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Approach to Alkali-Metal Chemisorption within the Anderson Model*

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A theory of chemisorption relevant to alkali atoms on metal surfaces is presented. The virtual-impurity-state problem is modeled in the manner presented by Kjöllerström, Scalapino, and Schrieffer for solving the Anderson impurity problem in the low-density approximation (LDA). It is assumed that the binding or chemisorption energy of the alkali metal is composed of two parts, a metallic and an ionic component. Since considerable charge transfer from the alkali atom to the metal occurs, the LDA is appropriate for describing the metallic part of the binding . Another consequence of the large charge transfer is that the major portion of the binding results from an ionic type of bond between the partially charged alkali ion on the surface and a polarization or screening charge inside the metal. The results of the theoretical calculations indicate that binding energies for alkali atoms adsorbed on clean single-crystal faces of metals generally fall with in the range of 1.5–2.5 eV, in accord with available experimental data on metals such as W, Mo, Ta, and Ni.

I. INTRODUCTION

Since Taylor and Langmuir's[1] classic work in which they studied the electronic properties of tungsten surfaces coated with partial cesium monolayers, the importance of alkali adsorption on metal surfaces has gained widespread recognition. It was found that the formation of roughly 0.6–0.7 of a monolayer of cesium on the tungsten surface caused the work function of the system to be reduced by as much as 3 eV. Subsequent experimental studies using various techniques (for example, thermionic, photoelectric, contact potential, and field emission) have both substantiated the original findings and built up an increasing quantity of reliable data on the electronic properties of single-crystal metal surfaces covered by adsorbed alkali-metal monolayers.[2–7] With the enhanced production of experimental data on these systems it has become increasingly important to have an acceptable theoretical framework in order that the data can be understood in a systematic manner.[8–11]

A critical review of most of the theoretical work on chemisorption prior to 1967 has been given.[12,13] Since this review, additional work has been done on chemisorption which is of importance to the present study.[14–21]

The basic ideas which seem most relevant to alkali-metal chemisorption are those pioneered by Gurney,[8] extended by Gomer and co-workers,[3] and developed further by others.[9–11] Within this school of thought, an alikali adsorbate is viewed as an ion with a virtual state, derived from the valence level, broadened and shifted by a configuration type of interaction with the continuum of metal states. The position of the virtual level on an energy-level diagram, relative to the occupied portion of the metal conduction band, determines the charge state of the impurity[10] or, equivalently, the type of chemical bond formed between the alkali and the metal.[11] This is analogous to the Anderson impurity, which may possess a localized magnetic moment.[22–25] In Fig. 1 the effective metal and virtual-impurity-level density of states are shown, both for the Anderson magnetic impurity and a hypothetical magnetic chemisorbed alkali adatom. The localized magnetic moment can occur if the splitting between

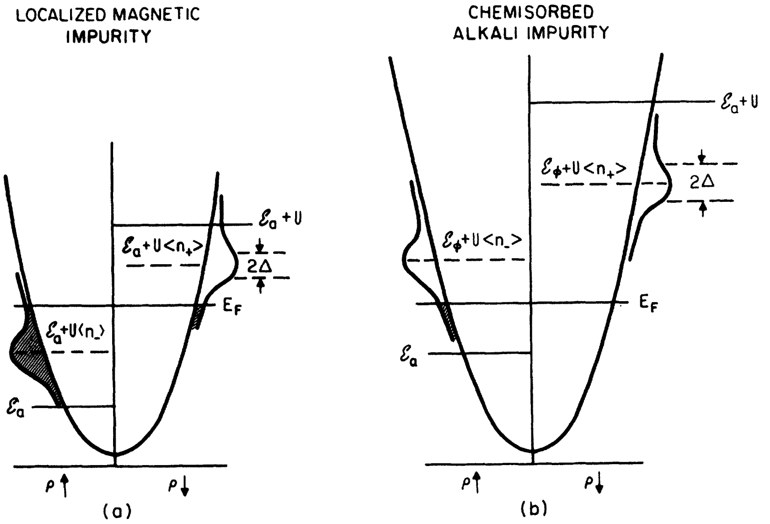

FIG. 1. (a) Density-of-states distributions for a magnetic impurity. The monotonic parabolic curve is a free-electron metal density of state. (b) Density of states for an electropositive adsorbate. The area in the cross-hatched section is the amount of electron charge on the adsorbate. The case of a low-density magnetic impurity is shown. A nonmagnetic impurity has $\langle n+\rangle = \langle n-\rangle$, so the two bell-shaped curves would then coincide in energy.

a spin-up and a spin-down level is sufficient to cause one level to be mostly below the Fermi energy and the other level mostly above. On the other hand, alkali chemisorption is characterized by both spin levels lying sufficiently above the Fermi level, so that the alkali adatom has lost most of its electron charge to the metal energy states at the Fermi level, and hence a fractionally charged ion results, in analogy with a localized magnetic moment whose magnitude is a fraction of a Bohr magneton. As a result of the low net electron charge on the adatom, past theory has been content to neglect any magnetic effects that might be associated with the alkali surface impurity and was formulated within an effective single-electron approximation in which spin properties were not introduced.[3,10,11]

The picture adopted in the present work is the following. The alkali surface impurity is regarded as an ionic impurity of nonintegral charge number due to the broadening and shifting of the virtual level. The effective adatom density of states has been observed in resonance tunneling experiments and has been interpreted in terms of the parameters characterizing the virtual impurity level (or scattering resonance), the position and width of the state on the atom-metal energy-level diagram.[26] Although, for experimental reasons, the measurements have been done on alkaline-earth rather than alkali-metal atoms, we feel that there is sufficient resemblance to allow certain rather general conclusions to be made concerning the alkali atoms based on both the experimental results in the alkaline-earth studies and past theoretical calculations on the alkali adsorption problem.[10,11,21] The major conclusion we shall use from these studies is that for chemisorbed atoms, such as Na, K, and Cs on metal substrates, the valence level of the atom is shifted upwards by 0.5–1.0 eV and achieves a width of about 0.3–1.5 eV. Considering that most metal surfaces have work functions between ~4.2 and 5.0 eV and that the ionization potentials of the cited alkali-metal atoms are in the range 3.9–5.1 eV, it is seen that the shifted level of the alkali atom will tend to be above the Fermi level of the metal. Only a small amount of overlap (or shared electron bonding) between the virtual state and the metal conduction band will occur owing to the finite width of the impurity level. Thus a small fraction of an electron charge will reside in the immediate neighborhood of the ion core ($\lesssim 0.25e$) and an ion with an effective charge number $Z_{\text{eff}} \gtrsim 0.75$ will exist on the surface polarizing the electrons in the conduction band. A spin-independent formulation of this model has been successful in providing numerical results of dipole moments for various combinations of atoms, metals, and crystal faces which are in reasonably good agreement with the experimentally determined values.[5,11] Here we will set up the procedure for calculating binding energies for alkali-like atoms on metal surfaces. The expressions will be obtained as a function of some undetermined hopping and overlap matrix elements. These formulas will be numerically evaluated for some reasonable choices of these parameters.

The plan and goals of the present paper are as follows. In Sec. II the self-consistent solutions to the Anderson Hamiltonian are obtained. The impurity charge is such that the appropriate solutions to the Anderson Hamiltonian tend to the nonmagnetic low-density-approximation (LDA) solutions given by Schrieffer and Mattis.[23] In Appendix A some problems associated with the utilization of an Anderson type of Hamiltonian for surface impurities are discussed. With LDA solutions and the results derived in Appendix A, the procedure of Kjöllerström, Scalapino, and Schrieffer (KSS)[24] is used to obtain an expression for the nonionic part of the binding energy of the surface impurity in Sec. III. A method for treating the ionic part of the binding energy based upon the results of detailed microscopic theories of dielectric screening in the surface region of an electron gas is provided in Sec. IV.[17–19,27] The results of model calculations for binding energies as a function of various combinations of system parameters such as the virtual-impurity-level position and width, the substrate work function, the electron affinity of the impurity atom, and the electron density in the conduction band are given in Sec. V together with a general synopsis and conclusions.

