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Variational *Ansatz* for the Anderson model of chemisorption[†]

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A variational *Ansatz* for the ground state of the Anderson Hamiltonian for hydrogen chemisorption is presented which becomes exact in three limiting cases and gives a very good interpolation for all values of parameters. The binding energy is calculated for three different model systems and turns out to yield more than 99.9% of the exact result for a finite metal cluster for all values of coupling strengths. The wave function is used to give criteria separating the weak-coupling regime from the strong-coupling regime.

I. INTRODUCTION

In a recent paper by the author[1] (hereafter referred to as I) a variational *Ansatz* for the ground state of a hydrogen atom chemisorbed on a metal surface has been proposed to give a proper description of the electron correlation effects which are known to play an important role. In most cases the Fermi energy of the metal lies between the ionization and the affinity level of the hydrogen atom and the hydrogen is adsorbed neutrally. For larger distances from the surface, when the intraatomic Coulomb energy U is large compared to the coupling strength, charge fluctuations on the hydrogen atom are strongly suppressed.

This correlation effect cannot be described within the restricted Hartree-Fock (RHF) theory where the ground-state wave function is given by a Slater determinant with identical orbits for different spins. For larger adatom distances solutions of the HF equations are known to exist[2,3] in which the spin symmetry is broken, i.e., one obtains different orbitals for different spins. This unrestricted HF (UHF) ground state gives qualitatively the correct behavior for the binding energy ΔE at large adatom distances ($\Delta E \rightarrow 0$ for $R \rightarrow \infty$), but the quantitative results for finite distances are not very good.[4,5]

The variational ansatz proposed in I uses the HF ground state (RHF or UHF) as a starting point but allows the components of the HF state with a definite number of electrons on the hydrogen atom to be determined by the variational principle for the ground state. This procedure leads to the correct behavior of the binding energy in the limit $R \rightarrow \infty$ also starting from the restricted HF ground state. The model calculations of I use the Anderson Hamiltonian for chemisorption in which the adatom-metal coupling is described by a one-electron hopping parameter V. For V larger than a critical value V_c only RHF solutions exist and the *Ansatz* of I yields important improvements in the binding energy when realistic values for the parameters are used. For $V < V_c$ both types of HF solutions exist and one can use both types of HF states as the starting point for the variational *Ansatz*. It turns out that the RHF ground state as a starting point leads to a lower energy for $\frac{1}{2} V_c \lesssim V$, while for $V \lesssim \frac{1}{2} V_c$ the *Ansatz* using the UHF ground state gives the lower energy. In this regime the RHF ground state becomes a poor starting point and one even can get slightly positive binding energies. This crossover behavior is unsatisfactory as one cannot use the same kind of wave function for all parameters of V.

In this paper we present an improved ansatz which does not show the shortcomings described above. This new *Ansatz* takes as a starting point a generalized RHF state which is built up from one-particle states which are solutions to a one-particle Hamiltonian with an effective coupling strength $\tilde{V}$ which is taken as a variational parameter.

In Sec. II we present the ansatz and show that it goes over to the exact solution in the three exactly solvable limits: (a) $U=0$, (b) $V=0$, and (c) bandwidth $B=0$. The evaluation of the matrix elements of the states appearing in our ansatz with the Hamiltonian is indicated in Sec. III, while all the details of the calculations are given in the Appendix. In Sec. IV we discuss the results for the binding energy for three different model systems which show that our *Ansatz* leads to excellent results for all values of parameters. We also show the results for an expectation value which is a measure for the transition from the weak-coupling to the strong-coupling (surface molecule) regime of chemisorption. This and another criterion for the transition involving the variational parameter $\tilde{V}$ are compared with a very simple criterion using the exact wave functions in the extreme weak- and strong-coupling limits. The modifications of our *Ansatz* for a more sophisticated model Hamiltonian to describe hydrogen chemisorption are briefly discussed.

