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Chemisorption with overcompleteness, nonorthogonality, and electron correlation: Nondegenerate ground state*

A. Bagchi† and Morrel H. Cohen
Department of Physics and James Franck Institute, The University of Chicago, Chicago, Illinois 60637
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A unified theory of hydrogen chemisorption on the surface of a metal is developed by taking overcompleteness and nonorthogonality of wave functions and electron correlation into account. The metal-atom system is described in terms of an overcomplete basis set consisting of the eigenstates (both occupied and unoccupied) of the metal and the occupied electronic state on the adatom. A pseudo-Green's-function formalism is set up to deal with the overcompleteness problem. The equations of motion of the pseudo-Green's-function elements are derived and the system energy is expressed in terms of them. The theory is applied in this paper to the situation where the intra-atomic Coulomb repulsion is assumed to be small so that hydrogen chemisorbs in a nonmagnetic configuration and the ground state is nondegenerate in spin. The Hartree-Fock approximation is worked out within the overcomplete basis, and the correspondence between our theory in this limit and previous work is established. Possible extensions of the perturbation procedure are discussed.

I. INTRODUCTION

Chemisorption—the chemical bonding of an atom or a molecule to a metal surface—is a process of central importance in the study of catalysis. Although chemisorption has enjoyed a long history[1] of experimental investigation, serious theoretical efforts at understanding the nature of the process have been made only for a limited number of simple adsorbates. This is hardly surprising, in view of the fact that a chemical bond which involves a metal as a component must necessarily be complex. The problem studied most extensively theoretically has been the chemisorption of hydrogen on transition metals.[2-5] Some theoretical work has also been done on the adsorption of CO,[6] which appears to retain its molecular character while participating in the bonding, and of transition metals on transition metals.[7,8] Considerable interest has developed lately in the adsorption of alkali atoms[9] with the accompanying change of the work function of the substrate metal.[10]

Of all the adsorbates mentioned above, hydrogen is by far the simplest. Data on chemical kinetics indicate that hydrogen chemisorbs on a transition metal atomically. The problem of hydrogen chemisorption is, therefore, essentially the problem of binding of a one-electron atom to the surface of a narrow-band metal. So far, the problem has been approached most fruitfully within the framework of a one-electron Hartree-Fock theory,[3] starting with a generalized version of the Anderson Hamiltonian.[11] This theory has been criticized[12] on the grounds that it fails to take into account properly the effect of the electron-electron correlation on the atom. In fact, the intra-atomic Coulomb repulsion U is 13 eV for hydrogen in free space and is quite large. Even though U must surely be reduced by dynamical screening when the atom is brought close to a metal surface, it still remains the largest parameter of the chemisorption problem and should be treated exactly as far as possible. One-electron theories of hydrogen adsorption are also believed[12] to give a larger charge transfer from the metal to the atom than is observed experimentally. The experimental evidence is based, however, on work-function changes which give direct information only on surface dipole moments. Any result drawn from it on the exact amount of charge transfer cannot be regarded as conclusive.

Schrieffer and co-workers[4,12] have tried to set up the theory of hydrogen chemisorption by allowing correlation effects to play the dominant role. They ignore the effect of charge transfer and assume that a hydrogen atom sticks to a transition metal in a neutral configuration. This assumption explains the experimental fact that the chemisorption of hydrogen on a transition metal produces an insignificant change in the metal work function. The mechanism of bonding is based on the coupling of the electronic spin on the hydrogen atom to spin fluctuations in the metal localized in the vicinity of the adsorbed atom. It is a direct generalization of the Heitler-London scheme for the formation of the H_2 molecule. The difference between the present case and that for H_2 formation is that one of the components participating in the chemical bond is this problem, viz., the metal, is spin saturated in its ground state. The spin fluctuations in the metal can arise both from Coulomb-exchange scattering and from scattering which involves the nonorthogonality of the electron wave functions in the metal and the atom. In fact, the overlap of wave functions is a crucial part of the theory and makes the exchange integral antiferromagnetic rather than ferromagnetic. A number of points are rather obscure in this theory. The starting hypothesis (i.e., zero charge transfer) on which the theory is based is presumably exact in the limit of an infinite U. For a realistic situation where U is finite and probably $\lesssim 10$ eV, the effect of charge-transfer terms on binding should be estimated before they can be considered truly negligible. There are also practical difficulties in carrying out a binding-energy calculation on this model for a real chemisorption system. Paulson and Schrieffer[4] give prescriptions for calculating the chemisorption energy in the two opposite limits when the coupling between the adatom and the neighboring atoms of the substrate metal is either very weak or very strong. It will be necessary to set up a reasonable interpolation scheme, joining the two limits, in order to calculate the chemisorption energy for the case of intermediate coupling, which is the situation prevailing experimentally.

It appears, therefore, that the adsorption of the simplest adsorbate, hydrogen, on a metal surface is a problem of fundamental theoretical interest, and it is by no means fully understood. The chemisorption problem is dominated by the large intra-atomic Coulomb correlation U which ought to be treated accurately before any approximation can be made. This implies that any simple one-electron picture is of limited validity. This is not a criticism of the Anderson model for chemisorption which has been widely treated[2,3,9] in the literature. Such theories are generally based on the Hartree-Fock approximation and must be correct when the Coulomb repulsion U is small. In other words, one-electron theories may be of great validity for a host of adsorbates other than hydrogen. Conversely, the theory of Schrieffer *et al.* is strictly valid in the $U\rightarrow\infty$ limit. It would be of interest to construct a theory which goes over smoothly from the small-U to the large-U limit. Another point of theoretical interest is the recognition[4] that the overlap of electronic wave functions plays an important role in the bonding of a one-electron atom. It is convenient, in setting up the theory of chemisorption, to deal with the combination of the set $\{\varphi_k\}$ of metallic wave functions and the set $\{\varphi_i\}$ of atomic wave functions. But the set of metallic wave functions (including both bound and running-wave states) is complete, so that the addition of atomic wave functions makes one deal with an overcomplete set of states. This introduces additional theoretical complications in the problem. In their theory,[4] Paulson and Schrieffer ignore the overcompleteness problem by confining their attention essentially to electronic wave functions bound within the metal. These constitute a subset of the complete set of states $\{\varphi_k\}$. Paulson and Schrieffer use the variational theorem to generalize the Rayleigh-Schrödinger perturbation theory in terms of a nonorthogonal set of states. They also outline a procedure[4] for writing down the many-body Hamiltonian in a second quantized notation after taking overlap into account properly.

In this and a succeeding paper, our main interest is to set up the theory of hydrogen chemisorption by dealing systematically with the questions of overcompleteness and nonorthogonality of metallic and atomic wave functions, and of the electron-electron interaction. Two limiting cases can arise, depending on the strength of the intra-atomic Coulomb repulsion U. When U is small compared to the other parameters of the problem, e.g., the bandwidth, the hydrogen atom chemisorbs in a nonmagnetic configuration, and the ground state of the system is nondegenerate with respect to spin. This is the situation studied in this paper. Standard procedures of the many-body perturbation theory can then be applied straightforwardly to the problem. If, on the other hand, the Coulomb correlation U is very large, the hydrogen atom carries an electronic spin and the chemisorption ground state is spin degenerate. This introduces further complications in the formal development of the theory. Our analysis of that situation will be contained in a later paper.

In this paper, then, we are concerned with small U when hydrogen chemisorbs in a nonmagnetic state. The total spin S of the system is zero, and the ground state in chemisorption is nondegenerate in spin.

We begin our study with the overcomplete basis set $(\{\varphi_k\}\cup\{\varphi_i\}, \langle\varphi_k|\varphi_i\rangle\neq 0)$ and construct a generalized many-body perturbation theory in terms of this set. We do this by introducing appropriate pseudo Green's functions. This is a generalization of the approach of Kanamori *et al.*[13] to the local-moment-formation problem when electron-electron interaction is taken explicitly into account. We define the model in Sec. II and work out, in Sec. III, the equations of motion of the pseudo Green's functions and the expression for the energy in terms of them. This analysis will form the core of our later study of a degenerate ground state in chemisorption. In Sec. IV, we first adopt previous procedures[13] and present a formal solution to the problem in terms of the undetermined proper self-energy. Next we introduce the Hartree-Fock approximation and relate the proper self-energy to the pseudo-Green's function elements. Finally, we display explicitly the simplifying assumptions that must be made in order to derive the Newns model[3] of hydrogen chemisorption from our work. We conclude in Sec. V with a discussion of possible improvements in the treatment of electron correlation by going beyond the Hartree-Fock theory. We indicate how higher-order many-body perturbative techniques can be adapted to the overcomplete basis, and point out possible areas of future investigation.