II. ANDERSON MODEL

The type of surface impurity or adsorbed atom and metal combination we shall consider is that system which is adequately described by the model Hamiltonian

$$H=\sum_{\lambda,\sigma}\epsilon_{\lambda\sigma}n_{\lambda\sigma}+\sum_{\sigma}\epsilon_{a\sigma}n_{a\sigma}+\sum_{\lambda,\sigma}(V_{\lambda a}c^{\dagger}_{\lambda\sigma}c_{a\sigma}+\text{H. c.})+Un_{a+}n_{a-}\ , \qquad (1)$$

where $c^{\dagger}$ and c are the Fermi creation and destruction operators, H.c. is the Hermitian conjugate, and $n_{\lambda\sigma}=c^{\dagger}_{\lambda\sigma}c_{\lambda\sigma}$ and $n_{a\sigma}=c^{\dagger}_{a\sigma}c_{a\sigma}$. Since Eq. (1), often referred to as the Anderson Hamiltonian, has been discussed at length in the literature,[16,22–25] we will only explain here the notation and quote the end results in the cited papers which will be required in the present description of alkali chemisorption. In the occupation number representation, Eq. (1) describes a continuum of metal states specified by the set of quantum numbers λ and spin σ with unperturbed eigenvalues $\epsilon_{\lambda\sigma}$. For example, in semi-infinite jellium, the quantum number $\lambda=(\vec{k}_T, |k_z|)$ with $\vec{k}_T$ the k vector transverse to the surface normal and $|k_z|$ the magnitude of the k vector normal to the surface. (This point is discussed in detail in Appendix A.) The alkali atom is characterized by a ground-state energy $\epsilon_{a\sigma}$ which may include static-potential-induced shifts in the energy level. All energies are measured relative to a zero at the Fermi level of the metal. The strength of the coupling between the discrete atomic state and the continuum of metal states is determined by the hopping integral

$$V_{\lambda a}=\int d^3r\,\psi^{*}_{\lambda}(\vec{r})\,V_m(\vec{r})\psi_a(\vec{r})\ , \qquad (2)$$

with ψ^{*}_{λ} being a metal eigenfunction, ψ_a an atomic wave function, and V_m an effective single-electron potential for the entire system of the metal plus atom, determined self-consistently. In the surface region, the single-electron potential of the metal would be similar to previously calculated surface potentials for perfect surfaces[28–30] modified to account for the presence of the impurity ion core. The last term in Eq. (1) represents an approximation to electron-electron correlation effects on the impurity site. Within the Hartree-Fock theory, this term is given by the Coulmob repulsion between spin-up and spin-down electrons,

$$U_{\text{HF}}=\int d^3r_1\,d^3r_2\,\psi^{*}_{a+}(\vec{r}_1)\psi^{*}_{a-}(\vec{r}_2)\times(e^2/|\vec{r}_1-\vec{r}_2|)\psi_{a+}(\vec{r}_1)\psi_{a-}(\vec{r}_2)\ . \qquad (3)$$

For an isolated single-electron-like atom, Eq. (3) represents the amount of energy in excess of the ionization potential needed to add a second electron to the atom in the Hartree-Fock approximation, and as such should be simply related to the electron affinity A and ionization potential V_i through $U=V_i-A$.[31] A direct calculation using Eq. (3) gives too large results, at least for hydrogen chemisorption, so Newns chose to redefine an effective Coulomb integral.[16] One would expect a somewhat smaller value of U for the "impurity problem" compared to the "atom problem" owing to screening effects in or on the solid. Because of the usually assumed properties of alkali-metal chemisorption on transition-metal surfaces (substantial charge transfer from the atom to the metal occurs), we consider that the LDA of Schrieffer *et al.*[22–25] most realistically treats the impurity-state correlation effects. As will be seen shortly, the LDA is used to define an approximate correlated Coulomb integral called U_{eff}.

In either the Hartree-Fock or Schrieffer-Mattis treatment, the correlation term is treated as an average self-energy in the sense that

$$\Sigma^{(\sigma)}(\omega)\equiv U\langle n_{a-\sigma}\rangle\ , \qquad (4)$$

so that the possibly spin-dependent unperturbed impurity eigenvalue is $\epsilon_{a\sigma}+\Sigma^{(\sigma)}(\omega)$. Allowing an impurity electron characterized by this energy to couple with the continuum of metal states via the hopping integral of Eq. (2) and treating this coupling in the manner prescribed by Anderson[22] and by KSS,[24] we can identify a spin-dependent virtual impurity Green's function

$$G^{\sigma}_{aa}(\omega)=\left(\omega-\epsilon_{a\sigma}-\Sigma^{(\sigma)}(\omega)-\sum_{\lambda}\frac{|V_{\lambda a}|^2}{\omega-\epsilon_{\lambda}+i\delta}\right)^{-1}=[\omega-\epsilon_{\phi}-\Sigma^{(\sigma)}(\omega)+i\Delta\,\text{sgn}\omega]^{-1}\ . \qquad (5)$$

The half-width of the virtual level is given by $\Delta=\pi\sum_{\lambda}\delta(\omega-\epsilon_{\lambda})|V_{\lambda a}|^2$. As a result of the perturbation of the metal on the atom, the center of the atomic band is shifted such that $\epsilon_{\phi}=\epsilon_{a\sigma}+\Delta\epsilon_m$. To the order we are working we have

TABLE I. Impurity energy-level nomenclature.

$\epsilon_{a\sigma}=\phi_e-V_i+\Delta\epsilon_1$:	Atomic state energy relative to Fermi level
$\Delta\epsilon_1$:	Static-potential-induced shift in atomic energy level due to such forces as the image charges
$\Delta\epsilon_m$:	Shift in real part of the atomic level due to the $V_{\lambda a}$ mixing; equal to zero if $\Delta\neq\Delta(\omega)$
$\epsilon_\Phi^\sigma=\epsilon_{a\sigma}+\Delta\epsilon_m$:	Impurity energy level before correlations at impurity site have been taken into account
$E_\Phi^\sigma=\epsilon_\Phi^\sigma+U_{\text{eff}}\langle n_{a-\sigma}\rangle$:	Impurity-virtual-state center of gravity including on-site correlations
$\Sigma^{(\sigma)}(\omega)=U_{\text{eff}}\langle n_{a-\sigma}\rangle$:	Correlations self-energy at impurity site

$$\Delta\epsilon_m=P\sum\nolimits_\lambda |V_{\lambda a}|^2/(\omega-\epsilon_\lambda)\ .$$

The first-order shift in the energy $\Delta\epsilon_1$ resulting from placing the atom in the self-induced field at the metal surface has been absorbed into $\epsilon_{a\sigma}$. This term has been explained in detail previously.[11,21,26] The term $\Delta\epsilon_m$ is a shift due to the real part of the self-energy and is equal to zero when one assumes that Δ is a constant. The density of states associated with each virtual impurity level of spin σ is

$$\rho_{aa}^{(\sigma)}(\omega)=-(1/\pi)\,\text{Im}G_{aa}^{(\sigma)}(\omega)$$

$$=\frac{1}{\pi}\frac{\Delta}{[\omega-\epsilon_\phi-\Sigma^\sigma(\omega)]^2+\Delta^2}\ . \tag{6}$$

At zero temperature, the total electronic charge on the impurity is

$$\langle n_{\text{tot}}\rangle=\sum_\sigma\int_{-\infty}^{0}\rho_{aa}^{(\sigma)}(\omega)\,d\omega$$

$$=\frac{1}{\pi}\left[\cot^{-1}\left(\frac{E_\Phi^+}{\Delta}\right)+\cot^{-1}\left(\frac{E_\Phi^-}{\Delta}\right)\right]\ , \tag{7}$$

where the Fermi level has been taken as the zero of energy. Here $E_\Phi^\sigma=\epsilon_{a\sigma}+U\langle n_{a-\sigma}\rangle+\Delta\epsilon_m$ with $\epsilon_{a\sigma}$ given by $\phi_e-V_i+\Delta\epsilon_1$, ϕ_e is the metal work function, and V_i is the first ionization potential of the isolated impurity atom. For convenience, a list of the energy-level nomenclatures is given in Table I.

As a result of the host-induced mixing between the "up" and "down" states, the lower-energy spin-up state is shifted upwards an amount $U\langle n_{a-}\rangle$ because of its repulsive interaction with the partially occupied spin-down state as shown in Fig. 1(b). (Note that since there are no magnetic fields, the up and down directions are quite arbitrary.) On the other hand, the spin-down state, whose energy is U above the energy of the spin-up electron in an isolated atom, is shifted downwards from the affinity level an amount $U(1-\langle n_{a+}\rangle)$ owing to the fact that the lower-energy level does not become totally occupied before the spin-down level begins filling. Hence, the repulsive electron-electron interaction felt by the higher-energy "bound" electron is not as great as when the atom is isolated. Consequently, the energy is somewhat lowered when the atom is adsorbed. Newns,[16] Schrieffer and Gomer,[20] and Gomer and co-workers[3] have indicated that such an effect could result in the apparent formation of a single virtual level in chemisorption, lying about halfway between the electron affinity level and the ionization potential. In the sense that the sum $\rho_{aa}(\omega)=\sum_\sigma\rho_{aa}^{(\sigma)}(\omega)$ obtained from Eq. (6) appears as a singly peaked distribution, this is correct. Within the context of the theory of Newns,[16] a level with a Lorentzian shape will occur halfway between the spin-up and -down levels only when one has a system which is adequately represented by a nonmagnetic ($n_+=n_-$) nonionic Hartree-Fock solution to the Anderson model. Since recent interpretations of oxygen chemisorption experiments, for example, have suggested that a single level may exist midway between the ionization potential and the electron affinity, this point should be considered further.[32]