II. VARIATIONAL *ANSATZ*

In the following we present a variational *Ansatz* for the ground state of the Anderson Hamiltonian for hydrogen chemisorption. We will not treat the nonorthogonality of the metal states and the hydrogen 1*s* function explicitly, as this can be put into a renormalization of the matrix elements of the Hamiltonian.[6] The Anderson Hamiltonian reads[2]

$$H=\sum_{k,\sigma}\epsilon_k n_{k\sigma}+\sum_{\sigma}\epsilon_a n_{a\sigma}+Un_{a\uparrow}n_{a\downarrow}$$
$$+\sum_{k,\sigma}V_{ak}(\psi^{\dagger}_{a\sigma}\psi_{k\sigma}+\text{H. c.})\ . \qquad (2.1)$$

The first term describes the free metal surface with k labeling the wave vector $\vec{\text{k}}$ and the band index the second and the third term the free hydrogen atom with U the intra-atomic Coulomb repulsion and the last one the coupling between the metal and the adsorbate.

The coupling term can be rewritten using the creation and annihilation operator of a normalized state $|b\rangle$ localized at the metal surface in the vicinity of the hydrogen atom[4]

$$|b\rangle=V^{-1}\sum_k V_{ak}|k\rangle\ ,$$

with

$$V^2=\sum_k|V_{ak}|^2\ . \qquad (2.2)$$

In the model calculation described in Sec. IV this state $|b\rangle$ will be simply a Wannier state of the metal atom next to the adatom. The coupling operator $\hat{V}$ can be written

$$\hat{V}=V\sum_{\sigma}(\psi^{\dagger}_{a\sigma}\psi_{b\sigma}+\text{H. c.})\ . \qquad (2.3)$$

Before we present our variational ansatz for the ground state $|\phi_0\rangle$ which works well for all values of parameters in the Hamiltonian we shortly discuss the three special cases for which the exact solution for the ground state is known:

(a) For $U=0$ the problem reduces to a single-particle problem, and the ground state is given by the Slater determinant constructed from the occupied single-particle states $\varphi_i=\psi^{\dagger}_i|\text{Vac}\rangle$

$$|\phi_0\rangle=\prod_{i<i_{\max},\sigma}\psi^{\dagger}_{i\sigma}|\text{Vac}\rangle\ . \qquad (2.4)$$

(b) For $V=0$ the adatom is not coupled to the metal surface, and in the ground state one has one electron at the hydrogen atom and the undisturbed Fermi sea $|F\rangle$. If the metal surface is replaced by a *finite* cluster of metal atoms one has to distinguish the cases of even or odd total numbers of electrons. For an even number of electrons the unperturbed ground state is degenerate, and one has to use a spin symmetric linear combination

$$|\phi\rangle\propto\psi^{\dagger}_{a\sigma}|F_{\sigma}\rangle+\psi^{\dagger}_{a,-\sigma}|F_{-\sigma}\rangle\ , \qquad (2.5)$$

while for an odd number of electrons or for a semi-infinite metal one simply can use

$$|\phi_0\rangle=\psi^{\dagger}_{a\sigma}|F\rangle\ . \qquad (2.6)$$

(c) In the limit of zero bandwidth $B=0$ the hydrogen 1*s* state is coupled to the state $|b\rangle$ defined in (2.2) which is *not* coupled to the rest of the solid. In this case the ground state is given by the ground state of the *a*-*b* surface molecule and a modified Fermi sea $|\tilde{F}\rangle$ constructed of the metal orbitals orthogonal to the state $|b\rangle$. For $\epsilon_a<\epsilon_F<\epsilon_a+U$ the lowest energy is obtained if there are two electrons in the surface molecule and they form a singlet state. The coefficient c_i in

$$|\phi_0\rangle=[c_0\psi^{\dagger}_{b\uparrow}\psi^{\dagger}_{b\downarrow}+c_1(\psi^{\dagger}_{a\uparrow}\psi^{\dagger}_{b\downarrow}+\psi^{\dagger}_{b\uparrow}\psi^{\dagger}_{a\downarrow})+c_2\psi^{\dagger}_{a\uparrow}\psi^{\dagger}_{a\downarrow}]|\tilde{F}\rangle \qquad (2.7)$$

can be obtained by solving the eigenvalue problem for the surface molecule alone.

In I we have described a variational *Ansatz* for the ground state which starts from a restricted HF wave function with identical orbitals for different spins which becomes exact in all three of these exactly solvable cases but for small V has the undesirable features described in the introduction. Another variational ansatz for the ground state of the Anderson Hamiltonian starting from a RHF state has been proposed in the context of the local moment problem by Coqblin and Toulouse[7] but their ansatz does not even give the limit $V=0$ correctly.