II. THEORETICAL MODEL

We define in this section the model that we use to study the chemisorption of an atom or a molecule on the surface of a transition metal. Specifically we wish to consider hydrogen as the adsorbate and treat it as an unpolarizable one-electron atom. Generalization to the case of many-electron adsorbates is easy to carry out. Let us suppose that there are N electrons in the conduction band of the metal which participate in the formation of the chemisorption bond. We assume that there are N_i ions in the substrate. If $-e$ denotes the electronic charge, and if $Z_m e$ is the charge on the mth ion in the metal, then charge neutrality requires that

$$N=\sum_{m=1}^{N_i} Z_m \; . \qquad (2.1)$$

In the absence of the adsorbate atom and at absolute zero, the N metal electrons occupy all states of the conduction band below the Fermi energy.

At large separation between the atom and the metal, we have a free atom and the metal without interaction. As the atom is brought close to the metal surface, electron-electron and electron-ion interactions lead to chemisorption. Figure 1 shows a hydrogen atom close to a metal surface. The metal potential is shown, for simplicity, as a square well and electrons fill up all states up to the Fermi energy ϵ_F. The Hamiltonian of the combined metal-atom system can be written

$$\mathcal{H}=\left\{\sum_{i=1}^{N}\left(\frac{p_i^2}{2m}-\sum_{m=1}^{N_i}\frac{Z_m e^2}{|\vec{r}_i-\vec{R}_m|}+\frac{1}{2}\sum_{j(\neq i)}^{N}\frac{e^2}{|\vec{r}_i-\vec{r}_j|}\right)+\frac{1}{2}\sum_{\substack{m,m'=1\\ m\neq m'}}^{N_i}\frac{Z_m Z_{m'} e^2}{|\vec{R}_m-\vec{R}_{m'}|}\right\}+\left(\frac{p_a^2}{2m}-\frac{e^2}{|\vec{r}_a-\vec{R}_a|}\right)$$
$$+\sum_{i=1}^{N}\frac{e^2}{|\vec{r}_i-\vec{r}_a|}-\sum_{i=1}^{N}\frac{e^2}{|\vec{r}_i-\vec{R}_a|}-\sum_{m=1}^{N_i}\frac{Z_m e^2}{|\vec{r}_a-\vec{R}_m|}+\sum_{m=1}^{N_i}\frac{Z_m e^2}{|\vec{R}_m-\vec{R}_a|}\;, \qquad (2.2)$$

where $\vec{r}_i(\vec{R}_m)$ denotes the position of an electron (ion) in the metal and $\vec{r}_a$ $(\vec{R}_a)$ refers to the electron (proton) of the atom. The Hamiltonian is expressed as a sum of parts which have a simple physical interpretation. We may rewrite Eq. (2.2) as

$$\mathcal{H}=\mathcal{H}_M+\mathcal{H}_a+W+\mathcal{H}_{\text{int}}\;, \qquad (2.3)$$

where $\mathcal{H}_M$ and $\mathcal{H}_a$ refer to the Hamiltonian of the metal and the free atom, respectively,

$$W=\sum_{m=1}^{N_i}\frac{Z_m e^2}{|\vec{R}_m-\vec{R}_a|} \qquad (2.4)$$

is the repulsive energy of interaction between the proton and the metal ions, and

$$\mathcal{H}_{\text{int}}=\sum_{i=1}^{N}\frac{e^2}{|\vec{r}_i-\vec{r}_a|}-\sum_{i=1}^{N}\frac{e^2}{|\vec{r}_i-\vec{R}_a|}$$
$$-\sum_{m=1}^{N_i}\frac{Z_m e^2}{|\vec{r}_a-\vec{R}_m|}\;. \qquad (2.5)$$

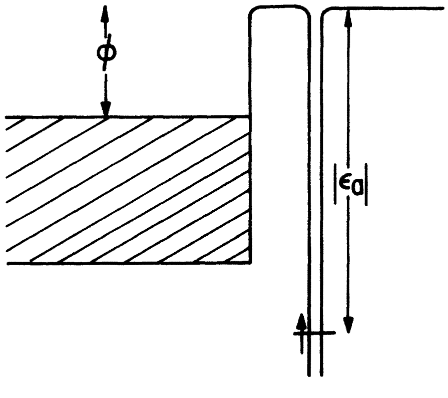

FIG. 1. Schematic representation of a hydrogen atom close to a metal surface. The Fermi energy is denoted by ϵ_F, ϕ is the work function, and ϵ_a the unperturbed energy of an electron on the adatom.

Although the separation of the Hamiltonian of Eq. (2.3) displays clearly the terms which are responsible for chemisorption, it is not in the most suitable form for the development of a Green's-function theory. For that purpose, it is more convenient to treat the $N+1$ electrons of the metal-adsorbate system on the same footing and write the Hamiltonian as ($\hbar=1$)

$$\mathcal{H}=\sum_{i=1}^{N+1}\left(-\frac{\nabla_i^2}{2m}+V_M(\vec{r}_i)+V(\vec{r}_i)\right)$$
$$+\frac{1}{2}\sum_{i,j}{}' U(\vec{r}_i-\vec{r}_j)+\mathcal{H}_R\;. \qquad (2.6)$$

Here

$$V_M(\vec{r}_i)=-\sum_{m=1}^{N_i}\frac{Z_m e^2}{|\vec{r}_i-\vec{R}_m|} \qquad (2.7)$$

represents the attractive one-electron potential due to the metal ions,

$$V(\vec{r}_i) = -e^2/|\vec{r}_i - \vec{R}_a| \tag{2.8}$$

is the potential of the proton, and

$$U(\vec{r}_i - \vec{r}_j) = e^2/|\vec{r}_i - \vec{r}_j| \tag{2.9}$$

is the electron-electron interaction. The prime over the second sum of Eq. (2.6) indicates that the term $i=j$ must be excluded. $\mathcal{H}_R$ stands for the repulsive energy of the ion cores,

$$\mathcal{H}_R = \frac{1}{2} \sum_{\substack{m,m'=1 \\ (m\neq m')}}^{N_i+1} \frac{Z_m Z_{m'} e^2}{|\vec{R}_m - \vec{R}_{m'}|} , \tag{2.10}$$

where $\vec{R}_{N_i+1} = \vec{R}_a$ is the location of the adsorbate nucleus. For fixed $\vec{R}_a$, $\mathcal{H}_R$ is a constant term in the energy and will be generally omitted unless otherwise specified.

Ignoring $\mathcal{H}_R$, then, the Hamiltonian of Eq. (2.6) may be written in second quantized notation as

$$\mathcal{H} = \int d^3x\, \psi^\dagger(\vec{x}) \left(-\frac{1}{2m}\nabla^2 + V_M(\vec{x}) + V(\vec{x}) \right) \psi(\vec{x}) + \frac{1}{2} \int\!\!\int d^3x\, d^3x'\, \psi^\dagger(\vec{x}) \psi^\dagger(\vec{x}') U(\vec{x} - \vec{x}') \psi(\vec{x}') \psi(\vec{x}) . \tag{2.11}$$

The $\psi(x)$'s obey the usual Fermi anticommutation rule

$$\{\psi(\vec{x}), \psi^\dagger(\vec{x}')\} = \delta(\vec{x} - \vec{x}'); \quad \{\psi(\vec{x}), \psi(\vec{x}')\} = 0 . \tag{2.12}$$

We consider here the case of small intra-atomic Coulomb repulsion when the chemisorption ground state is nondegenerate. The single-particle Green's function is then defined as the expectation value of the time-ordered product

$$\mathcal{G}(\vec{x}t; \vec{x}'0) = -i \langle T\psi(\vec{x}t)\psi^\dagger(\vec{x}'0) \rangle . \tag{2.13}$$

The notation $\langle \cdots \rangle$ stands for the expectation value in the full interacting ground state of the entire system. The equation of motion of $\mathcal{G}$ is easily worked out:

$$i \frac{\partial \mathcal{G}(\vec{x}t; \vec{x}'0)}{\partial t} = \delta(t)\delta(\vec{x} - \vec{x}') - i \langle T[\psi(\vec{x}t), \mathcal{H}]\psi^\dagger(\vec{x}'0) \rangle = \delta(t)\delta(\vec{x} - \vec{x}') + \left(-\frac{1}{2m}\nabla^2 + V_M(\vec{x}) + V(\vec{x}) \right) \mathcal{G}(\vec{x}t; \vec{x}'0) - i \int d^3x_2\, U(\vec{x} - \vec{x}_2) \langle T\psi^\dagger(\vec{x}_2 t^{++})\psi(\vec{x}_2 t^{+})\psi(\vec{x}t)\psi^\dagger(\vec{x}'0) \rangle . \tag{2.14}$$

