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Universal features of bonding in metals

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Binding-energy-distance relations for metallic systems are shown to exhibit a universal behavior under a simple two-parameter scaling. All currently available *ab initio* calculations for the cohesion and adhesion of metals, as well as the chemisorption of gas atoms on metal surfaces, are shown to be determined by this single relation. Further, the energetics of diatomic molecules are determined by the same relation, despite the existence of strong volume-dependent forces for metals. These findings suggest a commonality of metallic bonding and a close relationship between molecular and metallic bonding. The universal nature of binding-energy-distance relations implies relations between seemingly disparate physical phenomena. As an example we show that the surface-binding-energy relation can be approximately expressed in terms of the bulk quantities. This leads to an explanation of the well-known empirical result that the surface energy per surface atom is proportional to the cohesive energy per bulk atom. Also, a simple relationship between adsorbate-substrate vibrational stretch frequencies and their desorption energies follows from the universal relationship.

I. INTRODUCTION

It has long been known that there are universal features associated with the bonding of diatomic molecules.[1] That is, potential-energy relations involving two, or at most, a few parameters in simple, analytic forms were found to represent well a rather wide variety of diatomic molecules.

Such two-atom or pair-potential functions are not appropriate for metals, however. For metals it is well known that there are strong volume-dependent forces which can never be expressed as pairwise interactions.[2] Despite this fact, it has recently been discovered[3–5] that certain metallic *total* ground-state energies as a function of atomic separation obey a universal relationship. So far, this universality has been found to extend to adhesion, cohesion, and chemisorption on metals. In this paper we will show that under a simple two-parameter scaling (of the energy and the length scale) all these systems, as well as the diatomic molecules, can be expressed in terms of a single binding-energy-distance relation.

As a consequence of this universality, many apparently disparate physical quantities are found to be, in fact, related. We will show (1) that the entire surface-energy-distance relation can be determined from bulk-metal properties and (2) that adsorbate-substrate vibrational stretch frequencies can be approximately related in a simple way to the local electron density, the geometry, and the desorption energy.

This paper is divided into two parts. In each we first give general results supporting universality. Then specific examples are given which relate the basic concept to practical problems. In the first part of the paper we identify the length scale with the screening length. Section II reviews our previous results which showed that with this choice of length scale, the available, first-principles calculations for adhesion, cohesion, and chemisorption binding-energy-distance relations could be scaled separately into universal functions. In Sec. III A we show that the universal feature of the results in Sec. II imply that the surface energy (per surface atom) is proportional to the cohesive energy per bulk atom. A second example, in Sec. II B, shows that the identification of the scaling length with the screening length leads to a simple, testable relation between the vibrational frequency of an adsorbate, its adsorption energy, and the local electron density for each geometry of bonding. The identification of the scaling length with the screening length yields important results when it is known. However, in some situations the screening length is not a well-defined quantity, e.g., in the energies of diatomic molecules. In the second part of this paper we determine the scaling length from the energy second derivative at equilibrium, i.e., from vibrational properties. From this we find that all binding-energy curves for adhesion, cohesion, chemisorption, and for the bonding energy of diatomic molecules as a function of interatomic spacing have the same approximately universal form under the two-parameter scaling. Section IV provides our evidence for this assertion, our most significant result. In Sec. V we show how to determine the length scale in terms of experimental quantities. We calculate bulk (cohesion) and surface (adhesion) scaling lengths for the fcc, bcc, and hcp metals. These surface and bulk lengths are shown to be proportional. The constant of proportionality is found empirically. In Sec. VI we use this fact to relate the energetics of cleavage to within experimental error to the properties of bulk metals. Section VII concludes the paper with a discussion.

II. SCALING OF METALLIC BINDING ENERGIES

Recently, we have shown that metallic binding-energy-distance curves can be approximately scaled into a single universal relation in each of the following cases: (1) chemisorption on a metal surface[5]; (2) metallic and bimetallic adhesion[3]; and (3) the cohesion of bulk metals.[3] A similar result was subsequently advanced by Vidali *et al.*[6] for the case of physisorption. In each case, the energy relation can be expressed as

$$E(a)=\Delta E\, E^*(a^*)\ . \tag{2.1}$$

Here $E(a)$ is the total energy as a function of the interatomic separation distance a, ΔE is the equilibrium binding energy, while $E^*(a^*)$ is an approximately universal function which describes the shape of the binding-energy curve. The coordinate a^* is a scaled length defined by

$$a^*=(a-a_m)/l\ . \tag{2.2}$$

Here a_m is the equilibrium separation and l is a scaling length which is to be determined. In each of the three systems we considered we found that l is reasonably well determined by the Thomas-Fermi (TF) screening[7] length

$$l_{\mathrm{TF}}=\frac{1}{3}\left[\frac{243\pi}{64}\right]^{1/6} n^{-1/6}(a_m)\ , \tag{2.3}$$

where $n(a_m)$ is the electron density at the equilibrium position of the atom. We note that such a choice is not appropriate for the case of physisorption, which we will consider no further.

The total-energy-distance curve for a given physical situation is determined from the two scaling parameters ΔE and l once the general form of $E^*(a^*)$ is established. The choice of ΔE as a scaling parameter is simply a convenient way to assure that all the curves for a given case (i.e., chemisorption) have a common value at the minimum. The identification of l with the screening length is somewhat less obvious. The screening length describes the range of the strong electronic forces created when an external point charge is introduced into a metal. As such, it sets the approximate scale for the distance over which electronic forces can act. These same electronic forces determine the cohesion of the atoms with each other. Speaking heuristically, we can say that the screening length defines the "size" of an atom in a metallic environment. The Thomas-Fermi approximation for the screening length was chosen due to its analytic simplicity and *a posteriori* due to its success in describing the data. More accurate expressions for electron-gas screening lengths[7] are also inversely proportional to the $\frac{1}{6}$ power of the electron density. The constant of proportionality is not important to the question of universality, and so the Thomas-Fermi approximation is as good as any for our purposes. However, it also introduces a certain arbitrariness since it depends on an appropriate definition of the electron density to be used.

The scaling of the three classes of metallic systems previously reported will be reviewed below. First, we will deal with the binding energy of chemisorbed atoms on a metallic surface. Then the adhesion energy of two metal surfaces will be considered. Finally, the cohesive binding energy of a bulk metal as a function of uniform dilatation is given.

Binding-energy-distance relationships in chemisorption have recently been computed for several adsorbates on jellium in a self-consistent *ab initio* fashion.[8–12] Hydrogen was first treated by Smith, Ying, and Kohn[8] using a linear response-gradient expansion method. Subsequently, Kahn and Ying[9] computed binding-energy curves for the alkalis using the same technique. Binding-energy-distance relations for the chemisorption of H, O, and Si on jellium surfaces which approximate Al and Mg have been computed via a solution of the Kohn-Sham equations.[10–12] For a review of these calculations, see Ref. 13.

