Electronic Structure of a Chemisorbed Layer at Electrochemical Interface: Copper Layer on Gold Electrode

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Though the importance of chemisorption at the electrochemical interface is well recognized, an electronic level description for the same still remains in a nascent stage. The present work specifically addresses this problem. An appropriate model Hamiltonian based formalism is proposed for a random adsorbate layer with arbitrary coverage and the ensuing two-dimensional band formation by metallic adsorbates in the monolayer regime. The coherent potential approximation is employed to handle the randomness. The adsorbate self-energy is evaluated explicitly using the density of states for the substrate band. This takes us beyond the conventional wide-band approximation and removes the logarithmic divergence associated with the binding energy calculations. The formalism is applied to the electrosorption of copper ion on gold electrode, and the coverage dependence of adsorbate charge, binding energy, and adsorbate density of states are determined. The analysis predicts a unique charge configuration of copper adsorbate, having a net positive charge, in the high-coverage regime, and multiple charge states when the coverage is low. Though one of the charge configurations of copper is nearly neutral at small coverage, its positive charge state is the most stable in the entire coverage range. The transition from the relative neutral state of copper at low coverage to a positive charge configuration occurs sharply at the intermediate-coverage region. This transition is caused due to the progressive desolvation of copper adion with increasing coverage. The energy calculations show that copper s-orbital bonding contributes maximally toward the binding energy at the metal−vacuum interface, whereas it is the copper d-orbital bonding which makes chemisorption feasible at the gold electrode. Finally, our numerical results are compared with the relevant experimental studies.

1. Introduction

Chemisorbed species significantly modify the physicochemical nature of an electrochemical interface.[1−3] In spite of their importance in the areas of heterogeneous electron-transfer reactions, catalysis, chemically modified electrodes, and double layer studies, an electronic level description of the electrosorption phenomenon is still elusive. However, the recent progress concerning in situ structure-sensitive techniques has made it possible to obtain the structural details of an adlayer in an electrochemical environment. In the present paper, we investigate the electronic states of a random adsorbate layer. To understand the similarities, as well as the critical differences between the chemisorption at the metal−vacuum and electrochemical interface, is the other motivation for undertaking this study.

In our studies, the adsorbate coverage factor θ is allowed to take any arbitrary value in the range (0,1). Thus the formalism remains valid all the way up to a monolayer regime, starting with a single adsorbate case. The analysis ultimately leads to the quantitative estimates of (i) average "occupation probability" and the "partial charge-transfer coefficient" of adsorbate, (ii) its density of states, and (iii) binding energy. The formalism also enables one to study how these quantities are affected due to coverage variation.

Electrochemisorbed copper on gold electrode represents a model experimental system, studied extensively through various structure-sensitive techniques.[4−7] Besides, this is also typical of the underpotential deposition phenomenon.[8−10] Double layer studies coupled with the thermodynamic analysis suggest that a copper adsorbed on gold electrode exists in a neutral state when the coverage is low.[11,12] On the other hand, Tadjeddine et al. have shown through in situ X-ray absorption spectroscopy of copper layer on gold(111) electrode surface that in the monolayer regime, the charge state of Cu adsorbate is close to Cu^+.[6] These studies show a large variation in copper adatom charge with increasing coverage. It will be pertinent here to restate that the electronic structure of a metallic adsorbate differs significantly in the low and higher coverage domains. In the former case, the electrons are essentially localized on the adatom whereas with increasing coverage, they tend to get delocalized over a large spatial region. These extended electronic states ultimately form a two-dimensional band in the monolayer regime. We have applied our general formalism to Cu/Au system. Our theoretical results are in conformity with the Tadjeddine et al. experimental observation of a positively charged copper adsorbate in the high coverage regime. For the low-coverage domain, analysis shows the existence of three different charge states of a copper adsorbate. Though one of these states corresponds to a nearly neutral configuration of the copper, energetic considerations make this state a metastable one. Also the transition from this neutral to a positive charge configuration is not smooth, but occurs discontinuously in the intermediate-coverage region. We show in sections 7 and 8 that the progressive desolvation of a metallic adsorbate with increasing coverage is the main reason behind this feature. The transition from multiple charge states of copper when coverage θ is small to a single charge state for intermediate value of θ is specific to electrochemical interface. This indicates that the

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chemisorption at the electrochemical and metal−vacuum interface can be qualitatively different, even when the adsorbate and substrate remain the same. In the context of multiple charge states of copper, we also note that when the net charge on an adsorbate at the electrochemical interface gets reduced, its solvation energy decreases. This in turn shifts adsorbate's energy toward a more positive value.

The present analysis employs, as the model Hamiltonian, a generalized version of the Anderson−Newns Hamiltonian,[13−16] which has been studied extensively in the context of chemisorption at a metal−vacuum interface. The generalization considered here refers to (i) modeling additional interactions which an adsorbate experiences at an electrochemical interface, (ii) considering a collection of adspecies along with their mutual interactions, instead of a lone adsorbate, and (iii) allowing a randomness in the occupancy status of adsorption sites. Obviously the formalism considered here is also valid for the adsorption at the metal−vacuum interface in the appropriate limiting conditions.

Kornyshev and Schmickler (KS) have earlier considered the coverage dependence of the adsorbate charge using a generalization of Anderson−Newns Hamiltonian, and have applied their formalism to study the adsorption of Cs and I at a mercury electrode.[17] The coverage dependence in their analysis arises due to nonlocal electrostatic interactions between adions.

The present formalism differs qualitatively from Kornyshev and Schmickler approach, both at the levels of Hamiltonian (cf. section 2) and analysis.

In the KS formalism, the other adsorbates essentially introduce a static shift in the energy level of an adatom. The quantum-mechanical aspect of the adlayer problem is still handled within a "single-adsorbate" model. In contrast, the present formalism takes into account the band structure of the metallic adlayer. Next, the KS approach is based on the wide-band approximation which has been extensively employed to study the chemisorption at the metal−vacuum (M−V) and electrode−electrolyte (E−E) interface. Herein, a part of adsorbate's self-energy arising due to the metal−adsorbate hybridization is approximated as an energy independent quantity $i\Delta$. This approximation leads to a logarithmic divergence in the energy calculation and necessitates an introduction of a lower cutoff parameter in order to arrive at a finite result.[18] Within the wide-band approximation, the adsorbate Green's function has a single pole structure (Lorentzian density of states) when the intraadsorbate Coulomb repulsion is treated using the Hartree−Fock approximation.

We have gone beyond the wide-band approximation in the present formalism. The relevant self-energy arising due to the electronic coupling between metal and adsorbate states is explicitly evaluated employing model density of states for the substrate. This removes the divergence in the energy calculation and, depending on the system parameters, allows the adsorbate Green's function to admit more than one pole even within the Hartree−Fock limit. The self-energy now depends on the energy variable, and the adsorbate density of states may exhibit non-Lorentzian structure.

In order to substantiate as well as compare our results with the wide-band limit based formalism, we have suitably extended the latter to the context of random adsorbate layer (sections 6 and 8).

In the next section, a model Hamiltonian describing the electrochemisorbed layer is constructed. The coherent potential approximation (CPA) scheme for the random adsorbate layer is considered in section 3. The adsorbate density of states and other relevant quantities are evaluated in the next two sections. Analytic expressions suitable for the numerical computations are derived in section 6 and the application of the formalism to the copper adsorption on gold electrode is considered in section 7. Section 8 is devoted to discussion, followed by section 9 on summary and concluding remarks.

2. The Model Hamiltonian

Chemisorbates forming a random layer over an electrode surface have extensive electronic coupling with the substrate band states as well as with other adspecies. In addition, they interact with the orientational, vibrational, and electronic polarization modes of a polar liquid in the electrolyte phase. This leads to the solvation energy of the adsorbate. Similarly, the coupling between the adsorbate and surface plasmons in the substrate is responsible for the image energy contributions. The various solvent polarizations and surface plasmon modes are described within the harmonic approximation, and their coupling with the adsorbates is modeled as diagonal fermion−boson terms. Taking into account all the above interactions along with the intraadsorbate Coulombic repulsion, a Hamiltonian for the electrochemisorbed system is written as[16,17]

$$H = \sum_{k,\sigma} \epsilon_k n_{k\sigma} + \sum_{i,\sigma} \hat{\epsilon}_{i\sigma}(\{b_\nu + b_\nu^\dagger\}, Un_{i\bar{\sigma}})n_{i\sigma} + \sum_{\upsilon=1}^{4} \omega_\nu b_\nu^\dagger b_\nu + \sum_{k,i,\sigma} \{\upsilon_{ik} c_{i\sigma}^\dagger c_{k\sigma} + \text{h.c.}\} + \sum_{i\neq j,\sigma} \upsilon_{ij} c_{i\sigma}^\dagger c_{j\sigma} - \sum_{\{i\},\nu=1}^{4} \{\lambda_{ic\nu}(b_\nu + b_\nu^\dagger) + Un_{i\sigma}n_{i\bar{\sigma}}\} \quad (2.1)$$

The first two terms describe the electronic states of electrode and the adsorbate layer. ϵ_k and $\hat{\epsilon}_{i\sigma}n_{i\sigma}$ are the energy of kth electronic level in the substrate and the energy operator for the site i in the two-dimensional adsorbate lattice. $\hat{\epsilon}_{i\sigma}$ includes the contributions to the adsorbate orbital energy due to its coupling to various boson branches, and from the intraadsorbate Coulomb repulsion U. $c_l^\dagger(c_l)$ and n_l are creation (annihilation) and number operators for the quantum state l. The set $(\{k\sigma\}, \{(i\sigma\})$ is assumed to form a complete orthonormal set. The third term corresponds to the three polarization branches in the solvent medium ($\nu = 1, 2, 3$) and the surface plasmon in the substrate ($\nu = 4$). The next two entries describe the respective hopping terms between the sites on adsorbate layer and substrate band states, and between the adsorbates in the two-dimensional lattice. The coupling between the adsorbate core charge and the boson modes is represented by the last term in eq 2.1. The U term here removes the double counting of the intraadsorbate repulsion. $\{i\}$ implies that the summation is over the sites occupied by the adsorbates.

At an electrochemical interface, the solvent layer adjacent to electrode is usually described, to a first approximation, as a structureless medium of dielectric constant 5.0.[19] There is no charge transfer between the dielectric medium and the electrode. It only provides the background in which the adsorbate lattice is embedded. The operator $\hat{\epsilon}_{i\sigma}$, when a site i is occupied by an adsorbate, is[20]

$$\hat{\epsilon}_{i\sigma}(\{b_\nu + b_\nu^\dagger\}, Un_{i\bar{\sigma}}) = E_a + \sum_{\nu=1}^{4} \lambda_{ia\nu}(b_\nu + b_\nu^\dagger) + Un_{i\bar{\sigma}} \quad (2.2)$$

where E_a is the adsorbate's orbital energy in the vacuum.

In case site i is unoccupied by an adsorbate, the expectation value of $\hat{\epsilon}_{i\sigma}$ is given by the relation

$$\langle \hat{\epsilon}_{i\sigma} \rangle \rightarrow \infty \tag{2.3}$$

This ensures no charge sharing between the electrode and vacant sites.

$\hat{\epsilon}_{i\sigma}$ is therefore a random entity, giving rise to a diagonal randomness in the problem. All other parameters, both diagonal and nondiagonal, are taken to be deterministic. They do not depend on the occupancy status of the sites.

It is pertinent here to consider how a system described through the above Hamiltonian differs from the system studied by Krastov and Mal'shukov (KM) for the structural phase transition in an adsorbate layer.[21] This clarification is also needed because the approach used by KS to study the coverage dependence of the adsorbate charge at an electrochemical interface[17] has a similarity with the KM formalism. Therefore, we mention the following basic differences between the two approaches:

(i) We consider a random distribution of adsorbate on the 2D lattice. No such randomness is inherent in KM formalism. We treat the randomness using the CPA approach. Being an effective medium theory, CPA averages out all the inhomogeneities in the system and provides us with a description in which all the adsorption sites are equivalent; though the effective self-consistent site energy is now a function of energy variable (cf. section 3).

(ii) We model the direct interaction between adsorbate through the hopping term $\sum_{i\neq j,\sigma} v_{ij} c_{i\sigma}^{\dagger} c_{j\sigma}$. This "one-body" interaction leads to the band structure of 2D adlayer (cf. section 3).

In contrast, the interadsorbate direct interaction is modeled in the KM analysis through a "two-body" Coulomb term $(1/2)\sum_{i\neq j} U\hat{n}_i\hat{n}_j$ describing the electrostatic interactions between the adions. The same is true for the KS studies on the coverage dependence of the adsorbate charge.

(iii) In the KM formalism, the shift in adsorbate orbital energy due to a boson mode is $\lambda^2/\omega_0\langle n\rangle$ for all coverages. The coverage dependence of this shift comes only through the coverage dependence of the average charge $\langle n\rangle$. To take into account the progressive desolvation of the adspecies with increasing coverage, the ensuing shift due to solvent polarization modes is scaled by a factor $(1 - \theta^2)$ in our formalism (cf. section 7).