In our new variational *Ansatz* we start from a generalized Hartree-Fock state $|\tilde{\Psi}_{\text{HF}}\rangle$ to be specified below and introduce projection operators $P_i(i=0,1,2)$ which project onto the subspaces with i electrons on the hydrogen atom. The P_i can be expressed in terms of the occupation number operator of the hydrogen 1*s* state

$$P_0=(1-n_{a\uparrow})(1-n_{a\downarrow})\ ,$$
$$P_1=n_{a\uparrow}(1-n_{a\downarrow})+n_{a\downarrow}(1-n_{a\uparrow})\ , \qquad (2.8)$$
$$P_2=n_{a\uparrow}n_{a\downarrow}\ .$$

With these projection operators our *Ansatz* reads

$$|\phi_0\rangle=\sum_{i=0}^{2}\lambda_i P_i|\tilde{\Psi}_{\text{HF}}\rangle+(\lambda_3P_0+\lambda_4P_2)\hat{V}P_1|\tilde{\Psi}_{\text{HF}}\rangle\ , \qquad (2.9)$$

with the λ_i variational parameters and $|\tilde{\Psi}_{\text{HF}}\rangle$ a state of the form (2.4) with the φ_i eigenstates of an effective single-particle Hamiltonian H_1

$$H_1=\sum_{k,\sigma}\epsilon_k n_{k\sigma}+\sum_{\sigma}(\epsilon_a+Un_0)n_{a\sigma}$$
$$+\tilde{V}\sum_{\sigma}(\psi^{\dagger}_{a\sigma}\psi_{b\sigma}+\text{H. c.})\ . \qquad (2.10)$$

For $n_0=n_{\text{HF}}$ and $\tilde{V}=V$ $|\tilde{\Psi}_{\text{HF}}\rangle$ goes over to the restricted Hartree-Fock ground state of the Anderson Hamiltonian (2.1). In the following we shall use the parameters $\tilde{V}$ and n_0 as extra variational parameters.

Apart from the difference $|\Psi_{\mathrm{HF}}\rangle \to |\tilde{\Psi}_{\mathrm{HF}}\rangle$ our new *Ansatz* (2.9) differs from the one used in I by the last two terms. As will be discussed below these terms give an important improvement in the weak coupling regime. In the state $\hat{V}P_1|\tilde{\Psi}_{\mathrm{HF}}\rangle$ one has two or zero electrons at the hydrogen atom and the free variation of both of these parts will be important if the energy of the doubly occupied adsorbate is much different from the empty one. As shown in the appendix the numerical effort in calculating matrix elements is not altered by this splitting of the $\hat{V}P_1|\tilde{\Psi}_{\mathrm{HF}}\rangle$ term. This *Ansatz* leads to the exact result for the three limiting cases discussed above and also gives the correct behavior for small V as shown in Sec. III. The exact results for the limiting cases can simply be obtained by taking special values for the variational parameters in (2.9):

(a) $U=0$: If we choose $\tilde{V}=V$, $\lambda_3=\lambda_4=0$, and $\lambda_0=\lambda_1=\lambda_2=1$, we obtain the exact result using $P_0+P_1+P_2=1$.

(b) $V=0$: In the limit $\tilde{V}\to 0$ and $n_0=(\epsilon_f-\epsilon_a)/U=n_{\mathrm{HF}}(\tilde{V}=0)$ $P_1|\tilde{\Psi}_{\mathrm{HF}}\rangle$ goves over to the exact limit [(2.5) and (2.6)] as we show in Sec. III.

(c) $B=0$: Choosing $\lambda_3=\lambda_4=0$ and $\tilde{V}\gtrsim V$ and n_0 arbitrary λ_i $(i=0,1,2)$ are just the exact expansion coefficients c_i of (2.7).

The variation of $\tilde{V}$ and n_0 will be shown to be necessary to ensure $\Delta E\leqslant 0$, while the last term in our *Ansatz* (2.9) leads to a binding energy $\propto V^2$ for small V.

To obtain explicit results we have to evaluate the matrix elements of the states in (2.9) with the Hamiltonian, as well as the overlap between these states.