The variety of binding-energy-distance relationships for the different adsorbates is exemplified in Fig. 1, where the results of Refs. 8 and 9 are given. Here $r_s=(3/4\pi n_+)^{1/3}$, where n_+ is the bulk electron density of the substrate. The alkalis show a much slower variation with separation (distance between the adsorbate and jellium surfaces) than does hydrogen. In combining the results of Refs. 8–12, we take note of the fact that the authors of Refs. 8 and 9 computed ionic binding-energy curves. For the ionic case, the desorbed particle is an ion with an electron left in the metal, whereas for the atomic case the desorbed particle is an atom. In the vicinity of the equilibrium position, electron exchange between adsorbate and substrate is rapid. Therefore one might expect that in this region the ionic curve would be essentially identical to the atomic curve. We will see that this is, in fact, the case, as evidenced by the result that the ionic and atomic curves can be scaled onto a single, universal curve. In order to make a proper comparison, we computed the atomic-desorption energies $E(a_m)$ from the ionic-desorption energies of Refs. 8 and 9 as follows. For the alkali results of Ref. 9, $E(a_m)$ was obtained by adding $I-\varphi_e$ to the values at the respective minima of the curves in Fig. 1, i.e., to the negative of the ion-desorption energies. I is the ionization potential of the

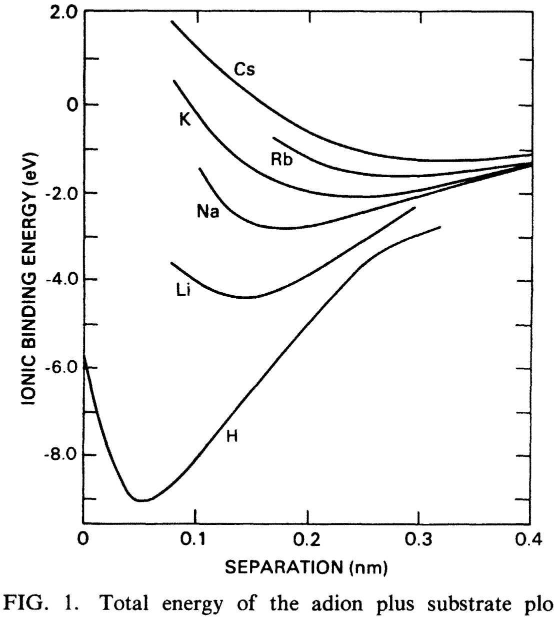

FIG. 1. Total energy of the adion plus substrate plotted against adion separation from the jellium surface. The (bulk) jellium $r_s=1.5$ a.u. The hydrogen results are from Ref. 8 and the alkali results are from Ref. 9.

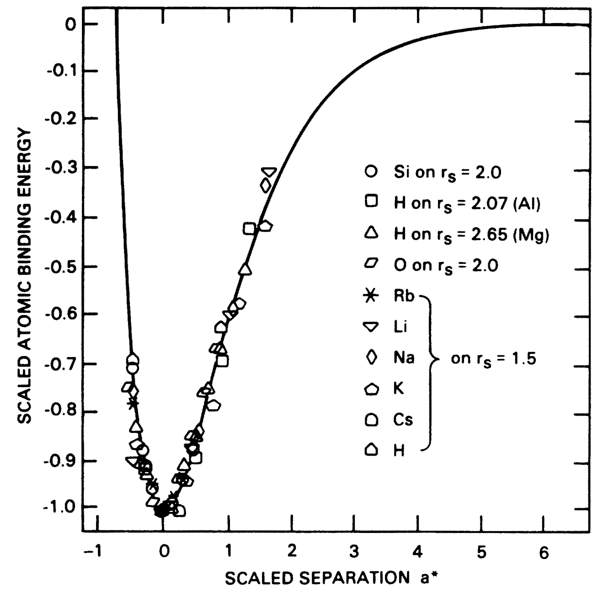

FIG. 2. Atomic-binding-energy curves for chemisorption on jellium surfaces scaled as described in the text. The jellium bulk densities are denoted by the corresponding r_s values listed in the figure. The O results are from Ref. 12, the H results on $r_s = 2.07$ (Al) and 2.65 (Mg) are from Ref. 11, the Si results are from Ref. 10, the H results on $r_s = 1.5$ are from Ref. 8, and the alkali results are from Ref. 9.

adsorbate atom and φ_e is the electron work function of the substrate. For $r_s = 1.5$, which is appropriate for the jellium density used in the ionic binding-energy calculations of Refs. 8 and 9, we took $\varphi_e = 3.88$ eV.[14] The hydrogen-ion curve of Fig. 1 indicates an ion-desorption energy of 9 eV, over 2 eV too low. Thus an accurate value of $E(a_m)$ could not be obtained by adding $I - \varphi_e$ to -9 eV. Instead, we set $E(a_m) = 3$ eV. The $E(a_m)$ value was chosen to agree with the experimental atomic-desorption energy (Ref. 15).

The inputs to the scaling relation Eq. (2.1) are given by $a^* = (a - a_m)/l_{\mathrm{TF}}$ and $E = E(a_m)$. Figure 2 shows the results of scaling. As can be seen, all the first-principles chemisorption energy-distance curves currently available describe a single universal energy-distance relation.

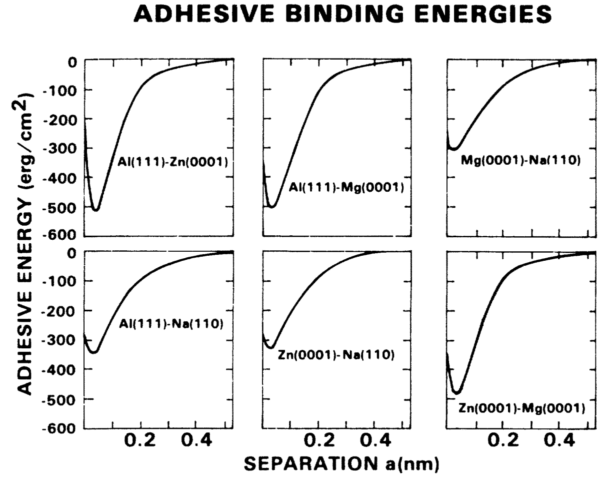

FIG. 3. Adhesive binding energy vs the separation a between the surfaces indicated.

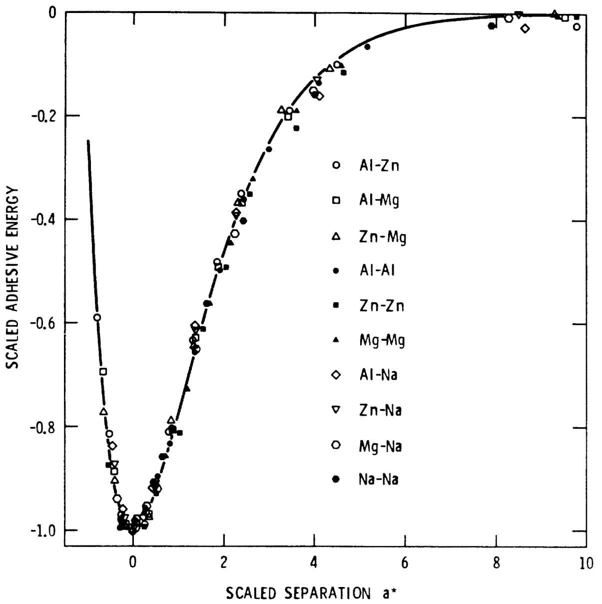

FIG. 4. Adhesive-energy results from Fig. 3 (above) and Fig. 4 of Ref. 17 scaled as described in the text.