(iv) The KM analysis employs "spin-less" approximation wherein the intraadsorbate Coulomb repulsion U is taken to be the largest energy parameter in the system. Thus, only one electron is allowed in a valence orbital. In Hamiltonian (2.1), no such approximation has been used.

(v) Both the KM and KS analysis are based on the wide-band approximation.

The above comparison shows that present formalism is qualitatively different from the KM and KS approach for the coverage-dependent properties of an adlayer. However, a suitable extension of the wide-band limit based approach for random adlayer would enable us to make a comparison between the present and the KM, KS formalism, at least when the coverage is small. We refer to section 6 and 8 for further details in this regard.

To summarize, the chemisorbed species are considered here to be distributed randomly over various adsorption sites on the substrate lattice. These sites form a 2D lattice in a medium of effective dielectric constant 5.0. We take this 2D lattice to be commensurate with the underlying substrate surface. This implies that the adspecies occupy "on-top" positions. At coverages less than unity, the sites unoccupied by adsorbates constitute the second component of the adlayer, the first being the occupied sites. At complete coverage ($\theta = 1$) the adsorbates form (1×1) ordered structure. The various system components and their interactions are described by the Hamiltonian (2.1).

2.1. An Effective Hamiltonian. The Hamiltonian (2.1) presents a complex problem, the reason being its many-body nature and the inherent randomness in the system. The many-body aspect follows from the intraadsorbate coulomb repulsion and the fermion−boson interactions. We treat the former within the Hartree−Fock approximation, which in effect raises the E_a by $U\langle n_{a\bar{\sigma}}\rangle$. In an earlier communication,[16] we had analyzed the fermion−boson coupling in a detailed manner through superoperator technique. Therein, it had been shown that for low-frequency boson modes, a mean field decoupling

$$\phi n_{a\sigma} \approx \langle\phi\rangle n_{a\sigma} + \phi\langle n_{a\sigma}\rangle \tag{2.4}$$

suffices ($\phi = b + b^{\dagger}$). Consequently, E_a gets further shifted by $\sum_{\nu=1,2} \lambda_{i\nu}\langle\phi_\nu\rangle$ where $\nu = 1, 2$ respectively refers to orientational and vibrational polarization modes of the solvent. For high-frequency modes, it becomes necessary to go beyond the mean field approximation. The resulting shift in E_a is now $\sum_{\nu=3,4}[2\lambda_{ic\nu}\lambda_{i\nu}/\omega_\nu - \lambda_{i\nu}^2/\omega_\nu]$, where indices 3 and 4 correspond to electronic polarization branch in the solvent and surface plasmon oscillations in the substrate.

With these simplifications, and after substituting the value of $\langle\phi_\nu\rangle$,[16] the Hamiltonian (2.1) gets replaced by an effective Hamiltonian:

$$\begin{aligned} H = {} & \sum_{k,\sigma}\epsilon_k n_{k\sigma} + \sum_{i,\sigma}\epsilon_{i\sigma} n_{i\sigma} + \sum_{i,k,\sigma}\{v_{ik}c_{i\sigma}^{\dagger}c_{k\sigma} + \text{h.c.}\} + \\ & \sum_{i\neq j,\sigma} v_{ij}c_{i\sigma}^{\dagger}c_{j\sigma} + \sum_{\nu=1}^{4}\omega_\nu b_\nu^{\dagger}b_\nu + \\ & \sum_{\{i\},\nu=1,2}(\lambda_{i\nu}(\sum_{\sigma}\langle n_{i\sigma}\rangle - \lambda_{ic\nu}))\phi_\nu - \\ & \sum_{\{i\}}\left(U - 2\sum_{\nu=3,4}\frac{\lambda_{i\nu}^2}{\omega_\nu}\right)\langle ni_\sigma\rangle\langle n_{i\bar{\sigma}}\rangle - \\ & \sum_{\{i\},\sigma,\nu=1,2}\frac{\lambda_{i\nu}^2}{\omega_\nu}\left(\frac{2\lambda_{ic\nu}}{\lambda_{i\nu}} - \sum_{\sigma}\langle n_{i\sigma}\rangle\right)\langle n_{i\sigma}\rangle - \sum_{\{i\},\nu=3,4}\frac{\lambda_{ic\nu}^2}{\omega_\nu} \end{aligned} \tag{2.5}$$

where

$$\begin{aligned} \epsilon_{i\sigma} \equiv \epsilon_{a\sigma} = {} & E_a + \sum_{\nu=1,2}\frac{2\lambda_{i\nu}^2}{\omega_\nu}\left(\frac{\lambda_{ic\nu}}{\lambda_{i\nu}} - \langle n_{i\sigma}\rangle\right) + \\ & \sum_{\nu=3,4}\left(\frac{2\lambda_{ic\nu}\lambda_{i\nu}}{\omega_\nu} - \frac{\lambda_{i\nu}^2}{\omega_\nu}\right) + \left(U - 2\sum_{\nu=1}^{4}\frac{\lambda_{i\nu}^2}{\omega_\nu}\right)\langle n_{i\bar{\sigma}}\rangle \end{aligned} \tag{2.6}$$

when a site i is occupied by an adsorbate; and as noted earlier, $\epsilon_{i\sigma}$ tends to infinity otherwise. $\{i\}$ implies a summation over occupied sites only. The second and third terms on the right side of (2.6) describe the shifts in the adsorbate orbital energy due to slow and fast bosons modes, respectively. The fourth term takes into account the renormalization of U caused by fermion−boson interactions. While evaluating the shift in $\epsilon_{i\sigma}$ due to bosonic coupling, the boson-mediated interactions between different sites are neglected. Next, since the adsorption of a single species is considered, we replace $\lambda_{i\nu}$ by $\lambda_{a\nu}$ and $\lambda_{ic\nu}$ by $\lambda_{c\nu}$.

3. Green's Function: A CPA Approach

While constructing the effective Hamiltonian (2.5) from (2.1), two important simplifications are made. (i) A decoupling

between the fermionic and bosonic components is achieved. (ii) The system is now described by a one-body Hamiltonian. But the problem associated with the random nature of $\{\epsilon_{i\sigma}\}$ still remains. We tackle it using the concept of coherent potential approximation.[20,22,23] Herein, the random adsorbate layer is replaced by an effective, nonrandom, 2D medium. This is achieved by replacing the random variable $\epsilon_{i\sigma}$ by a deterministic energy parameter $k_\sigma(\epsilon)$ which is same for all the sites. $k_\sigma(\epsilon)$ depends on the energy variable ϵ. It has to be evaluated self-consistently using the condition that the configuration averaged t-matrix for an arbitrary site i, i.e., $\langle t_i\rangle_c$ is zero. $\langle ...\rangle_c$ denotes the configuration average. The physical reasoning behind this step is linked to the fact that random potentials at different sites cause a scattering of incident particles. In an effective medium, potential is the same at all the sites and hence there is no scattering; thus $\langle t_i\rangle_c = 0$.

The fermion Green's function (GF) matrix elements corresponding to sites on adsorbate layer satisfy the relation[20,23]

$$G_{ij} = G^0_{ij}\delta_{ij} + \sum_l G^0_{ii} W_{il} G_{lj} \tag{3.1}$$

where

$$G^{0\sigma}_{ij} = \left\langle c_{i\sigma} \frac{1}{\epsilon - \sum_{i\sigma}\epsilon_{i\sigma} n_{i\sigma}} c^\dagger_{j\sigma} \right\rangle \tag{3.2}$$

$\langle ...\rangle$ denotes the quantum mechanical average. The unperturbed GF is

$$G^{0\sigma}_{ij} = \frac{1}{\epsilon - \epsilon_{a\sigma}} \quad \text{if } i = j \text{ and site } i \text{ is occupied by an adsorbate}$$
$$= 0 \qquad \text{otherwise} \tag{3.3}$$

$$W_{il} = v_{il} + \sum_k \frac{v_{ik} v_{kl}}{\epsilon - \epsilon_k} = v_{il} + W'_{il} \tag{3.4}$$

is an energy dependent, but deterministic quantity. Expression 3.1 can be rewritten as an operator equation

$$G = G^0 + G^0 W G \tag{3.5}$$

which is valid only for the two-dimensional adsorbate lattice. Equation 3.5 implies

$$G = \frac{1}{\epsilon - \sum_{i\sigma}\epsilon_{i\sigma} n_{i\sigma} - W} \tag{3.6}$$

As noted earlier, CPA essentially replaces $\epsilon_{i\sigma}$ in (3.6) by $k_\sigma(\epsilon)$, i.e.,

$$\sum_{i,\sigma} \epsilon_{i\sigma} n_{i\sigma} \rightarrow \sum_{i\sigma} k_\sigma(\epsilon) n_{i\sigma} \equiv K(\epsilon) \tag{3.7}$$

Consequently, the configuration averaged Greenian operator is

$$\langle G\rangle_c \equiv \bar{G} = \frac{1}{\epsilon - K(\epsilon) - W} \tag{3.8}$$

The coherent potential $k_\sigma(\epsilon)$ is to be determined self-consistently through the expression[20]

$$\bar{G}^\sigma_{ii} = \frac{1-\theta}{\epsilon_{a\sigma} - k_\sigma(\epsilon)} \tag{3.9}$$

In order to determine $k_\sigma(\epsilon)$, an explicit expression for $\bar{G}^\sigma_{ii}$ is needed. As the effective medium replacing the random adsorbate layer is periodic, the configuration-averaged GF matrix elements are diagonal in two-dimensional Bloch representation. Hence for every site

$$\bar{G}^\sigma_{ii} = \left\langle i \left| \frac{1}{\epsilon - K - W} \right| i \right\rangle = \frac{1}{N_{||}} \sum_u \frac{1}{\epsilon - k_\sigma(\epsilon) - W(\epsilon,u)} \tag{3.10}$$

The summation over momentum u is restricted to the first Brillouin zone of 2D lattice having $N_{||}$ number of sites. $W(\epsilon,u)$ is the Fourier transform of W_{ij}.

$$W(\epsilon,\mathrm{u}) = \sum_j \mathrm{e}^{i\mathbf{u}\cdot\mathbf{R}_{ji}} [v_{ij} + W'_{ij}(\epsilon)]$$
$$= \epsilon_u + \sum_j \mathrm{e}^{i\mathbf{u}\cdot\mathbf{R}_{ji}} W'_{ij}(\epsilon)$$
$$= \epsilon_u + W'(\epsilon, u) \tag{3.11}$$

Using (3.9) and (3.10), the self-consistency equation for $k_\sigma(\epsilon)$ can be written as

$$\bar{G}^\sigma_{ii} = \frac{1}{N_{||}} \sum_u \frac{1}{\epsilon - k_\sigma(\epsilon) - \epsilon_u - W'(\epsilon, u)} = \frac{1-\theta}{\epsilon_{a\sigma} - k_\sigma(\epsilon)} \tag{3.12}$$

In the next section, we consider the evaluation of the adsorbate density of states and its occupation probability using the adsorbate GF $\bar{G}^\sigma_{ii}$.

4. Adsorbate Density of States and Occupation Probability

To evaluate the adsorbate density of states at site i, we introduce a restricted configuration averaged GF $\langle G^\sigma_{ii}\rangle_{i=a}$. Here the restricted configuration average means that we a priori consider the site i to be occupied by an adsorbate. For the remaining sites, whose occupancy status is left unspecified, configuration average is performed. The adsorbate density of states at the site i is given as

$$\rho^\sigma_i(\epsilon) = \frac{1}{\pi}\mathrm{Im}\,\langle G^\sigma_{ii}(\epsilon)\rangle_{i=a} \tag{4.1}$$

The imaginary part of the Green's function is evaluated by taking $\epsilon \equiv \epsilon - i0^+$. A further configuration average at site i leads to

$$\langle\langle G^\sigma_{ii}\rangle_{i=a}\rangle = \theta\langle G^\sigma_{ii}\rangle_{i=a} = \bar{G}^\sigma_{ii} \tag{4.2}$$

From (4.1) and (4.2)

$$\rho_i^\sigma(\epsilon) = \frac{1}{\pi\theta}\mathrm{Im}\,\bar{G}_{ii}^\sigma \tag{4.3}$$

Given $\rho_i^\sigma(\epsilon)$, the average occupation probability is determined through the relation

$$\langle n_{i\sigma}\rangle = \int_{-\infty}^{\epsilon_f} \rho_i^\sigma(\epsilon)\,\mathrm{d}\epsilon \equiv \langle n_{a\sigma}\rangle \tag{4.4}$$

where ϵ_f is the Fermi energy. As $\bar{G}_{ii}^\sigma$ implicitly depends on $\langle n_{i\sigma}\rangle$, a self-consistent determination of $\langle n_{i\sigma}\rangle$ is required. We determine it in the nonmagnetic limit, i.e., $\langle n_{i\sigma}\rangle = \langle n_{i\bar{\sigma}}\rangle$. Thus, in the present formalism, we need two self-consistency calculations, one for the coherent potential $k_\sigma(\epsilon)$, and the other for $\langle n_{i\sigma}\rangle$.