III. EVALUATION OF MATRIX ELEMENTS

To obtain the ground-state energy from (2.9), the variation of the λ_i leads to a 5×5 eigenvalue problem of the form $\det(H-\epsilon S)=0$. The lowest eigenvalue gives the ground-state energy as a function of n_0 and $\tilde{V}$. To calculate the matrix elements H_{ij} $(i,j=0,1,\ldots,4)$ it is convenient to rewrite the Hamiltonian (2.1) using the one-particle Hamiltonian H_1 (2.10)

$$H=H_1+H_U+\Delta\hat{V}\ , \tag{3.1}$$

with

$$H_U=U[n_{a\uparrow}n_{a\downarrow}-n_0(n_{a\uparrow}+n_{a\downarrow})]=U[(1-2n_0)P_2-n_0P_1]$$

and

$$\Delta\hat{V}=V-\tilde{V}\ .$$

The state $|\tilde{\Psi}_{\mathrm{HF}}\rangle$ has been chosen to be the ground state of the system of noninteracting electrons described by $H_1=H_0+\tilde{V}$

$$H_1|\tilde{\Psi}_{\mathrm{HF}}\rangle=\tilde{E}_0|\tilde{\Psi}_{\mathrm{HF}}\rangle\ . \tag{3.2}$$

In the following $\langle\ \rangle$ denotes the expectation value in the state $|\tilde{\Psi}_{\mathrm{HF}}\rangle$.

The matrix elements H_{ij} $(i,j=0,1,2)$ are quite simply to evaluate and have been given in a similar form in I. For the diagonal terms one obtains using

$$[H_0,P_i]=0\ ,\quad P_i\hat{V}P_i=0\ ,$$

$$\begin{aligned}H_{ii}&=\langle P_iHP_i\rangle=\langle H_0P_i\rangle+\langle H_UP_i\rangle \\ &=\{\tilde{E}_0+U[(1-2n_0)\delta_{i,2}-n_0\delta_{i,1}]\}S_{ii}-\langle\tilde{V}P_i\rangle\ .\end{aligned} \tag{3.3}$$

For $\tilde{V}=0$ the last term vanishes and one obtains for $i=1$

$$\frac{H_{11}}{S_{11}}=2\sum_{k<k_F}\epsilon_k+2(\epsilon_a+Un_0)f(\epsilon_a+Un_0)-Un_0\ , \tag{3.4}$$

with $f(\epsilon)$ the Fermi function. As stated in Sec. II this goes over to the unperturbed ground-state energy

$$E_0^{(0)}=2\sum_{k<k_F}\epsilon_k+\epsilon_a$$

for $n_0=(\epsilon_F-\epsilon_a)/U$. As this result is independent of V it ensures $\Delta E\leqslant 0$ for all V. For $\tilde{V}\neq 0$ the last term in (3.3) does not vanish and can be calculated using the product form (2.4) of $|\tilde{\Psi}_{\mathrm{HF}}\rangle$. If we consider again the case $i=1$ we obtain

$$\begin{aligned}\langle\tilde{V}P_1\rangle=\tilde{V}\sum_\sigma[&\langle\psi^\dagger_{a\sigma}\psi_{b\sigma}\rangle\langle n_{a-\sigma}\rangle \\ &+\langle\psi^\dagger_{b\sigma}\psi_{a\sigma}\rangle\langle(1-n_{a-\sigma})\rangle]=2\tilde{V}\rho_{ab}\ ,\end{aligned} \tag{3.5}$$

with $\rho_{ab}=\langle\psi^\dagger_{a\sigma}\psi_{b\sigma}\rangle$. As H_1 is of the form of the effective HF one particle Hamiltonian for the Anderson model,[2] the expectation value ρ_{ab} can be obtained from the corresponding Green's function via the fluctuation-dissipation theorem[8]:

$$\begin{aligned}\tilde{V}\rho_{ab}&=-\frac{\tilde{V}}{\pi}\int\mathrm{Im}g_{ba}(\epsilon+io)f(\epsilon)\,d\epsilon \\ &=-\frac{1}{\pi}\int\mathrm{Im}(\Gamma g_{aa})f(\epsilon)\,d\epsilon \\ &=\int_{-\infty}^{\epsilon_F}[\epsilon-(\epsilon_a+Un_0)]\rho_a(\epsilon)\,d\epsilon\ ,\end{aligned} \tag{3.6}$$

with

$$\begin{aligned}\rho_a(\epsilon)&=-(1/\pi)\mathrm{Im}[\epsilon+io-\epsilon_a-Un_0-\tilde{\Gamma}(\epsilon+io)]^{-1}\ , \\ \tilde{\Gamma}(z)&=\tilde{V}^2\sum_k\frac{|\langle b|k\rangle|^2}{z-\epsilon_k}\ .\end{aligned} \tag{3.7}$$