Two of the authors have recently computed[16] the electronic structure and adhesive energetics for contacts between all combinations of Al(111), Zn(0001), Mg(0001), and Na(110). The Kohn-Sham equations were solved self-consistently using methods similar to those discussed in Ref. 17. Computed binding energies agreed well with experimental surface energies, and agreement was obtained between computed elastic constants and experiment. In Fig. 3 are plotted the adhesive binding energies as a function of separation in bimetallic contacts made between all combinations of the four metals. The adhesive energy is defined as

$$E_{ad}(a) = [E(a) - E(\infty)]/2A\ , \qquad (2.4)$$

where E is the total energy, A is the cross-sectional area, and a is the distance between the surfaces of the metals ($a = 0$ when surface atoms of the two half-spaces are separated by the average of the two bulk lattice spacings).

The inputs to the scaling relation are given by (1) setting ΔE equal to the adhesion energy at $a = a_m$, and (2) using $(l_{\mathrm{TF},1} + l_{\mathrm{TF},2})/2$ as the scaling length. Here $l_{\mathrm{TF},1}$ and $l_{\mathrm{TF},2}$ are the Thomas-Fermi screening lengths of the two separate metals. Figure 4 shows the results of scaling the calculated energies. The closeness of the scaled results is truly remarkable.

Recently theoretical binding-energy curves have become available for several bulk metals (Carlsson *et al.*[18] (Mo, K, and Cu) and Herbst[19] (Sm^{2+} $[4f^2(5d,6s)^2]$, Sm^{3+} $[4f^2(5d,6s)^3]$, and Ba). These total cohesive-energy curves were calculated as a function of the separation between atoms for a uniformly dilated lattice. We characterize the separation between atoms in terms of the Wigner-Seitz radius $r_{\mathrm{WS}} = (3/4\pi n_A)^{1/3}$, where n_A is the atom density. As input to scaling relation, we choose $a^* = (r_{\mathrm{WS}} - r_{\mathrm{WS}m})/l_{\mathrm{TF}}$ where $r_{\mathrm{WS}m}$ is the equilibrium Wigner-Seitz radius. The Thomas-Fermi screening length is evaluated using the equilibrium interstitial electron den-

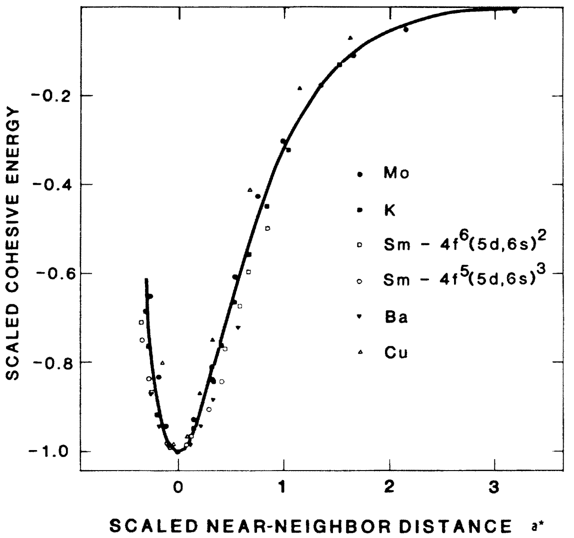

FIG. 5. Bulk energy of various metals scaled as described in the text.

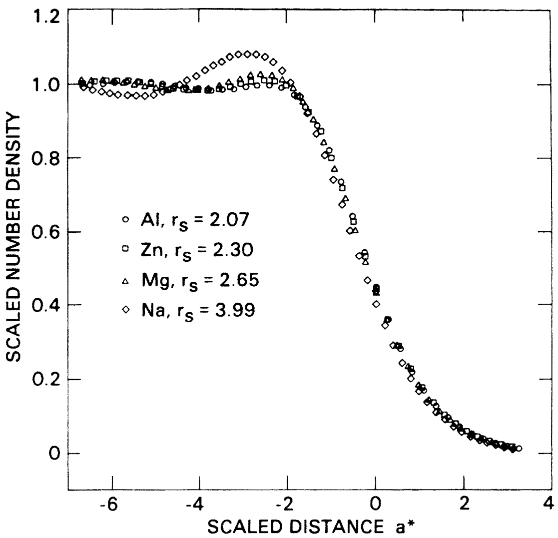

FIG. 6. Electron number density at a jellium surface as a function of a scaled coordinate perpendicular to the surface where $a^* = a/l_{\mathrm{TF}}$ and l_{TF} is determined from the corresponding r_s value shown in the figure. The number-density amplitudes are divided by the bulk density.

sity.[19,20] ΔE is the energy per atom needed to separate the atoms to infinity while keeping them in the ground-state configuration. Thus ΔE is not quite the cohesive energy although it is closely related to it. Figure 5 shows the scaled results. The binding energy of Mo, K, Ba, Sm^{2+}, and Sm^{3+} falls closely on a single curve. The results for Cu have the same shape but lie somewhat off the common curve. Note that this agreement is not as good as we found earlier for chemisorption and adhesion.

The cohesive-energy calculations of Carlsson *et al.* [augmented spherical wave (ASW) density-functional theory] and Herbst (relativistic Hartree-Fock) are quite different from each other and from the perturbative density-functional results of Refs. 16 and 17 for E_{ad}. The nature of cohesive bonding in these metals is quite varied. Ba is a divalent band overlap metal, Sm is an *f*-electron metal, Mo and Cu have important *d*-band interactions, while K is a simple metal. That such different metals calculated in quite different ways fall on a single curve indicates the generality of the scaling relations.

Finally, we note that the charge densities for a well-known zero-order model of the simple metal surfaces scale with the Thomas-Fermi screening length, as do total energies. We have calculated the electron densities at the surface of a jellium half-space for $r_s = 2$–4. Then those results were scaled assuming

$$n(z) = n_+ n^*(z^*) \tag{2.5}$$

and

$$z^* = z/l_{\mathrm{TF}} \; . \tag{2.6}$$

Here $n(z)$ is the physical density as a function of the distance from the jellium edge z. The bulk density is given by n_+, z^* is a scaled distance, and $n^*(z^*)$ is the universal form for the electron density. Figure 6 shows the result of scaling these curves. The densities are rather accurately given by a common relation except for the Friedel oscillations. This is to be expected since the Friedel oscillations are characterized by the Fermi wave vector. The scaling of the density with l_{TF} was anticipated in a variational ansatz for the surface density introduced by Perdew.[21] A rough charge conserving fit which ignores Friedel oscillations is given by

$$n^*(z^*) = \begin{cases} (1 - 0.54 e^{1.02 z^*}), & z^* < 0 \quad (2.7) \\ 0.46 e^{-1.02 z^*}, & z^* > 0 \; . \quad (2.8) \end{cases}$$

The quality of this fit could presumably be further improved by including a second term which includes the oscillation in the electron density and which is scaled with the Fermi wave vector. The fact that these surface-density profiles scale can be used in a plausibility argument for the existence of universality in adhesion (Ref. 3).

III. RELATIONSHIPS BETWEEN DIFFERENT ENERGIES

A. Relation of surface and cohesive energies

As an example of relationships that can be derived from the knowledge that universality exists, we look for a relationship between surface energies σ and cohesive energies E_{coh}. From Eqs. (2.1)–(2.3),

$$\left[\frac{d^2 E(a)}{da^2} \right]_{a = a_m} = \frac{\Delta E}{l^2} \left[\frac{d^2 E^*(a^*)}{da^{*2}} \right]_{a^* = 0} . \tag{3.1}$$

For adhesion, the above expression can be approximated in terms of the elastic stiffness constant associated with the direction perpendicular to the interface C'_{11} as

$$\frac{2\sigma}{l^2} \left[\frac{d^2 E^*_{ad}(a^*)}{da^{*2}} \right]_{a^* = 0} = \frac{C'_{11}}{d} , \tag{3.2}$$

where d is the interplanar spacing.