5. Interaction Energy

The interaction energy for the chemisorbed system is defined as

$$\Delta\bar{E} = \langle H\rangle - \langle H^0\rangle \tag{5.1}$$

where H is the Hamiltonian (2.5), with $\epsilon_{i\sigma}$ replaced by $k_\sigma(\epsilon)$. H^0 is the Hamiltonian of the far-separated substrate−adsorbate system.

$$H^0 = \sum_{k,\sigma}\epsilon_k n_{k\sigma} + \theta N_{||}[\sum_\sigma E_a n_{a\sigma} + U n_{a\sigma}n_{a\bar{\sigma}}] + \sum_{\nu=1}^{4}\omega_\nu b_\nu^\dagger b_\nu + \theta N_{||}[\sum_{\nu=1}^{3}(\lambda_{a\nu}^0 n_{a\sigma} + \lambda_{c\nu}^0)](b_\nu + b_\nu^\dagger) \tag{5.2}$$

$\lambda_{\alpha\nu}^0(\alpha = a, c;\ \nu=1, 2, 3)$ is the coupling coefficient between the adsorbate in the bulk electrolyte and solvent polarization modes. An adsorbate far removed from the electrode surface does not experience any image effect, so we take $\lambda_{\alpha 4}^0 = 0$. $\lambda_{\alpha\nu}^0$ differs from the respective $\lambda_{\alpha\nu}$ because the solvation energies of an adsorbate, when it is located at the interface and when it is in the bulk, are different. $\theta N_{||}$ is the total number of adsorbates that have migrated from the bulk region to form the 2D adlayer at the interface.

As in section 2, we again decouple the fermionic and bosonic components in H^0. Subsequent averaging of the bosonic operators[16] in H and H^0 leads to

$$\Delta\bar{E} = \Delta\bar{E}_1 + \Delta\bar{E}_2 + \Delta\bar{E}_3 \tag{5.3}$$

where

$$\Delta\bar{E}_1 = \langle[\sum_{k,\sigma}\epsilon_k n_{k\sigma} + \sum_{i,\sigma}k_\sigma(\epsilon)n_{i\sigma} + \sum_{i,k,\sigma}(v_{ik}c_{i\sigma}^\dagger c_{k\sigma} + \text{h.c.}) + \sum_{i\neq j,\sigma}v_{ij}c_{i\sigma}^\dagger c_{j\sigma}]\rangle \tag{5.4}$$

$$\Delta\bar{E}_2 = -\langle[\sum_{k,\sigma}\epsilon_k n_{k\sigma} + \theta\, N_{||}\{\sum_\sigma \epsilon_{a\sigma}^0 n_{a\sigma} + U n_{a\sigma}n_{a\bar{\sigma}}\}]\rangle^0 \tag{5.5}$$

$$\Delta\bar{E}_3 = \theta N_{||}\left[\sum_{\nu=1,2}\frac{\lambda_{a\nu}{}^2}{\omega_\nu}(\sum_\sigma\langle n_{a\sigma}\rangle)^2 - \sum_{\nu=1}^{4}\frac{\lambda_{c\nu}{}^2}{\omega_\nu} - \left(U - 2\sum_{\nu=3}^{4}\frac{\lambda_{a\nu}{}^2}{\omega_\nu}\right)\langle n_{a\sigma}\rangle\langle n_{a\bar{\sigma}}\rangle - \left\{\sum_{\nu=1}^{2}\frac{\lambda_{a\nu}^0{}^2}{\omega_\nu}(\sum_\sigma\langle n_{a\sigma}\rangle^0)^2 - \sum_{\nu=1}^{3}\frac{\lambda_{c\nu}^0{}^2}{\omega_\nu}\right\}\right] \tag{5.6}$$

$$\epsilon_{a\sigma}^0 = E_a + \sum_{\nu=1}^{2}\frac{2\lambda_{a\nu}^0{}^2}{\omega_\nu}\left(\frac{\lambda_{c\nu}^0}{\omega_\nu} - \sum_\sigma\langle n_{a\sigma}\rangle^0\right) - 2\frac{\lambda_{a3}^0{}^2}{\omega_3}\langle n_{a\bar{\sigma}}\rangle^0 + 2\left(\frac{\lambda_{c3}^0\lambda_{a3}^0}{\omega_3} - \frac{\lambda_{a3}^0{}^2}{\omega_3}\right) \tag{5.7}$$

$\langle ...\rangle$ and $\langle ...\rangle^0$, respectively, imply the averaging with respect to the states of interacting and far-removed adsorbate−substrate systems.

Using the Heisenberg equation of motion for Green's functions along with the relation (4.3) and

$$\rho_k^\sigma(\epsilon) = (1/\pi)\mathrm{Im}\,\bar{G}_{kk}^\sigma(\epsilon) \tag{5.8}$$

$\Delta\bar{E}_1$ and $\Delta\bar{E}_2$ can be expressed in terms of substrate and the adsorbate layer density of states

$$\Delta\bar{E}_1 + \Delta\bar{E}_2 = \sum_\sigma\{\int_{-\infty}^{\epsilon_f}\epsilon\rho_m^\sigma(\epsilon)\,\mathrm{d}\epsilon - \int_{-\infty}^{\epsilon_f^0}\epsilon\sum_k\rho_k^{0\sigma}(\epsilon)\,\mathrm{d}\epsilon\} - \theta N_{||}\{\sum_\sigma\epsilon_{a\sigma}^0\langle n_{a\sigma}\rangle^0 + U\langle n_{a\sigma}\rangle^0\langle n_{a\bar{\sigma}}\rangle^0\} \tag{5.9}$$

where we have used

$$\langle n_{a\sigma}n_{a\bar{\sigma}}\rangle^0 = \langle n_{a\sigma}\rangle^0\langle n_{a\bar{\sigma}}\rangle^0$$

for an isolated adsorbate. In this case, $\langle n_{a\sigma}\rangle^0$ and $\langle n_{a\bar{\sigma}}\rangle^0$ can take values 0 or 1 only. ϵ_f and ϵ_f^0 are the Fermi energies in the presence and in the absence of chemisorption.

$$\rho_m^\sigma(\epsilon) = \sum_k\rho_k^\sigma(\epsilon) + \sum_i\rho_i^\sigma(\epsilon) \tag{5.10}$$

is the total electronic density of states for chemisorbed system.

Using the charge conservation criterion

$$\sum_\sigma\int_{-\infty}^{\epsilon_f}\rho_m^\sigma(\epsilon)\,\mathrm{d}\epsilon = \sum_{k,\sigma}\int_{-\infty}^{\epsilon_f^0}\rho_k^{0\sigma}(\epsilon)\,\mathrm{d}\epsilon + \theta N_{||}\sum_\sigma\langle n_{a\sigma}\rangle^0 \tag{5.11}$$

we have

$$\Delta\bar{E}_1 + \Delta\bar{E}_2 = \sum_\sigma\int_{-\infty}^{\epsilon_f^0}(\epsilon - \epsilon_f^0)(\rho_m^\sigma(\epsilon) - \sum_k\rho_k^{0\sigma}(\epsilon))\,\mathrm{d}\epsilon - \theta N_{||}\{\sum_\sigma(\epsilon_{a\sigma}^0 + \epsilon_f^0)\langle n_{a\sigma}\rangle^0 + U\langle n_{a\sigma}\rangle^0\langle n_{a\bar{\sigma}}\rangle^0\} \tag{5.12}$$

To obtain $\rho_m^\sigma(\epsilon)$, we need both adsorbate (cf. eq 3.12) and the substrate Green's functions. The latter is obtained from the relation

$$\bar{G}^{\sigma}_{kk'} = \bar{G}^{0\sigma}_{kk}\delta_{kk'} + \sum_{i,j} \bar{G}^{0\sigma}_{kk} v_{ki} \bar{G}^{\sigma}_{ij} v_{jk'} \bar{G}^{0\sigma}_{kk'}$$

$$= \bar{G}^{0\sigma}_{kk'}\delta_{kk'} + \frac{1}{N_{\|}} \sum_{i,j} \frac{\bar{G}^{0\sigma}_{kk}\, e^{i\mathbf{u}\cdot\mathbf{R}_{ij}}\, v_{ki} v_{jk'} \bar{G}^{0\sigma}_{kk'}}{\epsilon - k_{\sigma}(\epsilon) - W(u,\epsilon)} \quad (5.13)$$

with

$$\bar{G}^{0\sigma}_{kk}(\epsilon) = (\epsilon - \epsilon_k)^{-1}$$

Equations 5.12 and 5.13 allow us to rewrite the interaction energy expression as

$$\Delta\bar{E} = \frac{1}{\pi}\mathrm{Im} \sum_{\sigma} \int_{-\infty}^{\epsilon_f} (\epsilon - \epsilon_f) \left(\sum_{u} \frac{1 - \dfrac{\partial W(u,\epsilon)}{\partial \epsilon}}{\epsilon - k_{\sigma}(\epsilon) - W(u,\epsilon)} \right) d\epsilon - \theta N_{\|} \{ \sum_{\sigma} \epsilon^{0}_{a\sigma} \langle n_{a\sigma} \rangle^{0} + U \langle n_{a\sigma} \rangle^{0} \langle n_{a\bar{\sigma}} \rangle^{0} \} + \Delta\bar{E}_3 \quad (5.14)$$

The expressions (4.3), (4.4), and (5.14) along with (5.6) constitute our main results for the adsorbate density of states, its average electronic charge, and the interaction energy.

The binding energy of a single adsorbate can be obtained by dividing $\Delta\bar{E}$ with $\theta N_{\|}$.

$$\Delta E = (1/\theta\, N_{\|})\Delta\bar{E} \quad (5.15)$$

Appropriate expressions suitable for the numerical calculations are derived in the next section.

6. Electrochemisorption: A Simple Model for Numerical Calculations

The results given in the last section require tedious summations over the momentum k of the metal states and the momentum u of the Bloch states in the 2D adsorbate layer. But we can achieve considerable simplification under the following conditions.[20]

1. It is mentioned in the section 2 that the adsorbate layer is commensurate with the underlying substrate. As a result, the Brillouin zones of the adsorbate layer and the underlying parallel two-dimensional substrate lattice are the same. Assuming the separability of the metal states energies $\{\epsilon_k\}$ in the directions parallel and perpendicular to the surface, one can write

$$\epsilon_k = \epsilon_{u,k_z} = \epsilon^{\|}_{u} + \epsilon^{\perp}_{k_z} \quad (6.1)$$

where the zero of the energy scale is taken at the substrate band center.

2. The density of states for the substrate in the direction perpendicular to surface is taken to be Lorentzian, whereas the same is assumed to be rectangular along the surface:

$$\frac{1}{N_{\perp}} \sum_{K_z} \delta(\epsilon - \epsilon^{\perp}_{k_z}) = \frac{1}{\pi} \frac{\Delta_{\perp}}{(\epsilon - \epsilon^{\perp}_{k_z})^2 + \Delta_{\perp}{}^2} \quad (6.2)$$

$$\frac{1}{N_{\|}} \sum_{u} \delta(\epsilon - \epsilon^{\|}_{u}) = 1/2\Delta_{\|}; \qquad -\epsilon < \Delta_{\|} < \epsilon$$

$$= 0 \qquad \text{otherwise} \quad (6.3)$$

$2\Delta_{\|}$ is the substrate bandwidth at the surface and Δ_t the total bandwidth of the substrate, is given as

$$2(\Delta_{\|} + \Delta_{\perp}) = \Delta_t \quad (6.4)$$

$N_{\perp}$ is the number of atomic layers in the substrate in the direction perpendicular to its surface.

3. An adsorbate occupying the "on-top" position on the substrate is assumed to couple with the underlying substrate atom only. Therefore,

$$v_{ik} = \frac{1}{\sqrt{N_{\perp} N_{\|}}}\, v e^{i\mathbf{k}\cdot\mathbf{R}_i} \quad (6.5)$$

where v is the "adsorbate−nearest substrate atom" coupling strength.

