculating physisorption interaction energies have been suggested in the literature, and have been reviewed by several authors.[18b,35] Of the quantum-mechanical calculations only a few[27-35] have been applied to computation of actual interaction energies. A pioneering attempt to account for both the attractive and repulsive contributions to the interaction energy has been presented by Pollard.[33] In this method the van der Waals interactions is described by classical dipole-dipole interaction[27] between the atom and the solid substrate. The repulsive term is evaluated as the exchange interaction resulting from a Heitler-London coupling scheme. Implicit in this approach is the formation of a "one-electron bond" between localized orbitals of the surface and valence orbitals of the adsorbate. Moreover, the model of the surface employed in the calculation does not allow for "leakage" of electronic charge into the vacuum. In addition, interactions of valence electrons of the adsorbate with the substrate electrons which may be of the same order as the Heitler-London bonding energy are neglected in the calculation. Coupled with a number of approximations used in the evaluation,[33] the results of the above method do not conform with more recent knowledge of surface structure characteristics[11,36] and are not in good agreement with available experimental data. The calculation of Mavroyannis,[30] on the other hand, is based on the work of Lifshitz[32] and Dzyaloshinskii *et al.*[29] It employs a uniform continuous model of the surface and in calculating the interaction energy ignores the presence of repulsive forces entirely. The calculation is performed by assuming that a noble-gas atom resides at a distance from the metal which is the average of the nearest-neighbor distances of the metal atoms in the metal and rare-gas atoms in a rare-gas crystal. The physisorption energy is then set equal to the van der Waals energy at the average distance and an approximate formula for the energy is used. The neglect of repulsive contribution to the energy of physisorption, the above assumption of equilibrium position, and the approximations introduced in the expression for the energy cause serious difficulties, as we have discussed in an earlier paper.[37] The semiclassical methods are phenomenological in type.[18a] In these calculations, a form of the individual adsorbed-atom–bulk-atom interaction energy is assumed and the total adsorbed-atom–bulk interaction energy is derived by summing over the bulk atoms. The validity of this procedure is doubtful for the van der Waals interaction, since Lifshitz and co-workers[29,32] have shown that the addition of individual atomic interaction energies is usually not valid in calculating the van der Waals forces between dielectric media. This is especially true in the case of metals, in which the electrons are delocalized.

The objective of this work is to derive a microscopic formulation of the physisorption interaction consonant with modern studies of bare-metal surfaces.[11] In a previous paper, we presented the results of such a consistent microscopic quantum-mechanical formulation of the problem and examined the systematic variations of the interaction energy of He atoms adsorbed on metal surfaces as a function of the parameters characteristic to the atom and metal under study.[37] In the present work derivations of the basic formulas and details of the calculations for atoms and molecules physisorbed on metal and additional results for He adsorption on metal surfaces are presented. Our fundamental assumption is that a physisorbed particle (i.e., atom or molecule) resides at a large distance from the surface, so that there is only weak coupling between the substrate and the incident particle. In equivalent terms, we can state that we assume that there is no chemical interaction (either charge transfer or charge rearrangement or other mechanism) involved: the particle and solid interact through the intermediary of the long-wavelength electromagnetic field.[38] This assumption agrees with the usual physical picture of physisorption.[16] The model determined by this hypothesis implies that the mechanisms responsible for attraction at short distances from the bulk (i.e., exchange, correlation, and electrostatic interactions) transform into the van der Waals attraction alone at physisorption distances. This is analogous to Bardeen's result for the image force.[25] Extending this picture further, we conclude that the repulsion between the physisorbed entity and the surface is provided by the remaining portion of the Hamiltonian: the electronic kinetic energy. This is a result familiar from the theory of diatomic molecules.[39]

In order to calculate the van der Waals energy,[29,32] it is necessary to measure the distance from the correct origin. It has been shown,[40] that for a stationary classical external charged particle the image-interaction energy should be measured from the centroid of the induced-charge density. Van der Waals forces, however, originate from the electromagnetic field fluctuations in the solid, extending beyond its boundaries, which perturb spontaneous fluctuations in the atom. In this case, we are, therefore considering a high-frequency interaction to which the electron density is not expected to be able to respond instantaneously. It has been shown[41] that the density fluctuations induced by a high-frequency external charge are related to the derivatives of the static isolated bare-metal electron density. In the framework of the jellium model of a metal surface (see, e.g., Ref. 11) the centroid of the induced-charge density is located very close to the edge of the jellium background, in contrast to the zero-frequency result of Lang and Kohn.[40] Since van der Waals forces have been derived from an image-charge method,[31] the distance in the expression for the van der Waals energy should be measured from the centroid of the derivative of the isolated-metal-electron density. However, in making consistent comparisons with the jellium model of a bare-metal surface we shall measure the van der Waals distance from the edge of the jellium background. Since the energies of the transitions involved in the van der Waals interaction are high but not infinite, one expects small corrections due to the diffuseness of the surface region of the bare metal.[41] In a forthcoming publication[42] we show the effect of varying the electronic surface boundary conditions upon the physisorption energies. The preceding remarks are intended to be a motivation of the physical picture consistent with the basic assumption of weak coupling and not, by any means, a rigorous proof of our assumptions. A rigorous proof requires an exact solution of the physisorption problem perhaps within the generalized[43] density-functional formalism.[44,45] Such a self-consistent solution entails considerable effort and does not yet exist.

This paper is organized into four sections. In Sec. II, we discuss the attractive portion of the interaction and indicate that it is represented by the van der Waals interaction at large physisorption distances in accordance with our basic assumption. We derive the general formula for van der Waals forces and show that it reduces to the usual expression[29-32] when the metal is represented as a uniform, homogeneous medium. Results of a detailed examination for He adsorption on metals reveal that adequate representation of the atomic polarization is *extremely* important for accurate numerical determination of the physisorption energy. In Sec. III we derive the equations for the repulsive energy of interaction within the density-functional formalism.[11,44,45] An important result is that in the case of weak coupling, the change in kinetic energy is expressible, to first order, in terms of the charge densities of the isolated atomic and metallic systems. This enables us to calculate the first-order correction to the repulsive energy *without* being required to derive the electron density of the combined system self-consistently. In applying the equations to physisorbed He, we examine the systematic behavior of the repulsive contribution as a function of the metallic adsorbent. In Sec. IV, we present results for the total physisorption interaction energy of He on metals. The predictions of the theory are in good agreement with results derived from He scattering experiments[46] and from heat of adsorption measurements.[47] A number of conclusions are forthcoming. First, the major contribution to the physisorption energy (i.e., the negative of the total interaction energy at the equilibrium position) originates from the van der Waals interaction. Thus, the physisorption energy is essentially temperature independent.[24,32] In addition, our results show that the equilibrium position of the adsorbed particle increases monotonically with increasing metallic electron density. The value of this equilibrium position is *not* related simply to the covalent radii of the He and metallic atoms as had been assumed in several previous studies.[30] Finally, for "ideal" metals in which the plasmon energy $\omega_p$ and the bulk electron densities $n_+$ are related by $\omega_p^2 = 4\pi n_+$ (in atomic units) the physisorption energy at high metallic electron densities (i.e., $\omega_p > 10$ eV) is found to increase with increasing electron density.