The superscripts on t mean $t^{++} = t^{+} + 0^{+}$ and $t^{+} = t + 0^{+}$. We introduce superscripts to resolve ambiguities in the definition of time ordering. Let us define the one-particle part of the Hamiltonian as $\mathcal{H}_1(\vec{x})$ such that

$$\mathcal{H}_1(\vec{x}) = -\frac{1}{2m}\nabla^2 + V_M(\vec{x}) + V(\vec{x}) . \tag{2.15}$$

We also define the two-particle Green's function[14]

$$G^{\mathrm{II}}(\vec{x}_1 t_1, \vec{x}_2 t_2; \vec{x}_3 t_3, \vec{x}_4 t_4) = \langle T\{\psi(\vec{x}_1 t_1)\psi(\vec{x}_2 t_2)\psi^\dagger(\vec{x}_3 t_3)\psi^\dagger(\vec{x}_4 t_4)\} \rangle . \tag{2.16}$$

The equation of motion of $\mathcal{G}$ is

$$i \frac{\partial \mathcal{G}(\vec{x}t; \vec{x}'0)}{\partial t} = \delta(t)\delta(\vec{x} - \vec{x}') + \mathcal{H}_1(\vec{x})\mathcal{G}(\vec{x}t; \vec{x}'0) + i \int d^3x_2\, U(\vec{x} - \vec{x}_2) G^{\mathrm{II}}(\vec{x}t, \vec{x}_2 t^{+}; \vec{x}_2 t^{++}, \vec{x}'0) . \tag{2.17}$$

The equation of motion can be formally simplified by introducing the self-energy operator. The proper self-energy $\Sigma(\vec{x}t; \vec{x}'t')$ is defined through the equation

$$-i \int d^3x_2\, U(\vec{x} - \vec{x}_2) \langle T\psi^\dagger(\vec{x}_2 t^{++})\psi(\vec{x}_2 t^{+})\psi(\vec{x}t)\psi^\dagger(\vec{x}'0) \rangle = \int \Sigma(\vec{x}t; \vec{x}''t'') \mathcal{G}(\vec{x}''t''; \vec{x}'0)\, d^3x''\, dt'' . \tag{2.18}$$

In terms of Σ, Eq. (2.17) reads

$$i \frac{\partial \mathcal{G}(\vec{x}t; \vec{x}'0)}{\partial t} = \delta(t)\delta(\vec{x} - \vec{x}') + \mathcal{H}_1(\vec{x})\mathcal{G}(\vec{x}t; \vec{x}'0) + \int \Sigma(\vec{x}t; \vec{x}''t'') \mathcal{G}(\vec{x}''t''; \vec{x}'0)\, d^3x''\, dt'' . \tag{2.19}$$

Equation (2.19) is the starting point of our subsequent development of a pseudo-Green's-function formalism. Our basic aim is simple. We should like to describe the metal-adsorbate system in terms of the eigenfunction of the atom plus the metallic eigenstates such that the energy of the combined system goes over trivially to the sum of energies of the atom and the metal for large separation of the two. The set of metallic eigenstates is complete, however, and the addition of the atomic eigenstate to this set makes it overcomplete. This introduces arbitrariness in the description of the problem. In the following sections we try to show how this arbitrariness can be used to our advantage in setting up a simple and physically meaningful perturbation theory. In particular, we discuss the Hartree-Fock factorization and show how previous theories of hydrogen chemisorption based on this approximation follow as simple limiting cases of the present formalism.

In Sec. III, we turn to the construction of a systematic many-body theory, taking overcompleteness and nonorthogonality into account.

III. PSEUDO-GREEN'S-FUNCTION FORMALISM WITH ELECTRON-ELECTRON INTERACTION

It is necessary, at this stage, to define precisely what we mean by the eigenstates of the metal and the atom that we talked about in Sec. II. The question of an overcomplete basis set must also be clarified before a pseudo-Green's-function formalism can be introduced. We are interested here in the chemisorption of an unpolarizable one-electron atom. This means that we have to consider only a single atomic wave function $\varphi_a(\vec{x})$. The eigenstate φ_a of the one-electron atom obeys the Schrödinger equation

$$\mathcal{H}_a(\vec{x})\varphi_a(\vec{x}) \equiv \left(-\frac{1}{2m}\nabla^2 + V(\vec{x})\right)\varphi_a(\vec{x}) = \epsilon_a\varphi_a(\vec{x}) , \tag{3.1}$$

with some appropriate boundary condition, where $V(\vec{x})$ is given by Eq. (2.8). For a free atom, the boundary condition demands that far from the nucleus, $\varphi_a(\vec{x})$ decays exponentially. The problem of the boundary condition is more involved when the atom is brought close to the metal surface, and it will be discussed briefly later on. The metal is described by a set of one-electron eigenstates $\{\varphi_k\}$ which are defined in the following manner. For the metal alone, without the adsorbate, the one-electron Green's function satisfies an equation similar to Eq. (2.19). Denoting functions with a superscript M (for metal), we have

$$\begin{aligned} i\,\frac{\partial \mathcal{G}^M(\vec{x}t;\vec{x}'0)}{\partial t} &= \delta(t)\delta(\vec{x}-\vec{x}') + \mathcal{H}_1^M(\vec{x})\mathcal{G}^M(\vec{x}t;\vec{x}'0) \\ &\quad + \int \Sigma^M(\vec{x}t;\vec{x}''t'')\mathcal{G}^M(\vec{x}''t'';\vec{x}'0)\,d^3x''\,dt'' , \end{aligned} \tag{3.2}$$

where

$$\mathcal{H}_1^M(\vec{x}) = -\frac{1}{2m}\nabla^2 + V_M(\vec{x}) . \tag{3.3}$$

Recognizing that $\mathcal{G}^M$ and Σ^M depend only on the time difference in their argument, and effecting a Fourier transform in time, we obtain

$$\begin{aligned} &[\omega - \mathcal{H}_1^M(\vec{x})]\mathcal{G}^M(\vec{x},\vec{x}';\omega) \\ &\quad - \int \Sigma^M(\vec{x},\vec{x}'';\omega)\mathcal{G}^M(\vec{x}'',\vec{x}';\omega)\,d^3x'' = \delta(\vec{x}-\vec{x}') . \end{aligned} \tag{3.4}$$

Here

$$\Sigma^M(\vec{x},\vec{x}';\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega(t-t')}\Sigma^M(\vec{x}t;\vec{x}'t') , \tag{3.5}$$

and a similar definition holds for $\mathcal{G}^M(\vec{x},\vec{x}';\omega)$. Now we are often interested primarily in electrons near the Fermi energy. The imaginary part of $\Sigma^M(\vec{x},\vec{x}';\omega)$ is small for ω near ϵ_F. We therefore ignore it, omitting finite lifetimes. Moreover, we are not very much interested in renormalization effects associated with the energy dependence of $\Sigma^M(\vec{x},\vec{x}';\omega)$. We choose to ignore these by setting $\partial\Sigma^M/\partial\omega = 0$, thus essentially evaluating $\Sigma^M(\vec{x},\vec{x}';\omega)$ at $\omega = \epsilon_F$. Equation (3.4) then reads

$$\begin{aligned} &\omega\mathcal{G}^M(\vec{x},\vec{x}';\omega) \\ &\quad - \int \mathcal{H}^M(\vec{x},\vec{x}'')\mathcal{G}^M(\vec{x}'',\vec{x}';\omega)\,d^3x'' = \delta(\vec{x}-\vec{x}') \end{aligned} \tag{3.6}$$

where

$$\mathcal{H}^M(\vec{x},\vec{x}') \equiv \mathcal{H}_1^M(\vec{x})\delta(\vec{x}-\vec{x}') + \Sigma^M(\vec{x},\vec{x}';\epsilon_F) . \tag{3.7}$$

If we rewrite Eq. (3.6) in operator notation as

$$[\omega\times\underline{1} - \mathcal{H}^M]\,\mathcal{G}^M(\omega) = 1, \tag{3.8}$$

then we are left with the result that the metallic electrons can be treated as though they move in the energy-independent single-particle effective Hamiltonian $\mathcal{H}^M$.