4. As the adsorbate layer is commensurate with the underlying substrate layer, both these layers have identical geometrical configurations. The matrix element v_{ij} depends on the distance R_{ij} and a universal constant specific to the system.[24] Since R_{ij} is same for the adsorbate and substrate layers, the hopping term v_{ij} for the adsorbate layer is proportional to v_{ij}', the hopping term in the substrate's surface layer. Taking μ as the proportionality constant, we have

$$v_{ij} = \mu v'_{ij} \quad (6.6)$$

and hence, using the Fourier transform (cf. eq 3.11)

$$\epsilon_u = \mu \epsilon^{\|}_{u} \quad (6.7)$$

Since the half-bandwidths of adsorbate layer, δ, and substrate surface, $\Delta_{\|}$, are proportional to v_{ij} and v'_{ij}, respectively, we can write

$$\mu = \delta/\Delta_{\|} \quad (6.8a)$$

The half-bandwidth δ in the above relation corresponds to the case of a complete monolayer. But, in fact, the bandwidth of adlayer depends on the coverage and tends to zero in the low-coverage limit. Following the methodology described in ref 22, we can write $\delta(\theta)$, the coverage-dependent half-bandwidth of the adlayer, as $\theta\delta$. Consequently, for a general coverage, eq 6.8a gets modified as

$$\mu = \theta\delta/\Delta_{\|} \quad (6.8b)$$

It may be noted here that when the coverage tends to zero, the configuration-averaged adsorbate Green's function (cf. eq 3.10) equals θ times the adsorbate GF obtained for the "lone-adsorbate" case. This remains valid for any strength of the v_{ij}.[20,23]

For a given material, if the total bandwidth Δ_t is known, the bandwidth $2\Delta_{\|}$ for its surface can be obtained using the relation[25]

$$2\Delta_{\|} = (N_s/N_b)\, \Delta_t \quad (6.9)$$

N_s and N_b are the respective coordination numbers for the surface and bulk atoms. Using eqs 3.12 and 6.1−6.7, the adsorbate GF and the self-consistency equation for the coherent potential $k_{\sigma}(\epsilon)$ can be rewritten as

$$\bar{G}^{\sigma}_{ii}(\epsilon) = \frac{1 - \theta}{\epsilon_{a\sigma} - k_{\sigma}(\epsilon)}$$

$$= \frac{1}{2\Delta_{\|}(B-A)\mu} \times \left[(A-C)\ln\left(\frac{A-\Delta_{\|}}{A+\Delta_{\|}}\right) - (B-C)\ln\left(\frac{B-\Delta_{\|}}{B+\Delta_{\|}}\right)\right] \tag{6.10}$$

with

$$A/B = {}^1/_2\left[(C+D) \pm \left\{(C+D)^2 - 4\left(CD - \frac{v^2}{\mu}\right)\right\}^{1/2}\right] \tag{6.11}$$

$$C = \frac{\epsilon - k_\sigma(\epsilon)}{\mu}; \quad D = \epsilon - i\Delta_\perp \tag{6.12}$$

Similarly, the interaction energy (cf. eqs 5.14 and 5.15) can be expressed as

$$\Delta\bar{E} = \frac{N_{\|}}{\pi}\mathrm{Im}\sum_\sigma \{\int_{-\infty}^{\epsilon_f}(\epsilon-\epsilon_f)\{\bar{G}_{ii}^\sigma + \xi^\sigma\}\,\mathrm{d}\epsilon\} - \theta N_{\|}\{\sum_\sigma(\epsilon_{a\sigma}^0 + \epsilon_f)\langle n_{a\sigma}\rangle^0 + U\langle n_{a\sigma}\rangle^0\langle n_{a\bar{\sigma}}\rangle^0\} + \Delta\bar{E}_3 \tag{6.13}$$

$\Delta\bar{E}_3$ and $\epsilon_{a\sigma}^0$ are given in eqs 5.6 and 5.7, and

$$\xi^\sigma = \frac{1}{2\Delta_{\|}}\left[\ln\left(\frac{D-\Delta_{\|}}{D+\Delta_{\|}}\right) + \frac{1}{B-A}\left\{(A-C)\ln\left(\frac{A-\Delta_{\|}}{A+\Delta_{\|}}\right) - (B-C)\ln\left(\frac{B-\Delta_{\|}}{B+\Delta_{\|}}\right)\right\}\right] \tag{6.14}$$

The expression 6.10 for the adsorbate GF contains μ in the denominator. Though μ tends to zero when the θ approaches zero, the $\bar{G}_{ii}^\sigma(\epsilon)$ remains finite in this limit. This can be verified either by suitable expansion of adsorbate GF, or by a priori taking v_{ij} (and hence μ) to be zero and reevaluating the adsorbate Green's function.[20,23]

In the above derivations for the adsorbate GF and the binding energy, $W'(\epsilon,u)$, the Fourier coefficient of W'_{ij} (cf. eqs 3.4 and 3.11), has been explicitly evaluated using the model density of states (eqs 6.2 and 6.3) and the relation 6.5. Alternatively, $\bar{G}_{ii}^\sigma$ and $\Delta\bar{E}$ can be evaluated using the wide-band approximation. As noted in the Introduction, this approximation has been extensively used in the chemisorption problems at electrochemical interface, as well as in the Kravstov and Mal'shukov work on adlayer.[21] Accordingly, we now have

$$W'_{il}(\epsilon) \approx i\Delta \tag{6.15}$$

where Δ is an energy-independent quantity and is a measure of adsorbate's energy width.[17,21] Within the above approximation, expression 6.10 for the adsorbate GF now becomes

$$\bar{G}_{ii}^{(w)\sigma}(\epsilon) = \frac{1-\theta}{\epsilon_{a\sigma} - k_\sigma(\epsilon)} = \frac{1}{2\Delta_{\|}\mu}\ln\left(\frac{\epsilon - k_\sigma(\epsilon) + \mu\Delta_{\|} - i\Delta}{\epsilon - k_\sigma(\epsilon) - \mu\Delta_{\|} - i\Delta}\right) \tag{6.16}$$

In the $\theta \to 0$ limit, the $\bar{G}_{ii}^{(w)\sigma}$ reduces to θ times the adsorbate GF $G_{aa}(\epsilon)$ obtained by Kornyshev and Schmickler.[17,20]

$$\bar{G}_{aa}^{(w)\sigma}(\epsilon) = \frac{\theta}{\epsilon - \epsilon_{a\sigma} - i\Delta} \tag{6.16a}$$

The superscript (w) here specifies the wide-band limit. While calculating the average adsorbate charge and the binding energy, the θ appearing in numerator of the right-hand side of the above expression gets canceled with a θ in the denominator (cf. eqs 4.3 and 5.15) and we recover the lone-adsorbate result of Kornyshev and Schmickler.

When the interaction energy is evaluated within the wide-band approximation, the ξ^σ appearing on the right-hand side of eq 6.13 is identically zero. Also the integral in this expression can be rewritten as (cf. eqs 4.3 and 4.4):

$$(1/\pi)\mathrm{Im}\int_{-\infty}^{\epsilon_f}(\epsilon-\epsilon_f)\bar{G}_{ii}^{(w)\sigma}\,\mathrm{d}\epsilon = (1/\pi)\mathrm{Im}\int_{-\infty}^{\epsilon_f}(\epsilon_{a\sigma} + (\epsilon - \epsilon_f - \epsilon_{a\sigma}))\bar{G}_{ii}^{(w)\sigma}\,\mathrm{d}\epsilon = \theta\epsilon_{a\sigma}\langle n_{i\sigma}\rangle + (1/\pi)\mathrm{Im}\int_{-\infty}^{\epsilon_f}(\epsilon-\epsilon_f-\epsilon_{a\sigma})\bar{G}_{ii}^{(w)\sigma}\,\mathrm{d}\epsilon \tag{6.17}$$

The last integral in the above expression diverges, and its lower limit needs a cutoff for obtaining a finite result. This energy cutoff is put at ϵ_Γ, the bottom of conduction band in the metal.[18] Thus, in the wide-band limit, the interaction energy expression (6.13) gets replaced by

$$\Delta\bar{E}^{(w)} = N_{\|}\sum_\sigma\{\theta\epsilon_{a\sigma}\langle n_{a\sigma}\rangle + (1/\pi)\mathrm{Im}\int_{\epsilon_\Gamma}^{\epsilon_f}(\epsilon-\epsilon_f-\epsilon_{a\sigma})\{\bar{G}_{ii}^{(w)\sigma}\}\,\mathrm{d}\epsilon\} - \theta N_{\|}\{\sum_\sigma(\epsilon_{a\sigma}^0 + \epsilon_f)\langle n_{a\sigma}\rangle^0 + U\langle n_{a\sigma}\rangle^0\langle n_{a\bar{\sigma}}\rangle^0\} + \Delta\bar{E}_3 \tag{6.18}$$

In the following sections, the details of the electronic structure of an copper layer adsorbed on gold electrode are considered. We give the results both for the general analysis and the wide-band approximation. A comparative study of these two approaches for the chemisorption problem is also provided.

7. Electrochemisorption of Copper on Gold Electrode

The relevance of substrate d band in the chemisorption phenomenon is well recognized. The importance of d band arises from its high density of states. Besides, the substrate d-orbitals provide strong, directed bonding with the adsorbate electronic states. Consequently, we model the gold substrate through its d band in the present calculations. But it may be mentioned here that the gold d band lies deeply under the Fermi level. In fact the gold Fermi level lies inside the sp-band. Therefore, one needs to include both d and sp bands of gold in the chemisorption calculations. In this regard, the Lorentzian density of states in eq 6.2 can be considered as the effective density of states which includes both d and sp bands of gold. It may be noted that the density of states for d band alone is semielliptical, and not Lorentzian.

In an earlier calculation for the electrosorption, the participation of only the s orbital of copper in the bonding was assumed.[26] But a proper analysis requires the inclusion of both s and d orbitals of copper in the model. There are three main reasons why a d-orbital of copper is also relevant to electrosorption process: (i) energetically it lies near the substrate d band when the intraadsorbate Coulomb repulsion U_d is taken into account, (ii) it has a large matrix element with the substrate states, and (iii) during the chemisorption of Cu^{2+}, a substantial amount of charge transfer occurs from the substrate to an unoccupied copper d-orbital. Therefore, both s and d orbitals of copper are included in the calculations. Subsequent analysis then requires a simultaneous self-consistent determination of the adsorbate

charges $\langle n_{s\sigma}\rangle$, $\langle n_{d\sigma}\rangle$, and the coherent potentials $k_{s\sigma}(\epsilon)$ and $k_{d\sigma}(\epsilon)$. In order to simplify this difficult task, we neglect the indirect interactions between s and d orbitals. Thus we treat the electrosorption of s and d orbitals separately. The self-consistency criterion is now applicable to individual pairs $(\langle n_{s\sigma}\rangle, k_{s\sigma}(\epsilon))$ and $(\langle n_{d\sigma}\rangle, k_{d\sigma}(\epsilon))$ only.

7.1. System Parameters. The energies of copper s and d orbitals lie at 7.72 and 20.14 eV below the vacuum level.[24] In the present calculations, energy zero is taken at the center of the substrate d band. Hence

$$E_s = \phi + \epsilon_f - 7.72; \quad E_d = \phi + \epsilon_f - 20.14 \tag{7.1}$$

ϕ is the substrate work function and ϵ_f is its Fermi level measured from the band center. The intraadsorbate repulsion energy for s and d orbitals, namely U_s and U_d, are 5.92 and 5.45 eV, respectively.[24,27]

We employ the Dogonadze, Kornyshev, and Schmickler scheme[26,28] to evaluate the contributions of various solvent polarization modes toward the total solvation energy. Accordingly, the contributions from the orientational, vibrational, and electronic polarization modes are respectively given as:

$$E_1 = \alpha X\left(\frac{1}{\epsilon_{ir}} - \frac{1}{\epsilon_s}\right)F(\lambda_1/r_i)$$

$$E_2 = \alpha X\left(\frac{1}{\epsilon_{opt}} - \frac{1}{\epsilon_{ir}}\right)F(\lambda_2/r_i)$$

$$E_3 = \alpha X\left(1 - \frac{1}{\epsilon_{opt}}\right)F(\lambda_3/r_i) \tag{7.2}$$

where

$$F(x) = 1 - (1 - e^{-x})/x \tag{7.3}$$

and the correlation lengths λ_1, λ_2, and λ_3 for the three polarization branches are 0.68, 0.12, and 0.10 nm respectively. The ionic radius is r_i (0.127, 0.096, and 0.072 nm for Cu^0, Cu^{1+}, and Cu^{2+}, respectively) and ϵ_{ir} (= 4.9), ϵ_{opt} (1.15), and ϵ_s (78.5) are the infrared, optical, and static dielectric constants for water. The radius of a fractionally charged adsorbate is obtained through the interpolation formula provided in ref 26. α is the degree of solvation of the adsorbate at the interface. The parameter X is so chosen that $z^2(E_1 + E_2 + E_3)/\alpha$ equals the solvation energy ΔG_S of an ion having charge z. X in fact accounts for any discrepancy in the calculated and experimental solvation energies. At a metal−vacuum interface, the image energy of a unit charge is taken as $-e^2/4(x + \kappa^{-1})$[29], where κ^{-1} is the Thomas−Fermi screening length. For gold, $\kappa^{-1} = 0.06$ nm. x is the distance of the charge from the electrode surface. We take the distance between the copper adsorbate and the underlying gold atom to be the same as the distance between two nearest adsorbed copper atoms in the monolayer configuration, i.e., 0.288 nm.[4] The electrode plane is considered to be located at the midpoint between the copper and gold atoms. Therefore, the distance x between the adsorbate and substrate surface is 0.144 nm. Substituting these values, we get the image energy $\epsilon_{im} = -1.76$ eV. Thus, we now have

$$\frac{\lambda_{a\nu}^2}{\omega_\nu} = E_\nu \qquad (\nu = 1, 2, 3 \text{ unless specified otherwise}) \tag{7.4}$$

and at the M−V interface

$$\lambda_{a4}^2/\omega_4 = -\epsilon_{im} = 1.76 \text{ eV} \tag{7.4a}$$

At an electrochemical interface, we use the Kornyshev and Schmickler formalism for determining the image energy.[26]

$$-\frac{\lambda_{a4}^2}{\omega_4} = \epsilon_{im} = \frac{e_0^2}{4\epsilon_{opt} r_i}\frac{(\epsilon_{opt} - 1) - \kappa^2 r_i^2}{(\epsilon_{opt} + 1) + \kappa^2 r_i^2} \tag{7.4b}$$

As noted earlier, $(E_1 + E_2 + E_3)/\alpha = \Delta G_s = 5.92$ eV is the solvation energy of a singly charged copper ion.[26] When the adsorbate is in the bulk solution region, $\lambda_{a\nu}^{02}/\omega_\nu = E_\nu/\alpha$.