When the total electron charge on the adsorbate, given by Eq. (7), is quite small ($\langle n_{\text{tot}}\rangle\lesssim 0.25$), the LDA of Schrieffer and Mattis[23] would be expected to describe electron-electron correlation effects on the impurity site more accurately than the Hartree-Fock approximation, whose physical consequences were discussed in the preceding paragraph. For a detailed discussion, the reader is referred to the original papers by Anderson[22] and by Schrieffer and co-workers[23–25] on the LDA application. For present purposes in the LDA, for choices of the parameters U and Δ relevant to alkali chemisorption, no magnetic solutions to the virtual-impurity-state problem exist. Furthermore the intra-atomic Coulomb integral Eq. (3) is replaced by an effective potential[23,24]

$$U_{\text{eff}}=U/[1+U\phi(0)]\ ,$$

with

$$\Phi(0)=\frac{1}{\pi(E_\Phi^++E_\Phi^-)}\left[\tan^{-1}\left(\frac{E_\Phi^+}{\Delta}\right)+\tan^{-1}\left(\frac{E_\Phi^-}{\Delta}\right)\right]$$

$$=\frac{1}{\pi E_\Phi}\tan^{-1}\left(\frac{E_\Phi}{\Delta}\right)$$

and

$$E_\Phi^+=E_\Phi^-\ .$$

The set of equations which must be solved self-consistently to obtain the nonmagnetic LDA description of an adsorbed alkali-atom impurity is thus

$$n_a = \frac{1}{\pi} \cot^{-1}\left(\frac{\epsilon_\phi + U_{\text{eff}} n_a}{\Delta}\right) \tag{8}$$

and

$$U_{\text{eff}} = U \Big/ \left[1 + \frac{U}{\pi(\epsilon_\phi + U_{\text{eff}} n_a)} \tan^{-1}\left(\frac{\epsilon_\phi + U_{\text{eff}} n_a}{\Delta}\right)\right] , \tag{9}$$

where use has been made of the fact that $n_{a+} = n_{a-} = n_a = \frac{1}{2} n_{\text{tot}}$ [see Eq. (7)]. Typically for alkali-atom chemisorption, ϵ_ϕ falls in the range $0.3 < \epsilon_\phi < 2.0$ eV since the ionization potential of the alkalis varies from ≈ 4 to 5 eV, $\phi_e \approx 4.5$ eV, and $\Delta\epsilon \approx 1$ eV, as noted both through calculations[11,21] and through resonance tunneling experiments.[26] For similar reasons, we expect the level width to fall within the range $0.3 \lesssim \Delta \lesssim 1.0$ eV for s levels of adsorbed alkali atoms at low surface coverage. (Note that the level width is $\Delta = \frac{1}{2}\Gamma$, where Γ is the width parameter used in some past work.[3,11]) Finally, the electron affinity of alkali atoms is about 1 eV.[31] Thus, the redefined Coulomb integral U_{eff} falls in the range $2.5 \lesssim U_{\text{eff}} \lesssim 4.0$ eV.

Physically electron-electron correlations on the alkali impurity result in the following situation. If the charge state is such that the LDA is valid, then the Coulomb self-energy Σ which is proportional to the electronic charge is not sufficiently repulsive to keep an electron of spin σ off the site if one of spin $-\sigma$ is already there. Thus there is no preferred spin and a nonmagnetic state occurs in which $\langle n_+ \rangle = \langle n_- \rangle$. The adatom density of states for spin-up and spin-down states occurs at the same energy $(\epsilon_\phi + U\langle n_a \rangle)$. The two Lorentzian curves in Fig. 1(b) line up, but not midway between ϵ_a and $\epsilon_a + U$. The integrated area under the "double-level" density of states will include two electrons. However, since the energy level is raised by the $U\langle n_a \rangle$ term, the total charge occupation on the adatom is not necessarily larger. In the so-called single-electron approximation (SE) used in the past,[10,11] the charge on the adsorbate is given by

$$\langle n_{\text{tot}} \rangle_{\text{SE}} = (1/\pi)\cot^{-1}(\epsilon_\phi/\Delta) ,$$

whereas the nonmagnetic LDA solution to the Anderson impurity gives the total adsorbate electron charge as

$$\langle n_{\text{tot}} \rangle_{\text{LDA}} = \frac{2}{\pi} \cot^{-1}\left(\frac{\epsilon_\phi + \frac{1}{2} U_{\text{eff}} \langle n_{\text{tot}} \rangle_{\text{LDA}}}{\Delta}\right) .$$

Thus, although we are dealing with a nonmagnetic solution of the Anderson problem, spin-correlation effects do have a definite effect on the energy levels and thus the charge state of the chemisorbed atom. This is a definite distinction from the results of the single-electron impurity theory.

A useful equation is formed by combining Eqs. (8) and (9) to yield

$$\frac{\Sigma}{\Delta} = \frac{\cot^{-1} y}{p^{-1} + y^{-1} \tan^{-1} y} , \tag{10}$$

with $y = (\epsilon_\phi + \Sigma)/\Delta$. Treating the quantity $p \equiv U/\pi\Delta$ parametrically, we have drawn Eq. (10) in Fig. 2, choosing appropriate ranges of p and y for alkali chemisorption. This result is useful in that it shows the manner in which the virtual-level position changes as a result of electron correlation effects at the impurity site. For example, we should know the value of U from either known values of V_i and A or from independent calculations for a given alkali atom. It is presumed that the level could be observed in a resonance tunneling experiment from which the experimental value of y and Δ would be immediately obtainable. Since we know y, Δ, U, and thus p, Eq. (10) allows us to ascertain the correlation self-energy. Alternatively, a completely theoretical approach is possible. Techniques for calculating approximate values of ϵ_ϕ and Δ have been put forth.[10,11,21] Thus, Eq. (10) could be solved self-consistently to obtain the value of Σ resulting from a given set of values for ϵ_ϕ, Δ, and U. We will demonstrate in Sec. V how to use the results of Fig. 2 to obtain an explicit calculation.

III. METALLIC CHEMISORPTION

The conceptual viewpoint of the present approach to alkali chemisorption is that the bond formed between the atom and the metal can be divided into an ionic part and a metallic part, somewhat in analogy with Pauling's approach[33] to chemical bonding in molecules. The fact that charge transfer is large in the cases considered here suggests that the principal contribution to the binding energy of a chemisorbed alkali atom arises from ionic-type bonds, in direct opposition to either transition-metal[14] or hydrogen adsorption[16,20] in which it is assumed that strong covalent bonds are formed. Because of the prominence of the ionic bonding, limited considerations have been given to a quantitative description and estimate of the energy associated with the metallic portion of the metal-alkali bond. This part of the bond energy, which might be called a delocalization energy, results from allowing the valence electron of the alkali to spread throughout the metal and the metal electrons to spread a bit into the region of the alkali atom. In this way the kinetic energies of all electrons are reduced by relaxing slightly the geometric confinement of both the metal and atomic electrons.

In the work of KSS,[24] they consider the energy associated with an impurity atom in a dilute alloy. An expression for the energy which is related to the metallic portion of the chemisorption energy is

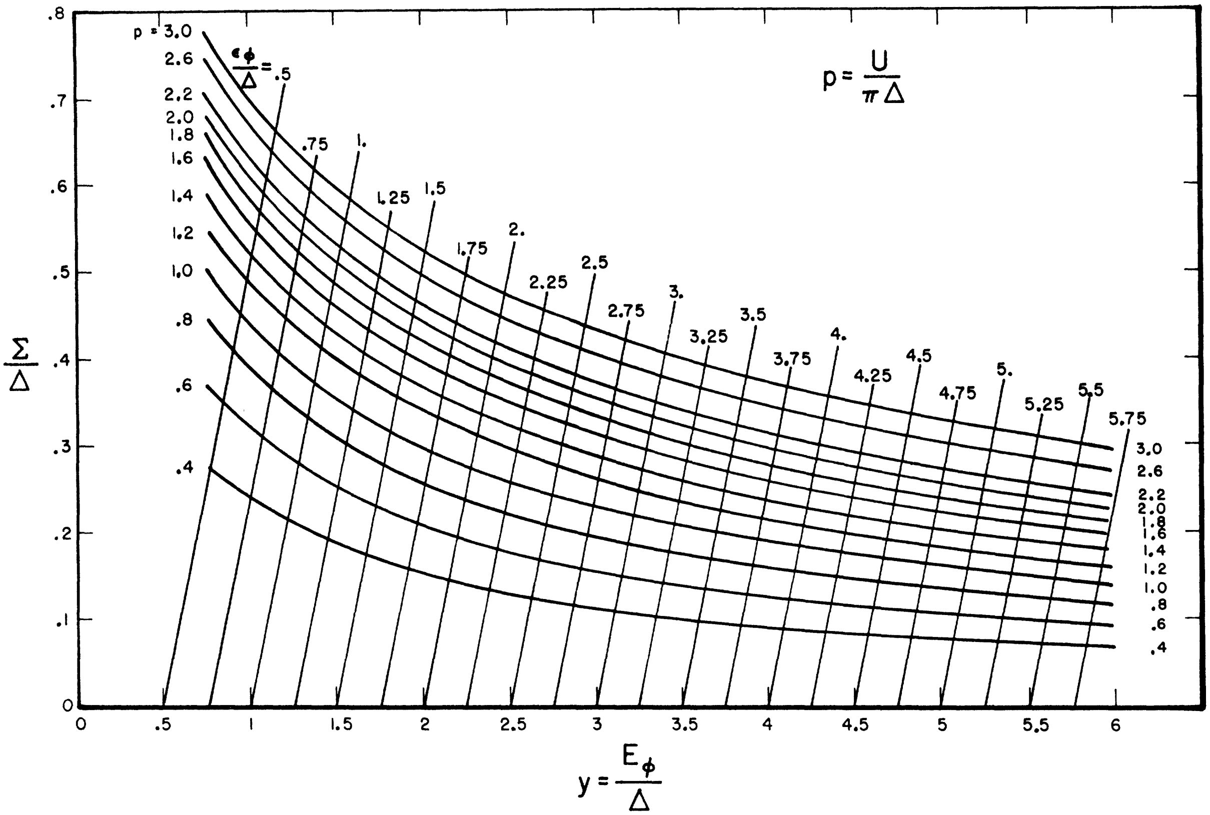

FIG. 2. Master curve from which self-consistent solutions to the virtual impurity state, in the LDA, are obtainable.

