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Chemical Trends in Atomic Adsorption on Simple Metals

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Essentially exact numerical solutions of the self-consistent atom-jellium model are used to show how the chemical concepts of electronegativity, shell-filling, and covalent or ionic bonding manifest themselves in the microscopic redistributions of charge and state density which accompany chemisorption. Realistic results are provided for chemisorbed Li, Cl, and Si, illustrating the three basic types of bonding—cationic, anionic, and covalent.

In the work reported here, the self-consistent atom-jellium model¹ is used to study the adsorption on a dense simple-metal surface of three atoms—Li, Si, and Cl—which are sufficiently different chemically that their binding to such a surface spans the phenomenology we expect to find in chemisorption on simple metals (when neither spin fluctuations nor permanent moments are important). This study is motivated by the conviction that we must abstract from our understanding of relatively simple systems, in which detailed analysis is possible, the concepts which will enable us to think effectively about more complex cases.

As an atom approaches a surface, those of its energy levels which are (or become) degenerate with the energy bands of the metal broaden into resonances, permitting nonintegral occupation. The final position of each resonance relative to the Fermi energy (E_F), and therefore its occupation, result from the competition among the atom's desire to fill its valence shell, the intra-atomic Coulomb repulsion energy required to do so, and the electron affinity of the metal. The range of possible behavior is illustrated in Fig. 1. The $2s$ resonance of Li lies primarily above² E_F and the $3p$ resonance of Cl lies below E_F , providing clear examples of positive and negative ionic chemisorption. The direction of charge transfer is consistent with the electronegativities of Li, Cl, and an Al¹ surface. Filling the valence shell of Cl and emptying that of Li both involve only a single electron; to fill or empty that of Si would involve four electrons. The energetic cost of this results in the partial occupation of the Si

$3p$ resonance seen in Fig. 1, which has important implications for the electron density. The states in the lower-energy part of any resonance have greater amplitude in the bond region than those in the upper part.³ For Si near its equilibrium separation, the scale of this amplitude difference is large and the preferential occupation of bonding states results in a clearly discernible covalent bond charge (see below).

The motivation for looking at electron densities is that they provide a spatially detailed picture of bonding which is independent of the analytical approach employed. Further, the existence of comprehensive analyses of electron densities in related molecular systems⁴ makes it possible to compare the chemical trends in these extensively

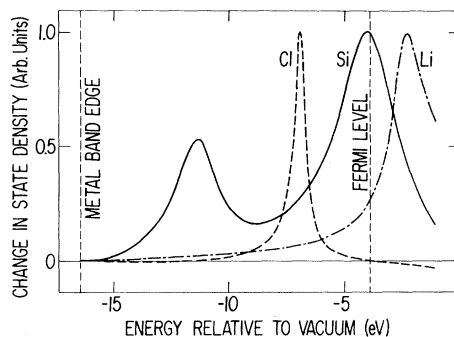


FIG. 1. Change in state density due to chemisorption (cf. Ref. 1). Curves correspond to positive-background-atom nucleus separations which minimize total energy [2.5 a.u. (Li), 2.3 a.u. (Si), 2.6 a.u. (Cl)]. Note that lower Si resonance corresponds to the $3s$ level of the atom; for Cl, this is a discrete state below the band edge.