The solvation energy of the interfacial adsorbate, as considered above, is appropriate for low-coverage regime. At the higher coverages, adsorbates progressively get desolvated. This is caused by (i) steric effects and (ii) delocalization of adsorbate electron over a large spatial region for metallic adsorbates. The delocalization of electrons causes a weakening of the adsorbate−solvent interaction and it also leads to an effective screening of the adsorbate core charge. In fact when $\theta = 1$, the electrons are delocalized over the entire 2D copper layer. This layer can be now considered to form the outermost surface of the electrode. Consequently, its interaction with the solvent polarization, as a first approximation, can be neglected. Since no theoretical study of the dependence of the adsorbate solvation energy ΔG_s^a on coverage seems to be available, we propose the following interpolative scheme for E_ν, and hence for $\Delta G_s^a(\theta)$, as a function of coverage

$$E_\nu(\theta) = (1 - \theta^2)E_\nu \tag{7.5}$$

The presence of θ^2 in a sense takes into account the correlation in a primitive way. The decrease in adsorbate solvation energy $E_\nu(\theta)$ depends on the probability of finding another adsorbate in its vicinity. The relation 7.5 satisfies the limiting cases corresponding to $\theta \to 0$ and $\theta = 1$. We now have

$$\frac{\lambda_{a\nu}^2(\theta)}{\omega_\nu} = E_\nu(\theta) = (1 - \theta^2)E_\nu = (1 - \theta^2)\frac{\lambda_{a\nu}^2}{\omega_\nu} \tag{7.6}$$

$$\sum_{\nu=1}^{3} E_\nu(\theta) = \Delta G_s^a(\theta) = \alpha(1 - \theta^2)\,\Delta G_s \tag{7.7}$$

In the calculation, we take $\lambda_{a\nu s} = \lambda_{a\nu d} = \lambda_{a\nu}$. The suffixes s and d denote s and d orbitals. We take the coupling strengths of a unit positive core charge and the orbital electron with solvent modes to be of the equal magnitude. In the neutral state, the copper s orbital is singly occupied, hence for the underlying core charge, $|\lambda_{c\nu s}|$ is equal to $|\lambda_{a\nu}|$. On the other hand, a d orbital is doubly occupied in the neutral state and so $|\lambda_{c\nu s}| = 2|\lambda_{a\nu}|$.

The ab initio calculation of the matrix elements $\{\upsilon\}$ (cf. eqs 6.5 and 6.11) between the orbitals of copper adsorbate and gold electrode is a difficult task. We treat them as adjustable parameters in our calculations. Reasonable estimates for these parameters can be obtained through the existing data. The υ_s for the hydrogen adsorption on transition metals is ≈4.00 eV.[13,23] Now υ_s varies as R^{-3}, where R is the interatomic spacing.[24] The equilibrium distance R_e for an hydrogen atom chemisorbed on copper, or other transition metals is ∼0.20 nm.[25] This is less than 0.288 nm, the separation between copper and the gold substrate. The R^{-3} dependence of υ_s implies that for the present system, υ_s is smaller than 4.0 eV. In our calculations, we have taken υ_s as 2.70 eV at the M−V interface and allowed for its

TABLE 1

ϕ	Δ_d	ϵ_f	E_s	E_d	ΔG_s (C_u^+)	ϵ_{im}	U_s
4.80	5.60	5.20[a]	2.28[a]	−10.14[a]	5.92	−1.76	5.92
U_d	$\Delta_{\parallel}$	$\Delta_{\perp}$	v_{sd}	v_{dd}	α	μ_s	μ_d
5.45	1.40	1.40	2.68	4.85	0.50	0.75	0.60

[a] These energies are relative to the d band center of Au. α, μ_s, and μ_d are dimensionless quantities. All other quantities are in the units of eV. α and ΔG_s are zero for chemisorption at a metal−vacuum interface. The ϵ_{im} is for the M−V interface.

variation at electrochemical interface. Schrieffer et al. have specified that for transition metals, v_d lies in the range 4−6 eV.[29] We take $v_d = 4.85$ eV. As subsequent calculations will demonstrate, these specific values of v_s and v_d enable us to recover the observed trends in the average adsorbate charge and give reasonable estimates of the binding energy both for the metal−vacuum and electrode−electrolyte interface.

Gold forms a fcc lattice. The coordination number N_b of a gold atom in the bulk is 12. The coordination number N_s of an atom at the Au(111) surface is 6. Δ_t, the total d bandwidth of gold, is 5.6 eV.[24] Using eq 6.9, we get $\Delta_{\parallel} = 1.40$ eV. From (6.4) $\Delta_{\perp} = 1.40$ eV. The d bandwidth of copper is 3.47 eV.[24] Through similar argument, we get δ, the half d bandwidth of 2D adsorbed copper layer as 0.87 eV. Hence from eq 6.8, $\mu_d =$ 0.6 for the copper monolayer. The bandwidth of unhybridized copper s band is taken as $E(\Gamma) - E(X)$ which equals 4.21 eV.[30] Consequently $\mu_s = 0.75$. The work function of gold electrode is 4.8 eV, and its Fermi level, measured from the d band center, is 5.20 eV.[24] We have taken α, the degree of solvation of the adsorbate, as 0.50. This value lies exactly at the midpoint of the prescribed range 0.33−0.66.[26] Finally, the energy ϵ_Γ of the conduction band bottom for the gold is taken at 8.10 eV below the Fermi energy.[22] We recall that this quantity is needed to calculate of binding energy in the wide-band approximation.

Unless stated otherwise, the various parameters employed in the calculations are summarized in Table 1.

8. Numerical Results and Discussion

8.1. Average Occupation Probability and Energetics. With a view to have a comparative study of chemisorption at the metal−vacuum and electrochemical interface, we begin our calculations with the same values of the matrix elements v_s (2.70 eV) and v_d (4.85 eV) for both the interfaces.

Two specific features concerning the copper d orbital occupancy $\langle n_{d\sigma}\rangle$ emerges through the calculations: (i) this orbital is almost completely filled upon chemisorption and, (ii) the variations in the coverage have little effect on $\langle n_{d\sigma}\rangle$. This is true both for the metal-vacuum ($\langle n_{d\sigma}\rangle \approx 0.97$) and electrochemical ($\langle n_{d\sigma}\rangle \approx 0.965$) interfaces. Since the level shift caused by external applied potential is not considered in the calculations, the results reported in this section pertain to the potential of zero charge. The plot for self-consistent evaluation of $\langle n_{d\sigma}\rangle$ at electrochemical interface is given in Figure 1. The point of interaction between the straight line and the curve describing the calculated values of charge on copper d orbital $N_{d\sigma}$, corresponding to various input of $\langle \bar{n}_{d\sigma}\rangle$ (cf. eq 4.4), gives the required self-consistent value.

In contrast to $\langle n_{d\sigma}\rangle$, the average occupancy $\langle n_{s\sigma}\rangle$ for copper s orbital is more sensitive to the coverage variation. As the Cu d orbital is almost completely filled, any variation in the adsorbate net charge arises through the changes in the $\langle n_{s\sigma}\rangle$. We first consider the case of metal−vacuum interface, wherein $\langle n_{s\sigma}\rangle$ is around 0.3. The increase in coverage results in a slight increase

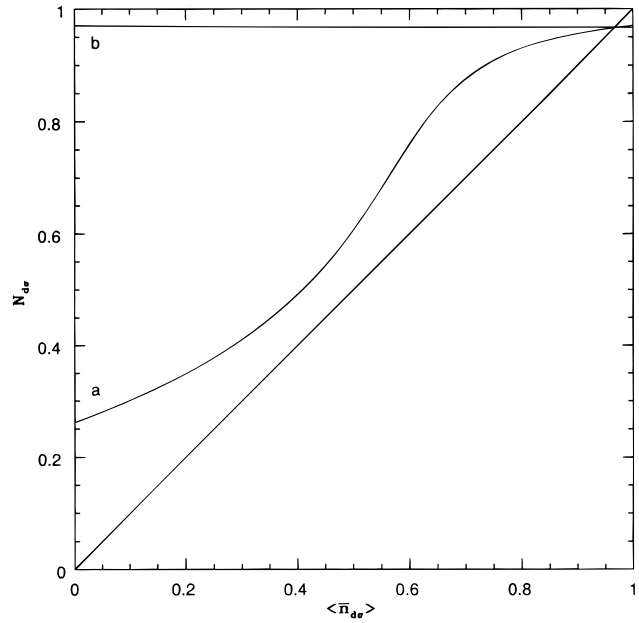

Figure 1. Self-consistent solution to d orbital occupancy of Cu chemisorbed on Au(111) electrode surface at electrochemical interface: (a) $\theta = 0.10$, $\langle n_{d\sigma}\rangle = 0.965$; (b) $\theta = 0.90$, $\langle n_{d\sigma}\rangle = 0.967$. Refer to Table 1 for parameters.

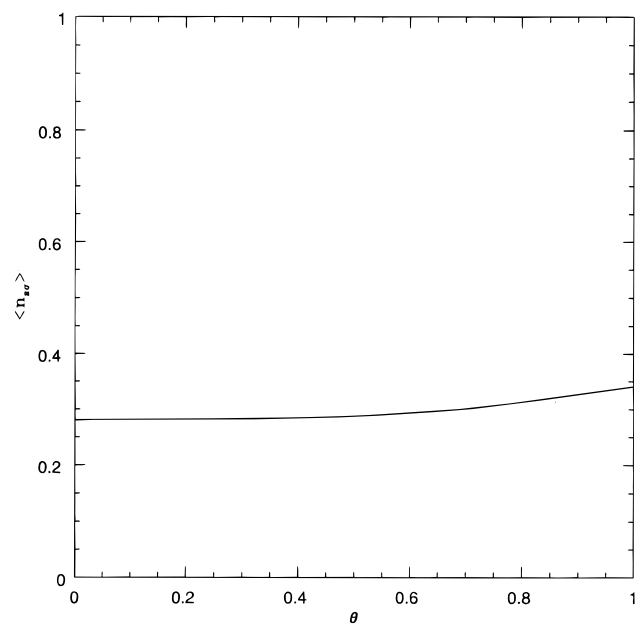

Figure 2. Coverage dependence of average s orbital occupancy $\langle n_{s\sigma}\rangle$ for Cu chemisorbed on Au(111) surface at the metal−vacuum interface.

in $\langle n_{s\sigma}\rangle$ (cf. Figure 2). The change is minimal in the low-coverage regime. The curve a in Figure 3 leads to the self-consistent evaluation of $\langle n_{s\sigma}\rangle$ when $\theta = 0.1$. The U term in the adsorbate's s orbital energy expression leads to an upward level shift with the increasing value of input $\langle \bar{n}_{s\sigma}\rangle$, which in turn reduces the calculated value of adsorbate charge $N_{s\sigma}$. We get a single self-consistent solution for $\langle n_{s\sigma}\rangle$ in the entire coverage range. The variation in the copper s orbital binding energy ΔE_s with respect to $\langle \bar{n}_{s\sigma}\rangle$ gives rise to an energy extremum at the self-consistent value of the orbital charge. For $\theta = 0.9$, and the corresponding self-consistent $\langle n_{s\sigma}\rangle$ at 0.327, the occurrence of the extremum in $|\Delta E_s|$ is shown in Figure 4. Note that in the present case, ΔE_s equals $-|\Delta E_s|$.

For the chemisorption at the metal−vacuum interface, the θ variation has a minimal effect on d orbital binding energy ΔE_d.

The major contribution to the total binding energy ΔE ($=\Delta E_s + \Delta E_d$) comes through ΔE_s (≈ -1.6 eV). The ΔE_d is ≈ -0.42 eV and the total binding energy is ≈ -2.00 eV.