given as

$$E_M(s)=\frac{1}{2\pi i}\sum_\sigma \oint (\omega-\tfrac{1}{2}U_{\mathrm{eff}}\, n_{a-\sigma})G^\sigma_{aa}(\omega)\,d\omega\ . \qquad (11)$$

The contour is such that it encloses the occupied states below the Fermi level. By folding the contour as described by KSS,[24] Eq. (11) takes a more obvious form. Realizing that for a well-behaved function $f(\omega)$ with no poles in the upper half-plane we have

$$\frac{1}{2\pi i}\oint f(\omega)G^\sigma_{aa}(\omega)\,d\omega=\frac{1}{\pi}\int_{-\infty}^{0} f(\omega)\,\mathrm{Im}G^\sigma_{aa}(\omega)\,d\omega\ , \qquad (12)$$

and using Eq. (6) for the impurity-level Green's function or density of states, Eq. (11) becomes

$$E_M(s)=\sum_\sigma \int_{-\infty}^{0} \omega\rho^\sigma_{aa}(\omega)\,d\omega-U_{\mathrm{eff}}\,n_{a+}n_{a-}\ . \qquad (13)$$

As discussed by KSS,[24] a problem arises when the Lorentzian impurity density of states given by Eq. (6) is used in Eq. (13) if Δ and Σ are considered to be constant. Under these circumstances, the non-ω-dependent lifetime Δ does not drop off fast enough to eliminate the ω term in the numerator as ω approaches $-\infty$. Either of two possible resolutions of this problem can be used here. The level width can be written as

$$\Delta(\omega)=\pi\rho_\lambda(\omega)\,|V_{\lambda a}(\omega)|^2\ ,$$

where both the host-conduction-band density of states ρ_λ and the hopping integral $V_{\lambda a}$ given by Eq. (2) are taken to be ω dependent. In this section we will assume $V_{\lambda a}=$ const, and take as an approximation

$$\rho_\lambda(\omega)=0 \ \text{ for } \omega<-E_F$$
$$=\rho_0 \ \text{ for } \omega\geq E_F\ ,$$

with ρ_0 a constant. This simply says that the impurity lifetime is influenced only by the allowed energy states in the metal. This is not an unreasonable picture. An alternative approximate treatment, in which an energy-dependent hopping integral is used, is discussed in Appendix B. Since the numerical results of either treatment are coincidentally quite similar, we will consider that the simpler approximation is valid within the uncertainty limits of our model.

In the case of ionic chemisorption, the initial state is an alkali ion and a metal separated by an infinite distance. The final state is an interacting alkali adatom and metal separated by an equilibrium distance s. Hence, using the Lorentzian impurity density of states, given by Eq. (6), and the metal density of states cut off at the bottom of the conduction band, the metallic chemisorption energy derived from Eq. (13) can then be expressed as

$$\begin{aligned} E_M &\equiv E_M(s) - E_M(\infty) \\ &= \sum_\sigma E_\phi^\sigma n_{a\sigma} - U_{\text{eff}}\, n_{a+} n_{a-} + \sum_\sigma \frac{\Delta}{2\pi} \ln\left(\frac{(E_\phi^\sigma)^2 + \Delta^2}{(E_F + E_\phi^\sigma)^2 + \Delta^2}\right) \\ &= \epsilon_\phi \langle n_{\text{tot}}\rangle + \tfrac{1}{4} U_{\text{eff}} \langle n_{\text{tot}}\rangle^2 + \frac{\Delta}{\pi} \ln\left(\frac{E_\phi^2 + \Delta^2}{(E_F + E_\phi)^2 + \Delta^2}\right) \end{aligned} \tag{14}$$

since we are adsorbing an ion and $\Delta \to 0$ when the metal and alkali adatom are separated. No explicit mention of the metal electrons has been made since they just contribute a constant energy to both the initial and final configurations, and hence the terms cancel in Eq. (14). Detailed numerical consequences of Eq. (14) will be given in Sec. V.

IV. IONIC CHEMISORPTION

In recent work, the physical picture of a massive point impurity inducing a screening charge within the surface region of the metal electron gas has been a useful approximation for ionic bonding.[17–19,27] In previous work, the ionic bond was described mostly within the context of the classical image force approximation.[1,9,12] Physically, this is equivalent to describing ionic adsorption on a perfect conductor, a reasonable approximation when the charge center is much further than a few inverse Fermi wave numbers from the surface. However, for ionic adsorption, the ion is about an ionic radius (~1.0–2.5 Å) from the surface, which is the same order of size as the characteristic screening distance. Thus, a means of treating finite dielectric screening effects in a nonuniform electron gas is required.

One rather useful simplification has emerged from the detailed microscopic theories of screening in the surface region.[17–19] As suggested by Gomer and Swanson,[3a] the corrections to the classical image force due to finite screening in a real metal can be handled in a reasonably easy manner. Essentially, they redefined the position of the effective image plane. The mathematical surface is depressed into the metal by an amount equal to some screening length. Hence, the classical image attraction of a charge Ze a distance s from the surface and given by $V_{\text{im}}^0 = (Ze)^2/4s$ is replaced by $V_{\text{im}} = (Ze)^2/4(s + k^{-1})$ when k is defined appropriately as the screening parameter. Newns[19] has shown that this procedure gives a very good representation of the true potential once a satisfactory expression for the screening length is obtained. Gadzuk[17] has shown how a screening parameter, based upon a detailed microscopic theory, can be obtained. On the basis of these analyses, the appropriate screening lengths are given by $k_s^{\text{Gomer}} = k_{\text{FT}}$, $k_s^{\text{Newns}} = \frac{4}{3} k_{\text{FT}}$, and $k_s^{\text{Gadzuk}} \approx 0.9 k_{\text{FT}}$. Here k_{FT}, the Fermi-Thomas screening length, is given by $k_{\text{FT}} = (6\pi n e^2/E_F)^{1/2} = 2.95/r_s^{1/2}$ Å^{-1}, $n =$ No. electrons/volume $= (\frac{4}{3}\pi a_0^3 r_s^3)^{-1}$, and a_0 is the Bohr radius. In using this result, the atom-metal separation s could be less than the particle radius.[11,17] This arises from the fact that an impurity at the surface of an electron gas bounded by an infinite potential can be considered to be equivalent to an impurity ≈0.3–1.0 Å away from the surface of an electron gas bounded by a finite potential of depth ≈10 eV. Using these screening results, a method is presented in which the ionic part of the chemisorption energy can be calculated when account is taken of the fact that the effective charge on the ion is a rapidly varying function of position due to the shifting and broadening of the alkali valence level.

In applying the modified image potential to a theory of alkali-atom chemisorption, another important point must be considered. In the preceding paragraph the ionic binding energy associated with bringing a unit of charge infinitely far removed from the metal up to a distance s from the surface has been described. It is apparent either physically or from Eq. (8) that the amount of electron charge centered around the impurity in a virtual bound state is strongly dependent on the separation and thus the energy-level spectrum. An alkali ion far from the surface has a net charge $Z_{\text{eff}}(\infty) = 1$. However, as the atom is brought to the surface, the sharp state broadens and overlaps a bit with the conduction band such that the effective charge of the ion is now a function of separation $Z_{\text{eff}}(s) = 1 - 2n_a(s)$ with $n_a(s)$ given by Eq. (8).

The classical image potential energy is derived in the following manner. If a charge $Z_{\text{eff}}\, e$ is a distance s' from a perfect-conductor surface, then the electric field of the test charge plus the induced screening charge will be such that the $s' + k_s^{-1} = 0$ plane is an equipotential surface. The resulting field will be that which would result if a negative image of $-Z_{\text{eff}}\, e$ were formed a distance $s' + k_s^{-1}$ into the metal. Consequently, the attractive force between the test charge and its image is $F(s') = -Z_{\text{eff}}^2 e^2/4(s' + k_s^{-1})^2$. The work or change in energy to bring the charge from $s'=\infty$ to $s'=s$ is, accordingly,

$$W=-e^2\int_s^\infty \frac{Z_{\text{eff}}^2(s')\,ds'}{4(s'+k_s^{-1})^2} \ . \tag{15}$$

Now we must examine the variation of Z_{eff} with s'. Here we will take a reasonable but approximate approach to the dependence of Z_{eff} on s'. The Z_{eff} is given by

$$Z_{\text{eff}}(s')=(2/\pi)\tan^{-1}[E_\Phi(s')/\Delta(s')] \ . \tag{16}$$

Since $E_\Phi(s')$ is a much more slowly varying function of s' than $\Delta(s')$, we will assume that it is approximately constant in the above relationship. The broadening Δ results from electrons tunneling through the barrier assumed to exist between the adsorbate and the substrate.[3,8-11] Thus, we would expect the width or tunneling probability to be proportional to an exponential of the usual WKB-type phase integral

$$\int_0^{s'} k(z)\,dz \approx [(2m/\hbar^2)\phi_e]^{1/2}s' \ .$$

As a simple approximation

$$\Delta(s')\approx\Delta_0\exp\{-2[(2m/\hbar^2)\phi_e]^{1/2}(s'-r_i)\} \ , \tag{17}$$

where ϕ_e is the work function of the metal and Δ_0 is the level width upon adsorption where $s'=r_i$. Hence, substituting Eq. (17) in Eq. (16), we find

$$Z_{\text{eff}}(s')=\frac{2}{\pi}\tan^{-1}\left\{\frac{E_\Phi}{\Delta_0}\exp\left[2\left(\frac{2m}{\hbar^2}\phi_e\right)^{1/2}(s'-r_i)\right]\right\} \ . \tag{18}$$

This result will be used in order to evaluate Eq. (15) numerically.