## II. ATTRACTIVE INTERACTION

The total Hamiltonian $H$ for the combined metal-atom system is represented by[38]

$$H = H_M + H_A + H_{\mathrm{em}} + H_{\mathrm{SR}} + H_{\mathrm{VW}}, \tag{2.1a}$$

in which $H_{\mathrm{em}}$ is the Hamiltonian of the vacuum-quantized electromagnetic field, $H_M$ and $H_A$ are the Hamiltonians of the isolated atomic and metallic systems, $H_{\mathrm{SR}}$ describes the short-range interactions between the atom and metal, and $H_{\mathrm{VW}}$ corresponds to the interaction between all the particles of the system and the quantized long-wavelength electromagnetic field (i.e., the van der Waals interaction). More explicitly,

$$H_{\mathrm{VW}} = -\int d^3r\, \vec{A}(\vec{r}) \cdot \vec{j}(\vec{r}) \,. \tag{2.1b}$$

The quantities $\vec{A}$ and $\vec{j}$ are the vector potential and particle current density operator, respectively. The integral in Eq. (2.1b) is cutoff at a small distance.[38] The ground-state energy of the system, $E$, is specified by the Schrödinger equation

$$H | G, d\rangle = E | G, d\rangle \,, \tag{2.2a}$$

where $| G, d\rangle$ is the ground state for separation $d$ between the metal and atom. At $T = 0\,^\circ\mathrm{K}$, the energy of interaction between the atom and metal is given by

$$U(d) = \langle G, d | H | G, d\rangle - \langle G, \infty | H_M + H_A + H_{\mathrm{em}} | G, \infty\rangle. \tag{2.2b}$$

At large values of $d$, the contribution from $H_{\mathrm{SR}}$ is negligible and

$$U(d) = \langle G, d | H_{\mathrm{VW}} | G, d\rangle \equiv E_{\mathrm{VW}}(d), \tag{2.2c}$$

in which $E_{\mathrm{VW}}$ is the van der Waals energy.

The Hamiltonians $H_{\mathrm{SR}}$ and $H_{\mathrm{VW}}$ give rise to the attractive forces between the atom and metal. The coupling to short-wavelength electromagnetic fluctuations, embodied in $H_{\mathrm{SR}}$, produces chemical binding (or chemisorption). In accordance with our basic hypothesis that physisorbed atoms reside at such large distances from the surface that there is no chemical mechanism involved in the adsorption process, we neglect the influence of $H_{SR}$ and identify the attractive energy of interaction with $E_{VW}$. At short distances from the surface, the attractive energy of interaction is usually described in terms of exchange, correlation, and electrostatic interaction energies. If calculated exactly, the contributions from these terms approach the van der Waals interaction at large separations. Thus, in a sense, the van der Waals energy at large distances contains the exchange, correlation and electrostatic terms, in agreement with Bardeen's[25] result for the image force. Consequently, consistent with the assumption of weak coupling, the van der Waals energy is the *whole* energy of attraction: Adding exchange or correlation contributions to the van der Waals energy would constitute overcounting and would contradict our basic assumption. It has been shown[30] that the van der Waals energy of interaction between an individual atom and a dielectric medium can be derived from the results of Lifshitz and co-workers[29,32] for the dispersion energy between two dielectric media, by assuming that one of the media is rarified (i.e., the density of atoms approaches zero). Casimir's idea[48] that the retarded dispersion forces between media is attributable to the zero-point energy of the quantum electromagnetic field, has been shown[49] to be equivalent to Lifshitz's approach,[32] where the dispersion forces arise from classical electrodynamics into which there has been introduced a random fluctuating field in matter. According to the formulation of Van Kampen *et al.*,[50] the van der Waal free energy of interaction between two semi-infinite dielectric media with planar faces of infinite area which are separated by a gap, $l$, is given by[51]

$$W(l)=\frac{kT}{4\pi c^2}\sum_n \xi_n^2 \int_1^\infty p\,dp\ln[g_a(i\xi_n,p)g_b(i\xi_n,p)], \tag{2.3a}$$

$$\xi_n=2\pi nkT/\hbar. \tag{2.3b}$$

The summation in Eq. (2.3a) is performed over integral values of $n$, where the $n=0$ term is given half-weight, $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $c$ is the velocity of light in vacuum. The quantities $g_a$ and $g_b$ are the dispersion relations of the normal modes (TM and TE) of the electromagnetic field. These modes have been identified with surface plasmons.[52] The variables $\xi$ and $p$ appearing in Eq. (2.3a) are related to the frequency $\omega$ and the component of the wave vector in the plane of the surface, $\vec{k}_{\parallel}$, by the following transformations[32]:

$$\xi=-i\omega, \tag{2.3c}$$

$$ck_{\parallel}=\xi(p^2-1)^{1/2}. \tag{2.3d}$$

The quantities appearing in Eq. (2.3a) are derived from the dispersion relations for the normal modes,

$$g_j(\omega,\vec{k}_{\parallel})=0 \quad (j=a \text{ or } b), \tag{2.3e}$$

by the transformations in Eqs. (2.3c) and (2.3d). In this formalism flexibility is achieved by reducing the calculation of the van der Waals forces to the solution of Maxwell's equations subject to the appropriate boundary conditions, in order to derive Eq. (2.3e) for specific systems. The energy in Eq. (2.3a) is independent of temperature for distances appropriate to physisorption (i.e., $l<20$ Å).[29,32] At these distances, therefore, $W$ is the zero-point energy of the total system. At large distances, $W$ is temperature dependent.[29] The force per unit area, $F$, is related to $W$ by the equation,

$$W(d)=\int_d^\infty F(l)\,dl, \tag{2.4a}$$

where we use the convention that an attractive force is positive. If one of the media of density $N_0$ is a rarified gas (i.e., $N_0\rightarrow 0$), then $W$ can be derived by summing over the van der Waals energy $E_{VW}$ of the individual atoms in the medium.[29] That is to say,