All other matrix elements H_{ij} can be reduced in a similar way to the calculation of moments of the density of states at the adsorbate corresponding to the one particle Hamiltonian H_1. The detailed results are given in the Appendix. It turns our that the matrix H_{ij} splits off a term proportional to the ground state energy $\tilde{E}_0$ of H_1, i.e., $H_{ij}=\tilde{E}_0S_{ij}+\tilde{H}_{ij}$.

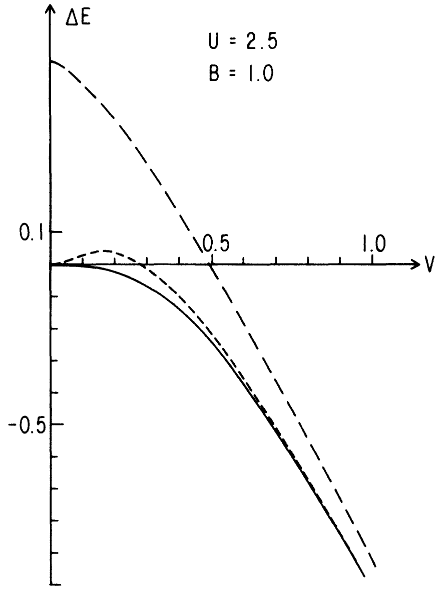

FIG. 1. Binding energy ΔE for adsorption on a one-dimensional infinite chain: long-dashed curve, RHF result; short-dashed curve, *Ansatz* used in I; solid curve, Eq. (2.9) as a function of V.

The binding energy ΔE is then given as the sum of $\tilde{E}_0 - E_0^{(0)}$ and the lowest eigenvalue of the 5×5 eigenvalue problem of $\tilde{H}_{ij}$. The calculation of a difference like $\tilde{E}_0 - E_0^{(0)}$ has been described in detail by Newns[3] and involves again only the adsorbate Green's function g_{aa}.

IV. RESULTS AND DISCUSSION

We have carried out model calculations using our *Ansatz* (2.9) for the one-dimensional chain used by Newns,[3] a simple cubic metal surface described by a tight-binding s band and the finite chain used by Einstein.[5] As the essential features of our *Ansatz* can already be seen in the symmetric case $2\epsilon_a + U = 2\epsilon_F$ most of our model calculations were performed in this limit.

In the symmetric case (with a half-filled symmetric band) our *Ansatz* can be simplified using the particle-hole symmetry of the problem. The doubly occupied and the empty adsorbate states obtain the same weight, i.e., $\lambda_0 = \lambda_2$, $\lambda_3 = \lambda_4$ which reduces the 5×5 eigenvalue problem to a 3×3 one. The more important simplification occurs from the fact that the particle-hole symmetry fixes the value of n_0 to $n_0 = n_a^{\mathrm{RHF}} = n_a^{\mathrm{exact}} = \frac{1}{2}$. The lowest eigenvalue then only depends on the one extra variational parameter $\tilde{V}$.

We have calculated the binding energies ΔE for given values of U and B as functions of V. For small values of V the variational parameter $\tilde{V}$ becomes very important and the ratio $\alpha = \tilde{V}/V$ turns out to be very small if U is large enough. This variational parameter allows the state $|\tilde{\Psi}_{\mathrm{HF}}\rangle$ to depend on U in contrast to the true HF state of the system which was used as a starting point in I. If we consider a fixed value of V and take the limit U, $|\epsilon_a| = \frac{1}{2}U \to \infty$, the true RHF state remains the same as for $U = 0$ while it is obvious that the exact ground state in this limit is just given by the unperturbed ground state [(2.5) and (2.6)]. We obtain this exact behavior of our Ansatz (2.9) by having $\alpha \to 0$, i.e., $\tilde{V} = 0$ as $U \to \infty$. The influence of the $\hat{V}P_1|\tilde{\Psi}_{\mathrm{HF}}\rangle$ term in (2.9) can be seen by noting that our ground-state energy will be lower than the one for the special choice $\lambda_0 = \lambda_2 = 0$, $\lambda_3 = \lambda_4 = \lambda$, and $\tilde{V} = 0$. For this choice our *Ansatz* reads with $|0\rangle = \psi^{\dagger}_{a\sigma}|F\rangle$