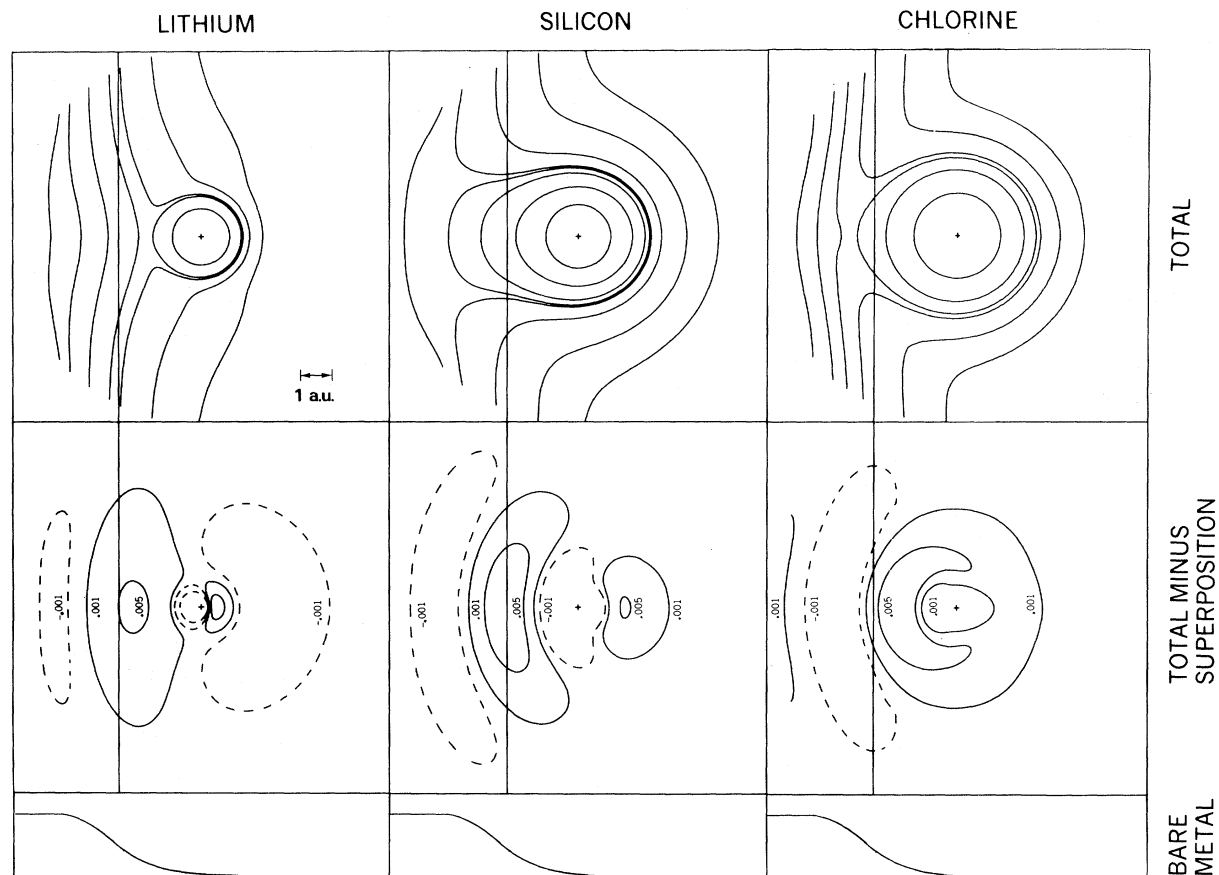


FIG. 2. Upper row: Contours of constant electron density in a (any) plane normal to the surface containing the adatom nucleus (indicated by +). Metal is to the left; solid vertical line is positive background edge. For computational convenience, contours are not shown beyond the inscribed circle of each square. Contour values were selected in each case to be visually informative. Center row: Contours of total electron density minus superposition of atomic and bare-metal electron densities [electrons/(a.u.)³]. The polarization in the core region, shown for Li, has been deleted from the Si and Cl plots because of its complexity. Bottom row: Profile of bare-metal electron density (shown for comparison). [Bulk density is 0.030 electrons/a.u.)³]

studied systems with those in chemisorption. (This comparison is also relevant to the adequacy of simulating surface complexes with small clusters.) Figure 2 shows contours of constant density for both the total electron density in the chemisorbed system and the total minus the superposition of the metal and atom⁵ electron densities.

The contours for the total distribution show the behavior expected from the degree of shell filling seen in Fig. 1. The outermost closed contours surrounding the Li and Cl nuclei are more circular than those for Si, which show a more prominent projection of charge into the bond region. The metal contours deflect toward the Li and away from the Cl, indicating the ionic attraction (Li) and repulsion (Cl).