Similarly, for uniform dilation of a bulk metal,

$$\frac{E_{\mathrm{coh}}}{l^2} \left[\frac{d^2 E^*(a^*)}{da^{*2}} \right]_{a^* = 0} = 12\pi B r_{\mathrm{WS}} , \tag{3.3}$$

where B is the bulk modulus. Combining Eqs. (3.2) and (3.3),

$$\frac{\sigma}{E_{\text{coh}}}=\left[\frac{d^2E^*(a^*)}{da^{*2}}\right]_{a^*=0}\left[\frac{d^2E^*_{\text{ad}}(a^*)}{da^{*2}}\right]^{-1}_{a^*=0}\times\frac{C'_{11}}{2d}\frac{1}{12\pi B r_{\text{WS}}}\ . \tag{3.4}$$

Because of the universality, the ratio of the second derivative in the large parentheses is independent of the metal considered. From Figs. 4 and 5 one can evaluate them, and

$$\frac{4\pi r^2_{\text{WS}}\sigma}{E_{\text{coh}}}=1.7\frac{C'_{11}}{2d}\frac{r_{\text{WS}}}{3B}\ . \tag{3.5}$$

As will be discussed in Sec. VI, the term $(C'_{11}/2d)(r_{\text{WS}}/3B)$ is a constant within $\pm 20\%$ for a wide range of metals. Thus, we find

$$(4\pi r^2_{\text{WS}})\sigma \propto E_{\text{coh}}\ . \tag{3.6}$$

This is a well-known empirical result. We see now that a simple proportionality relation between a metal's cohesive and surface energies per atom is due to universal behavior exhibited by the binding-energy relations.

It is difficult to obtain an accurate constant of proportionality from first-principles and, in fact, the constant in Eq. (3.5) is too small by a factor of approximately 2. This is presumably due to approximations made in the calculations discussed earlier. In Sec. VI an empirical approach will be taken which leads to a more accurate constant.

B. Chemisorption on transition metals

A further example of the utility of the relations given in the preceding section deals with chemisorption. Given the perhaps surprising accuracy of the relation described in Fig. 2 for adsorbates on jellium, one might well ask if a similar relation exists for adsorbates on crystalline transition metals. In this case a number of complexities arise with respect to the results shown for the jellium surface. First, in the relatively open structure of the crystalline solid an adsorbate in, e.g., the fourfold symmetric site may penetrate between the surface atoms. It is hard to imagine that a scaling length simply related to local electron density as in Eq. (2.3) would describe the binding of an adsorbate in that case as well as an adsorbate located far from the surface. Second, the nature of the bonding is rather different depending on the surface geometry at the adsorbate's site (e.g., the on-top, the twofold, or the fourfold symmetric site).

We have met the first difficulty by considering only adsorbates which bond in the exponential tail region of the substrate electron density. Those adsorbates which penetrate so far into the metal surface as to lie between surface atoms are neglected. The fact that the relationship between the electron density and the scaling length varies from site to site can be used to advantage. Here the variation will aid in deciding on the site for a given observed adsorbate.

TABLE I. Comparison of adsorbate-substrate vibrational-stretch mode frequencies computed from Eq. (3.8) with those of Ref. 22 for the onefold site on Ni(100).

Adsorbate	Vibrational frequencies (meV) Ref. 22	Eq. (3.8)
H	283	242
Cl	43.6	
Na	19.3	22.7

In order to test this extension of the universal scaling hypothesis, we will derive the simple relation which it implies between the adsorbate-substrate vibrational stretch excitation energy ω and its desorption energy ΔE. Then we will test this relation for a variety of adsorbates on Ni(100). From Eqs. (2.1) and (2.2),

$$\omega=\left[\frac{1}{M}\frac{d^2E(a)}{da^2}\right]^{1/2}_{a=a_m}=\left[\frac{\Delta E}{Ml^2}\frac{d^2E^*(a^*)}{da^{*2}}\right]^{1/2}_{a^*=0}\ . \tag{3.7}$$

We ignore modes in which the vibration of the substrate atoms is important.

Here M is the mass of the adsorbate. One might hope to determine $(d^2E^*/da^{*2})_{a^*=a_m}$ by scaling $E(a)$ as in Figs. 1 and 2. In fact, no such curves of $E(a)$ are available for transition-metal surfaces. However, one can eliminate $[d^2E^*(a^*)/da^{*2}]_{a^*=a_m}$ by considering only ratios of vibrational stretch frequencies for different atomic adsorbates, all at the same site. The vibrational energy of one adsorbate, ω_2, given that of another adsorbate is

$$\omega_2=\omega_1\left[\frac{\Delta E_2}{\Delta E_1}\frac{M_1}{M_2}\frac{n_2^{1/3}(a_m)}{n_1^{1/3}(a_m)}\right]^{1/2}\ . \tag{3.8}$$

Here we have used the local-density result for the screening length Eq. (2.3). The densities, as in Sec. II, are given by the bare-metal surface. Equation (3.8) follows immediately from Eqs. (2.3) and (3.7).

One can test Eq. (3.8) in the following way. Upton and Goddard[22] have used the generalized valence-bond method to treat chemisorption of gas atoms on a 20-atom Ni cluster, yielding values of ω and ΔE for various adsorption sites on the cluster. The clean-surface electron densities $n(a_m)$ are obtained from a self-consistent local-orbital calculation for a Ni(100) film.[23] While there are expected to be some differences between the cluster and film substrates, this provides an approximate test. For the onefold

TABLE II. Comparison of adsorbate-substrate vibrational-stretch mode frequencies computed from Eq. (3.8) with those of Ref. 22 for the twofold site on Ni(100).

Adsorbate	Vibrational frequencies (meV) Ref. 22	Eq. (3.8)
Cl	32.4	59.9
Na	16.9	22.9
S	48	
O	65	56.1
O	68	72.9

TABLE III. Comparison of adsorbate-substrate vibrational-stretch mode frequencies computed from Eq. (3.8) with those of Ref. 22 for the fourfold site on Ni(100).

	Vibrational frequencies (meV)	
Adsorbate	Ref. 22	Eq. (3.8)
Cl	30.4	31.8
Na	16.9	13.8
S	37	
O	46	50.7

or on-top site of Ni(100), the results are given in Table I. The reference adsorbate was taken to be Cl, although the choice is arbitrary and does not affect the test. The agreement on adsorbate vibrational frequencies is rather good, considering the large range between H and Na. For this site the adsorbate equilibrium positions are relatively far from the surface. For the twofold and fourfold sites, the H equilibrium positions are quite close to the surface, and the penetration problem discussed above is severe. Vibrational frequencies for H from Eq. (3.8) are two to three times too large for these sites. For the other adsorbates, the results are generally good, however, as shown in Tables II and III. Here the reference adsorbate was taken to be S. For O there are two chemisorbed states in the twofold site and only one for the fourfold site. In every case, there is reasonably good agreement, with the lone exception of Cl on the Ni(100) twofold site. We have no explanation for the one Cl result at this time. The results for the other sites and adsorbates do suggest that universality approximately extends to chemisorption on crystalline transition metals, provided that the adsorbate does not penetrate the surface atomic layer.