$$|\phi_0\rangle = |0\rangle + \lambda\hat{V}|0\rangle\,, \tag{4.1}$$

which leads to a ground-state energy given by the second step of a continued fraction expansion of the resolvant $\langle 0|(z-H)^{-1}|0\rangle$ which gives the correct behavior $\Delta E \propto -V^2/U$ for small V. For large V our *Ansatz* goes over to the exact ground state and provides an excellent interpolation scheme between the weak-coupling and the strong-coupling regime.

Figure 1 shows the binding energy ΔE for the symmetric case as a function of V for the adsorption on the one-dimensional metal chain discussed by Newns.[3] The energy unit is given by the half-bandwidth $B = 1$ and the intra-atomic Coulomb repulsion has been chosen to be $U = 2.5$. The restricted HF curve shows the well known incorrect behavior $\Delta E \to \frac{1}{4}U$ for $V \to 0$. The other broken curve shows the result for the RHF *Ansatz* of I. For small V the binding energy is positive and this *Ansatz* is a poor approximation. This behavior is not so drastic for the finite-chain calculation given in I and appears only for extremely small V. For larger V the results for the binding energy become nearly as good as the results of our new *Ansatz* (2.9) (full curve) and both results approach the exact solution as discussed in Sec. II. To test our *Ansatz* we have also calculated binding energies for the finite-chain model used by Einstein.[5] For chains consisting of three metal atoms Einstein has calculated the exact binding energies by diagonalizing a 36×36 matrix on a computer. These exact results are compared with our approximate solution from (2.9) for $U = 2.5$ in Table I. In the second column we also give the results for $\alpha = \tilde{V}/V$ which goes from 0 to 1 for increasing V. Our results for the binding energies are in very good agreement with the exact results giving more than 99.9% of the binding energy for all values of V. The calculation of binding energies for parameters different from the symmetric case requires a little more computer time, as the lowest eigenvalue of our 5×5 eigenvalue problem now depends on two parameters n_0 and $\tilde{V}$. The most important effect

TABLE I. Binding energies ΔE for the finite chain used by Einstein in comparison with the exact results. ($U=2.5$).

V	$(\tilde{V}/V)$	ΔE	ΔE_{exact}[a]
0.15	0.221	−0.041 21	−0.0412
0.25	0.357	−0.111 88	−0.1119
0.375	0.505	−0.240 77	−0.2410
0.5	0.618	−0.403 80	−0.4041
1.0	0.833	−1.226 49	−1.2266
1.5	0.906	−2.151 49	−2.1515
2.0	0.935	−3.109 90	−3.1099

[a] T. L. Einstein (private communication).

again comes from the variation of $\tilde{V}$ if one chooses n_0 to go from $(\epsilon_F-\epsilon_a)/U$ to $\frac{1}{2}$ when $\tilde{V}$ goes from zero to infinity, which is just the behavior of the restricted HF expectation value n_a^{HF}.

We have calculated the binding energy of H on a simple cubic metal surface described by a tight-binding s band using the parameters for Ni given by Newns.[3] For V in the region of the equilibrium distance the $\tilde{V}$ variation is no longer very important as the system can be described quite well by the surface molecule picture. For $V=3.4$ eV we obtain a binding energy 0.7 eV larger than the HF value, which is about 25% of the total binding energy. This shows that our *Ansatz* gives quite important corrections to the HF results for realistic values of parameters.

Our *Ansatz* also enables us to calculate expectation values of various operators of physical interest. In the following we discuss the expectation value $\langle n_{a\sigma} n_{b\sigma}\rangle$ which gives information about the transition from the weak-coupling to the strong-coupling case.