Before taking up the evaluation of Cu s orbital occupancy at the gold electrode in the electrochemical environment, let us restate some relevant experimental facts. The partial charge transfer coefficient λ is one of the important parameters in the electrosorption studies. It equals to the difference of charges on the adsorbate when it is in the bulk, and when it lies at the interface. For the chemisorption of ionic Cu^{2+}

$$\lambda = 2(\langle n_{s\sigma}\rangle + \langle n_{d\sigma}\rangle) - 1 \tag{8.1}$$

Though λ itself is not a measurable quantity, its numerical value lies close to the experimentally determined electrosorption valency γ_n.[11,12] In the $\theta \rightarrow 0$ limit, γ_n for Cu/Au system is 2.0.[12] Thus the double layer studies coupled with the thermodynamic analysis indicate that the copper adsorbed at a gold electrode is neutral when the coverage is small.

On the other hand, Tadjeddine et al. have shown using the in situ X-ray absorption spectroscopy that in the higher coverage domain, charge on the copper adatom on a gold electrode is close to $+1.0$.[6]

This substantial reported variation in $\langle n_{s\sigma}\rangle$ with changing coverage prompts us to make a simple calculation for $\Delta E'_s$, the energy required to bring a single Cu^+ ion from the bulk electrolyte to the interface when the bonding is very weak ($\upsilon_s \rightarrow 0$), but the occupancy of the copper's s spin−orbital in the interfacial region is $\langle n_{s\sigma}\rangle$. In this case of negligible bonding, the main contribution to the energetics would come from (i) partial desolvation of the ion at the electrode, (ii) image energy contribution, (iii) change in energy while transferring charge $2\langle n_{s\sigma}\rangle$ from the Fermi level of the electrode to the unbroadened orbital of the adsorbate at the interface, and (iv) intraadsorbate coulomb repulsion U_s. In the case $\langle n_{s\sigma}\rangle = \langle n_{s\bar{\sigma}}\rangle = 0$, the charge on Cu at the interface remains $+1$. Therefore, the energy $\Delta E'_s$ is $-\sum_{\nu=1}^{4} \lambda_{a\nu}^2/\omega_\nu + \Delta G_s$. As noted earlier, we have taken $\lambda_{ac\nu} = \lambda_{a\nu}$. Substituting the numerical values, we get $\Delta E'_s = +1.29$ eV. Next, when $\langle n_{s\sigma}\rangle = \langle n_{s\bar{\sigma}} = 0.5\rangle$, i.e., the copper adsorbate is neutral (each spin−orbital being half occupied), $\Delta E'_s = \phi - I + U_s/4 - 0.5 \sum_{\nu=3}^{4} \lambda_{a\nu}^2/\omega_\nu + \Delta G_s$. Taking the first ionization energy I for copper as 7.72 eV, we get $\Delta E'_s$ as $+3.53$ eV for a neutral copper atom at the interface. Finally, when $\langle n_{s\sigma}\rangle = \langle n_{s\sigma}\rangle = 1.0$, that is, the copper atom at the electrode has a net charge -1.0, $\Delta E'_s = 2(\phi - I) + U_s - \sum_{\nu=1}^{4} \lambda_{a\nu}^2/\omega_\nu + \Delta G_s$, which is equal to $+1.41$ eV. Note that the analysis given here corresponds to the lone-adsorbate case; the influence of the other adsorbates has been neglected. We have taken the degree of solvation α of the copper ion at the interface as 0.5. The expressions given here for $\Delta E'_s$ for various cases can be obtained either directly, or taking $\upsilon_s = 0$ appropriately in eqs 5.3−5.7 and 5.15. These elementary calculations show that in the absence of bonding ($\upsilon_s = 0$), bringing a Cu^{1+} ion from the bulk phase to the interface is energetically unfavorable, irrespective of the charge state of copper at the interface. This remains true for entire plausible range of α between 0.33 and 0.66. Next the ionic configurations of copper at the interface have relatively lower energy than the neutral copper atom, with Cu^{1+} being the least energy configuration.

In the above calculations, we have taken υ_s to be zero. But in order to have different charge states of copper at the interface, we need a finite υ_s, howsoever infinitesimal its magnitude may be. In addition, it has to be verified that we indeed get more than one self-consistent solutions for $\langle n_{s\sigma}\rangle$, so that all the charge states of copper considered above are realized at the interface. Taking $\upsilon_s = 0.02$ eV (which is 2 orders of magnitude lower than its earlier value of 2.70 eV), and $\theta = 0.1$ (leading to very low concentration of the adsorbates), we get all the three charge states of copper adsorbate. The self-consistent values of $\langle n_{s\sigma}\rangle$ are 0.0, 0.504, and 1.0. Their respective binding energies (cf. eqs 5.15 and 6.13) are 1.32, 3.51, and 1.50 eV, which compare well with the $\Delta E'_s$ values obtained earlier.

Next when we allow υ_s to take the value 2.70 eV, it is pertinent to examine whether (i) one still gets three different charge states of copper, (ii) the binding energy becomes negative, and (iii) a less ionic state of copper adsorbate is more stable? The calculations corresponding to $\theta = 0.1$ confirm the first point but the answers to the next two queries are in the negative. The self-consistent values of $\langle n_{s\sigma}\rangle$ are now 0.074, 0.665, and 0.98. The associated s orbital binding energies ΔE_s are -2.32×10^{-2}, 1.85, and 1.34 eV, respectively. This shows that even a strong coupling between the copper s orbital and the metal states does not make neutral copper atom relatively more stable than the positively charged copper adsorbate in the low-coverage regime, nor does it lower the energy sufficiently so as to make the chemisorption of copper at gold electrode feasible. As we shall shortly show, the adsorption is possible due to the bonding of copper d orbital. Subsequent calculations with progressive increasing coverage show that the roots of $\langle n_{s\sigma}\rangle$ lying at 0.074 and 0.665 shift toward higher values, whereas the one at 0.98 moves downward. At $\theta = 0.52$ the lowest root shifts to 0.09 ($\Delta E_s = 0.52$ eV) and the remaining two roots merge and take a common value 0.89 ($\Delta E_s = 2.01$ eV). Beyond this coverage, we get only one self-consistent solution for $\langle n_{s\sigma}\rangle$ giving rise to a positively charged copper adsorbate. Thus when $\theta = 0.75$, $\langle n_{s\sigma}\rangle = 0.14$ ($\Delta E_s = 1.02$ eV) and the same for $\theta = 1.0$ is 0.33 ($\Delta E_s = 1.23$ eV).

When $\theta = 0.1$ and $\upsilon_s = 2.70$ eV, the net charge Q on copper corresponding to various self-consistent values of $\langle n_{s\sigma}\rangle$ is $+0.92$, -0.26, and -0.89. These values are obtained by adding the d orbital and core charges to $2\langle n_{s\sigma}\rangle$.

$$Q = -2(\langle n_{s\sigma}\rangle + \langle n_{d\sigma}\rangle) + 3 \tag{8.2}$$

The least charge on copper is -0.26, which does not make the Cu adatom exactly neutral. In fact it has been shown earlier that the neutral state of copper is obtained when $\upsilon_s = 0.02$ eV. Thus, in order to lower the relative large negative charge -0.26, we now take $\upsilon_s = 2.0$ eV. The charge -0.26 now gets reduced to -0.11. The other motivation for taking υ_s as 2.0 eV, apart from its earlier considered value of 2.70 eV, is that it allows us to understand the effect of υ_s variation on chemisorption characteristics. We also note that the variation of υ_d has least effect on the d orbital occupancy.

The self-consistent plot for $\langle n_{s\sigma}\rangle$ when $\upsilon_s = 2.0$ eV is given in Figure 3. For $\theta = 0.10$, we get three self-consistent values at 0.04, 0.59, and 0.99. The change in the locations of various roots with increasing coverage follows a trend identical to the $\upsilon_s = 2.70$ eV case. But instead of at $\theta = 0.52$, the merger of the two higher roots takes place at $\theta = 0.65$. At this point, the common value of these roots are 0.88. The remaining root lies at 0.079. Beyond $\theta = 0.65$, only the smallest root survives, whose magnitude keeps on increasing with further increase in coverage. Finally, at $\theta = 1.00$, the $\langle n_{s\sigma}\rangle$ is 0.39 which is 0.06 more than the corresponding value when $\upsilon_s = 2.70$ eV.

It may be noted that the slow boson terms, weighted by $\langle n_{s\sigma}\rangle$, now lower the adsorbate orbital energy with increasing $\langle n_{s\sigma}\rangle$ (cf. eq 2.6). As the magnitude of these quantities are greater

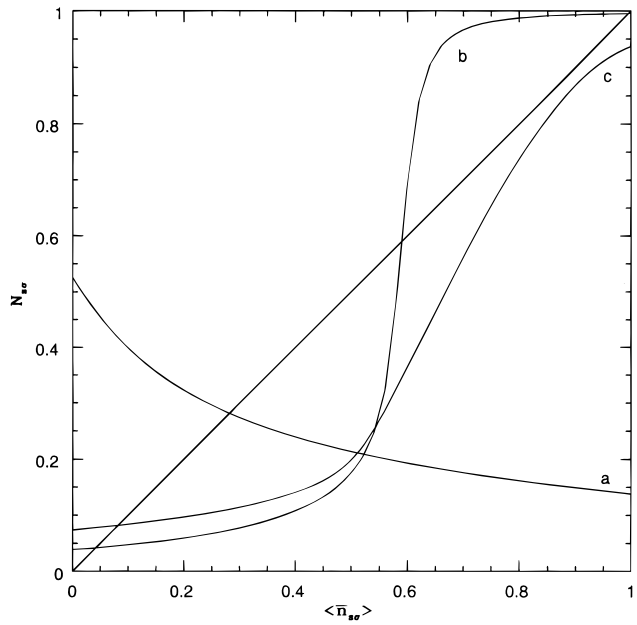

Figure 3. Self-consistent solutions to s orbital occupancy of Cu chemisorbed on Au(111): (a) $\theta = 0.10$, $\langle n_{s\sigma}\rangle = 0.285$ (M−V interface, $\upsilon_s = 2.70$ eV); (b) $\theta = 0.10$, $\langle n_{s\sigma}\rangle = 0.04$, 0.59 and 0.99 (E−E interface, $\upsilon_s = 2.0$ eV); (c) $\theta = 0.67$, $\langle n_{s\sigma}\rangle$ 0.082 (E−E interface, $\upsilon_s = 2.0$ eV).

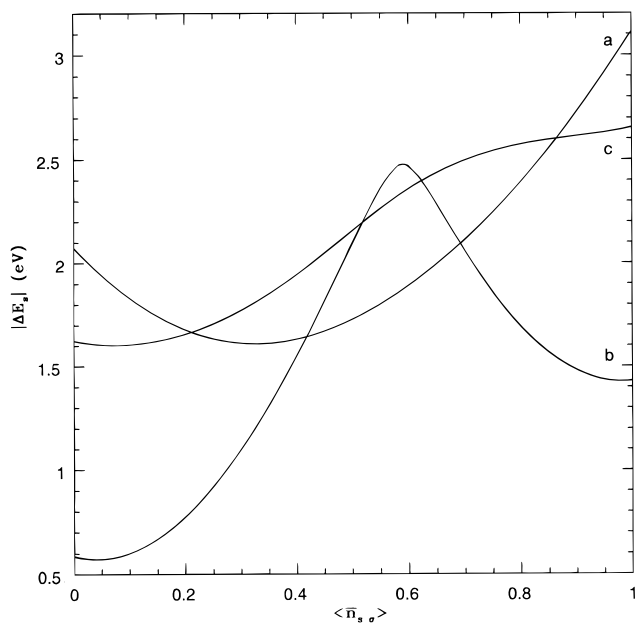

Figure 4. Extremum in the binding energy ΔE_s at the self-consistent values of average electronic charge on copper s orbital: (a) $\theta = 0.90$, $\langle n_{s\sigma}\rangle = 0.327$ (M−V interface, $\upsilon_s = 2.70$ eV); the parameters for (b) and (c) are same as for curves b and c in the Figure 3.

than the U term (unless θ is quite large (cf. eq 7.7)), calculated $N_{s\sigma}$ increases with increasing value of input $\langle \bar{n}_{s\sigma}\rangle$.

The occurrence of extremum in $|\Delta E_s|$ for $\theta = 0.1$ ($\langle n_{s\sigma}\rangle = 0.04, 0.59, 0.99$) and $\theta = 0.67$ ($\langle n_{s\sigma}\rangle = 0.082$) at electrochemical interface is shown in Figure 4. Note that presently $\Delta E_s = |\Delta E_s|$.