It is now possible to introduce the eigenstates $\{\varphi_k\}$ of the metal Hamiltonian $\mathcal{H}^M$ such that

$$\mathcal{H}^M\varphi_k = \epsilon_k\varphi_k . \tag{3.9}$$

In an actual situation, it is often difficult to find the states φ_k and the energies ϵ_k explicitly. We assume, however, that these are known. Since $\mathcal{H}^M$ of Eq. (3.7) is Hermitian, the set $\{\varphi_k\}$ is complete. It represents the entire set of one-electron eigenstates of the metal, including occupied states below the Fermi energy and unoccupied states for both positive and negative energies. The atomic eigenstate φ_a can be expanded, of course, in terms of the complete set $\{\varphi_k\}$. If $|k\rangle$ and $|a\rangle$ denote the state vectors corresponding to the wave functions $\varphi_k(\vec{x})$ and $\varphi_a(\vec{x})$, respectively, then

$$|a\rangle = \sum_k \Delta_{ka}|k\rangle , \tag{3.10}$$

where $\Delta_{ka} = \langle k|a\rangle$ is the overlap integral. We propose to describe the metal-adsorbate system in terms of the manifestly overcomplete set of states $\{\varphi_k, \varphi_a\}$. Considerable literature exists on the use of an overcomplete basis set of states in describing a system of (effectively) noninteracting electrons. The problem has been studied in connection with magnetic impurities in a nonmagnetic host metal,[13,15,16] the band-structure calculation[17,18] of d-band metals, and pseudopotential theory.[19] The principal feature which distinguishes the present paper from previous work is that we take electron-electron interaction explicitly into account. We should note, however, that some of the previous work was concerned with the many-body effect in band-structure calculations[20] and foreshadowed our investigation.

We begin by expanding the field operator $\psi(\vec{x})$ in terms of the overcomplete basis:

$$\psi(\vec{x}) = \sum_k \varphi_k(\vec{x}) c_k = \sum_k \varphi_k(\vec{x}) b_k + \varphi_a(\vec{x}) b_a . \qquad (3.11)$$

The spin subscript σ is understood in Eq. (3.11). We regard $\varphi_a(\vec{x})$ as the solution of Eq. (3.1) with the boundary condition appropriate for a free atom. Such a choice is in the spirit of the previous work[3,4] on hydrogen chemisorption, but is by no means essential. For the purpose of this work, it is simply necessary to assume that $\varphi_a(\vec{x})$ and ϵ_a are known, and any boundary condition[13,21] can be incorporated naturally into the formalism. It follows from the orthonormality of the functions $\{\varphi_k(\vec{x})\}$ that

$$c_k = \int d^3x \, \varphi_k^*(\vec{x}) \psi(\vec{x}) . \qquad (3.11a)$$

The expansion of $\psi(\vec{x})$ in terms of the complete set $\{\varphi_k\}$ is unique, and the operators c_k, which are the coefficients of expansion, obey the Fermi anticommutation rule:

$$\{c_k, c_{k'}^\dagger\} = \delta_{kk'} ; \quad \{c_k, c_{k'}\} = 0 . \qquad (3.12)$$

The expansion in terms of the overcomplete basis, however, is not unique. We see this by noting that Eq. (3.11a) implies

$$c_k = b_k + \Delta_{ka} b_a , \qquad (3.13)$$

where Δ_{ka} is defined in Eq. (3.10). This means that the operators b_k are arbitrary so long as b_a is not specified explicitly. The b_k's and b_a will not, in general, obey any definite commutation relation. A choice of b_a specifies the expansion uniquely. For example,

$$b_a = 0 \Rightarrow b_k = c_k , \qquad (3.14a)$$

and

$$b_a = c_a \Rightarrow b_k = c_k - \Delta_{ka} c_a , \qquad (3.14b)$$

where c_a is the destruction operator for an electron in the state $|a\rangle$, i.e.,

$$c_a = \int d^3x \, \varphi_a^*(\vec{x}) \psi(\vec{x}) . \qquad (3.15)$$

Equation (3.14b) shows that, for the given choice of b_a, b_k creates the OPW state from $\varphi_k(\vec{x})$. We find, with the help of Eq. (3.10), that

$$c_a = \sum_k \Delta_{ak} \int d^3x \, \varphi_k^*(\vec{x}) \psi(\vec{x}) = \sum_k \Delta_{ak} c_k . \qquad (3.16)$$

The conjugate operator can be expanded as

$$c_a^\dagger = \sum_k c_k^\dagger \Delta_{ka} . \qquad (3.17)$$

We now define pseudo Green's functions as the ground-state expectation values of the time-ordered products:

$$G_{kk'}(t) = -i \langle T b_k(t) c_{k'}^\dagger \rangle , \qquad (3.18a)$$

$$G_{ak'}(t) = -i \langle T b_a(t) c_{k'}^\dagger \rangle , \qquad (3.18b)$$

$$G_{ka}(t) = -i \langle T b_k(t) c_a^\dagger \rangle , \qquad (3.19a)$$

$$G_{aa}(t) = -i \langle T b_a(t) c_a^\dagger \rangle . \qquad (3.19b)$$

If Eq. (3.17) is combined with Eqs. (3.19), we obtain

$$G_{ka}(t) = (-i) \sum_{k'} \langle T b_k(t) c_{k'}^\dagger \rangle \Delta_{k'a} = \sum_{k'} G_{kk'}(t) \Delta_{k'a} . \qquad (3.20a)$$

Similarly

$$G_{aa}(t) = \sum_{k'} G_{ak'}(t) \Delta_{k'a} , \qquad (3.20b)$$

which shows that $G_{kk'}(t)$ and $G_{ak'}(t)$ are the only independent elements of the pseudo Green's function. We call the functions defined in Eqs. (3.18) pseudo Green's functions in contrast to the real Green's function whose elements, in the representation of the φ_k's are

$$\mathcal{G}_{kk'}(t) = -i \langle T c_k(t) c_{k'}^\dagger \rangle . \qquad (3.21)$$

Equation (3.13) enables us to relate the real and pseudo Green's functions as

$$\mathcal{G}_{kk'}(t) = G_{kk'}(t) + \Delta_{ka} G_{ak'}(t) . \qquad (3.22)$$

At first sight, the definitions of Eqs. (3.18) and (3.19) seem puzzling. But we have achieved our objective of expressing the one-particle propagator in terms of an overcomplete basis set of states. We have done this by resorting to an asymmetrical definition of the elements of the pseudo Green's function. Our next task is to relate the pseudo Green's function to quantities of physical interest. This is done very simply for the single-particle density of states, which is related to the trace of the real Green's function, and the trace can be written as

$$\sum_k \mathcal{G}_{kk} = \sum_k G_{kk} + \sum_k G_{ak} \Delta_{ka} = \sum_k G_{kk} + G_{aa} , \qquad (3.23)$$

where Eqs. (3.22) and (3.20b) have been used. The trace of the pseudo Green's function is, therefore, the same as the trace of the true propagator.

It is possible to derive the equations of motion of the pseudo Green's function from Eq. (2.19) in terms of the proper self-energy. Combining Eqs. (2.13), (3.21) and (3.22), we obtain

$$\mathcal{G}(\vec{x}t;\vec{x}'0)=\sum_{kk'}\varphi_k(\vec{x})\varphi^*_{k'}(\vec{x}')\mathcal{G}_{kk'}(t)=\sum_{kk'}\varphi_k(\vec{x})\varphi^*_{k'}(\vec{x}')\left[G_{kk'}(t)+\Delta_{ka}G_{ak'}(t)\right]\,. \tag{3.24}$$

We subsitute this equation into Eq. (2.19) and make use of the orthonormality and completeness of the metal eigenstates,

$$\langle k|k'\rangle=\delta_{kk'}\,;\quad\sum_k|k\rangle\langle k|=1\,. \tag{3.25}$$

The result is

$$\sum_{kk'}\varphi_k(\vec{x})\varphi^*_{k'}(\vec{x}')\left(i\frac{\partial G_{kk'}(t)}{\partial t}+\Delta_{ka}i\frac{\partial G_{ak'}(t)}{\partial t}\right)=\delta(t)\sum_{kk'}\varphi_k(\vec{x})\varphi^*_{k'}(\vec{x}')\delta_{kk'}+\mathcal{H}_1(\vec{x})\sum_{kk'}\varphi_k(\vec{x})\varphi^*_{k'}(\vec{x}')[G_{kk'}(t)+\Delta_{ka}G_{ak'}(t)]$$
$$+\int d^3x''\,dt''\,\Sigma(\vec{x}t;\vec{x}''t'')\sum_{kk'}\varphi_k(\vec{x}'')\varphi^*_{k'}(\vec{x}')[G_{kk'}(t'')+\Delta_{ka}G_{ak'}(t'')]\,. \tag{3.26}$$

Let us define the Fourier transform of the self-energy as

$$\Sigma_{ij}(\omega)=\int dt\,e^{i\omega(t-t')}\int d^3x\int d^3x'\,\varphi^*_i(\vec{x})\Sigma(\vec{x}t;\vec{x}'t')\varphi_j(\vec{x}')\quad(\varphi_i=\varphi_{k'}\,\varphi_a)\,. \tag{3.27}$$

Then the orthonormality of φ_k's may be utilized to rewrite Eq. (3.26), after transforming to the frequency space, as

$$\sum_{k''}\{\langle k|(\omega-\mathcal{H}_1)|k''\rangle-\Sigma_{kk''}(\omega)\}G_{k''k'}(\omega)+\sum_{k''}\{\langle k|(\omega-\mathcal{H}_1)|k''\rangle-\Sigma_{kk''}(\omega)\}\Delta_{k''a}G_{ak'}(\omega)=\delta_{kk'}\,. \tag{3.28}$$

Making use of the completeness condition of Eq. (3.10), we obtain

$$[\langle k|(\omega-\mathcal{H}_1)|k''\rangle-\Sigma_{kk''}(\omega)]G_{k''k'}(\omega)+[\langle k|(\omega-\mathcal{H}_1)|a\rangle-\Sigma_{ka}(\omega)]G_{ak'}(\omega)=\delta_{kk'}\,, \tag{3.29}$$

where we have introduced the summation convention over repeated k indices in order to avoid any confusion with the self-energy operator. The summation convention over k indices will be followed in the rest of the paper, unless otherwise specified.