We suspect that Eq. (3.8) may be of use to experimentalists who are looking for a rough check of their vibrational and/or desorption-energy results. In that connection, it is perhaps important to note that Eq. (3.8) applies *only* to adsorbates on the same symmetry site. That is, one gets quite inaccurate results if adsorbate 1 of Eq. (3.8) is on, e.g., a onefold site and adsorbate 2 is on, e.g., a fourfold site. This difference may be useful in experimentally determining the adsorption site. For example, if a set of measured desorption energies and vibrational frequencies scales nicely using Eq. (3.8) for one particular site (e.g., the onefold site) but not for the others, then one has some indication that the site is, in fact, onefold symmetric. The determination of relative vibrational frequencies depends on knowing the electron number density for the clean substrate and the adsorbate's position. Such clean-substrate densities may be either obtained from the overlapping atom approximation or from a first-principles calculation[23] as in our example.

Since the dependence on the density is weak ($n^{1/6}$), Eq. (3.8) can be roughly approximated as

$$\omega_2 \sim \omega_1 \left[\frac{\Delta E_2}{\Delta E_1} \frac{M_1}{M_2} \right]^{1/2} . \tag{3.9}$$

While Eq. (3.9) is not as accurate as Eq. (3.8), it may nevertheless be useful in correlating experimental data. The vibrational-frequency trends listed in Tables I—III are preserved when Eq. (3.9) is used.

IV. SINGLE RELATION FOR DIATOMICS, ADHESION, COHESION, AND CHEMISORPTION

Scaling interatomic separation by a screening length has an intuitive appeal because of the effective atomic-size picture discussed earlier. While it is quite successful for chemisorption and adhesion (Figs. 2 and 4), the universality was a little less apparent for cohesion (Fig. 5). More importantly, it would be highly desirable to relate the metallic universality to the energetics of diatomic molecules. Screening lengths have little meaning for molecules, however.

Thus we must take a somewhat different approach. We will see that it will lead not only to the desired relationship between universality in diatomic molecules and metals, but also will help to explain how a universal binding-energy relation can exist for metals despite the inadequacies of a pairwise-interaction picture.

The theory of cohesion and structure for simple metals has been successfully carried out in terms of perturbation theory.[2] In that theory, the difference between the free-electron potential and that of a crystalline array is treated as a small perturbation. This perturbing potential is typically chosen to be a pseudopotential. From that theory, it is possible to separate the total-energy—atomic-separation relation into so-called volume-dependent (structure-independent) terms and terms which can be expressed as pairwise interactions. It will be seen below that both the pairwise and the volume-interaction terms can be treated on the same footing.

The pairwise-interaction terms can be expressed in terms of a spherically symmetric potential. This potential is, in turn, specified in terms of the pseudopotential. A class of pseudopotentials which has been rather good for studies of cohesion and structure is due to Ashcroft.[24] It depends on only two parameters, the net charge of the ion core and an ion-core radius. Thus the pairwise-interaction part of the total-energy—interatomic-separation relation for a range of simple metals can be written in terms of these two parameters. As such, it has a universal form not unlike that found in diatomic molecules. This result is perhaps not surprising in that pairwise-interaction terms are reminiscent of potential-energy—atomic-separation distance relations for diatomic molecules.

There is no apparent similarity between the volume or structure-independent part of the total-energy—atomic-separation relation and diatomic interaction potentials, however. These volume terms also can be specified in terms of the perturbing pseudopotential. If one again uses the Ashcroft pseudopotential, one finds that even these volume-dependent terms can be written as a function of the two parameters, the net charge of the ion core, and an ion-core radius. Thus *both* the structure-independent and pairwise-interaction parts of the total energy can be written in terms of the same two parameters. Thus it is plausible that one could find a total-energy—atomic-separation relation of universal form—even for metals.

Further, the above argument suggests that the universal form could be a two-parameter family. As such, these parameters can be determined in a variety of ways. *This suggests a way to bridge the gap between diatomic molecules and metals.* We choose to specify ΔE through the equilibrium binding energy as before. Because screening

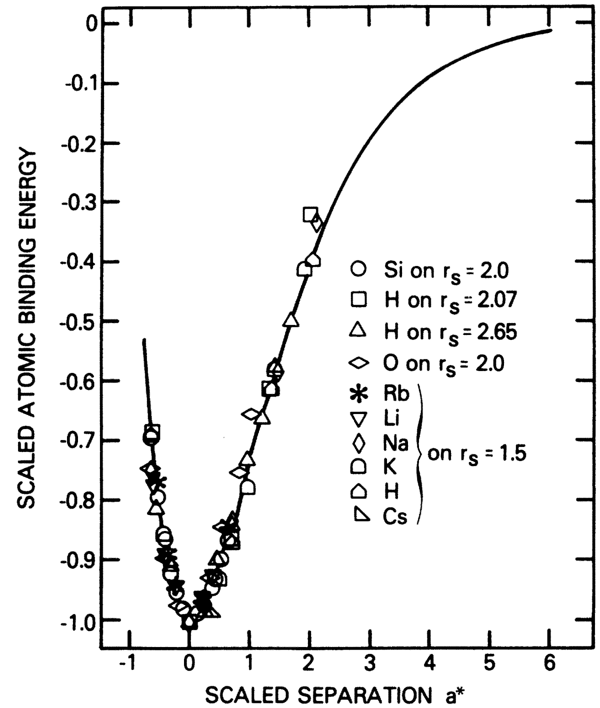

FIG. 7. Atomic-binding-energy curves for chemisorption jellium surfaces with distances scaled via Eqs. (4.1), (2.1), and (2.2). The jellium bulk densities are denoted by the corresponding r_s values listed in the figure. The unscaled $E(a)$ was taken from Fig. 2.

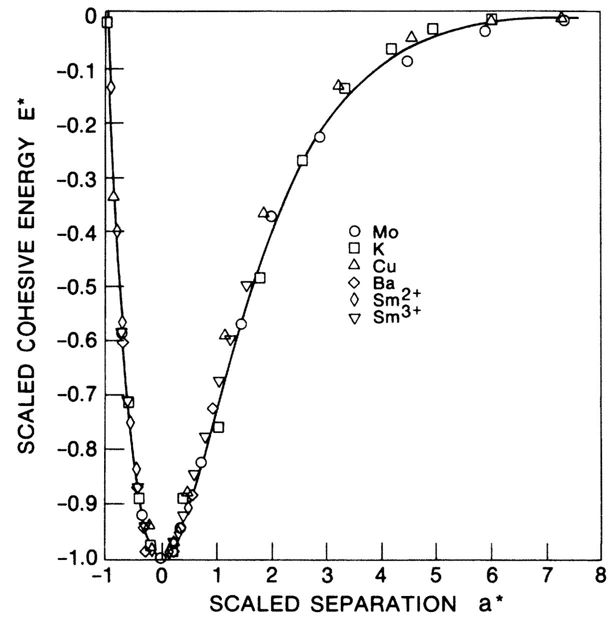

FIG. 9. Bulk energies of various metals scaled using Eqs. (4.1), (2.1), and (2.2).