V. RESULTS AND DISCUSSION

Some numerical consequences of this theory of alkali-metal chemisorption are discussed in this section to illustrate the applicability of the formulation. The procedure for carrying through a detailed calculation of the binding energy is provided. Some physical conclusions which emerge from the numerical computations are presented. Some illustrative theoretical binding-energy comparisons for systems which have been studied experimentally are also considered.

The ultimate goal is the computation of binding energy from a given set of parameters characterizing the noninteracting atom and host surface. In the absence of a complete theory or defined set of parameters, we must content ourselves with a theoretical treatment which is given also in terms of parameters characterizing the interacting system but whose values are accessible either through independent experiments or through alternative theoretical calculations. The theoretical binding energy $E_B=E_M+W$ with E_M and W given by Eqs. (14) and (15), respectively, has therefore been reformulated in terms of the following parameters: (a) noninteracting system—ϕ_e, the work function of a particular crystal face of the host; V_i, the alkali ionization potential; A, the alkali electron affinity; and k_s, the host screening parameter. (b) Interacting systems—Δ, the virtual-impurity-level width; ΔE, the level shift; U, the screened intra-atomic Coulomb integral; s, approximately the ionic radius, but more precisely the atom-metal separation upon adsorption.

The parameters falling in category (a) are all defined. In category (b), the level width Δ is, in principle, calculable theoretically, although completely reliable calculations require better treatments of the surface potential than are presently available.[10,11] Alternatively, Δ can be determined through a proper analysis of resonance tunneling data.[26] Consequently, we feel that Δ can be regarded as an accessible parameter. Nearly the same can be said for the level shift ΔE and the screened Coulomb integral U. But there is one important distinction: In both Eqs. (14) and (15) we require knowledge of $E_\Phi=(\phi_e-V_i+\Delta E)+\Sigma=\epsilon_\Phi+\Sigma$. Past theory has suggested possible ways to calculate ΔE or ϵ_Φ.[11,21,26] If the Anderson theory is a valid model for alkali chemisorption as herein proposed, then the self-energy term Σ must be computed from the theory outlined in Sec. II. Thus, the self-consistency condition Eq. (10), which leads to the master curve of Fig. 2, becomes necessary. By knowing ϵ_Φ, Δ, and U one can find the self-consistent value of Σ which is given by the intersection of the curve specified by $p=U/\pi\Delta$ with the linear curve specified by ϵ_Φ/Δ in Fig. 2. As an explicit example, the results in Fig. 2 have been used to compute the self-energy as a function of ϵ_Φ, choosing reasonable values for the parameter Δ of 0.33-1.0 eV, and $U=\pi$ eV for convenience. The result is shown in Fig. 3. From these results we see that the apparent position of the alkali level is shifted upwards by about 0.3 eV because of Coulomb repulsion between up- and down-spin electrons on the impurity.

The last parameter requiring specification is the atom-metal separation s which is explicitly required in the calculation of the ionic part of the binding energy Eq. (15) and implicitly needed in calculations of Δ and ΔE. Ideally, this quantity should be obtained by solving

$$\left.\frac{\partial E_{\text{chem}}(s)}{\partial s}\right|_{s=s_{\text{equil}}}=0 \ .$$

For several reasons this procedure is not justified

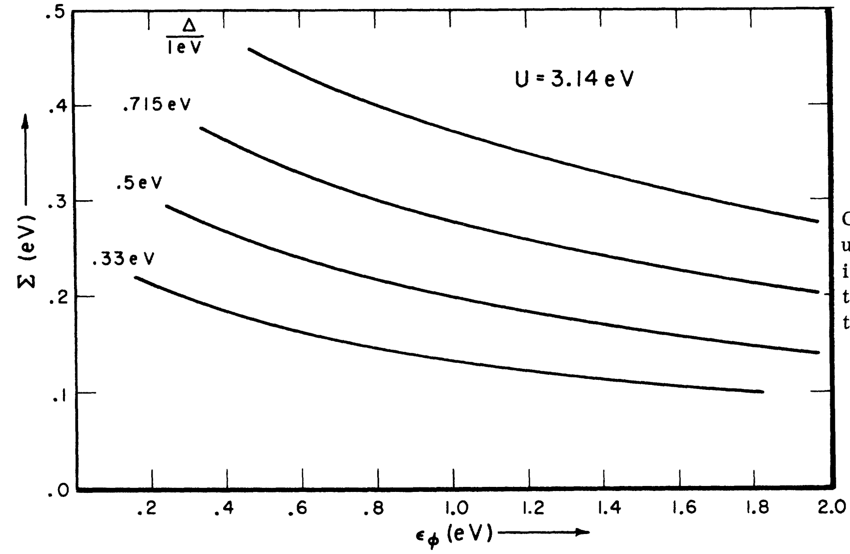

FIG. 3. Typical self-energy or Coulomb repulsion energy between up- and down-spin electrons at the impurity site as a function of the initial energy level. The level width is treated parametrically with $U = 3.14$ eV.

here. First, the key quantities Δ and ΔE are not sufficiently well defined as functions of s. More critical is the absence of a realistic strongly repulsive term between the alkali and the metal as the separation decreases. In effect we have used a hard-core repulsion and thus dictate the "equilibrium" separation. Fortunately, it appears reasonable to take s as proportional to the ionic radius of the particular adsorbate and, as the obvious first approximation, to set s equal to the ionic radius. Lastly, an excessively large computer effort would be required to obtain the theoretical extremum and it is doubtful that the microscopic theories providing functional forms for Δ, ΔE, and the repulsive term are sufficiently well defined to warrant the large numerical efforts required to calculate $s = s_{\text{equil}}$. The main justification of the present theory is therefore that, given the parameters in (a) and (b), it is useful to calculate the chemisorption energies directly from the graphical relationships proposed here.

The so-called metallic part of the chemisorption energy E_M given by Eq. (14) can be written in a convenient nondimensional manner as

$$\frac{\pi E_M}{\Delta} = 2y \cot^{-1} y - \frac{(\cot^{-1} y)^2}{p^{-1} + y^{-1} \tan^{-1} y} + \ln\left(\frac{y^2 + 1}{(E_F/\Delta + y)^2 + 1}\right) , \quad (19)$$

where $p = U/\pi\Delta$. Treating the quantity p parametrically and fixing E_F/Δ at a value appropriate for a typical metal, Eq. (19) is plotted in Fig. 4 as a function of y. In effect, this graph is a master curve for the metallic part of the chemisorption energy. Also shown, drawn with a dashed line, is the electron density given by Eq. (8). The information contained by Figs. 2 and 4 should be sufficient to calculate the nonionic contribution to the binding energy. As an explicit example, E_M is given in Fig. 5 for a system in which $U = 3.14$ eV and $E_F = 7.50$ eV, values which would be reasonable approximations for typical experimental systems. A range of relevant values for ϵ_Φ is chosen. Since ϵ_Φ, U, and Δ are known the self-energy and hence E_Φ are ascertained from Fig. 2. Going back to Fig. 4, we determine the nondimensional metallic part of the chemisorption energy, knowing E_Φ and p. The nondimensional energy is then converted to dimensional form and plotted in Fig. 5. It should be noted that for a given ϵ_Φ in Fig. 5, the magnitude of the metallic contribution to the binding energy increases as Δ increases, which is what one might expect from more physical considerations. One final point should be made. Since we are working in the LDA, care must be taken to make sure that this theory is applied only within the valid limits of the LDA. For instance, as Δ and hence n_a increase, the LDA is less valid and, in fact, magnetic solutions for the impurity might become energetically favorable. In this case, the present analysis must be considerably modified.

It is also informative to consider the ionic part of the chemisorption energy given by Eq. (15), the modified image type of interaction. In Eq. (17), $[(2m/\hbar^2)\phi_e]^{1/2} = 1.09$ Å^{-1} is a reasonable approximation for real systems. Having normalized Eq. (15), we evaluate $W[e^2/4(s + k_s^{-1})]^{-1}$ as a function of s. Treating

$$y = \frac{E_\Phi}{\Delta_0} \exp\left[-2\left(\frac{2m}{\hbar^2}\phi_e\right)^{1/2} r_i\right]$$