Equation (3.29) cannot determine all of the unknown pseudo-Green's-function elements, $G_{kk'}(\omega)$ and $G_{ak'}(\omega)$. In fact, there are fewer equations than there are unknowns, so that Eq. (3.29) can be used merely to express $G_{kk'}$'s in terms of the $G_{ak'}$'s. Thus far, the elements $G_{ak}(\omega)$ are totally arbitrary, and this arbitrariness is related to the freedom in the choice of b_a discussed earlier. We follow the procedure of Kanamori *et al.*[13] and take care of this arbitrariness by introducing a further set of equations

$$\langle a|\Phi|k''\rangle G_{k''k'}(\omega)$$
$$+[\langle a|(\omega-\mathcal{H}_1)|a\rangle-\Sigma_{aa}(\omega)]G_{ak'}(\omega)=\Delta_{ak'} \tag{3.30}$$

where the coefficients $\langle a|\Phi|k''\rangle$ are unknown and at our disposal. Equation (3.30) transfers the arbitrariness in $G_{ak'}$ to the arbitrariness in the choice of $\langle a|\Phi|k''\rangle$. Conversely, once the coefficients $\langle a|\Phi|k''\rangle$ are chosen, the description of the interacting-electron system in terms of the pseudo Green's function is complete. Equations (3.29) and (3.30) are the generalization of the pseudo-Green's-function equations of Kanamori and collaborators[13] when electron-electron correlation is taken into account. We should emphasize the fact that, although the choice of $\langle a|\Phi|k''\rangle$ is arbitrary, not all choices will correspond to a sensible separation of the chemisorption problem into a metallic part and an atomic part. We may start from a meaningful choice of b_a and derive the coefficients $\langle a|\Phi|k''\rangle$ from it. Since one of our major aims is to set up a theory which goes over to an independent atom and the metal in the limit of large separation, a reasonable choice of $\langle a|\Phi|k''\rangle$ is of crucial importance to the theory.

Equation (3.29) can be simplified considerably if we use the metal part of the self-energy, $\Sigma^M(\vec{x},\vec{x}';\epsilon_F)$, and the effective one-particle metal Hamiltonian $\mathcal{H}^M$. Equation (2.15) defining $\mathcal{H}_1(\vec{x})$ can be written with the help of Eqs. (3.1) and (3.3) as

$$\mathcal{H}_1(\vec{x})=\mathcal{H}_a(\vec{x})+V_M(\vec{x})=\mathcal{H}^M_1(\vec{x})+V(\vec{x})\,. \tag{3.31}$$

Therefore

$$\langle k|\mathcal{H}_1|k''\rangle=\langle k|\mathcal{H}^M_1|k''\rangle+\langle k|V|k''\rangle \tag{3.32a}$$

and

$$\langle k|\mathcal{H}_1|a\rangle=\langle k|\mathcal{H}_a|a\rangle+\langle k|V_M|a\rangle\,. \tag{3.32b}$$

If we define

$$\Sigma^M_{ij}=\int d^3x\,d^3x'\,\varphi^*_i(\vec{x})\Sigma^M(\vec{x},\vec{x}';\epsilon_F)\varphi_j(\vec{x}')\,, \tag{3.33}$$

where i and j stand for any of the k states and/or a, then Eqs. (3.7) and (3.9) lead to

$$\langle k|\mathcal{H}^M|k'\rangle=\langle k|\mathcal{H}^M_1|k'\rangle+\Sigma^M_{kk'}=\epsilon_k\delta_{kk'}\,. \tag{3.34}$$

In deriving this relation, we have used the orthonormality of the φ_k's. Using this result in Eq. (3.32a), we obtain

$$\langle k|\mathcal{H}_1|k''\rangle = \epsilon_k\delta_{kk''} + \langle k|V|k''\rangle - \Sigma^M_{kk''} \ . \quad (3.35a)$$

Also Eq. (3.32b) can be combined with Eq. (3.1) to give

$$\langle k|\mathcal{H}_1|a\rangle = \epsilon_a\Delta_{ka} + \langle k|V_M|a\rangle \ . \quad (3.35b)$$

Let us now define the self-energy S of metal-adsorbate interaction through the equation

$$S_{kk'}(\omega) = \Sigma_{kk'}(\omega) - \Sigma^M_{kk'} \ . \quad (3.36)$$

When Eqs. (3.35) and (3.36) are substituted in Eq. (3.29), we obtain

$$\{(\omega-\epsilon_k)\delta_{kk''} - [\langle k|V|k''\rangle + S_{kk''}(\omega)]\}G_{k''k'}(\omega) + \{(\omega-\epsilon_a)\Delta_{ka} - [\langle k|V_M|a\rangle + \Sigma_{ka}(\omega)]\}G_{ak'}(\omega) = \delta_{kk'} \ . \quad (3.37)$$

Similarily, Eq. (3.30) can be rewritten as

$$\langle a|\Phi|k''\rangle G_{k''k'}(\omega) + \{(\omega-\epsilon_a) - [\langle a|V_M|a\rangle + \Sigma_{aa}(\omega)]\}G_{ak'}(\omega) = \Delta_{ak'} \ . \quad (3.38)$$

It should be noted that $\Sigma_{ka}(\omega)$ and $\Sigma_{aa}(\omega)$ can also be written as the sum of two contributions—one originating in the metal and the other in the metal-adsorbate interaction. For example,

$$\Sigma_{ka}(\omega) = S_{ka}(\omega) + \Sigma^M_{ka} \ , \quad (3.39)$$

and similarly for $\Sigma_{aa}(\omega)$. Such a separation in Eq. (3.37) is of no immediate advantage, however, and we prefer to retain $\Sigma_{ka}(\omega)$ at this stage.

We complete the formal development of this section by writing down the ground-state energy of the metal-adsorbate system in terms of the pseudo Green's function. The use of Eq. (10.18) of Fetter and Walecka[22] gives

$$E = \langle\mathcal{H}\rangle = -\frac{i}{2}\sum_\sigma \int d^3x \int \frac{d\omega}{2\pi} e^{i\omega\eta} \times \lim_{\vec{x}'\to\vec{x}} \left(\omega - \frac{\nabla^2}{2m} + V_M(\vec{x}) + V(\vec{x})\right) \times \mathcal{G}^\sigma(\vec{x},\vec{x}';\omega) + \mathcal{H}_R \ , \quad (3.40)$$

where $\eta\to 0^+$ and sum over the spin label σ is indicated. $\mathcal{G}^\sigma(x,x';\omega)$ is the Fourier transform of

$$\mathcal{G}^\sigma(\vec{x}t;\vec{x}'0) = -i\langle T\psi_\sigma(\vec{x}t)\psi^\dagger_\sigma(\vec{x}'0)\rangle \ . \quad (2.13a)$$

But Eq. (3.24) implies that

$$\mathcal{G}^\sigma(\vec{x},\vec{x}';\omega) = \varphi_k(\vec{x})\varphi^*_{k'}(\vec{x}) \times [G^\sigma_{kk'}(\omega) + \Delta_{ka}G^\sigma_{ak'}(\omega)] \ , \quad (3.41)$$

so that

$$E = -\frac{i}{2}\sum_\sigma \int d^3x \int \frac{d\omega}{2\pi} e^{i\omega\eta} \varphi^*_{k'}(\vec{x})[\omega + \mathcal{H}_1(\vec{x})] \times \varphi_k(\vec{x})[G^\sigma_{kk'}(\omega) + \Delta_{ka}G^\sigma_{ak'}(\omega)] + \mathcal{H}_R \ . \quad (3.42)$$