$$W(d)=\int_d^\infty N_0E_{VW}(l)\,dl. \tag{2.4b}$$

The individual atomic dispersion energy is, thus, given by the relation

$$E_{VW}(d)=\lim_{N_0\rightarrow 0}\left(\frac{1}{N_0}F(d)\right). \tag{2.5}$$

In order to illustrate the application of Eq. (2.5), we describe the metal as a uniform, homogeneous medium characterized by a dispersionless dielectric function, $\epsilon_M(\omega)$. In numerical calculations, we let $\epsilon_M(\omega)=1-(\omega_p/\omega)^2$, where $\omega_p$ is the plasma frequency characteristic to the metal. For a free-electron metal, $\omega_p=(4\pi ne^2/m)^{1/2}$, where $n$ is the electron volume density, and $e$ and $m$ are the electron charge and mass, respectively. We characterize the rarefied gas of atoms by a dielectric constant, $\epsilon_A(\omega)=1+4\pi N_0\alpha_A(\omega)$, in which $\alpha_A$ is the dynamic polarizability of the atom[53,54] and $N_0$ is the density of atoms. The resultant force at small distances is given by[29]

$$F(d)=\frac{\hbar}{8\pi^2d^3}\int_0^\infty d\xi\,\frac{[\epsilon_A(i\xi)-1][\epsilon_M(i\xi)-1]}{[\epsilon_A(i\xi)+1][\epsilon_M(i\xi)+1]}$$

$$=\frac{N_0C_{VW}}{d^3}=N_0E_{VW}(d), \tag{2.6a}$$

$$C_{VW}\equiv\frac{\hbar}{4\pi}\int_0^\infty d\xi\,\alpha_A(i\xi)\frac{[\epsilon_M(i\xi)-1]}{[\epsilon_M(i\xi)+1]}. \tag{2.6b}$$

In Eqs. (2.6), the dynamic dielectric functions $\epsilon_A$ and $\epsilon_M$ are evaluated on the imaginary frequency axis $\omega = i\xi$, i.e., $\epsilon = \epsilon(i\xi)$. The result for $E_{\mathrm{VW}}$ in Eq. (2.6a), which was derived through the relation in Eq. (2.5), is completely equivalent to the results of calculations of the dispersion forces between a single atom and a metal surface.[30,31] The procedure we have outlined is, therefore, a viable one for calculating the van der Waals interaction energy between a single atom and a dielectric medium. In the present work we represent the metal as a uniform, structureless medium with a local dielectric constant (i.e., no dispersion), as in Eqs. (2.6). The effects of dispersion and varying electronic surface boundary conditions, are described in a forthcoming publication.[42]

In order to apply Eqs. (2.6), it is necessary to determine the origin from which $d$ in Eq. (2.6a) is measured in the context of the jellium model of a metal surface. Explicit in Lifshitz's derivation,[32] based upon a random fluctuation field,[55] is the observation that the van der Waals coupling is due to electromagnetic field fluctuations in the metal which extend beyond its boundaries and induce spontaneous transitions in the atom. The van der Waals interaction is, therefore, highly dynamic.[29,49] This is expressed in Eq. (2.6a) by the integral over all imaginary frequencies. In particular, He has a very strong continuum polariability,[56] so that the contributions from frequencies which are much larger than energies characteristic to the metal (e.g., the plasma and Fermi energies) are important in calculating $E_{\mathrm{VW}}$, as we shall show below. In the case of such a high-frequency external field, the metallic electron density cannot respond instantaneously. For example, the centroid of the density fluctuations induced by a very high-velocity external charge are related to the derivatives of the static-charge density,[41] in contrast to the zero-frequency result.[40] When applied to the jellium model, this result implies[41] that the centroid of the induced charge lies very close to the edge of the jellium background. In the context of an image force calculation, the image plane is located at the centroid of the induced charge.[40,57] Thus, for a high-frequency external field, the image plane is located at a distance close to the edge of the jellium background. Since van der Waals forces can be calculated by using an image method,[31] we measure $d$ from the jellium-model origin.[58]

The polarizability of an atom as a function of imaginary frequency is given in atomic units by[54]

$$\alpha(i\xi) = \sum_{j=1}^{\infty} \frac{f_j}{\xi^2 + \omega_j^2} + \int_{E_{\mathrm{IP}}}^{\infty} dE\, \frac{f_c(E)}{\xi^2 + E^2} \quad . \tag{2.7a}$$

The quantities $f_j$ and $\omega_j$ represent the discrete oscillator strengths and transition frequencies, respectively, while $f_c(E)$ and $E_{\mathrm{IP}}$ represent the continuum oscillator strength and ionization potential, respectively. Values of discrete transition frequencies and oscillator strengths used in the calculation for He were taken from Ref. 59. The continuum oscillator strength for He was determined by curve fitting of accurate calculations.[56] The result of the curve fitting (in atomic units) is specified in the following form:

$$\begin{aligned} f_c(E) &= 2A + 2B(2\pi c a_B/E) \quad (E_{\mathrm{IP}} \le E \le E_0), \\ &= 2F(2\pi c a_B/E)^2 \qquad (E_0 \le E). \end{aligned} \tag{2.7b}$$

In Eq. (2.7b), $a_B$ is the numerical value of the H Bohr radius expressed in angstroms, $A = -0.56054$, $B = 2.0263 \times 10^{-3}$, $F = 2.5645 \times 10^{-6}$ and $E_0 = 2.0019$. These coefficients were determined by requiring that the $f$ sum rule be satisfied. The continuum polarizability calculated with Eq. (2.7b) is given by

$$\begin{aligned} \alpha_c(i\xi) &\equiv \int_{E_{\mathrm{IP}}}^{\infty} dE\, \frac{f_c(E)}{\xi^2 + E^2} \\ &= \frac{2\pi c}{\xi^2} \left[ \frac{\xi A}{\pi c} [\tan^{-1}(X_{\mathrm{IP}}) - \tan^{-1}(X_0)] \right. \\ &\quad \left. + B' \ln\left( \frac{(1 + X_{\mathrm{IP}}^2)}{(1 + X_0^2)} \right) + \frac{2\pi c F'}{\xi} [X_0 - \tan^{-1}(X_0)] \right] \quad , \end{aligned} \tag{2.8a}$$

where

$$\begin{aligned} &X_0 \equiv \xi/E_0, \qquad X_{\mathrm{IP}} \equiv \xi/E_{\mathrm{IP}}, \\ &B' \equiv 2\pi c B a_B, \quad F' \equiv 2F(2\pi c a_B)^2. \end{aligned} \tag{2.8b}$$

As a check, the static polarizability, calculated with the first twelve discrete He levels[59] and $\alpha_c$, given in Eq. (2.8a), is 1.334 (in atomic units), which is to be compared with the exact $\alpha(0) = 1.384$.[53]