lengths are ill defined for diatomic molecules, we choose instead to specify the second parameter l by requiring that the second derivative of the total energy with respect to atomic separation at the equilibrium separation is equal to 1.0. That is [see Eqs. (2.1) and (2.2)],

$$l = \left[\Delta E \left[\frac{d^2E(a)}{da^2} \right]^{-1}_{a=a_m} \right]^{1/2} . \tag{4.1}$$

We first apply this procedure to adhesion, cohesion, and chemisorption on metals, and the results are shown in Figs. 7—9. One can see that the excellent scaling found earlier (Figs. 2 and 4) for adhesion and chemisorption is again found here. The scaling of cohesive energies is considerably improved over earlier screening-length scaling. This is presumably because of the difficulty of defining a

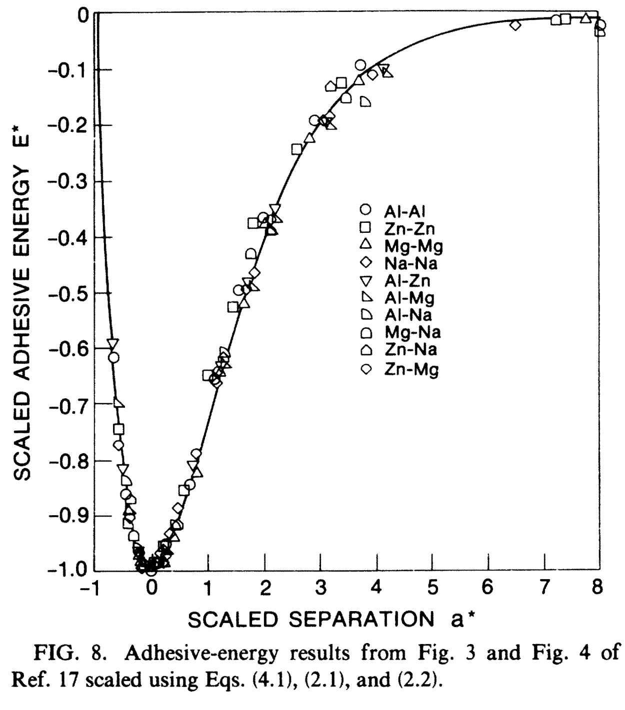

FIG. 8. Adhesive-energy results from Fig. 3 and Fig. 4 of Ref. 17 scaled using Eqs. (4.1), (2.1), and (2.2).

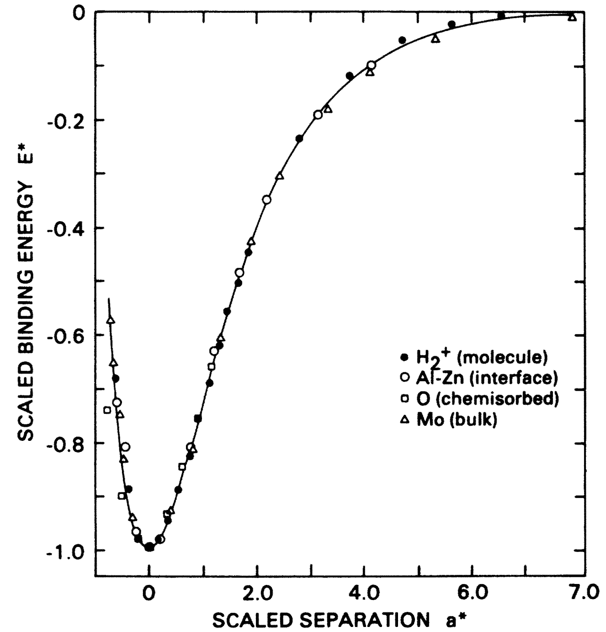

FIG. 10. Binding energy as a function of interatomic separation for four systems as noted, scaled using Eqs. (4.1), (2.1), and (2.2).

sufficiently accurate screening length for a bulk metal.

Finally, we compare in Fig. 10 the universal binding-energy relations for diatomic molecules and metallic cohesion, adhesion, and chemisorption. The molecule $H_2{}^+$ was chosen because it is a member of a broad family of diatomic molecules whose binding-energy relations are well represented by Morse or Rydberg functions and hence all have the universal relation shown in Fig. 10. The three other examples of Fig. 10 are quite representative as well, as shown in Figs. 7–9.

One can see that all the universal relations fall on top of each other. Thus there is a single universal relation for all these seemingly diverse systems. This is perhaps our most significant result. It shows that the metallic bond at an interface or in the bulk maintains a common dependence on interatomic spacing. This commonality extends to gas atoms interacting with metals and to the diatomic molecular bond. The degree to which these points all fall on a common curve in Fig. 10 is rather astounding. It tells us that there is an underlying simplicity in nature that was not recognized heretofore. Note that the ground-state energy of $H_2{}^+$ has been solved exactly and that, together with the variety of approximations used for the three other systems in Fig. 10, argues that this universality is not due to any theoretical approximation.

IV. DETERMINING ΔE AND l EMPIRICALLY

The universal scaling described in Eqs. (2.1) and (2.2) depends only on the two parameters ΔE and l. These parameters can be fixed by choosing any two physical measurements which depend on the total-energy curve. We assume that the equilibrium binding energy can be measured, thus establishing ΔE directly. We choose the length scale so that it can be measured also. We choose to fix l from a measurement of $(d^2E/da^2)_{a=a_m}$ as in Eq. (4.1). For a bulk solid this quantity can be inferred from the elastic constant or the bulk modulus. For chemisorbed atoms and dimers, $(d^2E/da^2)_{a=a_m}$ is directly related to a vibrational frequency. The complete energy versus distance curve can be found by determining the binding energy and its second derivative evaluated at the equilibrium position.

The length scales appropriate to the surface and bulk binding energies of a metal are expected to be closely related given the screening arguments of Sec. II. First, consider the surface-energy relation. When the metal is cleaved the change in energy per unit area is twice the surface energy $\Delta E = 2\sigma$. On the other hand, the corresponding $(d^2E/da^2)_{a=a_m}$ for cleavage is somewhat complicated and depends on the precise way cleavage is defined (see Refs. 25 and 26). We have expressed it in our calculations below as

$$\left[\frac{d^2E_s}{da^2}\right]_{a=a_m}=\frac{C'_{11}}{d}\ . \tag{5.1}$$

Here C'_{11} is the elastic constant appropriate to strain normal to the surface, while d is the interplanar separation in this direction. Thus

$$l_s=\left[\frac{2\sigma d}{C'_{11}}\right]^{1/2}\ . \tag{5.2}$$

Here the subscript s denotes a surface quantity. The corresponding length scale for a uniform dilatation of the bulk metal is

$$l_b=\left[\frac{\Delta E}{12\pi B r_{\mathrm{WS}}}\right]^{1/2}\ . \tag{5.3}$$

The length scales l_b and l_s can be estimated from Eqs. (5.2) and (5.3) using experimental data. We take the cohesive energy and lattice properties from Kittel,[27] the elastic properties from Simmons and Wang,[28] and surface energies from Tyson and Miller.[29] We will estimate the length scale for the most densely packed face of each metal. This will, in fact, introduce a certain error since the

TABLE IV. Surface and bulk length scales l_b and l_s in Å, and their ratios are calculated from Eqs. (5.2) and (5.3) using experimental data.