Here $\mathcal{H}_1(\vec{x})$ is the one-particle part of the Hamiltonian as defined in Eq. (2.15). Carrying out the integration over $\vec{x}$ and making use of the completeness of the k states, we obtain

$$E = -\frac{i}{2}\sum_\sigma \int \frac{d\omega}{2\pi} e^{i\omega\eta}\{\langle k'|(\omega+\mathcal{H}_1)|k\rangle G^\sigma_{kk'}(\omega) + \langle k'|(\omega+\mathcal{H}_1)|a\rangle G^\sigma_{ak'}(\omega)\} + \mathcal{H}_R \ . \quad (3.43)$$

This equation simplifies somewhat when used in conjunction with Eqs. (3.35). The result is

$$E = -\frac{i}{2}\sum_\sigma \int \frac{d\omega}{2\pi} e^{i\omega\eta}\{[(\omega+\epsilon_k)\delta_{k'k} - \Sigma^M_{k'k} + \langle k'|V|k\rangle]G^\sigma_{kk'}(\omega) + [(\omega+\epsilon_a)\Delta_{k'a} + \langle k'|V_M|a\rangle]G^\sigma_{ak'}(\omega)\} + \mathcal{H}_R \ . \quad (3.44)$$

With this result, we have achieved two of our objectives. We have the equations of motion of the pseudo Green's functions which can be solved in terms of the proper self-energy Σ. We also have an expression for the ground-state energy in terms of the pseudo-Green's-function elements. The problem, of course, is that the proper self-energy is not known, and it is necessary to set up some approximation scheme for finding Σ. Once the approximation scheme is decided upon, we must determine the matrix elements of G and Σ in a self-consistent manner. As a prototype example we may adopt the Hartree-Fock factorization to find Σ, and this is discussed in detail in Sec. IV.

IV. FORMAL SOLUTION AND THE HARTREE-FOCK APPROXIMATION

In Sec. III, we set up a formalism to deal with the problem of hydrogen chemisorption in terms of an overcomplete basis set comprising the eigenfunction of the atom and the eigenstates of the metal. We introduced appropriate pseudo Green's functions, derived their equations of motion in terms of the proper self-energy, and expressed the total energy of the system as a function of the pseudo-Green's-function elements. In this section, we first solve the equations of motion formally in terms of the proper self-energy Σ. We next derive the self-consistency condition relating

Σ to the matrix elements of G within the Hartree-Fock approximation, and finally show how the Newns model for hydrogen chemisorption can be recovered from our generalized description of the problem.

We mentioned earlier that the physical interpretation of the pseudo-Green's-function elements depends critically on the choice of the arbitrary coefficients $\langle a|\Phi|k\rangle$ of Eqs. (3. 30) and (3. 38). These can, in turn, be related to the choice of b_a in Eq. (3. 11). We shall have occasion to use, in much of the rest of the paper, the particular, physically meaningful choice $b_a = c_a$. In that case, Eqs. (3. 14b) and (3. 16) show that

$$\Delta_{ak} b_k = \Delta_{ak} c_k - c_a = 0 \ . \tag{4. 1}$$

(Sum over repeated k indices understood.) This equation, when coupled with the definition of Eq. (3. 18a), implies that

$$\Delta_{ak} G^s_{kk'}(\omega) = 0 \ , \tag{4. 2}$$

where the spin label s is now displayed explicitly. This particular choice for b_a is physically sensible because it leads to the identification of $G^s_{aa}(\omega)$ with the projection, on the adatom level, of the true Green's function itself, i. e.,

$$\begin{aligned}\Delta_{ak}\mathcal{G}^s_{kk'}(\omega)\Delta_{k'a} &= \Delta_{ak}G^s_{kk'}(\omega)\Delta_{k'a} + G^s_{ak'}(\omega)\Delta_{k'a} \\ &= G^s_{aa}(\omega) \ .\end{aligned} \tag{4. 3}$$

Furthermore, Eq. (4. 2) gives rise to a consistency condition between Eqs. (3. 29) and (3. 30), viz.,

$$\begin{aligned}\langle a|\Phi|k\rangle &= -\langle a|\mathcal{H}_1|k\rangle - \Sigma_{ak;s}(\omega) \\ &= -\epsilon_k\Delta_{ak} - \langle a|V|k\rangle - S_{ak;s}(\omega) \ ,\end{aligned} \tag{4. 4}$$

where

$$\begin{aligned}S_{ak;s}(\omega) &= \Delta_{ak''}[\Sigma_{k''k;s}(\omega) - \Sigma^M_{k''k;s}(\omega)] \\ &= \Sigma_{ak;s}(\omega) - \Sigma^M_{ak;s}(\omega) \ .\end{aligned} \tag{4. 5}$$

This definition should be compared with Eq. (3. 36).

A. Formal solution

We shall follow closely the work of Kanamori *et al.*[13] in presenting the formal solution to the equations of motion for the pseudo-Green's-function elements. We first derive the results and then discuss their structure. Multiplying Eq. (3. 38) by Δ_{ka} and subtracting it from Eq. (3. 37), we obtain

$$\begin{aligned}L^s_{kk''}G^s_{k''k'}(\omega) + M^s_{ka}G^s_{ak'}(\omega) &= \delta_{kk'} - \Delta_{ka}\Delta_{ak'} \\ &\equiv P_{kk'} \ ,\end{aligned} \tag{4. 6}$$

where

$$\begin{aligned}L^s_{kk''} = (\omega - \epsilon_k)\delta_{kk''} &- [\langle k|V|k''\rangle + S_{kk'';s}(\omega)] \\ &- \Delta_{ka}\langle a|\Phi|k''\rangle\end{aligned} \tag{4. 7a}$$

and

$$\begin{aligned}M^s_{ka} = &-[\langle k|V_M|a\rangle + \Sigma_{ka;s}(\omega)] \\ &+ \Delta_{ka}[\langle a|V_M|a\rangle + \Sigma_{aa;s}(\omega)] \ .\end{aligned} \tag{4. 7b}$$

Assuming the existence of the inverse of the matrix L^s which is not Hermitian, in general, we find

$$\langle a|\Phi|k''\rangle G^s_{k''k'} + \langle a|\Phi|k''\rangle(L^s)^{-1}_{k''k'''}M^s_{k'''a}G^s_{ak'} = \langle a|\Phi|k''\rangle(L^s)^{-1}_{k''k'''}P_{k'''k'} \ . \tag{4. 8}$$

Combining this with Eq. (3. 38), we obtain

$$\{\omega - \epsilon_a - \langle a|V_M|a\rangle - \Sigma_{aa;s}(\omega) - \langle a|\Phi|k\rangle(L^s)^{-1}_{kk''}M^s_{k''a}\}G^s_{ak'}(\omega) = \Delta_{ak'} - \langle a|\Phi|k\rangle(L^s)^{-1}_{kk''}P_{k''k'} \ . \tag{4. 9}$$

Also since the projection operator $P_{kk'}$ of Eq. (4. 6) projects out states orthogonal to $|a\rangle$,

$$P_{kk'}\Delta_{k'a} = 0 \tag{4. 10}$$

and the diagonal element of the pseudo Green's function on the adatom is

$$G^s_{aa}(\omega) = G^s_{ak'}(\omega)\Delta_{k'a} = \{\omega - \epsilon_a - \langle a|V_M|a\rangle - \Sigma_{aa;s}(\omega) - \langle a|\Phi|k\rangle(L^s)^{-1}_{kk''}M^s_{k''a}\}^{-1} \ . \tag{4. 11}$$

Equations (4. 9) and (4. 11) are the formal solutions for $G^s_{ak}(\omega)$ and $G^s_{aa}(\omega)$. They are not immediately useful because the results involve the self-energy Σ which is not known. It is nevertheless possible to understand some of the general features of the solutions. For a physically sensible choice of $\langle a|\Phi|k\rangle$ [e. g., that given by (4. 4)], Eq. (4. 11) can be interpreted as the Green's function of an electron on the adatom, renormalized to take electron-electron interaction into account. The term

$$\langle a|\Phi|k\rangle(L^s)^{-1}_{kk''}M^s_{k''a}$$

mixes the electron state on the atom with those in the metal, and produces both a level shift and a broadening in energy. Its influence will be small if the energy difference between the adatom level and an electronic state in the metal is large. In terms of $G^s_{aa}(\omega)$, we rewrite Eq. (4. 9) as

$$\begin{aligned}G^s_{ak'}(\omega) &= G^s_{aa}(\omega)\Delta_{ak'} \\ &\quad - G^s_{aa}(\omega)\langle a|\Phi|k\rangle(L^s)^{-1}_{kk''}P_{k''k'} \ .\end{aligned} \tag{4. 12}$$

The first factor on the right is related to the renormalized Green's function of an electron on the adsorbed atom. The second term depends explicitly on the tunneling of an electron from the atom to the metal or vice versa, through the matrix elements $\langle a|\Phi|k\rangle$. The contribution of the second term to the energy formula of Eq. (3.43) is small when the energy difference between the atomic and metallic electron levels is large. It is also possible to write down formal solutions for $G^s_{kk'}(\omega)$ in terms of $G^s_{ak'}(\omega)$ of Eq. (4.12), but it is not very useful and we turn instead to the question of determining the proper self-energy.