The difference contours show clearly the displacements of electronic charge which accompany bonding. In Li, we see that electrons are transferred from the vacuum side of the adatom toward the metal. The kidney-shaped depletion contour on the vacuum side, and even the reverse dipole contours in the core region, are strikingly similar to those found by Bader and co-workers⁴ in the LiH and LiF molecules. The nearly empty Li resonance of Fig. 1 suggests that the transferred electrons are best thought of as residing in "metal" states. (Our calculations, it should be remembered, do not define distinct atom and metal states.) Note also that for Li, as well as for the other two cases, the sequence of contours continues into the metal in the form of Friedel oscillations induced by the perturbing atom. The

difference contours for Cl provide a picture of a polarized negative ion very similar to that found for H and F in the molecular calculations just mentioned.

The difference contours for Si show a depletion of charge near the nucleus and accumulations on both the bond and vacuum sides. The same general configuration of contours is found in all the diatomics studied in Ref. 4 which exhibit p -orbital covalent bonding. The accumulation on the vacuum side is due to the interaction of the $3s$ and $3p_{\sigma}$ orbitals which leaves the former polarized into the bond and the latter out of the bond.

Adatom resonances play a uniquely important role in our efforts to understand chemisorption because they lead to readily identifiable structure in measured excitation spectra (photoemission, for example). Figure 3 shows the change

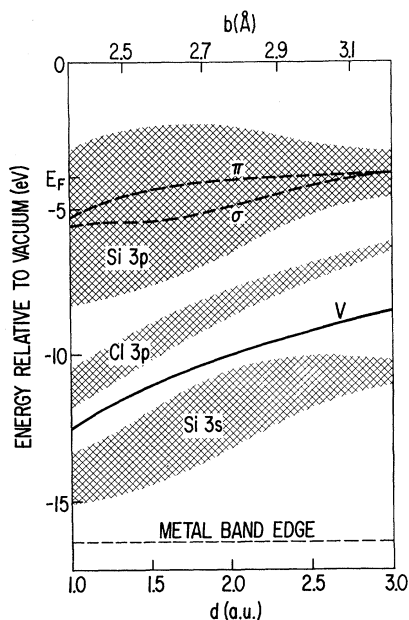


FIG. 3. Characteristics of Si and Cl resonances (cf. Fig. 1) as a function of metal-adatom separation. Boundaries of shaded regions indicate half-maximum energies. Lower axis d is separation of adatom nucleus from positive background edge. The plane through the outermost substrate nuclei is half an interplanar spacing behind the background edge. Thus d , the crystal structure of the substrate, and the adsorption site determine the adatom to metal-atom bond length b . The upper axis provides b for a threefold site on a (111) surface of Al as an example. Dashed curves show peak positions for σ ($m=0$) and π ($m=1$) components of Si $3p$ resonance. (Not shown for Cl.) Curve V gives effective one-electron potential (v_{eff} of Ref. 1) of bare metal (displaced downward 5.6 eV for pictorial reasons).

in resonance structure with metal-adatom separation for Si and Cl.⁹ The relative narrowness of the $3p$ resonance for Cl is due to Cl's greater core charge and can be viewed as part of a trend extending from alkali adatoms (where the resonance is unoccupied) to rare-gas adatoms. The changes in resonance width with decreasing separation result from a competition between two effects, broadening due to increasing metal-adatom interaction and narrowing due to the decreasing density of metal states seen by the resonance as it moves toward the bottom of the metal band. [Note the tendency of the resonances, particularly those which are filled, to follow the effective one-electron potential of the bare metal (as they would in first-order perturbation theory).]

It is Fig. 3 rather than Fig. 1 that should be used in the direct interpretation of experimental data, because the atom-jellium model represents an average of the properties of the adatom over all adsorption sites. In particular, the actual metal-adatom separation at favorable adsorption sites will be somewhat smaller than this average value. The difference from the average separation is greatest for small, strongly electronegative adatoms, such as oxygen, which at particular sites can dig their way into the surface.⁷ (We have estimated this difference for the larger adatoms considered here by reintroducing the discrete lattice as a perturbation, using pseudopotentials.⁸) The usefulness of Fig. 3 in interpreting experimental data rests on the conclusion of Ref. 7 that, for close-packed faces, the resonance position and width are less affected by the perturbation than is the equilibrium separation itself.⁹

We are delighted to thank J. E. Demuth, W. A. Lester, Jr., and M. C. Gutzwiller for useful discussions.