The values of $C_{\mathrm{VW}}$ for He are illustrated in Fig. 1. The dependence of the van der Waals constant $C_{\mathrm{VW}}$ upon $\omega_p$ can be readily determined by inserting Eq. (2.7a) into Eq. (2.6b). Letting $\epsilon_M(i\xi) = 1 + (\omega_p/\xi)^2$, we obtain

$$C_{\mathrm{VW}} = \frac{1}{8} \frac{\omega_p}{\sqrt{2}} \int_0^{\infty} dE\, \frac{f(E)}{E(E + \omega_p/\sqrt{2})} \quad , \tag{2.9a}$$

$$f(E) \equiv \sum_j f_j \delta(E - \omega_j) + f_c(E). \tag{2.9b}$$

Equations (2.9) are expressed in atomic units. Figure 1 clearly demonstrates that an accurate representation of the atomic properties is *essential* to an adequate calculation of the van der Waals energy. Curves (a), (b), and (c) correspond, respectively, to Eq. (2.9a) calculated with only the first transition), the first twelve transitions, and the first twelve transitions plus the continuum con-

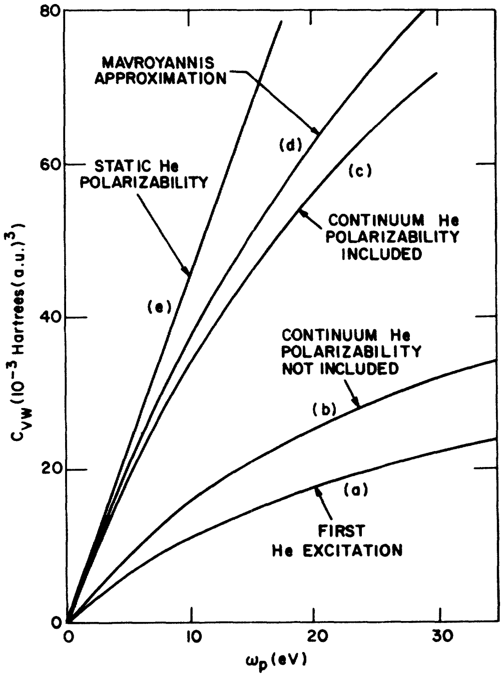

FIG. 1. He van der Waals constant $C_{VW}$ in Eq. (2.6b) as a function of plasma frequency $\omega_p$. $C_{VW}$ increases monotonically with $\omega_p$ for curves (a)–(e). Five models are considered: (a) only the first excitation is included; (b) twelve discrete ground-state excitations; (c) twelve discrete ground-state excitation and transitions to the continuum; (d) one excitation with oscillator strength of 2 and energy $\sqrt{2/\alpha(0)}$; (e) static polarizability alone. The importance of an adequate description of the frequency response of the atom is illustrated.

tribution of the He atom. The curve labeled (d) represents the approximation[30] in which the polarizability of He is modeled by one level with an oscillator strength of 2 (i.e., the total He oscillator strength) with a corresponding energy equal to $\sqrt{2/\alpha(0)}$. Finally, curve (e) results from replacing $\alpha(i\xi)$ by $\alpha(0)$ in Eq. (2.6b). This represents an upper bound on approximations to $C_{VW}$. Evidently a major contribution to $C_{VW}$ originates in the continuum levels. Moreover, the approximation in curve (d) deviates from the more accurate result in (c) by about 10%. Significant errors occur, therefore, when crude approximations of the atomic properties (i.e., the polarizability), are used in evaluating the van der Waals energy. In addition, we note a systematic increase in attraction correlated with increasing plasma frequency of the metal.

## III. REPULSIVE INTERACTION

Whereas the attraction between an atom and a metal surface arises from exchange, correlation, and electrostatic interactions, as we discussed previously, the repulsion derives from the increase in electronic kinetic energy upon assembling the system. This increase is a consequence of the Heisenberg uncertainty principle, since assemblage restricts the electrons to a smaller volume. A convenient method for calculating the change in kinetic energy is the density-functional formalism.[44,45] According to this theory, the ground-state energy of an interacting many-electron system in an external potential is a unique functional of the electron density $n(\vec{r})$. Formally the ground-state energy $E_v[n]$ can be written[44]

$$E_v[n] = T[n] + F[n], \tag{3.1a}$$

$$F[n] \equiv E_{xc}[n] + E_{es}[n], \tag{3.1b}$$

$$E_{es}[n] \equiv \int v(\vec{r})n(\vec{r})\,d^3r + \frac{1}{2}\int\int \frac{n(\vec{r})n(\vec{r}\,')d^3r d^3r'}{|\vec{r} - \vec{r}\,'|} \,. \tag{3.1c}$$

The quantities $T$ and $E_{xc}$ represent kinetic and exchange-correlation energies, respectively, which are unique functionals of $n$. In addition, we have extracted the electrostatic energy $E_{es}$ as usual.[44] In Eq. (3.1c), $v$ is the external potential which we define as the potential produced by all the ion cores in the system.

In the following we derive the change in kinetic energy, $\Delta T$, which is produced by juxtaposing the atom and metal surface. Under the assumption of weak coupling, $\Delta T$ can be expressed in terms of the isolated atomic and metallic electron densities, to first order in the coupling parameter. It is not necessary, therefore, to determine the self-consistent electron density of the combined system to this order of approximation. The ground-state energy satisfies the following variational principle[44]:

$$\mu = \frac{\delta E_v[n]}{\delta n} = \frac{\delta T[n]}{\delta n} + V(v, n, \vec{r}) + \epsilon_{xc}[n], \tag{3.2a}$$

$$V(v, n, \vec{r}) \equiv v(\vec{r}) + \int \frac{n(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}\, d^3r' , \tag{3.2b}$$

$$\epsilon_{xc} \equiv \delta E_{xc}[n]/\delta n. \tag{3.2c}$$

The symbol $\mu$ represents the chemical potential of the system. An equivalent system of self-consistent one-electron equation is given, in atomic units by[45,60]

$$\{h[n] + V(v, n, \vec{r})\}\psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}) , \tag{3.3a}$$

$$h[n] \equiv -\tfrac{1}{2}\nabla^2 + \epsilon_{xc}[n(\vec{r})] , \tag{3.3b}$$

$$T[n] = \sum_{i=1}^{N} \epsilon_i - \int d^3r \{V(v, n, \vec{r}) + \epsilon_{xc}[n(\vec{r})]\} n(\vec{r}) , \tag{3.3c}$$

$$n(\vec{r}) = \sum_{i=1}^{N} |\psi_i(\vec{r})|^2. \tag{3.3d}$$

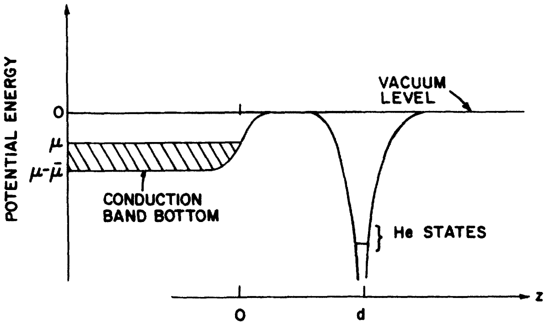

FIG. 2. Schematic illustrations of weak coupling. Metal wave-function amplitudes near the nucleus are small if the atom resides at large distance. The absence of overlap between the He state energies and the metal energy spectrum indicate that the weak coupling assumption is justifiable for He, *a fortiori*. Our energy conventions are illustrated.