B. Hartree-Fock approximation

In the previous subsection, we obtained formal expressions for the pseudo-Green's-function elements as functions of the proper self-energy Σ. The self-energy, in its turn, is defined through the relation

$$-i\sum_{s'}\int d^3x_2\, U(\vec{x}-\vec{x}_2)\langle T\psi^\dagger_{s'}(\vec{x}_2 t^{++})\psi_{s'}(\vec{x}_2 t^{+})\psi_s(\vec{x}\,t)\psi^\dagger_s(\vec{x}'0)\rangle=\int \Sigma_s(\vec{x}\,t;\vec{x}''t'')\mathcal{G}^s(\vec{x}''t'';\vec{x}'0)\,d^3x''\,dt'' , \tag{4.13}$$

and it depends on the one- and two-particle Green's functions. Equation (4.13) must be solved along with the equations of motion (3.37) and (3.38) for a self-consistent determination of G and Σ. The set of equations is not closed, however, because the two-particle Green's function appearing in (4.13) is not known. It is possible to derive the equation of motion of the two-particle Green's function in terms of the three-particle Green's function and so on, thus setting up a hierarchy of Green's-function equations. The series must then be truncated at some stage in order to obtain a closed system of equations. The simplest approximation is to employ Hartree-Fock factorization in Eq. (4.13), decomposing the two-particle Green's function into an antisymmetrized product of two single-particle Green's functions. Such a decoupling procedure leads to the self-consistent Hartree-Fock theory for the chemisorption problem, and we shall study it in some detail. Since the ground state under study is nondegenerate, the self-energy, in this approximation, assumes the form [cf. Eq. (10.4) of Ref. 22]

$$\Sigma^{\mathrm{HF}}_s(\vec{x}\,t;\vec{x}'t')=\delta(t-t')\sum_\sigma\left\{-i\delta(\vec{x}-\vec{x}')\int d^3x_2\,U(\vec{x}-\vec{x}_2)\,\mathcal{G}^\sigma(\vec{x}_2 t;\vec{x}_2 t^+)+i\delta_{s\sigma}U(\vec{x}-\vec{x}')\,\mathcal{G}^\sigma(\vec{x}\,t;\vec{x}'t^+)\right\} \tag{4.14}$$

Here s and σ label spin and the superscript HF stands for Hartree-Fock. If we use Eq. (3.24) to express the propagator in terms of the pseudo-Green's-function elements, and if Eq. (3.27) defining Σ_{ij} is used, we find, in a straightforward manner, that

$$\Sigma^{\mathrm{HF}}_{ij;s}(\omega)=-i\sum_\sigma\{\langle ik'|U|jk\rangle[G^\sigma_{kk'}(0^-)+\Delta_{ka}G^\sigma_{ak'}(0^-)]-\delta_{s\sigma}\langle ik'|U|kj\rangle[G^\sigma_{kk'}(0^-)+\Delta_{ka}G^\sigma_{ak'}(0^-)]\} . \tag{4.15}$$

The self-energy is seen to be independent of ω in this approximation. We separate out the contributions coming from $G_{kk'}$ and $G_{ak'}$, respectively. The former has to do mainly with the interaction among metal electrons; the latter involves the metal-adsorbate interaction. Noting that

$$G^\sigma_{ij}(t)=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\,e^{-i\omega t}G^\sigma_{ij}(\omega) \tag{4.16}$$

and making use of the completeness of the $|k\rangle$ states, we obtain

$$\Sigma^{\mathrm{HF}}_{ij;s}(\omega)=-i\sum_\sigma[\langle ik'|U|jk\rangle-\delta_{s\sigma}\langle ik'|U|kj\rangle]\int\frac{d\omega'}{2\pi}e^{i\omega'\eta}G^\sigma_{kk'}(\omega')-i\sum_\sigma[\langle ik'|U|ja\rangle$$
$$-\delta_{s\sigma}\langle ik'|U|aj\rangle]\int\frac{d\omega'}{2\pi}e^{i\omega'\eta}G^\sigma_{ak'}(\omega') . \tag{4.17}$$

Here $\eta\to 0^+$ and i and j stand for any of the k states and/or a. Within the same approximation, the metal part of the self-energy is given by

$$\Sigma^M_{k_1k_2;s}=\sum_k\sum_\sigma[\langle k_1k|U|k_2k\rangle$$
$$-\delta_{s\sigma}\langle k_1k|U|kk_2\rangle]n_{k\sigma} , \tag{4.18}$$

where $n_{k\sigma}$ is the Fermi function, i.e., the electron occupation number. When this is subtracted from $\Sigma^{\mathrm{HF}}_{k_1k_2;s}(\omega)$, we obtain an expression for $S_{k_1k_2;s}(\omega)$ valid for the present approximation scheme.

Equation (4.17) may be used to find Σ for a given approximation for G. With the definition (3.36) of $S_{kk'}(\omega)$ in mind, we have expressed the self-energy as the sum of a part coming from the metal electrons and a part arising from the atom-metal interaction. These contributions must be evaluated self-consistently with the solutions of Eqs. (3.37) and (3.38). The diagonal self-energy of an electron on the atom is given within our approximation scheme by

$$\Sigma^{\mathrm{HF}}_{aa;s}(\omega)=-i\sum_{\sigma}\left[\langle ak'|U|ak\rangle-\delta_{s\sigma}\langle ak'|U|ka\rangle\right]\int\frac{d\omega'}{2\pi}\,e^{i\omega'\eta}G^{\sigma}_{kk'}(\omega')-i\langle ak'|U|aa\rangle\int\frac{d\omega'}{2\pi}\,e^{i\omega'\eta}G^{-s}_{ak'}(\omega')\;. \tag{4.19}$$

We note that the diagonal self-energy of an electron of spin s depends only on the off-diagonal pseudo Green's function $G_{ak'}(\omega)$ of spin $-s$. This result arises from the Pauli principle restriction whereby two electrons can occupy the adatom level φ_a only if they have antiparallel spin. With the help of (4.12), we may rewrite the above equation as

$$\Sigma^{\mathrm{HF}}_{aa;s}(\omega)=-i\sum_{\sigma}\left[\langle ak'|U|ak\rangle-\delta_{s\sigma}\langle ak'|U|ka\rangle\right]\int\frac{d\omega'}{2\pi}\,e^{i\omega'\eta}G^{\sigma}_{kk'}(\omega')+i\langle ak'|U|aa\rangle\int\frac{d\omega'}{2\pi}\,e^{i\omega'\eta}G^{-s}_{aa}(\omega')$$
$$\times\langle a|\Phi|k\rangle(L^{s})^{-1}_{kk''}P_{k''k'}-iU\int\frac{d\omega'}{2\pi}\,e^{i\omega'\eta}G^{-s}_{aa}(\omega')\;, \tag{4.20}$$

where we have introduced the definition

$$U\equiv\langle a{\uparrow}a{\downarrow}|U|a{\uparrow}a{\downarrow}\rangle \tag{4.21}$$

as the intra-atomic Coulomb repulsion.

C. Newns theory

This approach[3] uses the Anderson Hamiltonian[11]—originally proposed to explain the formation of local moments—to describe the chemisorption of hydrogen. The atomic wave function is introduced as an extra orbital necessary for the full description of the problem. No direct overlap between atomic and metallic wave functions is considered, so that Δ_{ak} must be set equal to zero in the equations of motion. The model also involves the following assumptions. Two electrons are believed to interact appreciably only if they are both in the metal or on the atom. This implies that

$$S_{kk'}(\omega)=0\;. \tag{4.22}$$

The electron-electron correlation on the adsorbed atom is treated within the Hartree-Fock approximation of the preceding subsection. Furthermore, one-body scattering mechanisms which can connect various electronic states of the metal are ignored. Accordingly

$$\langle k|V|k'\rangle=0\;. \tag{4.23}$$

The term $\langle a|V_M|a\rangle$ may be used to renormalize ϵ_a. Finally, a hopping matrix element $\tilde{V}_{ka}$ is defined, allowing for an electron to jump from the atom to the metal, such that

$$\langle k|V_M|a\rangle+\Sigma_{ka;s}(\omega)=\tilde{V}_{ka}\;, \tag{4.24}$$

and it is assumed to be independent of ω. (The assumption is trivially correct if the Hartree-Fock form for Σ_{ka} is used.)

