

## Universal binding-energy relation in chemisorption

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We have discovered a universal relationship between chemisorbed-atom-metal-substrate interaction energies and separation distances. For a variety of adatoms and substrates, the adatom binding energy as a function of the distance between the adatom and metal surface has been accurately determined by a simple scaling of the universal relationship. We also reveal an accurate, simple relationship between the electron-number density distributions at jellium surfaces and the bulk electron density.

Recently it has become possible to compute adatom binding energies as a function of the distance between the adatom and metal surface in an *ab initio* fashion.<sup>1-4</sup> Such calculations are difficult and quite rare, however. Moreover, energy-distance relationships for chemisorption cannot be obtained using modern experimental techniques. Such relationships would be very useful, however, because they are basic to surface energetics. For example, energy-distance relationships are central to the prediction of surface equilibrium atomic configurations and reaction kinetics.<sup>5</sup>

In the following, we provide evidence for the existence of a universal energy-distance relationship for chemisorption on jellium surfaces. We have found that every chemisorption binding-energy-distance relation computed to date—for a wide variety of adatoms—can be accurately obtained via a simple scaling of a universal relation which we provide. The equilibrium binding energy and the host (substrate) electron density at the equilibrium position of the adsorbate are the only necessary inputs.

Binding-energy-distance relationships in chemisorption have been computed for several adsorbates on jellium in a self-consistent, *ab initio* fashion. Hydrogen was first treated by Smith, Ying, and Kohn<sup>1</sup> using a linear-response-gradient expansion method. Subsequently, Kahn and Ying<sup>2</sup> 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<sup>3,4,6</sup> via a solution of the Kohn-Sham<sup>7</sup> equations. For a review of these calculations, see Ref. 8.

The variety of binding-energy-distance relationships for the different adsorbates is exemplified in

Fig. 1, where the results of Refs. 1 and 2 are given. The alkalis show a much slower variation with separation (distance between the adsorbate and jellium surfaces), than does hydrogen. Despite these apparent differences, we shall see that there is a universal relationship which links together these results and those of Refs. 3, 4, and 6. That is, all of these

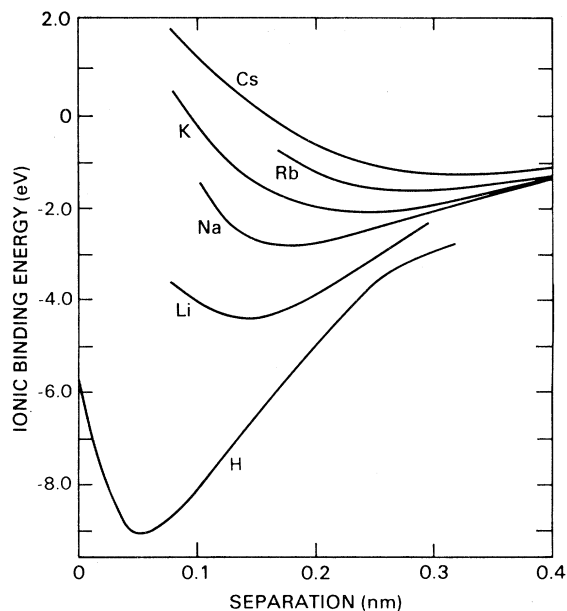


FIG. 1. Total energy of the adion plus substrate plotted against adion separation from the jellium surface. The (bulk) jellium  $r_s = 1.5$  a.u. The hydrogen results are from Ref. 1 and the alkali results are from Ref. 2.

results can be simply scaled onto a single curve.

The effective "size" of the adatom depends primarily on surface screening lengths. Longer screening lengths mean that the adatom samples the substrate surface potential distribution over a larger volume. The more rapid variations in the potential tend to be averaged out over a larger volume for the case of longer screening lengths. Conversely, it is plausible to expect adatoms which encounter shorter screening lengths when chemisorbed to effectively desorb or lose contact with the metal over a smaller separation range. That is, for these adatoms it would be expected that the atomic binding energy curves would rise to zero from the minimum or equilibrium position over a smaller range of separations. We will scale the adatom-jellium surface separation  $a$  by the Thomas-Fermi screening length  $\lambda = \frac{1}{3}(9\pi/4)^{1/3}r_{s1}^{1/2}$  a.u. where  $r_{s1}$  is determined from the clean surface electron density  $n_0$  at the equilibrium position of the adsorbate.<sup>9,10</sup> That is,  $r_{s1} = (3/4\pi n_0)^{1/3}$ .

In combining the results of Refs. 1-4 and 6 we take note of that fact that the authors of Refs. 1 and 2 computed ionic binding energy curves, while those of Refs. 3, 4, and 6 computed atomic 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.