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⁵Free-atom properties were calculated using a spin-polarized Kohn-Sham program written by J. F. Janak (private communication). The free-atom electron density was made spherically symmetric by partially filling the discrete-atom levels where necessary.

⁶The calculations used for Fig. 3 are self-consistent at every distance; only one of these distances minimizes the total energy of a given system. [The calculated atomic binding energies (cf. Refs. 1 and 5) are 1.3 eV (Li), 3.0 eV (Si), and 3.6 eV (Cl)]

⁷K. Y. Yu, J. N. Miller, P. Chye, W. E. Spicer, N. D. Lang, and A. R. Williams, *Phys. Rev. B* (to be published).

⁸This calculation used first-order perturbation theory. The magnitude of the first-order terms suggests that second-order terms can be important (Ref. 7). For adsorption in a threefold site on Al(111), the first-order treatment gives physically reasonable results for Si

($d = 1.6$ a.u., corresponding to an Al-Si bond length $b = 2.6$ Å) and Li ($d = 2.1$ a.u., corresponding to $b = 2.8$ Å), but indicates that the Cl atom sits further out than in the jellium calculation, which is presumably not the case. The use of first-order perturbation theory in this context cannot therefore be considered to represent a generally adequate treatment of discrete-lattice effects.

⁹Data of J. E. Rowe (private communication) for Cl adsorbed on Cd show a resonance ~ 2 eV wide centered 5.8 eV below E_F , with a shoulder on the low-energy side suggestive of a σ - π splitting of ~ 0.8 eV. This is consistent with Fig. 3, in conjunction with a bond length deduced from covalent or metallic radii as discussed by P. M. Marcus, J. E. Demuth, and D. W. Jepsen [*Surface Sci.* **53**, 501 (1975)] (which corresponds to a d of ~ 1 a.u.). The calculated σ component of the resonance for this d is 0.7 eV further below E_F than the π component.

Infrared Cyclotron Resonance in Semiconducting Surface Inversion Layers*

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The frequency-dependent conductivity $\sigma(\omega)$ of a two-dimensional interacting electron gas in the presence of a random array of scattering centers and a dc magnetic field is studied. Electron-electron interaction effects enter $\sigma(\omega)$ through the holomorphic memory function $M(\omega)$ whose imaginary part is the inverse of the frequency-dependent relaxation time $\tau(\omega)$. A qualitative explanation of some of the perplexing results observed in infrared cyclotron resonance, including how electron-electron interactions affect both the fundamental and harmonics, is given.

The concentration-dependent enhancement of the effective mass¹ and g value² of electrons in the surface inversion layer of a semiconductor obtained by studying the amplitude of the Shubnikov-de Haas oscillations in the surface conductance has been attributed³⁻⁵ to many-body interactions among the inversion-layer electrons. These observations spurred interest in observing dynamic cyclotron resonance in these systems.^{6,7} A simple argument shows that dynamic cyclotron resonance excited by a spatially uniform ac electric field cannot be affected by many-body interactions among the conduction electrons in a free electron gas.⁸ For this reason the many-body enhancement observed in the dc experiments would not be expected to occur in infrared cyclotron reso-

nance. Recent experimental observations have yielded some unexpected results.⁹⁻¹¹ The most striking result is the appearance of "harmonics" of cyclotron resonance at not quite integral multiples of the fundamental resonance. The amplitude of harmonics is relatively large (up to the order of 10% of the fundamental in the derivative spectrum) and dependent on the electron concentration. The mass obtained by equating the resonance frequency to an integral multiple of eB/m^*c displays, as a function of concentration, a behavior similar to that of the effective mass observed in the dc experiments. In the absence of electron-electron interactions, impurity scattering leads to the occurrence of "harmonics" at exact multiples of the bare cyclotron frequency.¹² In addi-