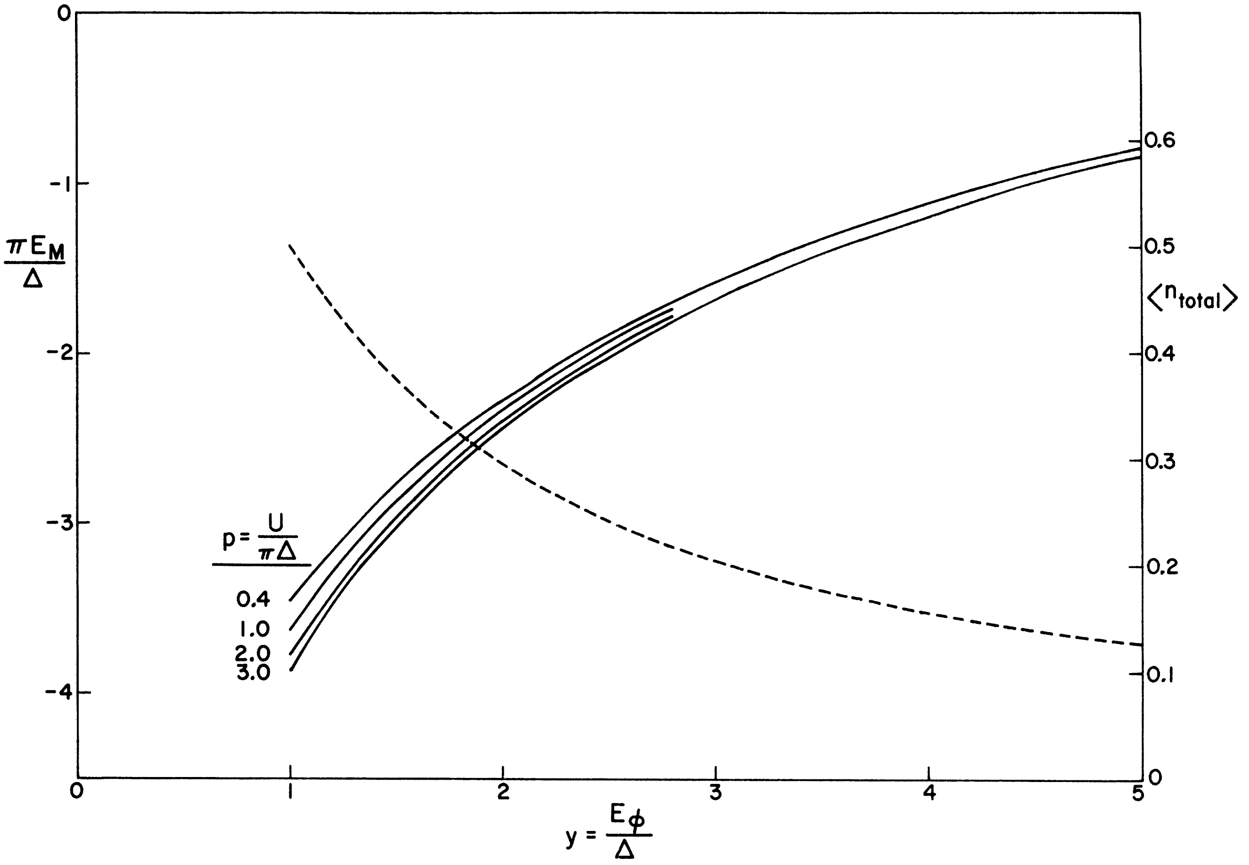

FIG. 4. Nondimensional metallic bond energy as a function of the self-consistent energy-level position. Also shown, by the dashed curve, is the electron charge number at the impurity site, given on the right-hand scale.

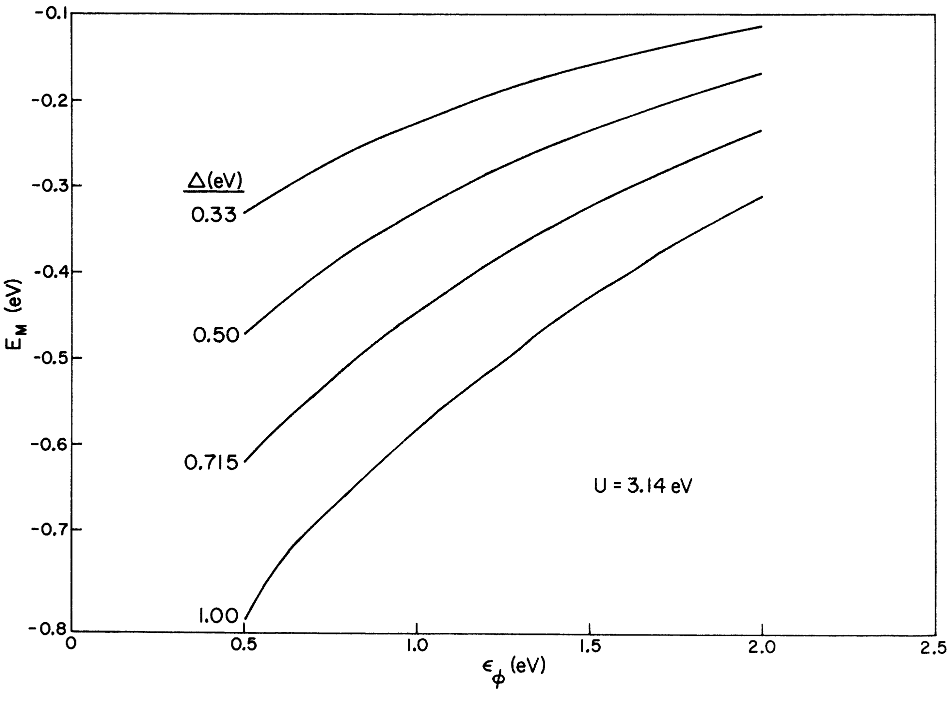

FIG. 5. Typical metallic binding energy as a function of the initial energy-level position treating the bandwidth parametrically and $U = \simeq \pi \simeq 3.14$ eV.

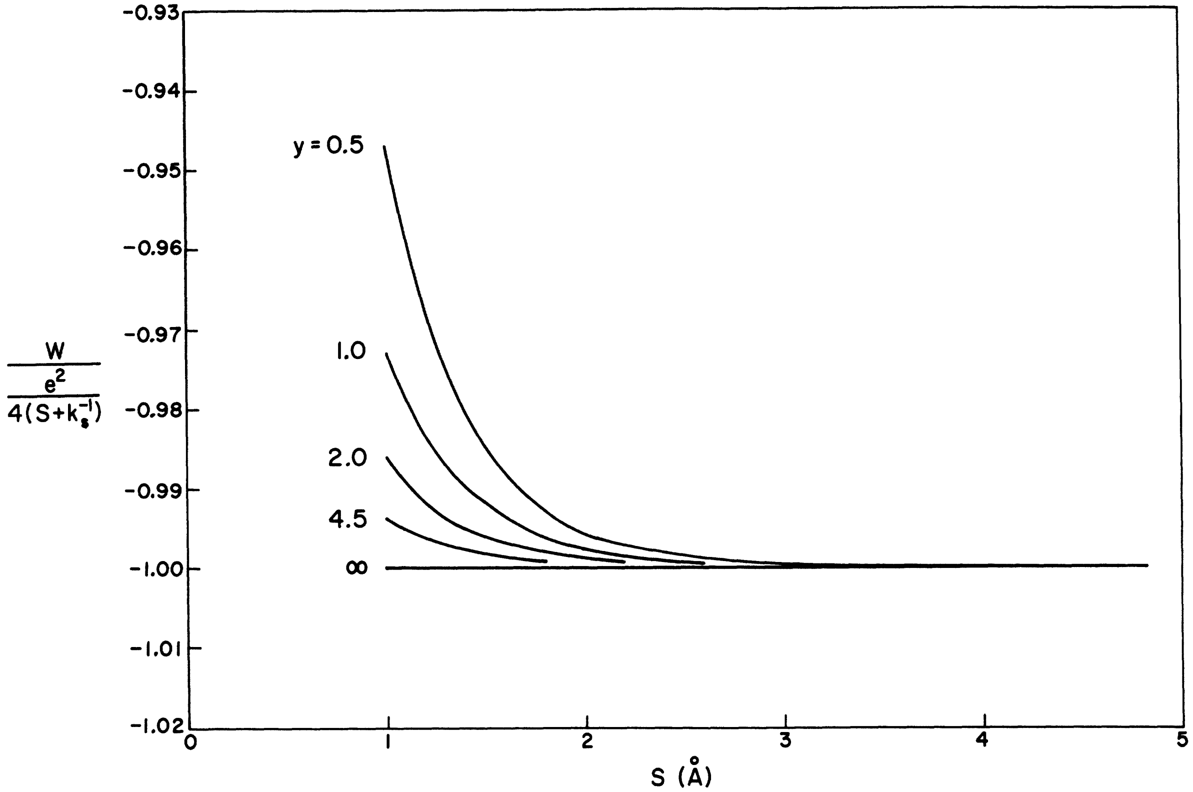

FIG. 6. Nondimensional ionic bond energy as a function of the atom-metal separation. The ratio of the self-consistent level position to the level width is treated parametrically.

parametrically, we draw the results in Fig. 6. It is seen that—although the effective charge on the alkali, when it is at its equilibrium position, might be a good deal less than unity—as the impurity is removed from the surface, the level width quickly shrinks, the charge goes to unity, and the ionic contribution becomes very similar to the modified image potential for a constant unit charge.

As a specific example of application of the present theory, the binding energies are calculated for a reasonable choice of input parameters relevant to specific alkali atoms and metal surfaces. In particular, the binding energies for Na through Cs on some hypothetical jellium metal with a typical electron density characterized by $r_s = 2.5$ are determined. The work function was set at 4.72 eV, which corresponds to the (110) face of Ni. The first three columns of numbers in Table II give the input data characterizing the alkali atoms. By using calculated values of ΔE and estimated values of Δ_0 based upon resonance tunneling experiments for alkaline-earth atoms (see columns 4 and 5), the self-consistent solutions to the impurity-level position are found from Fig. 2. The charge transfers from Fig. 4 are given in column 6. The metallic part of the binding energy is found from Fig. 5 since ϵ_ϕ and Δ are known. These results are indicated in column 7. Obtaining the value of y as

TABLE II. Input data characterizing the metal-alkali systems and derived and experimental binding energies. The ionization potentials and ionic radii were obtained from Ref. 34 and the electron affinities from Ref. 31. The experimental values are from Ref. 5, modified to correspond to ionic desorption energies. $k_s = 0.9 k_{FT}$; $r_s = 2.5$; $\phi_e = 4.72$ eV.