In the extreme weak-coupling case (2.6) this expectation value can be factorized $\langle n_{a\sigma} n_{b\sigma}\rangle = \langle n_{a\sigma}\rangle\langle n_{b\sigma}\rangle$ and equals $\frac{1}{4}$ in the symmetric case. In the strong-coupling limit (2.7) one has $\langle n_{a\sigma} n_{b\sigma}\rangle = 0$ as the surface molecule state is a singlet state. Figure 2 shows that the larger the U the longer the system remains in the weak-coupling regime. These expectation values have been calculated again for the one-dimensional half-infinite metal chain. As a criterion for the transition from the weak to the strong-coupling regime one could now (somewhat arbitrarily) take the value where $\langle n_{a\sigma} n_{b\sigma}\rangle$ has fallen to half of its maximum value, i.e., for values of parameters yielding $\langle n_{a\sigma}\rangle\langle n_{b\sigma}\rangle \geq \langle n_{a\sigma} n_{b\sigma}\rangle \geq \frac{1}{2}\langle n_{a\sigma}\rangle\langle n_{b\sigma}\rangle$ one is in the weak-coupling regime, while for parameters leading to $\langle n_{a\sigma} n_{b\sigma}\rangle \leq \frac{1}{2}\langle n_{a\sigma}\rangle\langle n_{b\sigma}\rangle$ one goes over to the strong-coupling regime. The left-hand full curve in Fig. 3 shows the boundary between the weak- and strong-coupling regimes in the U-V plane using this criterion. Another, more obvious criterion to distinguish these two regimes is to look at the form of the eigenstates of our one-particle Hamiltonian $\tilde{H}_1$. For values of $\tilde{V}$ greater than a value V_{SO} depending on the form and the width of the metal band, localized split-off states appear in $\rho_a(\epsilon)$ (3.7) as first discussed by Newns.[3] For the one dimensional semi-infinite chain this critical value is given by $V_{\text{SO}}=(1/\sqrt{2})B$. Using this criterion one obtains as a boundary between the two regimes the right-hand full curve in Fig. 3 which shows a similar functional behavior as the left-hand curve. These two curves would nearly coincide if we would choose not half the maximum value of $\langle n_{a\sigma} n_{b\sigma}\rangle$ in the first criterion but about a quarter of the maximum value.

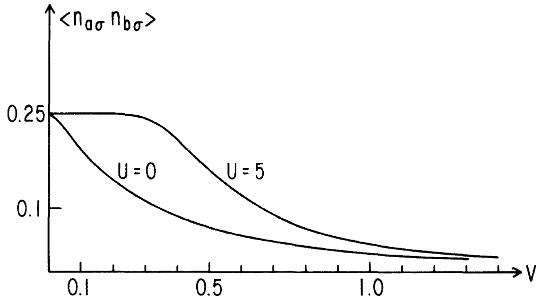

FIG. 2. Expectation value $\langle n_{a\sigma} n_{b\sigma}\rangle$ as a function of V for two different values of U.

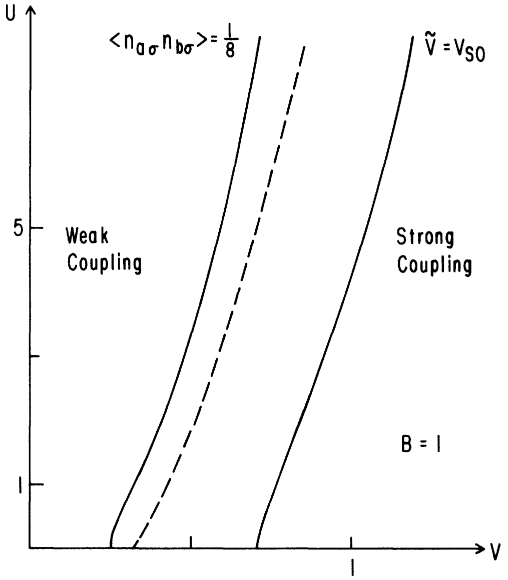

FIG. 3. Boundaries separating the weak- and strong-coupling regime in the U-V plane: left-full-curve criterion using $\langle n_{a\sigma} n_{b\sigma}\rangle$, right-full-curve criterion using $V = V_{\text{SO}}$ and dashed line criterion (4.5).