In applying the above equations to the physisorption problem, it is important to realize that Eqs. (3.1) and (3.3) are formally exact, even though we do not, at present, know the form of $E_{xc}$. Thus, these equations are correct for both atoms and condensed matter. $N$ is the total number of electrons in the system (i.e., the $\psi_i$ are a complete set of orthonormal states labeled in order of increasing energy). In the context of physisorption, all energies are measured relative to the vacuum, in agreement with the zero energy of the van der Waals forces. These conventions are illustrated in Fig. 2. According to our assumption of weak coupling the electron densities of the combined system undergo only small changes from their isolated systems values. In particular, in the case of He and other rare-gas atoms, this consequence is further supported by the chemical inertness of these elements. As illustrated schematically in Fig. 2, the ionization potential of He is much greater than the inner potential of common metals resulting in weak coupling. In other words, the metal electrons "see" the atom as almost neutral, while the atomic electrons experience a small perturbation due to the metal electron density in the surface region. Thus, electron states in the combined system can be identified with states of the isolated systems. We label the atomic He states by $i=1$, 2 and the metal states by $i=3, \ldots, N+2$, where $N$ is the number of electrons in the metal. The states and energy eigenvalues of the isolated system are symbolized by $\phi$ and $W$, respectively, while those of the combined system are labeled by $\psi$ and $E$, respectively. The quantity of interest is the change in kinetic energy, $\Delta T$, of the combined

$$\Delta T[n_c] = T_d[n_c] - T_\infty[n_A, n_M], \tag{3.4}$$

where $T_d$ and $T_\infty$ are the kinetic energies of the atom and metal electrons at a distance $d$ and at infinite separation, respectively. $n_c$, $n_A$, and $n_M$ are the electron number densities of the combined atom-surface system, isolated atom and metal, respectively. Within the context of the self-consistent (Kohn-Sham) equations,[45] the isolated system is specified by the following equations:

$$(h[n_A] + V_A)\phi_i = W_i\phi_i \quad (i=1,2), \tag{3.5a}$$

$$(h[n_M] + V_M)\phi_i = W_i\phi_i \quad (i=3,\ N+2), \tag{3.5b}$$

$$n_A = \sum_{i=1}^{2} |\phi_i|^2; \quad n_M = \sum_{i=3}^{N+2} |\phi_i|^2, \tag{3.5c}$$

$$V_A \equiv V(v_A, n_A, \vec{r}), \quad V_M \equiv V(v_M, n_M, \vec{r}) \quad . \tag{3.5d}$$

$v_A$ ($v_M$) is the external potential of the atomic nucleus (metal-ion cores). The combined system is described by

$$(h[n_c] + V_c)\psi_i = E_i\psi_i \quad (i=1,\ N+2), \tag{3.6a}$$

$$n_c = \rho_A + \rho_M, \tag{3.6b}$$

$$\rho_A = \sum_{i=1}^{2} |\psi_i|^2; \quad \rho_M = \sum_{i=3}^{N+2} |\psi_i|^2, \tag{3.6c}$$

$$V_c \equiv V(v_c, n_c, \vec{r}). \tag{3.6d}$$

$v_c$ is the external potential of all the ion cores. Although we separate the isolated atomic and metallic wave functions in Eqs. (3.5), these equations can be written in the form of Eqs. (3.6), since $n_A$ and $n_M$ do not overlap (i.e., $n_c \to n_A + n_M$ as $d \to \infty$). The quantities $\rho_A$ and $\rho_M$ represent the atomic and metallic densities in the combined system. Since the metallic states comprise a nondegenerate continuum, the energies $E_i$ ($i=3$, $N+2$) are parameters rather than eigenvalues. Their spectrum is determined by the bulk metal, i.e., $z \to -\infty$. That is to say, the Fermi degeneracy, $\bar{\mu}$, is given by[60]

$$\bar{\mu} = \tfrac{1}{2} k_F^2 + \epsilon_{xc}[\bar{n}_M], \tag{3.7}$$

where $\bar{n}_M$ is the bulk electron density as $z \to -\infty$ and $k_F$ is the Fermi momentum of a degenerate electron gas with the above density. The metal electron spectrum is, therefore, unchanged by assembling the system.

In order to demonstrate the effect of the weak coupling, we rewrite Eqs. (3.3) as follows:

$$\{h[\rho_M] + V(v_M, \rho_M, \vec{r}) + V_{MA}\}\psi_i = E_i\psi_i \quad (i=3,\ N+2), \tag{3.8a}$$

$$\{h[\rho_A] + V(v_A, \rho_A, \vec{r}) + V_{AM}\}\psi_i = E_i\psi_i \quad (i=1,\ 2), \tag{3.8b}$$

$$V_{MA} \equiv V(v_A, \rho_A, \vec{r}) + \epsilon_{xc}[n_c] - \epsilon_{xc}[\rho_M], \tag{3.8c}$$

$$V_{AM} \equiv V(v_M, \rho_M, \vec{r}) + \epsilon_{xc}[n_c] - \epsilon_{xc}[\rho_A]. \tag{3.8d}$$

The consistency of our assumption of weak coupling can be verified by insepection of Eqs. (3.8). If $\rho_A \approx n_A$, then $V_{AM}$ must be a small perturbation. This, in turn, requires that $\rho_M \ll n_A$ in the region of the nucleus (i.e., $n_c \approx \rho_A$ in this region). As a result we conclude that

$$V_{MA} \approx V(v_A, n_A, \vec{r}) + \epsilon_{xc}[n_A]. \qquad (3.9)$$

The expression in Eq. (3.9) is just the potential of an electron in the isolated atom. We expect, therefore, that $\rho_M \approx n_M$ when the one-electron eigenstates of the atom do not overlap the metal spectrum. This condition is fulfilled for He. Independently, $\rho_M \approx n_M$ when the atom resides at large distances from the surface, so that the metal wave functions have small amplitudes in the region of the nucleus (i.e., see Fig. 2). As a consequence of the above consideration, we derive through first order in $V_{AM}$,

$$E_i \simeq W_i + \int d^3r \, |\phi_i|^2 \, V_{AM} \quad (i=1, 2) \, . \qquad (3.10a)$$