Element	l_b	l_s	l_b/l_s
(fcc)			
Ir	0.23	0.43	0.53
Ni	0.27	0.52	0.52
Pd	0.24	0.56	0.43
Pt	0.24	0.54	0.44
Cu	0.27	0.55	0.50
Ag	0.27	0.58	0.47
Au	0.24	0.54	0.43
Al	0.34	0.66	0.51
Pb	0.30	0.67	0.45
Average			0.48
(bcc)			
Li	0.55	1.03	0.54
Na	0.56	1.09	0.52
K	0.65	1.28	0.51
Rb	0.66	1.32	0.50
Cs	0.71	1.44	0.50
V	0.31	0.72	0.43
Nb	0.34	0.75	0.45
Ta	0.33	0.68	0.49
Cr	0.25	0.53	0.48
Mo	0.27	0.55	0.48
W	0.27	0.53	0.49
Fe	0.27	0.56	0.48
Average			0.49
(hcp)			
Be	0.31	0.41	0.76
Co	0.26	0.52	0.50
Hf	0.37	0.74	0.50
Mg	0.32	0.78	0.40
Re	0.25	0.48	0.52
Ru	0.25	0.45	0.54
Tl	0.33	0.74	0.45
Ti	0.34	0.70	0.49
Zr	0.40	0.76	0.52
Average (Neglecting Be)			0.52

surface energies of Tyson and Miller represent an unknown average over many crystal faces, and not just the most densely packed face. For the bulk cohesion, $(d^2E/da^2)_{a=a_m}$ has been expressed in terms of the bulk modulus and r_{WS}. ΔE is defined as the energy to separate the atoms to infinity while maintaining the *equilibrium* ground-state electronic configuration. Thus ΔE is not necessarily equal to the cohesive energy E_{coh} due to the possibility of electronic phase transitions, such as the metal-insulator transition at low densities. Nonetheless, lacking a more accurate determination of ΔE, we will approximate it by E_{coh} in the calculations presented below.

We have seen that both cohesive- and adhesive-energy separation relations could be successfully scaled by the bulk screening length (Figs. 2 and 4). They were also successfully scaled by relations (5.2) and (5.3) (Figs. 8 and 9). Thus l_s and l_b must each be proportional to the bulk scaling length for each metal. In turn, l_b must be proportional to l_s for each metal. This consequence of universality can not be tested by experiment.

Table IV shows the results of evaluating the length scales l_b and l_s from experimental data for the closely packed fcc, hcp, and bcc metals. With the exception of Be, the ratio of l_b/l_s for all these metals is nearly 1/2. For all the metals except Mg (which is slightly too low) and Be (which is completely anomalous), the ratio of the bulk scaling length to the surface scaling length can be expressed to within ±10% by its average value

$$l_b \simeq 0.48(5) l_s \; . \tag{5.4}$$

The deviations of l_b/l_s from constancy are consistent with (1) the approximately ±20% uncertainties in the zero-temperature surface energies and (2) the similarly sized errors introduced by our approximations of ΔE for the bulk. Improvements in the evaluation of these quantities are needed to determine if l_b and l_s can be related more exactly in a simple way. The proportionality between l_b and l_s seems quite plausible given their interpretation in terms of the screening length as discussed in Sec. II.

VI. RELATIONS BETWEEN SURFACE AND BULK PROPERTIES

The surface energy, the surface scaling length, and, consequently, the surface-binding-energy curve can be approximately determined from (1) the approximations made in the evaluation of l_b and l_s, and (2) the consequent discovery of an approximate proportionality between them. Combining Eqs. (5.2) and (5.3) we obtain

$$\frac{4\pi r_{\mathrm{WS}}^2 \sigma}{E_{\mathrm{coh}}} = \left[\frac{l_s}{l_b} \right]^2 \frac{C'_{11}}{2d} \frac{r_{\mathrm{WS}}}{3B} \; . \tag{6.1}$$

Equation (6.1) is the same as Eq. (3.5) except that the constant $(l_s/l_b)^2$ replaces 1.7 in that equation. The ratio l_s/l_b has been evaluated approximately in the preceding section [see Eq. (5.6)]. We will substitute this *empirically* determined value into the following equations. Replacing l_s/l_b by its average value, Eq. (5.6), and noting that for the cubic metals d is simply expressed in terms of r_{WS}, we find for the cubic metals,

$$4\pi r_{\mathrm{WS}}^2 \sigma \simeq 0.48 \frac{C'_{11}}{B} E_{\mathrm{coh}} \; . \tag{6.2}$$

For the hcp's the c/a ratio is variable and d is not uniquely related to r_{WS}. For the hcp close-packed metals (excepting Be), we find

$$4\pi r_{\mathrm{WS}}^2 \sigma = 0.71 \left[\frac{r_{\mathrm{WS}}}{d} \frac{C'_{11}}{B} \right] E_{\mathrm{coh}} \; . \tag{6.3}$$

Zn and Ga were not considered since they are not close packed. Their c/a ratio is much larger than ideal. Other elements such as the rare earths have been excluded since the experimental data needed to evaluate the relevant expressions were not available.

For the (111) face of an fcc metal, Eq. (6.1) can be rewritten as

$$\sigma \simeq 0.25 \frac{(C_{11}+2C_{12}+4C_{44})}{C_{11}+2C_{12}} \frac{E_{\mathrm{coh}}}{a^2} \; . \tag{6.4}$$

For the (110) face of a bcc metal,

$$\sigma = 0.24 \frac{(C_{11}+C_{12}+2C_{44})}{C_{11}+2C_{12}} \frac{E_{\mathrm{coh}}}{a^2} \; . \tag{6.5}$$

For the (0001) face of a close-packed hcp metal we find,

$$\sigma = 0.17 \left[\frac{C_{33}}{C_{11}+2C_{12}} \right] \frac{E_{\mathrm{coh}}}{a^2} \; . \tag{6.6}$$

Here the C's are the elastic constants and a is the lattice parameter for the fcc and bcc metals. Equations (5.6) and (6.1)–(6.6) show that the energetics of cleavage are entirely controlled by the energetics of the bulk solid within the approximations to universality which we have made.

Below we will test the accuracy of our expressions for the surface energy. In Fig. 11 we plot the left-hand side of Eq. (6.2) against the right-hand side and obtain a 45° straight line. This represents the theoretical predictions. We have also plotted the experimental values of the same quantities. Deviations of experimental values from the

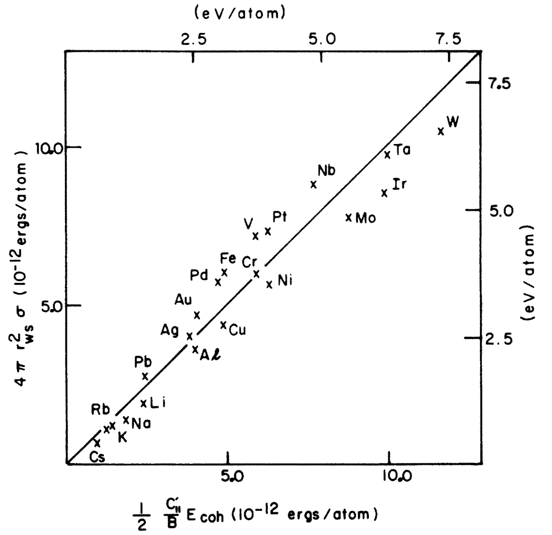

FIG. 11. Plot of the left-hand side of Eq. (6.2) vs the right-hand side yielding the straight line. The ×'s show the results of plotting the experimental data.