Alkali	V_i(eV)	A(eV)	r_i(Å)	ΔE(eV)	Δ(eV)	$\langle n_{tot}\rangle$	E_M(eV)	W(eV)	E(eV) (theor)	E(eV) (expt)	E(eV) (cycle)
Na	5.12	0.54	0.95	0.99	0.5	0.33	0.42	1.53	1.95	2.56	4.19
K	4.32	0.47	1.33	0.66	0.5	0.24	0.31	1.59	1.90	2.15	2.30
Rb	4.16	0.42	1.48	0.59	0.5	0.22	0.28	1.52	1.80	···	1.87
Cs	3.89	0.39	1.69	0.52	0.5	0.20	0.25	1.43	1.68	1.87	1.30

previously indicated, the ionic contribution is found from Fig. 6 and appears in the column 8. The theoretical total binding energies are shown in column 9, together with the experimental measurements of Gerlach and Rhodin[5] for the binding energies (these values are modified to correspond to ionic desorption energies) of Na, K, and Cs on the (110) face in Ni given in column 10. For purposes of comparison, the binding energy

$$E_{\text{cycle}} = V_i - \phi_e + e^2/4r_i \ ,$$

found from thermodynamic cycle and classical image force arguments, is presented in column 11. The agreement between experiment and theory is reasonably good. Both the trends and magnitude of the binding energies are in good accord using the theory presented here. This illustrates the basic validity of the present analysis but does not, of course, detract from the usefulness of the thermodynamic cycle approach.

In conclusion, we have seen that theory developed in the study of magnetic impurities in solids has provided a basic framework upon which an approach to a theory of alkali chemisorption on metal surfaces can be formulated. The present theory is distinguished from past theories of alkali chemisorption effects in that the latter have neglected the subtle ramifications related to magnetic effects of the virtual impurity level.[3,9-11] These theories are ineffective with regard to distinguishing between virtual states with or without a net spin. Consequently, effects related to the difference in energy between magnetic and nonmagnetic virtual states were not treated. Since these theories were most concerned with calculating dipole moments or charge distributions rather than energies, the neglect of the magnetic effects was not serious. The present theory, in which binding energies are calculated, does include interaction terms resulting from electron-electron interactions at the impurity site. By regarding the charge on the alkali atom as a function of atom-metal separation, it is possible to show that the ionic contribution to the chemisorption energy is not as sensitive to the virtual-level width as had been previously concluded. Master curves have been provided which enable one to calculate binding energies by knowing the critical parameters, which can be independently determined, characterizing the atom and the metal.

One of the significant realizations from this study, useful to the experimental physicist, is that the binding energies are not particularly sensitive to the particular alkali metal that is adsorbed. For instance, a difference in binding energy between Na^+, the most tightly bound ion considered, and Cs^+, the most loosely bound, was found to be only about 0.7 eV with $1.9 \lesssim E_{\text{binding}} \lesssim 2.6$ eV. This is to be contrasted with the dipole moment associated with the metal-alkali comples. Work-function measurements[5] for Na, K, and Cs on Ni (110) show that the dipole moment follows the sequence $\mu_{\text{Na}} = 1.85$, $\mu_{\text{K}} = 2.92$, $\mu_{\text{Cs}} = 4.05$ Debye units. Thus, as the binding energy varies by about 25%, the dipole moment associated with the bound complex varies by more than a factor of 2, almost an order of magnitude more. This, of course, comes from the fact that the dipole moment results from charge distribution associated with a distortion of the atomic and metallic wave functions. Since the energy of the system is stable with respect to a slight variation in the wave function, there results an nth-order change in chemisorption energy when the charge distribution or dipole displays an $n+1$ order variation. Hence, it seems that it might be more advantageous to measure dipole moments since they are more sensitive to the critical parameters of the adatom-metal system. With the promise of spectroscopic data obtainable from resonance tunneling experiments and improved theoretical formulation, the microscopic factors defining the phenomena of alkali-metal chemisorption will become increasingly more quantitatively understood.

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APPENDIX A

The coupling term in the Anderson Hamiltonian is

$$H_{\text{int}} = \sum_{\lambda,\sigma} \left(V_{\lambda a}\, c^{\dagger}_{\lambda\sigma}\, c_{a\sigma} + \text{H.c.} \right) . \qquad \text{(A1)}$$

The symbol λ represents the set of quantum numbers specifying the host states and σ is the spin quantum number. For an infinite material, in the extended zone scheme, λ represents the three-dimensional k vector with $-\infty < \vec{\text{k}} < \infty$. The hopping integral describing the coupling of the impurity orbital to a band state in jellium is

$$\begin{aligned} V_{\vec{\text{k}}a} &= \Omega^{-1/2} \int d^3r\, \Psi_a^*(\vec{\text{r}})\, V_m(\vec{\text{r}})\, e^{i\vec{\text{k}}\cdot\vec{\text{r}}} \\ &= a(\vec{\text{k}}) + ib(\vec{\text{k}}) \qquad \text{(A2)} \end{aligned}$$

if

$$a(\vec{k}) = \Omega^{-1/2} \int d^3r\, \Psi_a^*(\vec{r}) V_m(\vec{r}) e^{i\vec{k}_T\cdot\vec{r}_T} \cos k_z z\ , \tag{A3a}$$

$$b(\vec{k}) = \Omega^{-1/2} \int d^3r\, \Psi_a^*(\vec{r}) V_m(\vec{r}) e^{i\vec{k}_T\cdot\vec{r}_T} \sin k_z z\ , \tag{A3b}$$

and $V_m(\vec{r})$ is an effective system (Hartree-Fock) Hamiltonian. The picture which results is that of an impurity with a level width

$$\begin{aligned}\Delta &= \sum_{\vec{k}} \pi\delta(\epsilon_{\vec{k}} - \epsilon_a)|V_{a\vec{k}}|^2 = \sum_{\vec{k}} \pi\delta(\epsilon_{\vec{k}} - \epsilon_a)(|a|^2 + |b|^2)\\ &\simeq \pi\rho(\epsilon_F)\langle |V_{a\vec{k}}|^2\rangle_{\text{av}}\\ &= \pi\rho(\epsilon_F)(|a|^2_{\text{av}} + |b|^2_{\text{av}})\ ,\end{aligned} \tag{A4}$$

where $\rho(\epsilon_F)$ is the electron density of states at the Fermi energy and $\langle |V_{a\vec{k}}|^2\rangle_{\text{av}}$ is some average value of the hopping integral.[22]

Next, we wish to consider an impurity in a host of large extent in the x, y $(\vec{r}_T)$ plane and of finite extent in the surface-normal direction from $0 \leq z' \leq L$. If we assume infinite barriers at the surfaces, then the appropriate "continuum" wave functions are running waves in the transverse direction and standing waves in the z direction. In the boundary condition of vanishing wave function at $z' = 0$, L is satisfied by choosing

$$\Psi_\lambda(\vec{r}) = (2/\Omega)^{1/2} e^{i\vec{k}_T\cdot\vec{r}_T} \sin k_z z'$$

and (A5)

$$k_z = n\pi/L\ .$$

The quantum numbers are $\lambda = (\vec{k}_T, |k_z|)$ and fall in the range $-\infty < \vec{k}_T < \infty$, $0 \leq k_z \leq \infty$. Second quantized operators for particles in the states specified by λ can be expressed as a sum of operators for states specified by k, for example, the destruction operator $c_\lambda = 2^{-1/2}\,(c_{k_z} - c_{-k_z}) c_{\vec{k}_T}$. Thus, the coupling term in Eq. (A1) can be written as

$$H_{\text{int}} = \sum_{\lambda,\sigma\,(k_z>0)} V_{\lambda a}\, c^\dagger_{\lambda\sigma}\, c_{a\sigma} \rightarrow \sum_{\vec{k},\sigma\,(\text{all } k_z)} V_{\vec{k}a}\, c^\dagger_{\vec{k},\sigma}\, c_{a,\sigma}\ ,$$

which is the mixing term for the impurity orbital and the band wave functions in the finite crystal with surfaces. The hopping integral must be given in terms of $\vec{k}$ and any explicit dependence, due to either surface or size effects, must be treated. To calculate the hopping integral, imagine that the impurity is a distance ξ from the edge of the slab. Then translating the origin of coordinates to the impurity center, the metal wave functions are

$$\Psi_\lambda = (2/\Omega)^{1/2} e^{i\vec{k}_T\cdot\vec{r}_T} \sin k_z(\xi + z)\ .$$

Just as in Eqs. (A2) and (A3), we have

$$\begin{aligned}V_{\vec{k}a} = (2/\Omega)^{1/2} \sin k_z\xi &\times \int d^3r\, \Psi_a^*(\vec{r}) V_m(\vec{\xi} + \vec{r}) e^{i\vec{k}_T\cdot\vec{r}_T} \cos k_z z + (2/\Omega)^{1/2} \cos k_z \xi\\ &\times \int d^3r\, \Psi_a^*(\vec{r}) V_m(\vec{\xi} + \vec{r}) e^{i\vec{k}_T\cdot\vec{r}_T} \sin k_z z\ .\end{aligned} \tag{A6}$$

The impurity wave function Ψ_a confines the integrand to a spatial region of the order of the impurity radius. If the impurity is further than a few times this radius into the host, then the Hartree-Fock potential $V_m(\vec{\xi} + \vec{r})$ is not influenced by surface effects and, at least for jellium, we can replace $V_m(\vec{\xi} + \vec{r})$ by $V_m(\vec{r})$ since absolute position plays no role as far as V_m is concerned.[29] Then the integrals in Eq. (A6) are the same as $a(\vec{k})$ and $b(\vec{k})$ given by Eqs. (A3a) and (A3b), and as a result, for the host of finite size we have

$$V_{\vec{k}a} = \sqrt{2}\,\sin(k_z\xi) a(\vec{k}) + \sqrt{2}\,\cos(k_z\xi) b(\vec{k})\ , \tag{A7}$$

which is somewhat different from Eq. (A2). We will examine the consequences of Eqs. (A3), (A4), and (A7) for a few different limiting cases.