The resulting atomic electronic kinetic energy is given by

$$\begin{aligned} T[\rho_A] &= \sum_{i=1}^{2} \int d^3r \, \psi_i^* (-\tfrac{1}{2}\nabla^2)\psi_i \\ &= \sum_{i=1}^{2} E_i - \int d^3r \, \rho_A (V_c + \epsilon_{xc}[n_c]) \\ &\cong \sum_{i=1}^{2} W_i + \int d^3r \, (n_A - \rho_A)(V_c + \epsilon_{xc}[n_c]) \\ &\quad - \int d^3r \, n_A \{ V(v_A, \rho_A, \vec{r}) + \epsilon_{xc}[\rho_A] \} \\ &\cong \sum_{i=1}^{2} W_i - \int d^3r \, n_A (V_A + \epsilon[n_A]) = T[n_A] \, . \qquad (3.10b) \end{aligned}$$

To first order in $V_{AM}$, the kinetic energy of the atomic electrons is unchanged. Upon assembling the system, the chemical potential $\mu_c$ (i.e., the negative of the work function in the above energy convention) is changed from its isolated value, $\mu_M$. Therefore, $E_i = W_i + \mu_c$ for $i = 3, \ldots, N+2$. Upon combining Eqs. (3.2a) and (3.3c), the kinetic energy of the metallic electrons is determined by

$$\begin{aligned} T[\rho_M] &= \sum_{i=3}^{N+2} W_i - \int d^3r \, \rho_M (V_M + \epsilon_{xc}[n_M]) \\ &\quad + \int d^3r \, \rho_M \left( \frac{\delta T[n_c]}{\delta n} - \frac{\delta T[n_M]}{\delta n} \right) \\ &\cong T[n_M] + \int d^3r \, n_M \left( \frac{\delta T[n_c^0]}{\delta n} - \frac{\delta T[n_M]}{\delta n} \right) , \qquad (3.11a) \end{aligned}$$

$$n_c^0 \equiv n_M + n_A(d) \, . \qquad (3.11b)$$

Neglecting terms in $\rho_M - n_M$ and $\rho_A - n_A$ the change in kinetic energy of the system is

$$\Delta T[n_c] \cong \int d^3r \, n_M \left( \frac{\delta T[n_c^0]}{\delta n} - \frac{\delta T[n_M]}{\delta n} \right) . \qquad (3.12)$$

Thus, the zeroth-order change in kinetic energy can be determined approximately without resorting to self-consistent solutions. The notation $n_A(d)$ indicates that the nucleus is located at separation $d$.

Our scheme of calculation involves choosing a functional $T[n]$, which is an adequate description of the kinetic energies of both the atomic and metallic electrons when they are separated by an infinite distance. The functional we use is derived from the extended Thomas-Fermi version of the density functional formalism.[44] For the case of slowly varying electronic densities one may perform an expansion of $T[n]$ in successive orders of the gradient operator which, to first order, yields the following expression:

$$T[n] = \int d^3r \, [0.3(3\pi^2)^{2/3} n^{5/3} + \tfrac{1}{72}(\vec{\nabla} n)^2/n] \, . \qquad (3.13)$$

In the case of the He atom, we represent $n_A$ by the hydrogenic variational solution of the Schrödinger equation.[61] The resulting form is a good approximation to the exact number density and is given by

$$n_A(r) = (2/\lambda^3\pi) e^{-2r/\lambda} \, . \qquad (3.14)$$

In Eq. (3.14), $\lambda = \frac{16}{27}$ and $r$ is measured from the He nucleus. The kinetic energy resulting from insertion of Eq. (3.14) into Eq. (3.13) is 91.8% of the variational kinetic energy. Since the variational ground-state energy is within 1.9% of the experimental value,[61] it follows from the virial theorem, that the variational result for the kinetic energy has the same degree of accuracy. Equations (3.13) and (3.14), therefore, constitute a good approximation for the atomic kinetic energy within the context of physisorption. Application of Eq. (3.13) to the description of bare metal surfaces[62] and work function calculations[63] resulted in adequate agreement with experimental values. Rather than using the density-functional variational solutions for the metal number density, we employ a parametrized form of $n_M$ specified by[62]

$$n_M = n_+ - \tfrac{1}{2} n_+ \exp[\beta z] \, , \quad z < 0 \, , \qquad (3.15a)$$

$$n_M = \tfrac{1}{2} n_+ \exp[-\beta z] \, , \quad z > 0 \, , \qquad (3.15b)$$

where $n_+$ is the positive jellium charge density and $\beta$ is a variational parameter. Equation (3.13) is a functional form for the kinetic energy which in conjunction with the electron densities in Eqs. (3.14) and (3.15) is an adequate representation of both the isolated atom and metal. In accord with the density-functional formalism, we assume that Eq. (3.13) describes the combined system. The resulting equation for the repulsive energy $E_R$ is therefore

$$E_R(d) \cong \int_{V_\beta} d^3r \, n_M \left[ 0.5(3\pi^2)^{2/3}(n_A^{2/3} - n_M^{2/3}) \right.$$

$$+\frac{1}{72}\left(\frac{(\vec{\nabla}n_A)^2}{n_A^2}-\frac{(\vec{\nabla}n_M)^2}{n_M^2}-\frac{2\nabla^2 n_A}{n_A}+\frac{2\nabla^2 n_M}{n_M}\right)\Bigg]\,. \qquad (3.16)$$

The approximate form in Eq. (3.16) results from noting that $n_M$ varies much more slowly than $n_A$ (i.e., $2/\lambda \simeq 3\beta$), and $n_A \gg n_M$ in the region of the nucleus. Consequently, from Eq. (3.12) we observe that the major contribution comes from the region around the nucleus. The region $V_B$ is a sphere of radius, $b$, centered at the nucleus such that $n_A \geq n_M$ for $r \leq b$. Contributions from regions such that $r > b$ are much smaller. The integral in Eq. (3.16) can be performed analytically, yielding

$$\begin{aligned}E_R(d) \cong 0.5(3\pi^2)^{2/3}\Bigg[&\frac{5n_+\pi}{3\beta}\left(\frac{2}{\lambda^3\pi}\right)^{2/3}\\ &\times e^{-\beta d}[F_1(\beta_-)-F_1(-\beta_+)]\\ &-\frac{\pi n_+}{\beta}\left(\frac{n_+}{2}\right)^{2/3} e^{-\beta' d}[F_1(\beta')-F_1(-\beta')]\Bigg]\\ &+\frac{\pi n_+}{72\beta^2}e^{-\beta d}[F_2(\beta)-F_2(-\beta)-16/\lambda]\,, \qquad (3.17\text{a})\end{aligned}$$

$$F_1(X) \equiv \frac{e^{Xb}}{X}\left(b-\frac{1}{X}\right)+\frac{1}{X^2}\,, \qquad (3.17\text{b})$$

$$F_2(X) \equiv e^{Xb}\left[\left(b-\frac{1}{X}\right)\left(X^2-\frac{4}{\lambda^2}\right)+\frac{8}{\lambda}\right], \qquad (3.17\text{c})$$

$$\beta_\pm \equiv \beta \pm 4/3\lambda\,, \quad \beta' \equiv 5\beta/3\,, \qquad (3.17\text{d})$$

$$b \equiv \frac{1}{\beta+2/\lambda}\left[\ln\left(\frac{4}{n_+\pi\lambda^3}\right)+\beta d\right]\,. \qquad (3.17\text{e})$$