The net charge on copper with varying coverage at the electrochemical interface is shown in Figure 5. Since the d orbital occupancy is virtually constant, the structure in charge variations solely arise due to $\langle n_{s\sigma}\rangle$. At the gold electrode, we get three different charged states of Cu up to $\theta = 0.65$. The states, which are almost completely ionic when θ is small, tend to lower their net charge when coverage increases. This variation is relatively faster for the positive charge state. On

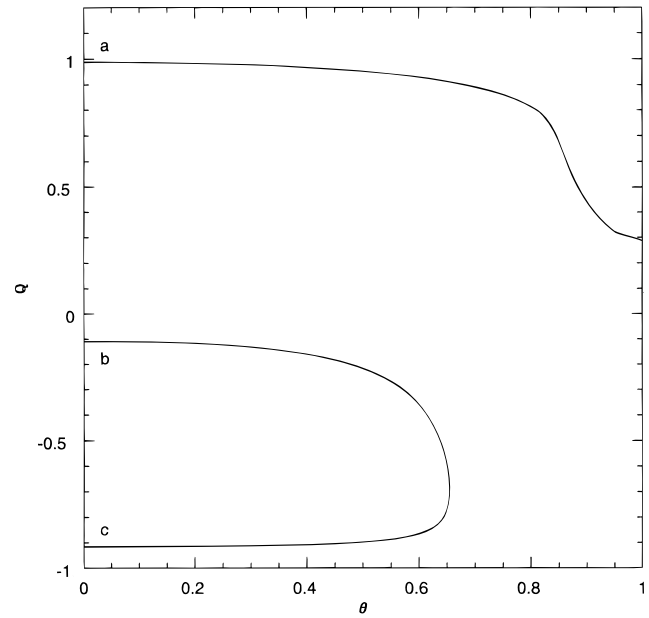

Figure 5. Total charge Q on Cu electrochemisorbed on Au(111) electrode: coverage dependence. The branches (a), (b), and (c) correspond to multiple self-consistent values of $\langle n_{s\sigma}\rangle$ ($\upsilon_s = 2.0$ eV). (a) and (b) merge together at $\theta = 0.65$ where the common value of Q is −0.69.

the other hand, the $Cu^{-0.11}$ configuration in the low-coverage region progressively acquires more electronic charge with increase in θ. But beyond a critical coverage ($\theta = 0.65$), both the negatively charged configurations of copper cease to exist. Only the state having positive charge, which is also the least energy configuration for all θ values, survives. Given the net charge Q on the copper adsorbate, the partial charge transfer coefficient can also be obtained using the relation $\lambda = 2 - Q$ (cf. eqs 8.1 and 8.2).

It is pertinent to analyze the reason behind the transition from multiple solutions to a single root for $\langle n_{s\sigma}\rangle$ with increasing coverage at electrochemical interface. We obtain only a single self-consistent solution for the adsorbate charge at metal−vacuum interface in the entire coverage ($0 < \theta \leq 1$) range. The multiple roots occur only at electrochemical interface, where the solvation of adspecies and its progressive desolvation with increasing coverage are the additional features. We note that presently the effect of external applied potential has not been considered. It is the presence of additional boson modes corresponding to the solvent polarization which are responsible for more than one self-consistent value for adsorbate charge.[21,31,32] The calculations show that all the three roots of $\langle n_{s\sigma}\rangle$ survive for all coverages if the desolvation of the adsorbate with the increasing coverage is disallowed. In fact it is this progressive desolvation which leads to the transition from multiple to a single charge state of copper. In the present formalism the desolvation effect has been modeled through the scaling factor $(1 - \theta^2)$. But the occurrence of this transition does not depend on this specific form of the scaling factor. Any factor $f(\theta)$ will do, provided $f(\theta) \rightarrow 0$ when $\theta \rightarrow 1$, and $f(\theta) \rightarrow 1$ when $\theta \rightarrow 0$. These limits imply that in the former case, the solvation energy of the adsorbate is $\alpha\Delta G_s$ and the same is zero when a metallic adsorbate forms a monolayer. We have, however, taken $f(\theta)$ as $(1 - \theta^2)$ since this implies that the decrease in the solvation energy of the adsorbate depends on the probability of finding another adsorbate in its vicinity.

The presence of multiple charge state for the copper s orbital, and the subsequent transition to a single charge state beyond a

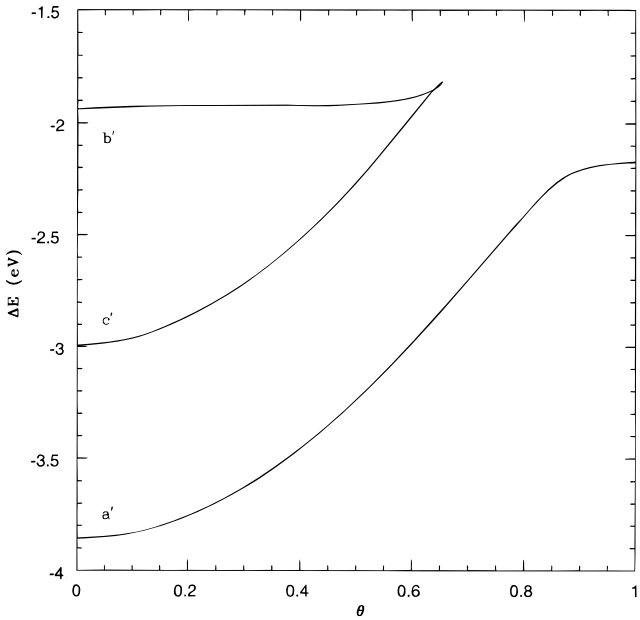

Figure 6. Coverage dependence of the total binding energy ΔE for Cu on Au(111) at electrochemical interface. The curves a′, b′, and c′ here depict the respective binding energies corresponding to the branches a, b, and c in Figure 5 for the total charge on copper.

critical coverage, also get reflected in the binding energy ΔE_s of the copper s orbital in the electrochemical environment. The change in ΔE_s with respect to coverage is substantial. But more importantly, ΔE_s is positive for all coverage regime. Therefore, the consideration of s orbital alone would not lead to the electrochemisorption of copper. This contrasts with the adsorption at the metal−vacuum interface wherein the s orbital bonding provides the major contribution to the chemisorption energy. The difference in the s orbital bonding nature at the metal−vacuum and electrode−electrolyte interface is a consequence of the fact that in the former case, a far separated copper adsorbate is in a neutral state, whereas in the latter case, s orbital is unoccupied in a solvated copper ion residing deep inside the bulk electrolyte. The desolvation of adsorbate upon chemisorption and energy difference between a neutral copper atom and a solvated Cu^+ ion leads to positive energy value for s orbital bonding. The binding energy contribution ΔE_d for copper d orbital does not vary much with coverage and it is sufficiently negative (≈ -4.4 eV). The negative chemisorption energy for the d orbital results from the large difference between the energies of the copper d orbital and gold Fermi level. Upon electrochemisorption, an unoccupied copper *d* -orbital gets almost completely filled and this leads to substantial decrease in the energy.

The total binding energy ΔE is a negative quantity, thus making electrosorption of copper on gold electrode feasible (cf. Figure 6), whatever may be the charge state of the copper adsorbate. But as we have noted earlier, configurations having more ionic character are more stable, with the positive charge state being most stable. The calculations have also shown that ΔE at the electrode−electrolyte interface is more negative than the ΔE at the metal−vacuum interface. Finally, we have also verified that a decrease in α, the degree of solvation for an interfacial adsorbate, reduces the binding energy.

The analysis presented here unambiguously supports the Tadjeddine et al. in situ experimental results showing a positive charge copper adatom when the coverage is large.[6] In this domain, only one self-consistent value of $\langle n_{s\sigma}\rangle$ exists. For the low coverages, the theory predicts that apart from ionic configurations, copper adsorbate can also exist in a relatively neutral state. But the energetic considerations make this state to be unstable. In fact when $\upsilon_s \rightarrow 0$, the stability of the various possible charge states of copper decreases in the order $Cu^+ > Cu^- > Cu^0$. The subsequent increase in υ_s does not alter this trend; it only lowers the respective energy values. So it seems that Tadjeddine et al., experimental observation of a positive charge copper adsorbate at higher coverage should be valid even for small θ (including the case of a single adsorbate). In such a case, the net charge on copper would decrease in a smooth way with the increasing coverage (curve a, Figure 5).

On the other hand, electrosorption valence data suggest that copper is neutral when the coverage is low. But this still requires a justification why the copper adsorbate on gold electrode should exist in a metastable configuration at low coverage. Notwithstanding the above energetic considerations, if the copper adsorbate is indeed neutral for small θ, the present formalism provides a method to verify this situation. The analysis carried out so far regarding the charge variation with coverage shows that the relatively neutral copper adatom first becomes more negative with increasing coverage. But beyond a critical coverage, it acquires a positive charge in a discontinuous fashion (cf. Figure 5). So in case copper adsorbate exists in two different charge configurations in the low and higher coverage regime, the switch over between them is not smooth. A sharp valence transition for the copper adatom in the intermediate coverage region thus signifies the presence of a neutral copper when coverage is low. We also note that decrease in υ_s shifts this critical coverage to higher values.

8.2. Wide Band Limit. We now provide a brief discussion on the applicability of the wide-band limit to copper adsorption on gold. We start with the lone adsorbate case (cf. eq 6.16a). Following refs 17 and 18, we take Δ_s as 1.0 eV. For the chemisorption at the M−V interface, only one self-consistent value of $\langle n_{s\sigma}\rangle$ equal to 0.49 is obtained. That the $\langle n_{s\sigma}\rangle$ lies near to 0.5 can be ascertained by comparing the copper s orbital energy with Δ_s. Taking the energy zero at the Fermi level, the $\epsilon_{s\sigma}$ is 0.04 eV when $\langle n_{s\sigma}\rangle$ is 0.5. As this value is much lower than Δ_s, the self-consistent expression

$$\langle n_{i\sigma}\rangle = (1/\pi)\cot^{-1}(\epsilon_{i\sigma}/\Delta_i); \quad \{i = \text{s, d}\}$$

$$\epsilon_{i\sigma} = \epsilon_a^0 - z_i\epsilon_{im} + (U_i + 2\epsilon_{im})\langle n_{i\bar{\sigma}}\rangle; \quad \{z_i = 1(3) \text{ for s(d) orbital}\} \quad (8.3)$$

leads to $\langle n_{s\sigma}\rangle \approx 0.5$ in the nonmagnetic limit.

The lower edge of conduction band ϵ_Γ for gold lies at 8.10 eV below the Fermi level.[22] With this cutoff, the s orbital binding energy ΔE_s when the charge is 0.49 is − 0.74 eV only. This binding energy at M−V interface is obtained by using the relation

$$\Delta E_i = \sum_\sigma \epsilon_{i\sigma}\langle n_{i\sigma}\rangle - (U_i + 2\epsilon_{im})\langle n_{i\sigma}\rangle\langle n_{i\bar{\sigma}}\rangle + \sum_\sigma (\Delta_i/2\pi)\ln\frac{\epsilon_{i\sigma}^2 + \Delta_i^2}{(\epsilon_\Gamma - \epsilon_{i\sigma})^2 + \Delta_i^2} + x_i^2\epsilon_{im} - \sum_\sigma \epsilon_{i\sigma}^0\langle n_{i\sigma}\rangle^0 - U_i\langle n_{i\sigma}\rangle^0\langle n_{i\bar{\sigma}}\rangle^0; \quad \{x_i = 1(2) \text{ for s(d) orbital}\} \quad (8.4)$$

The above expressions for the average charge and binding energy for a single adsorbate at M−V interface follows from eqs 6.16a, 6.18, 5.15, and 7.4.

For the copper d orbital, the self-consistent $\langle n_{d\sigma}\rangle$ at the M−V interface is 0.96 when $\Delta_d = 1.0$ eV. The corresponding binding

energy ΔE_d is +1.98 eV. If Δ_d is taken as 2.0 eV, the above two quantities are 0.925 and +3.07 eV, respectively. The reason behind getting such positive values for ΔE_d is that the argument of the ln function in eq 8.4 is greater than unity when the cutoff is taken at the bottom of conduction band. The binding energy value is also sensitive to the lower cutoff limit. For example, if the cutoff is taken arbitrarily at −15.0 eV, the ΔE_d gets reduced from +3.07 to +1.48 eV. This strong dependence of binding energy on cutoff parameter is also true for the copper s orbital. With lower cutoff at −15.0 eV, ΔE_s corresponding to $\Delta_s = 1.0$ eV is −1.13 eV. Finally in all the cases, the total binding energy remains positive.

Thus we find that the wide-band approximation predicts no binding even for the single adsorbate case at the M−V interface, and the copper adsorbate exists in almost neutral state.

Application of this formalism to a lone copper adsorbate at gold electrode again gives rise to three self-consistent solutions for $\langle n_{s\sigma}\rangle$ at 0.085 ($\Delta E_s = 1.25$ eV), 0.51 ($\Delta E_s = 2.21$ eV), and 0.91 ($\Delta E_s = 2.00$ eV) when $\Delta_s = 1.0$ eV and the lower cutoff is placed at the ϵ_Γ in the energy calculations. The corresponding $\langle n_{d\sigma}\rangle$ is 0.96 ($\Delta E_d = -2.14$ eV) for $\Delta_d = 1.0$ eV.