(a) *Volume impurity in large host.* From Eqs. (A4) and (A7), the level width is

$$\begin{aligned}\Delta = \sum_{\vec{k}} \pi\delta(\epsilon_{\vec{k}} - \epsilon_a)[&2\sin^2(k_z\xi)|a|^2 + 2\cos^2(k_z\xi)|b|^2\\ &+ 4\sin(2k_z\xi)|a|\,|b|]\ .\end{aligned} \tag{A8}$$

For large ξ, the $\cos^2$ and $\sin^2$ terms oscillate rapidly between 0 and 1 as the k_z sum is performed, compared to the slowly varying functions a and b. Thus, we can replace the squared trigonometric functions by their average value, which is $\frac{1}{2}$. Similarly, the average value of $\sin 2k_z\xi$ is zero. With these steps Eq. (A8) becomes

$$\Delta = \sum_{\vec{k}} \pi\delta(\epsilon_k - \epsilon_a)(|a|^2 + |b|^2)\ ,$$

which is identical with Eq. (A4), as it must be.

(b) *Surface impurity upon large host.* Our model surface impurity is placed at $\xi = 0$, directly upon the mathematical surface.[27] In view of the quantization rules of Eq. (A5), the hopping integral in Eq. (A6) becomes

$$V^{\text{surf}}_{\vec{k}a} = (2/\Omega)^{1/2} \int d^3r\, \Psi_a^*(\vec{r}) V_m(\vec{r}) e^{i\vec{k}_T\cdot\vec{r}_T} \sin k_z z\ ,$$

and the Anderson formalism can be simply adapted to the treatment of surface impurities by an appropriate choice of matrix elements.[16] We should note also that if the impurity was slightly removed from $z = 0$, then the same types of arguments as in case (a) could be used to eliminate the rapidly oscillating terms. Extra complications in practice but not in principle result from the fact that here V_m cannot be replaced by a constant inner potential for jellium. In fact, $V_m(\vec{r})$ would be similar to already calculated surface potentials[28–30] suitably modified to account for the presence of the impurity.

APPENDIX B

An alternative approach to the divergence of the quantity

$$E_{am} \equiv E_M(s) + U_{\text{eff}}\, n_{a+} n_{a-} = \textstyle\sum_\sigma \int_{-\infty}^{0} \omega \rho_{aa}^{\sigma}(\omega)\, d\omega \ , \qquad \text{(B1)}$$

in which an approximate but reasonable energy dependence on the hopping integral of Eq. (2) is used, as indicated. In the chemisorption problem, the alkali valence level broadens as a result of electron tunneling through the barrier which is assumed to exist between the adsorbate and the substrate.[3,8–11] Thus, one could expect the width, or tunneling probability, $\Delta(\omega)$ to be proportional to an exponential of the barrier height multiplied by the atom-metal separation s. As a simple approximation take

$$\Delta(\omega) \simeq \gamma e^{-2k(\omega)s} \ , \qquad \text{(B2a)}$$

with

$$\begin{aligned} 2k(\omega)s &= 2s\,[(2m/\hbar^2)(\phi_e - \omega)]^{1/2} \\ &= \alpha(\phi_e - E_\phi)^{1/2}\left(1 - \frac{(\omega - E_\phi)}{\phi_e - E_\phi}\right)^{1/2} \ , \end{aligned} \qquad \text{(B2b)}$$

when $\alpha = 2s(2m/\hbar^2)^{1/2}$. The barrier, for present purposes, is taken to be a simple square barrier whose height is ϕ above the Fermi level. Expanding the square root in Eq. (B2) and letting $\Delta_0 = \gamma\, e^{-\alpha(\phi - E_\phi)^{1/2}}$ and $\kappa = \alpha/2(\phi_e - E_\phi)^{1/2}$, Eqs. (B2a) and (B2b) yield

$$\Delta(\omega) \approx \Delta e^{\kappa(\omega - E_\phi)} \ . \qquad \text{(B3)}$$

Combining Eqs. (6) and (B1), defining a new variable $x = \omega - E_\phi$, and recognizing that $\Delta = \Delta(x + E_\phi)$, we obtain

$$E_{am} = \sum_\sigma \frac{1}{\pi} \int_{-\infty}^{-E_\phi} \frac{(x + E_\phi)\Delta}{x^2 + \Delta^2}\, dx \ . \qquad \text{(B4)}$$

The second integral does not depend upon the fact that Δ is energy dependent in the sense that

$$\sum_\sigma \frac{E_\phi}{\pi} \int_{-\infty}^{-E_\phi} \frac{\Delta}{x^2 + \Delta^2}\, dx = \sum_\sigma E_\phi n_{a\sigma} + 2U_{\text{eff}}\, n_{a+} n_{a-} \qquad \text{(B5)}$$

is independent of the form of Δ. Thus using Eqs. (B1)–(B5), the metallic binding energy in Eq. (14) is

$$E_M = \sum_\sigma E_\phi n_{a\sigma} + U_{\text{eff}}\, n_{a+} n_{a-} + E_\Delta \ ,$$

where

$$E_\Delta \equiv \sum_\sigma \frac{\Delta}{\pi} \int_{-\infty}^{-E_\phi} \frac{x e^{\kappa x}}{x^2 + \Delta^2 e^{2\kappa x}}\, dx \ . \qquad \text{(B6)}$$

E_Δ is the quantity playing the role analogous to that of the logarithm term in Eq. (14). For the alkali adsorption considered here, we must have $\Delta < E_\phi$ in order that charge transfer be dominant, as assumed here in binding. Thus we write the denominator as an infinite series:

$$\frac{1}{x^2 + \Delta(\omega)^2} = \frac{1}{x^2} \sum_{n=0}^{\infty} (-1)^n \left(\frac{\Delta(\omega)^2}{x^2}\right)^n \ . \qquad \text{(B7)}$$

The nth-order exponential integral is defined as

$$E_n(z) \equiv \int_1^\infty \frac{e^{-zt}}{t^n}\, dt \qquad \text{(B8)}$$

and has been tabulated.[35] If the Lorentzian is expressed according to Eq. (B7) and inserted into Eq. (B6), then it can be seen that the nth term in the summation is of the form of an nth-order exponential integral as in Eq. (B8) when z is suitably defined. Performing the indicated manipulations and solving for E_Δ, we arrive at the final expression

$$E_\Delta = \sum_\sigma \frac{\Delta}{\pi} \left[\sum_{n=0}^{\infty} \left(\frac{\Delta}{E_\phi}\right)^{2n} (-1)^{n+1} E_{2n+1}[(2n+1)\kappa E_\phi] \right] . \qquad \text{(B9)}$$

This is a very rapidly converging series whose numerical value is ~0.2 eV for values of the critical parameters pertaining to alkali-metal chemisorption. In comparison, the quantity

$$E_\Gamma \equiv \sum_\sigma \frac{\Delta}{2\pi} \ln\left(\frac{E_\phi^2 + \Delta^2}{(E_F + E_\phi)^2 + \Delta^2}\right) ,$$

which was obtained by taking a constant matrix element but an energy-dependent metal density of states (Sec. III), has a numerical value ~0.3 eV. These values are sufficiently close to each other so that either approximation provides a reasonable relationship to be used in the present treatment.

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Atomic Configurations in Binary Alloys

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The complete probability distribution of nearest-neighbor configurations has been inferred for a number of cubic binary alloys from their experimentally determined short-range order parameters. The probability variation method, derived previously, was used to perform the calculations. This procedure, which is used to generate n-site probabilities from experimentally measured pair probabilities, requires the physical assumption that the configurational energy of the system can be adequately represented by pairwise interactions whose range does not exceed the diameter of the cluster. Results are presented here for β-CuZn, Cu_3Au, CuAu, Au_3Cu, $Cu_{85.5}Al_{14.5}$, $Cu_{52}Ni_{48}$, and $Au_{60}Pd_{40}$, and the implications for ordering (or clustering) behavior are discussed. Finally, tables of coefficients for the bcc and fcc lattice are given to enable one to carry out this type of analysis for any cubic binary system.

I. INTRODUCTION

In a previous paper[1] (hereafter referred to as I) a systematic procedure was presented for using the measured values of Warren short-range order (SRO) parameters $\{\alpha_i\}$ in binary alloys to make a "best" prediction of the probability distribution of n-site atom configurations (where n can be 10 or more). These multisite probability distributions are potentially important for understanding nuclea-