In Fig. 3, we display the repulsive energy presented in Eqs. (3.17) for three different positive jellium charge densities. The systematic strengthening of $E_R$ with increasing $\omega_0^2 \equiv 4\pi n_+$ (in a.u.) is evident.

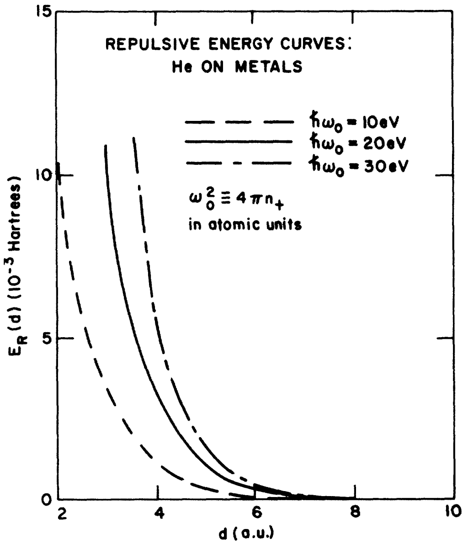

FIG. 3. The repulsive energy $E_R$ for He on metals. As $\omega_0$ increases $E_R$ becomes stronger.

## IV. He PHYSISORPTION ENERGY RESULTS AND CONCLUSIONS

In Secs. II and III, we treated the attractive and repulsive components of the physisorption energy. The total energy of interaction $U(d)$ is derived by combining them:

$$U(d) = -E_{\text{vW}}(d) + E_R(d). \qquad (4.1)$$

The van der Waals and repulsive energies used in the calculations are taken from Eqs. (2.6) and (3.17), respectively. In applying these equations we must specify the plasmon frequency $\omega_p$ needed to calculate $E_{\text{vW}}$ and the electron density $n_+$ necessary for $E_R$ (i.e., $\omega_0^2 \equiv 4\pi n_+$). We determine $\omega_p$ from electron-loss experiments,[64,65] using the criterion that the plasmon energy corresponds to the most prominent loss common to measurements taken in different laboratories. The value of $\omega_p$ for tungsten was taken from inelastic-low-energy-electron-diffraction (ILEED) measurements.[66] For free-electron metals, $\omega_0$ is determined by the number of conduction electrons per atom, so that there is no ambiguity in the value of this parameter (i.e., $\omega_0$ is the free-electron plasmon energy), and the observed value of $\omega_p$ differs only slightly from $\omega_0$ because of interbands transitions.[64]

In the case of transition metals, there is a potential problem because the choice of a free-electron density appropriate for a surface calculation is not clearly indicated. Fortunately, a prescription has been formulated[67] for choosing the "free" valence electrons in these metals. This prescription, which identifies the free electrons with the most stable oxidation state of the isolated atom, has been shown to be an excellent parametrization of surface energy data in the density parameter, $r_s$, i.e., $r_s \equiv (4\pi n_+/3)^{-1/3}$. Even though there is some disagreement[68] about the validity of the theory, nevertheless the parametrization can be considered as phenomenological, giving strong support to the correctness of the prescription. In the following, we denote the plasma frequency used in computing $E_{\text{vW}}$ by $\omega_p$ and that used in calculating $E_R$ by $\omega_0$.

Illustrated in Fig. 4 are $U(d)$, $E_{\text{vW}}(d)$, and $E_R(d)$ for a "typical" metal (i.e., $\omega_p = \omega_0 = 20$ eV). At the equilibrium position (vertical arrow), the van der Waals energy is the major component of the physisorption energy. From our discussion in Sec. II, we conclude that $U(d_{\text{eq}})$, where $d_{\text{eq}}$ is the equilibrium position of the atom is largely independent of temperature. Another interesting feature illustrated in Fig. 4 is that, as the particle approaches the surface, $E_R$ first decreases because the atomic

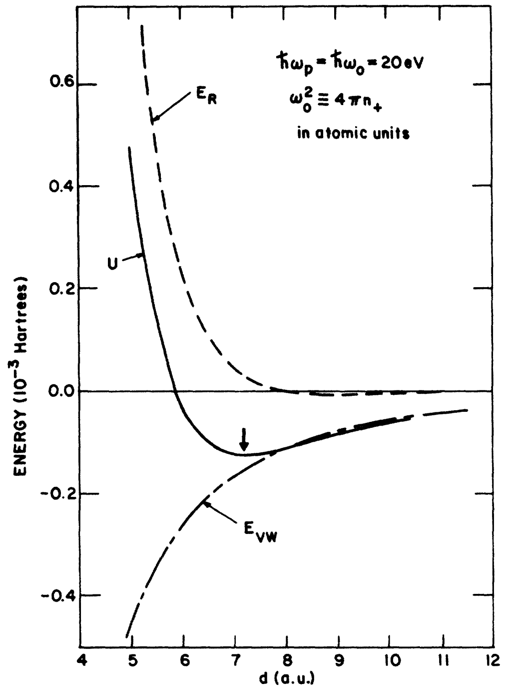

FIG. 4. Illustration of the relation between $U$, $E_{\mathrm{VW}}$ and $E_R$ for a typical "ideal" metal (i.e., $\omega_p = \omega_0 = 20$ eV). The arrow indicates the equilibrium position, $d_{\mathrm{eq}}$. The largest contribution to $U$ is from $E_{\mathrm{VW}}$, indicating that $U(d_{\mathrm{eq}})$ is mostly independent of temperature at physisorption distances.