The above calculation again shows that as $\theta \rightarrow 0$, the $Cu^{+0.91}$ is the most stable configuration, followed by $Cu^{-0.74}$. The nearly neutral charge state of copper ($Cu^{+0.06}$) is the least stable one. The respective total binding energies corresponding to these three charge configurations are −0.89, −0.14, and 0.07 eV.

Calculations based on eqs 4.3−4.4 and 6.16 show that the two roots of $\langle n_{s\sigma}\rangle$ again merge at $\theta = 0.63$. Beyond this coverage, the $\langle n_{s\sigma}\rangle$ is single valued, and it equals 0.23, 0.39, 0.474, 0.486, and 0.49 when θ is 0.64, 0.7, 0.8, 0.9, and 1.0, respectively. Thus wide-band approximation leads to a relatively neutral configuration of copper in the high-coverage regime.

The above analysis shows that the gross features like multiple roots for $\langle n_{s\sigma}\rangle$ at the E−E interface, relative stability of these solutions, and existence of a single solution beyond a critical coverage can be obtained through the wide-band limit based approach. But it gives poor result for binding energy. Besides, it predicts the existence of almost neutral copper adsorbate for large coverages which is contrary to the observations of Tadjeddine et al.[6]

8.3. Adsorbate's Density of States. The present calculations have shown that the average occupancy of copper d orbital remains constant with respect to change in the coverage, whereas $\langle n_{s\sigma}\rangle$ exhibits steep variation. The underlying reason for this feature can be understood through the respective density of states. The copper d orbital density of states for $\theta = 0.1$ in the electrochemical environment is plotted in Figure 7. The two peaks in the density of states, lying below the Fermi level (at 5.20 eV above the energy zero which is taken at the gold d band center) are to be ascribed to the bonding and antibonding states, broadened due to their interactions with the substrate band. Only the tail portion of the density of states lies near the Fermi level. A change in the coverage, though inducing a slight shift in the peaks positions and reducing their heights, does not alter the density of states near the Fermi level. Thus the d orbital average occupancy, which is the integrated density of states up to Fermi level, remains constant with the varying coverage. When $\theta = 0.10$, we get three density of states for the copper s orbital corresponding to the three self-consistent values of $\langle n_{s\sigma}\rangle$ at E−E interface. The density of states (dos) for $\langle n_{s\sigma}\rangle = 0.04$ and 0.99 lie much above and below the Fermi level, respectively (Figure 8). The former has a single narrow peak and the latter is broad and exhibits a diffuse satellite peak. The dos ρ_a corresponding to $\langle n_{s\sigma}\rangle = 0.59$ is peaked around the Fermi level

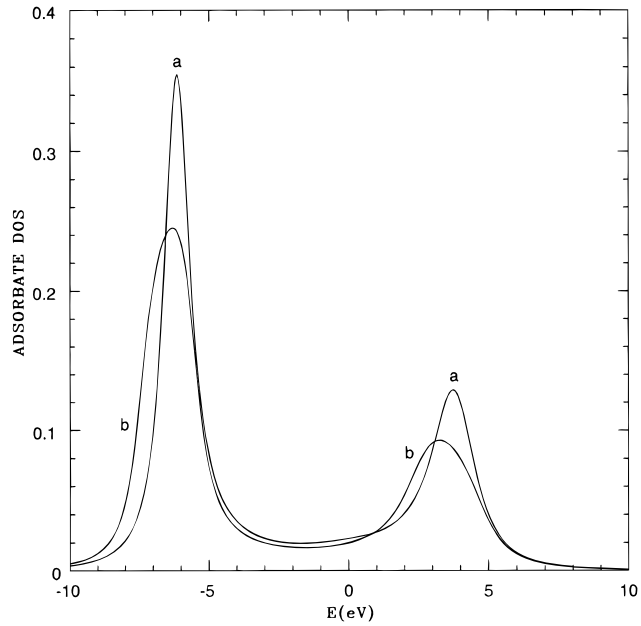

Figure 7. d orbital density of states for Cu electrochemisorbed on Au(111) electrode: (a) $\theta = 0.10$, $\langle n_{d\sigma}\rangle = 0.965$; (b) $\theta = 0.90$, $\langle n_{d\sigma}\rangle = 0.967$. Au d band center is at 0.0 eV. $\epsilon_f = 5.20$ eV, vacuum level at 10.00 eV.

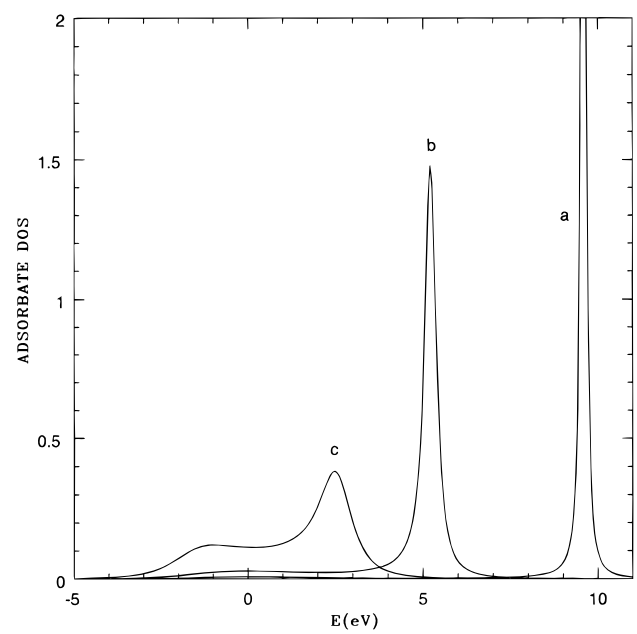

Figure 8. s orbital density of states for Cu electrochemisorbed on Au(111) electrode. $\theta = 0.10$, $\upsilon_s = 2.0$ eV. (a) $\langle n_{s\sigma}\rangle = 0.04$, the height of dos peak is 4.01; (b) $\langle n_{s\sigma}\rangle = 0.59$; (c) $\langle n_{s\sigma}\rangle = 0.99$.

and has a small satellite peak. As the coverage is increased, peaks in the dos for the least and largest $\langle n_{s\sigma}\rangle$ move toward the Fermi level whereas the dos peak corresponding to middle root shifts below the ϵ_f (Figure 9). This explains the ensuing variation in the adsorbate charge with coverage. The ionic configurations tend to reduce their net charge, whereas the neutral state becomes more negative with increasing θ (cf. Figure 5). Note that the increase in θ leads to a broader density of states along with reduced peak height. Whenever a dos peak lies in the vicinity of ϵ_f, any change in its position or shape, resulting either from the increase in coverage, or through variations in the other system parameters, has a pronounced effect on the magnitude of the corresponding charge. This explains the large variation

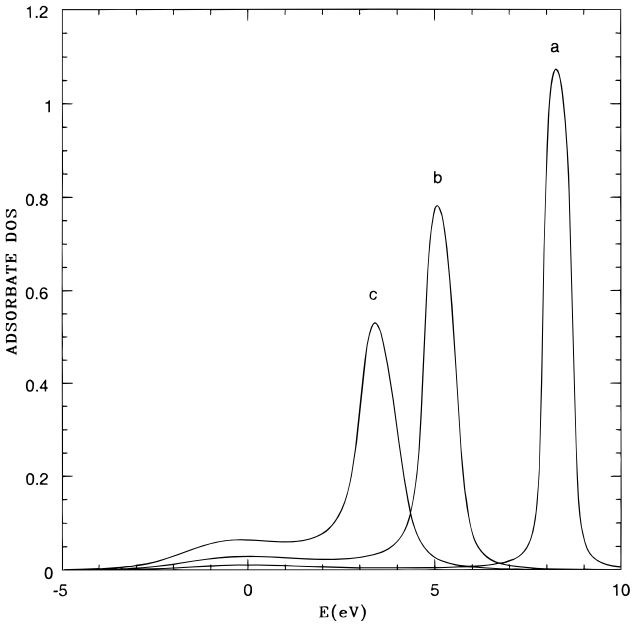

Figure 9. s orbital density of states for Cu electrochemisorbed on Au(111) electrode. $\theta = 0.50$, $\upsilon_s = 2.0$ eV. (a) $\langle n_{s\sigma}\rangle = 0.06$; (b) $\langle n_{s\sigma}\rangle = 0.64$; (c) $\langle n_{s\sigma}\rangle = 0.98$.

in the net charge Q in different coverage domains (branches a, b in Figure 5).

The adsorbate density of states are primarily considered here to explain the trends in the adsorbate average occupation probability, and it is also needed for the binding energy calculation. But ρ_a also plays a central role in the charge transfer processes involving metal−adsorbate complex, be it radiative, nonradiative, or related to STM studies. In this context, earlier results for the adsorbate dos by Schmickler, Kuznetsov, and Ulstrup for electron transfer via adspecies[31,33−35] and the more recent work by Schmickler for STM studies[36,37] of redox couple and in situ electron tunneling through thin water layer at electrode are notable. Recently we have obtained a closed form expression for ρ_a within the semiclassical approach for solvent and wide-band approximation. The density of states thus derived admits Lorentzian, Gaussian, and delta function structure in appropriate limits.[38] The voltage spectroscopy of adsorbate ions, preferably through STM measurements, can give information about the in situ adsorbate density of states.[39] Though this approach has been used extensively to obtain ρ_a at the M−V interface,[40] to our knowledge no such experimental result in the context of E−E interface is available. We shall report in future papers how the various electron transfer processes noted above are affected by the coverage dependence of the adsorbate density of states.

9. Summary and Conclusions

In order to understand the electronic structure of a chemisorbed layer in an electrochemical environment, an appropriate model Hamiltonian based formalism is constructed. Starting with the lone adsorbate case ($\theta \rightarrow 0$), the formalism is valid up to monolayer regime ($\theta = 1$). The adsorbates are assumed to occupy the on-top positions over the substrate atoms and the adsorbate layer is commensurate with the underlying electrode surface lattice. At coverages less than unity, the adsorbates are distributed randomly over various adsorption sites, and give rise to a 2D electron band in the monolayer regime. The randomness in the system is treated self-consistently through the CPA approach. The adsorbate self-energies arising due to its hybridization with the substrate states are evaluated using appropriate density of states for the substrate band. This allows us to go beyond the wide-band approximation, removes the divergence associated with the binding energy calculation in the wide-band limit, and leads to non-Lorentzian adsorbate density of states.

The formalism is applied to a chemisorbed layer of copper on gold electrode. The following are our main results:

1. Double layer studies have suggested that at low coverages, copper electrochemisorbed on gold electrode exists in a neutral state. The in situ X-ray absorption spectroscopy indicates that in the monolayer regime, copper adion is positively charged. Present theoretical analysis supports the latter. When the coverage is low, three self-consistent charge states for copper are possible. Though one of them is relatively neutral, binding energy calculations make it to be the least stable. The positive charge configuration of copper is most stable at all coverages.

2. The transition from multiple to unique charge configuration for copper is caused due to the progressive desolvation of copper adion with the increasing coverage. In spite of the energetic considerations, if the copper adsorbate is indeed neutral in the low, and positively charged in the higher coverage domains, the switchover between these two configurations is not smooth. It occurs through a sharp valence transition in the copper adatom in the intermediate-coverage region.

3. The coverage variation has a little effect on copper d-orbital occupancy. All the different charge configurations of the copper adsorbate result due to changes in its s orbital occupancy with varying coverage.

4. Density of states for the d orbital of the chemisorbed copper exhibits a two-peak structure. Both the peaks lie well below the Fermi level of gold. Thus, a shift in the peak positions, either because of the coverage variation or due to change in other parameters, would have minimal effect on the observables pertaining to the copper d orbital. On the other hand, the major peak corresponding to at least one of the density of states for s orbital always lies near the Fermi level. Consequently, the s orbital properties are more sensitive to the coverage and other parametric variations.

5. Calculations have shown that for the copper chemisorption on gold at the metal−vacuum interface, it is the s orbital bonding which contributes maximally toward the binding energy. But in the electrochemical environment, the binding energy for the s orbital is positive. The binding is possible only when the d orbital energy contributions are also taken into account in the energy calculations.

6. The wide-band limit based approach has been generalized to study the electronic properties of a random chemisorbed layer. The subsequent analysis shows that it gives poor results for binding energy. Besides, it predicts the existence of almost neutral copper adsorbate for large coverages which is contrary to the experimental observations of Tadjeddine et al.[6]

We have presently treated the randomness in the system through coherent potential approximation, which is an effective mean-field theory. To take into account the possible short-range order in the system, one needs to go beyond the CPA approach.

The copper adsorption in the presence of anions and the electron transfer through adsorbed layer represent possible extensions of the present work. Our results on these important problems will be reported in future communications.

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