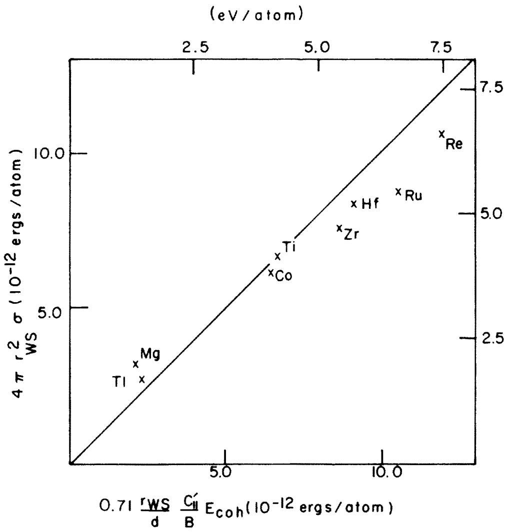

FIG. 12. Plot of the left-hand side of Eq. (6.3) vs the right-hand side yielding the straight line. The ×'s show the results of plotting the experimental data.

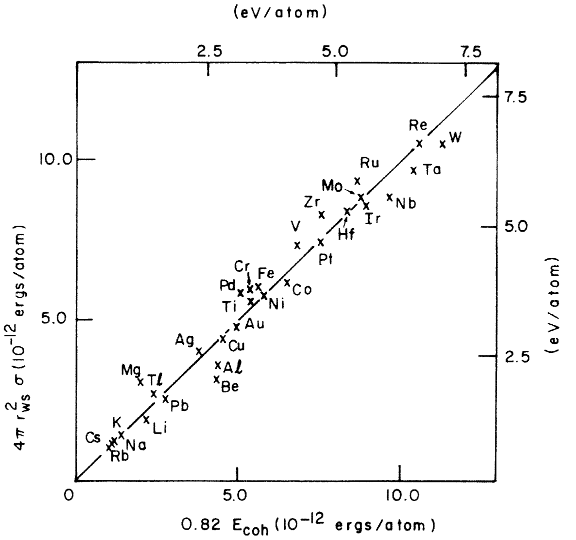

FIG. 13. Plot of the left-hand side of Eq. (6.7) vs the right-hand side yielding the straight line. The experimental data are shown by the ×'s.

theoretical estimate indicate either experimental error or inaccuracies in the theoretical prediction. In Fig. 11 we see that the experimental values for the cubic metals agree with the theory to within ±20%, which is comparable to the accuracy to which the surface energy of the densest faces are known for these metals. Figure 12 shows a similar treatment for the hcp metals in terms of Eq. (6.3). The equation (6.3) scatter in this case is considerably greater than the cubic metals. However, except for Mg, the agreement is within ±25%.

In developing the relationship l_b and l_s we used the surface energies proposed by Tyson and Miller.[29] As mentioned before, they represent an average over many crystal faces and are not an entirely adequate representation of the surface energy of the most densely packed face of a metal. Let us consider how this might enter a relationship such as Eq. (6.2) for the surface energy. Here we would take an average over crystal face for both sides of the equation. On the right-hand side this means averaging the face-dependent elastic constant. Already C/B for the cubic metals is approximately the constant 1.70 within a ±20% variation. After C is averaged over the various low-index crystal faces, we might expect to find that C/B is even closer to a constant for the cubic metals. The average value of C will be more isotropic and closer to the bulk modulus. Replacing C/B with its average value of 1.70, we obtain

$$4\pi r_{WS}^2\sigma \cong 0.82E_{coh}\ . \tag{6.7}$$

Figure 13 shows a plot of the left-hand side of Eq. (6.7) versus the right-hand side. The experimental quantities are also plotted. As can be seen, the scatter in the data is reduced compared to Figs. 11 and 12. This suggests that the face dependence represented by C/B is somewhat inconsistent with the averaged values of the surface energies obtained by Tyson and Miller.[29] For these averaged quantities, Eq. (6.7) is to be preferred. Equation (6.7) is very similar to a well-known empirical relation for the surface energy. For example, Tyson[30] discusses this relation and gives empirically

$$E_{coh} = 4A\sigma\ . \tag{6.8}$$

Here A is an appropriately defined surface area exposed per surface atom in the cleavage process. When A is expressed in terms of r_{WS}, Eqs. (6.7) and (6.8) are essentially identical. Tyson[30] and others have justified Eq. (6.8) on the basis of a pair-potential model for the solid. Our theory gives a similar relation while treating the strong volume-dependent forces and the pair-potential forces in a unified manner.

VII. DISCUSSION

As it appears, the occurrence of a universal form for the binding-energy-distance relation appears to have many implications. For example, we have used universality in demonstrating that the energetics for cleavage of metals can be determined from bulk properties. The well-known empirical relation between bulk and cohesive energies was also derived in this manner. As a further example, we have shown that for an adsorbed gas atom on a metal surface the (1) desorption energy, (2) the vibrational frequency, and (3) the bare-metal density at the position of the adsorbate are related via a simple expression. Other works which support the validity of the universal relationship are as follows. Rose and Dobson[31] have explored the implication of the scaling results for the surface energy in terms of the Thomas-Fermi screening length. McMullen, Perdew, and Rose[32] have used those results to discuss the stripping of surface atoms from a metal surface by an intense electric field. Other relationships are currently being considered by the authors including the thermophysical properties of metals. The fruitfulness of these studies will depend on how exactly the various systems can, in fact, be mapped into a single universal relationship. The answer to this question for metals is perhaps best approached for the cohesive-energy calculations which are the best understood and most realistic of those discussed. This suggests the need for accurate calculations of the cohesive-energy curves over a wide range of lattice parameters and for many different metals.

Perhaps the most surprising result of universality is that the universal binding-energy relations for certain types of diatomic bonding, as well as adhesion, cohesion, and chemisorption in solids are *one and the same.* How could that be? It is apparently not due to a theoretical approximation, since exact H_2^+ as well as local-density, generalized valence-bond,[22] and Hartree-Fock[19] results were considered. We have up to now only provided plausibility arguments for the existence of separate, universal binding-energy relations for individual phenomena, e.g., adhesion or cohesion. If the energetics of all the phenomena can be well represented by a two-parameter function, then the scaling described in Eqs. (4.1) and (4.2) leads to a single universal curve for each function. It has long been known that Morse or Rydberg functions work well for diatomics, but one cannot assume that they might accurately represent *total*-energy variations for metallic adhesion, cohesion, and chemisorption because of the presence of strong volume-dependent forces in metals.

One might well ask whether our findings of universality for diatomics and metals could serve as a justification for the use of pair potentials in physical metallurgy (Ref. 33). The answer is, unfortunately, no. The pair potential leaves out the strong volume-dependent terms. The latter are included in the *total* energy, which we argued does have a universal form. But, because the total energy is typically different from the pairwise contribution, our findings relative to the total energy do not speak to the validity of pair potentials.

Finally, the connection between diatomic and metallic energetics which evolved from the discovery of universality is perhaps significant. We saw earlier that there was a good analogy between molecular bonding and bonding between metal surfaces. The kind of agreement exhibited in Fig. 10 strengthens and broadens this conclusion to include a rather close relationship between the general metallic bond and molecular bonds.

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