and metallic electrons overlap and then increases because the electrons are "squeezed" into a smaller volume. This is exactly analogous to the situation for the binding in diatomic molecules.[39] In a previous paper,[37] we presented results for $d_{\mathrm{eq}}$ and $-U(d_{\mathrm{eq}})$ for the physisorption of He on free and transition metals. In Figs. 5 we summarize these results by plotting the physisorption energy versus the equilibrium position for a range of metals. The solid line in the Fig. 5(a) corresponds to ideal metals (i.e., $\omega_0 = \omega_p$). It is apparent that, for these metals, $U(d_{\mathrm{eq}})$ first increases (weaker binding) with increasing $d_{\mathrm{eq}}$ and then decreases with further increase of $d_{\mathrm{eq}}$. In Fig. 5(b) it is demonstrated that $d_{\mathrm{eq}}$ increases monotonically with increasing $\omega_0$. This increase is first very rapid (i.e., for $\omega_0 \lesssim 10$ eV) and then markedly slower. The transition metals listed in Table I follow this curve closely. It is important to note that the values of the equilibrium position are not simply related to the sum of covalent radii of the metallic and He atoms. The physisorption energy exhibits a maximum for $\omega_0 \simeq 10$ eV, as illustrated in Fig. 5(a). This feature can be appreciated by observing that the van der Waals energy (i.e., $C - C_{\mathrm{VW}}/d_{\mathrm{eq}}^3$) is the major contribution to the physisorption energy, as we show in Fig. 4. Comparison of Figs. 1 and 5(b) reveals that for increasing $\omega_0$, first $C_{\mathrm{VW}}$ increases less rapidly than $d_{\mathrm{eq}}^3$ and then (for $\omega_0 \gtrsim 10$ eV) the reverse occurs. It is, therefore, the rapid increase of $d_{\mathrm{eq}}$ for small values of $\omega_0$ and slower increase for higher $\omega_0$ which produces the maximum in the energy versus equilibrium-distance curve shown in Fig. 5(a). In Table I we display results of the calculations of the physisorption energies for various free-electron and transition metals, along with parameters used in the calculations, and compare our results with available experimental values. In comparing our results with experiments, we use values derived from He scattering experiments,[46,47] which were performed under controlled conditions. Other adsorption measurements have been made[69,70] on substrates whose surface conditions have not been specified; we, therefore, make no further reference to these experiments.

In conclusion, we have presented a formulation of a microscopic theory of physisorption derived from the assumption of weak coupling and the ap-

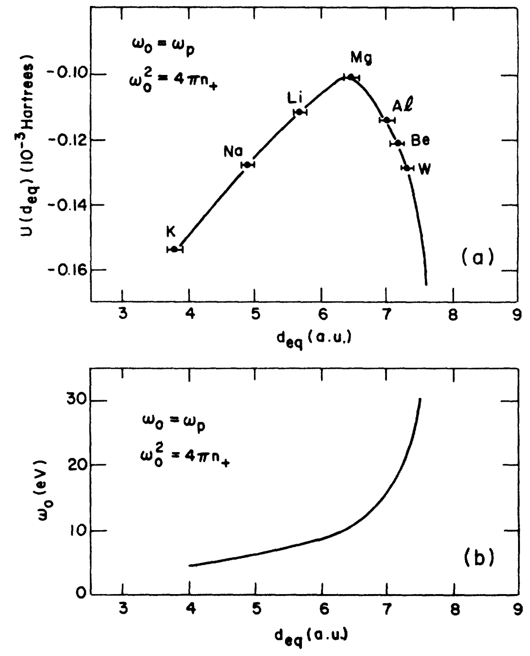

FIG. 5. (a) Physisorption energies for He adsorbed on "free-electron" metals. The decrease of $-U(d_{\mathrm{eq}})$ for small electron densities reflects the sharp increase in $d_{\mathrm{eq}}$ at these densities. The increase in $-U(-U(d_{\mathrm{eq}}))$ for high electron densities is a result of the slow variation of $d_{\mathrm{eq}}$. Error bars indicate the uncertainty in the values of $d_{\mathrm{eq}}$ due to the numerical distance grid of 0.1 a.u. used in the calculations. (b) Equilibrium position, $d_{\mathrm{eq}}$, of physisorbed He atoms on metals characterized by the plasma frequency $\omega_0$. The monotonic increase of $d_{\mathrm{eq}}$ as a function of the plasma frequency is illustrated.

TABLE I. Physisorption energies, equilibrium positions, and parameters used in the calculation of He adsorption on "free" and transition metals. The column labeled $E_{\text{expt}}$ represents values of the scattering well depth in He scattering studies (Refs. 46 and 47).

| Metal | $\omega_0$(eV) | $\omega_p$(eV) | $\beta$ | $d_{\text{eq}}$(a.u.) | $-U(d_{\text{eq}})$ ($10^{-3}$ hartree) | $E_{\text{expt}}$ ($10^{-3}$ hartree) |
|---|---|---|---|---|---|---|
| K | 4.3 | 3.9 | 1.32 | 3.8 | 0.129 | |
| Na | 5.9 | 5.9 | 1.27 | 4.9 | 0.123 | |
| Li | 8.0 | 7.1 | 1.24 | 5.9 | 0.097 | |
| Mg | 10.9 | 10.6 | 1.22 | 6.5 | 0.103 | |
| Al | 15.8 | 15.3 | 1.24 | 7.0 | 0.109 | |
| Be | 19.0 | 19.0 | 1.26 | 7.1 | 0.121 | |
| Ag | 12.7 | 23.0 | 1.22 | 6.3 | 0.179 | 0.128[a] |
| Zn | 13.5 | 22.9 | 1.22 | 6.4 | 0.169 | |
| Cu | 15.3 | 20.0 | 1.24 | 6.8 | 0.140 | |
| Co | 19.3 | 21.0 | 1.27 | 7.1 | 0.129 | |
| Ni | 19.4 | 22.9 | 1.27 | 7.1 | 0.138 | |
| Mo | 23.0 | 25.0 | 1.30 | 7.3 | 0.137 | |
| W | 23.0 | 23.0 | 1.30 | 7.3 | 0.129 | 0.159[b] |
| Pt | 19.1 | 23.0 | 1.34 | 7.6 | 0.141 | 0.167[a] |

[a] Reference 46.
[b] Reference 47.

plication of the local-dielectric-function formalism and the density-functional method. The systematic observation that the potential energy minimum does not occur at a distance equal to the hard-sphere radius of the metal-atom–gas-atom system as was assumed in several previous studies, but rather at larger distances [see also Fig. 5(b)], indicates the necessity for a complete theory which includes both the attractive and repulsive terms. Such a theory, subject to the approximations and assumptions indicated above, with the neglect of mutual interadsorbate interactions has been used in this study. The *ab initio* predictions of the theory for adsorption interaction energy curves of He atoms on metals are illustrated and compared with experimentally available data. Consequently, a systematic dependence of the interaction energy on parameters characterizing the metal surface and adsorbed atom were derived.

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