We will scale the amplitudes of these atomic binding-energy curves by their respective values at the minima. The distance and amplitude scaling is then explicitly,

$$E(a) = \Delta E E^*(a^*) \quad (1)$$

Here  $a^* = (a - a_m)/\lambda$  and  $\Delta E = E(a_m)$ , where  $a_m$  is the equilibrium separation, so that  $\Delta E$  is the theoretical energy to remove the adsorbate to infinite separation as a neutral atom (atomic desorption energy).<sup>11-13</sup>  $E^*(a^*)$  is the scaled atomic binding energy function and the  $E(a)$  are the atomic binding functions computed by the authors of Refs. 1-4 and 6.

It remains to find  $n_0$  so that  $\lambda$  can be determined. To simply find  $n_0$ , we make note of an accurate scaling of electron number density distributions at clean jellium surfaces. We have solved<sup>14</sup> the Kohn-Sham<sup>7</sup> equations for jellium surfaces with densities appropriate to Al, Zn, Mg, and Na. We scaled the distance coordinate by the Thomas-Fermi screening length corresponding to the bulk  $r_s$  and the density amplitude by the bulk (jellium) density. As shown in Fig. 2, the scaled electron number density distributions

fall rather closely on a single curve in the region where the equilibrium positions of the chemisorbed particles lie, 0 to +3 a.u. This enables a simple determination of  $n_0$  for the substrates of interest by scaling back from the curve in Fig. 2. Alternatively, a simple relationship is shown to exist between the bulk electron density and the surface density distribution.

In Fig. 3 we plot the scaled atomic binding energies  $E^*(a^*)$ . One can see that the scaled binding energies fall closely on top of each other so that Eq. (1) becomes a universal binding energy relation for chemisorption. This is true despite there being a variety of adsorbates and four different substrate bulk electron densities. That, e.g., the hydrogen results should fall on top of the alkali results is truly remarkable given the differences evidenced in Fig. 1.

It is interesting that the different theoretical methods (i.e., linear-response-gradient-expansion method and the solution of the Kohn-Sham equations), used in Refs. 1-4 and 6 yield results which fall closely on a single curve. This would suggest that the apparent universality is not due to a particular theoretical approximation.

This is consistent with what we have found<sup>15</sup> for cohesive and adhesive binding. For those phenomena, using identical scaling procedures, we found universal adhesive and cohesive binding energy relations. The results that we scaled came from a variety of theoretical methods, which gives further evidence of the universality not being due to a particular theoretical method. In addition, the cohesive energy

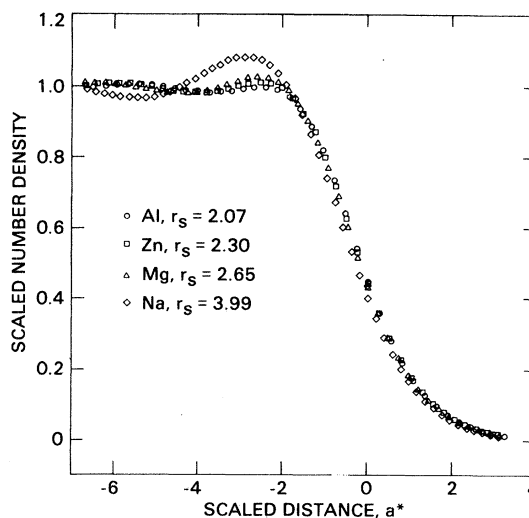


FIG. 2. Electron number densities at a jellium surface as a function of scaled coordinate perpendicular to the surface, where  $a^* = a/\lambda$  and  $\lambda$  is determined from the corresponding  $r_s$  value shown on the figure. The number density amplitudes are divided by the bulk density.

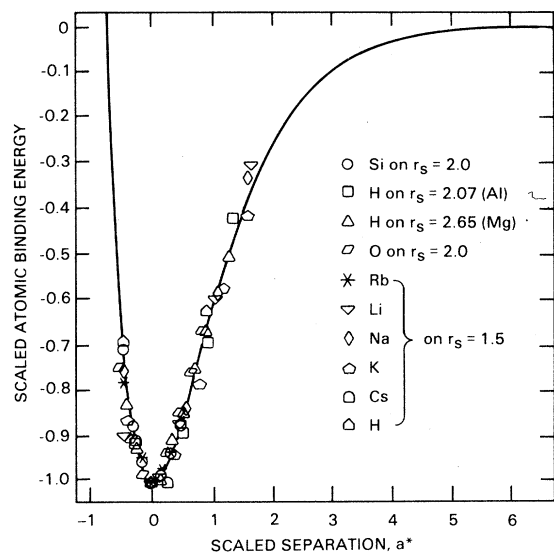


FIG. 3. Atomic binding energy curves for chemisorption on jellium surfaces scaled as described in the text. The jellium bulk densities are denoted by the corresponding  $r_s$  value listed in the figure. The O results are from Ref. 6, the H results on  $r_s = 2.07$  (Al) and  $2.65$  (Mg) are from Ref. 4, the Si results are from Ref. 3, the H results on  $r_s = 1.5$  are from Ref. 1, and the alkali results are from Ref. 2. The solid curve is drawn as an aid to the eye.

results included those from transition metals. This suggests that chemisorption on transition metals might fall within the universal character discussed here. A testing of this must await calculation of binding energy curves for chemisorption on transition metals.