In order that our pseudo-Green's-function theory may go over directly to the Green's function of the Newns model, it is necessary to make the choice given in Eq. (4.4) for $\langle a|\Phi|k\rangle$. Making use of (3.31) we obtain

$$\langle a|\Phi|k\rangle=-\langle a|\mathcal{H}_a+V_M|k\rangle-\Sigma_{ak;s}(\omega)$$
$$=-\epsilon_a\Delta_{ak}-\langle a|V_M|k\rangle-\Sigma_{ak;s}(\omega)$$
$$=-\tilde{V}_{ak} \tag{4.25}$$

after setting $\Delta_{ak}=0$ and using the definition of (4.24). With the assumptions and definitions noted above, we are led to the following equations of motion for the elements of the (pseudo) Green's function:

$$(\omega-\epsilon_k)G^{s}_{kk'}(\omega)-\tilde{V}_{ka}G_{ak'}(\omega)=\delta_{kk'}\;, \tag{4.26a}$$

$$-\tilde{V}_{ak''}G^{s}_{k''k'}(\omega)+\left[\omega-\epsilon_a-\Sigma_{aa;s}(\omega)\right]G^{s}_{ak'}(\omega)=\Delta_{ak'}=0. \tag{4.26b}$$

The remaining two equations are obtained by using Eqs. (3.20) in conjunction with the above equations. The point to note is that once we ignore the overlap of wave functions, all elements of G are independent and Eqs. (3.20) are no longer meaningful. The latter equations may be used formally, however, to derive the equations of motion of all components of G before letting $\Delta_{ak}\to 0$. We find, as a result,

$$(\omega-\epsilon_k)G^{s}_{ka}(\omega)-\tilde{V}_{ka}G^{s}_{aa}(\omega)=\Delta_{ka}=0 \tag{4.27a}$$

and

$$-\tilde{V}_{ak''}G^{s}_{k''a}(\omega)+\left[\omega-\epsilon_a-\Sigma_{aa;s}(\omega)\right]G^{s}_{aa}(\omega)$$
$$=\sum_{k}|\Delta_{ak}|^2=1\;. \tag{4.27b}$$

Equations (4.26) and (4.27) are the well-known equations of motion for the Anderson Hamiltonian.[11] Newns solved these equations self-consistently,[3] after making the Hartree-Fock assumption for $\Sigma_{aa;s}(\omega)$. The model, by definition, ignores matrix elements like $\langle ak'|U|ak\rangle$ and $\langle ak'|U|aa\rangle$. The self-consistency criterion, therefore, is [cf. Eq. (4.20)]

$$\Sigma_{aa;s}(\omega) = -iU\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}\, e^{i\omega'\eta}\, G_{aa}^{-s}(\omega') \tag{4.28}$$

$$= U\int_{-\infty}^{E_F} d\omega'[-(1/\pi)\,\mathrm{Im}\,G_{aa}^{-s}(\omega'+i0^{+})], \tag{4.28a}$$

where we have used the analytic property of $G_{aa}^{-s}(\omega)$ to write the line integral as the integral over a cut. Equations (4.26) and (4.27) should be solved subject to Eq. (4.28a). The Green's function $G_{aa}^{-s}(\omega)$ can be obtained from Eq. (4.11), where the condition $\Delta_{ak} = 0$ along with the other assumptions of the model implies

$$L_{kk''}^{s} \cong (\omega - \epsilon_k)\delta_{kk''} \tag{4.29a}$$

and

$$M_{ka}^{s} \cong -[\langle k|V_M|a\rangle + \Sigma_{ka;s}(\omega)] = -\tilde{V}_{ka}\;. \tag{4.29b}$$

Accordingly,

$$G_{aa}^{-s}(\omega) = \left\{\omega - \epsilon_a - \langle a|V_M|a\rangle - \Sigma_{aa;s}(\omega) - \sum_k \frac{|\tilde{V}_{ak}|^2}{(\omega - \epsilon_k)}\right\}^{-1}. \tag{4.30}$$

The system energy can be obtained from the matrix elements of G by using either (3.43) or (3.44). Newns treated the $\tilde{V}_{ak}$ as parameters in his theory to fit the binding-energy data after assuming a simple model for the density of states of the substrate metal. We therefore see that the Newns model for hydrogen chemisorption can be derived as a limiting case of our formalism when the Hartree-Fock theory is used to describe electronic correlation, and certain simplifying assumptions are made about the various matrix elements. The assumption of a small U, on which our present study is based, implies that the Hartree-Fock approximation should be an adequate description of electron-electron interaction in this case. However, the requirement that $\Delta_{ak} \to 0$ implies a tightly bound adsorbate wave function, which is inconsistent with the requirement of a small U.

V. DISCUSSION

We have discussed in this paper the problem of hydrogen chemisorption on a metal surface by dealing systematically with the questions of overcompleteness of wave functions and electron correlation. The intra-atomic Coulomb repulsion is assumed to be small so that the ground state of the system is nondegenerate in spin. Some literature exists on the role of overcompleteness in the chemisorption problem, when the electron-electron interaction is considered only on the adatom and treated within the simplest Hartree-Fock theory. Such studies constitute various special cases of the formalism presented above. Anderson and McMillan[15] studied the overcompleteness issue within the context of the Anderson Hamiltonian.[11] A slightly modified version of their work has been used by Penn[21] and by Bagchi, Gomer, and Penn[23] to analyze the asymptotic behavior of the adsorbate wave function far from the metal surface. These authors establish the validity of certain assumptions made in previous work[24] on the theory of field emission from adsorbate-covered surfaces. The model used by these authors[23] can be obtained from the formalism of this paper if we choose

$$\langle a|\Phi|k\rangle = \langle a|(\omega - \mathcal{H}_1)|k\rangle$$

and ignore the two-particle part of the Hamiltonian altogether. The Green's function employed by Penn[21] and by Bagchi *et al.*[23] is the function $\mathcal{G}_{kk'}(\omega)$ of Eq. (3.21) and it is related to the pseudo Green's function through Eq. (3.22). The effect of overcompleteness on the calculation of chemisorption binding energies[3] should be a fruitful area of study.

The formal results that we have derived in this paper in terms of the pseudo Green's function are exact. They are independent of the choice of $\langle a|\Phi|k\rangle$ if the equations of motion can be solved exactly. If, however, a perturbative solution of the equations of motion is attempted, the choice of the coefficients $\langle a|\Phi|k\rangle$ becomes important in order to justify the perturbation procedure. Also the choice of the coefficients is crucial if $G_{aa}(\omega)$ is to have a simple interpretation as the Green's function on the adatom.

A major new consideration of this paper is the problem of electron correlation within the framework of an overcomplete basis set of states. As an example of the method for determining the proper self-energy Σ, we have worked out the Hartree-Fock approximation in detail in Sec. IV. This is by no means essential, and higher-order many-body perturbation techniques can be applied to the problem in a straightforward manner. All that is necessary is to set up the perturbation theory in the coordinate representation and then introduce the pseudo Green's functions through the definition of Eq. (3.41). The proper self-energy, for example, can be evaluated within the random-phase approximation (RPA)[25] in terms of the matrix elements of G. Since the equations of motion for G involve matrix elements of Σ, it will be necessary at each stage to evaluate these quantities self-consistently. Improved treatment of electron correlation beyond the RPA is also possible. For example, the Coulomb line appearing in the diagrammatic representation of the electron self-energy may be screened by a more accurate dielectric function[26,27] than that given by the RPA. A dielectric formulation runs into difficulties, though, because the problem lacks translational symmetry. Some of these questions are currently under study to see how a better treatment of correlation may affect the theory of chemisorption.

The Hartree-Fock theory worked out here leads directly to the Newns theory when the overlap of adsorbate wave function with the metallic wave functions vanishes. This requires tightly bound adsorbate wave functions for which U would be large. Thus the simultaneous requirement of the Newns theory for small U and small Δ_{ka} makes it doubtful whether that theory has any well defined domain of validity.

In conclusion we note that from a physical standpoint, the most important assumption that we have made in this work involves the nondegeneracy of the chemisorption ground state. This is valid for small intra-atomic Coulomb repulsion U, and the Hartree-Fock theory presumably works best in that case. But U in practice is not small, and the use of the Hartree-Fock approximation has been criticized by Schrieffer and Mattis[28] in the magnetic impurity problem, and by Schrieffer and coworkers[4,12] for the problem of hydrogen chemisorption. For very large U, however, the chemisorbed atom may behave like a local magnetic moment, the ground state is degenerate, and further formal developments are required. This situation will be studied in a later paper.

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†Present address: Battelle Memorial Institute, 505 King Avenue, Columbus, Ohio 43201.

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