Chemisorption binding energy curves on simple metal crystalline surfaces can be quite site dependent.<sup>16</sup> It is unlikely that one could scale the curves for different sites onto one universal curve. It would be interesting, however, to attempt to scale the

curves for different adsorbates on the same site onto a universal curve for each site merely from a knowledge of the electron densities at the equilibrium positions. The fact that universal adhesive and cohesive energy relations were found<sup>15</sup> for crystalline solids suggests that they might be found for chemisorption on crystalline surfaces. A predictive capability for these surfaces could be formulated as follows. There is increasing evidence that bond lengths for chemisorption on metal surfaces can be determined relatively simply to a reasonable accuracy. For example, by summing covalent radii<sup>17</sup> or by using Pauling's bond-length-bond-order relation<sup>18</sup> some authors have successfully predicted chemisorption bond lengths. Once we know the bond length, the electron density  $n_0$  due to the clean substrate at the site of the adsorbate can be approximated by overlapping atomic charge densities. The accuracy criterion is not too critical for  $n_0$  since it enters into  $\lambda$  as  $n_0^{1/6}$  as shown above. There are a number of clean surface charge distributions now in the literature,<sup>19</sup> and these could be used when available. An experimental test of this predictive procedure could be had by comparing predicted vibrational spectra with electron energy-loss data. When binding energy curves are computed for crystalline transitional metal surfaces (there are none available in the literature to our knowledge), then a direct theoretical test of universality can be made for transition-metal surfaces.

In summary, our results suggest that a universal relation exists for the binding energy as a function of the separation distance between a chemisorbing atom and a jellium surface. This universality has been seen to extend to a wide variety of adsorbates on substrates of several different bulk electron densities. In a subsequent, longer paper, we will present a more quantitative argument as to why one might expect to find such a universal relationship. Taking advantage of the simple, exponential form for the universal binding energy relation, we will present analytic relationships between observables such as adsorbate vibrational frequencies and desorption energies.

<sup>1</sup>J. R. Smith, S. C. Ying, and W. Kohn, Phys. Rev. Lett. **30**, 610 (1973); S. C. Ying, J. R. Smith, and W. Kohn, Phys. Rev. B **11**, 1483 (1975).

<sup>2</sup>L. M. Kahn and S. C. Ying, Surf. Sci. **59**, 333 (1976); see especially Fig. 2.

<sup>3</sup>N. D. Lang and A. R. Williams, Phys. Rev. B **18**, 616 (1978).

<sup>4</sup>H. Hjelmberg, Phys. Scr. **18**, 481 (1978).

<sup>5</sup>J. C. Tully, J. Vac. Sci. Technol. **18**, 427 (1981).

<sup>6</sup>J. K. Norskov and N. D. Lang, Phys. Rev. B **21**, 2131 (1980).

<sup>7</sup>W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

<sup>8</sup>Topics in Current Physics, *Theory of Chemisorption*, edited by J. R. Smith (Springer, New York, 1980), Vol. 19.

<sup>9</sup>The Thomas-Fermi screening length  $\lambda$  is thought to be rather inaccurate, but the only property important to the scaling is the proportionality between  $\lambda$  and  $r_s^{1/2}$ . It is known (Ref. 10) that more accurate expressions for screening lengths retain the proportionality to  $r_s^{1/2}$ .

<sup>10</sup>See, e.g., S. Raimes, *Wave Mechanics of Electrons in Metals* (North-Holland, Amsterdam, 1967), especially Eq. 10.85, p. 305.

<sup>11</sup>For the alkali results of Ref. 2,  $E(a_m)$  was obtained by adding  $I - \phi_e$  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 adsorbate and  $\phi_e$  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. 1 and 2, we took  $\phi_e = 3.88$  eV. The authors are indebted to N. D. Lang for providing us with this value for the work function, which he obtained by solving the Kohn-Sham equations.

<sup>12</sup>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  $I - \phi_e$  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. 13).

<sup>13</sup>See, e.g., T. E. Madey and J. T. Yates, Jr., *Structure et Propriétés des Surfaces des Solides* (Editions du Centre Na-

tional de la Recherche Scientifique, Paris, 1970), No. 187, p. 155.

<sup>14</sup>John Ferrante and John R. Smith, Phys. Rev. B 19, 3911 (1979).

<sup>15</sup>J. H. Rose, John Ferrante, and John R. Smith, Phys. Rev. Lett. 47, 675 (1981).

<sup>16</sup>O. Gunnarsson, H. Hjelmberg, and B. I. Lundquist, Phys. Rev. Lett. 37, 292 (1976).

<sup>17</sup>J. C. Buchholz and G. A. Somorjai, Acc. Chem. Res. 9, 333 (1976).

<sup>18</sup>K. A. R. Mitchell, Surf. Sci. 100, 225 (1980).

<sup>19</sup>See, e.g., J. G. Gay, J. R. Smith, F. J. Arlinghaus, and T. W. Capehart, Phys. Rev. B 23, 1559 (1981).