Another boundary (dashed line in Fig. 3) which shows a similar functional behavior can be obtained from a very simple argument. Let us simply take the wave functions in the extreme weak- [(2.5) and (2.6)] and strong- (2.7) coupling limit and see which one leads to the lower energy. In the weak-coupling case we obtain

$$\langle\phi_0|H|\phi_0\rangle = E_0^{(0)} = 2\sum_{k<k_F}\epsilon_k + \epsilon_a \ , \tag{4.2}$$

while in the strong-coupling limit one obtains with $|\phi_0\rangle$ given by (2.7)

$$\langle\phi_0|H|\phi_0\rangle = E_0^{(0)} + \Delta E_{\text{SM}} + E_b \ , \tag{4.3}$$

where ΔE_{SM} is the binding energy of the surface molecule and E_b is the energy required to separate the singly occupied state $|b\rangle$ from the rest of the metal. The weak-coupling energy is a constant as a function of V, while in the strong-coupling case one has $\langle\phi_0|H|\phi_0\rangle \geq E_0^{(0)}$ for small V. The criterion for the boundary is given by

$$\Delta E_{\text{SM}} + E_b = 0 \ . \tag{4.4}$$

In the symmetric case an explicit expression for ΔE_{SM} can be given and one obtains defining γ by $E_b = \gamma B$

$$\tfrac{1}{4}U - [(\tfrac{1}{4}U)^2 + 4V^2]^{1/2} + \gamma B = 0$$

or

$$U = 8V^2/\gamma B - 2\gamma B \ . \tag{4.5}$$

For the half-infinite one-dimensional chain one obtains $\gamma = 2/\pi$ for the half-filled band case and $\gamma \to 1$ when the Fermi energy reaches the band edges (note that we have defined B as the *half*-bandwidth). Quite generally we expect E_b to be of the order of half the bandwidth. As the symmetric case is also not too far from reality in hydrogen chemisorption,[3] the criterion (4.5) provides a very simple first estimate to see whether the weak-coupling or the strong-coupling picture is a better description of the chemisorptive bond.

The transition from the weak-coupling regime to the strong-coupling regime is obviously not a sharp one and in the intermediate region (between the full curves in Fig. 3) neither the weak-coupling wave function (2.5) nor the strong-coupling ground state (2.6) will be a very good starting point for perturbation theory.[5]

Newns[3] has determined the coupling strength V doing an HF calculation and fitting V to give the experimental binding energy and obtained $V \sim 3.75$ eV for Ti, Cr, and Ni. If we take into account the correlation energy obtained from our *Ansatz* this value for the V will be reduced by about 0.4 eV. Using these values for V and using the criteria given above we come to the conclusion that the surface molecule (strong coupling) picture is a good description for the chemisorption of hydrogen on the narrow d-band transition metals at the equilibrium geometry.

V. CONCLUSION

In Secs. I–IV we have presented a variational *Ansatz* for the ground state of the Anderson Hamiltonian for chemisorption which turned out to work for all values of parameters providing in particular a smooth interpolation between the weak-coupling and strong-coupling or surface molecule picture. As our *Ansatz* has spin symmetry it can be used to calculate expectation values like the charge on the adsorbate without getting the unphysical behavior which occurs in an HF calculation due to the spurious breaking of the spin symmetry.[3] The *Ansatz* can quite easily be generalized for more sophisticated model Hamiltonians to describe hydrogen chemisorption. If one starts with the same basis set, i.e., $\{\varphi_k, \varphi_a\}$ one could work with the same form of the *Ansatz*, only replacing the coupling operator in $\hat{V}P_1|\tilde{\Psi}_{\text{HF}}\rangle$ by the more general coupling operator which would be no longer a single-particle operator as in the Anderson model. With this replacement the argument given in (4.1) would still apply leading to a result for the binding energy below the one for a second step of a continued fraction expansion of the resolvent matrix element $\langle 0|(z-H)^{-1}|0\rangle$ in the weak-coupling limit. We would also expect the generalized Ansatz to interpolate smoothly to the strong-coupling limit which will come out exactly also for a more general Hamiltonian. As we would expect a generalized *Ansatz* to work also quite well, we believe the major problem in the description of the hydrogen chemisorption bond is to find a more realistic model Hamiltonian and to perform an *ab initio* calculation of the matrix elements appearing in it.

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APPENDIX

In this appendix we give the expressions for the overlap matrix S_{ij} and the matrix elements H_{ij} of the Hamiltonian H between the states $|i\rangle$, $i = 0, \ldots, 4$ appearing in our Ansatz (2.9).

Using the explicit form the states $|3\rangle$ and $|4\rangle$

$$\begin{aligned} |3\rangle &= V\sum_\sigma \psi_{b\sigma}^\dagger \psi_{a\sigma}(1-n_{a-\sigma})|\tilde{\Psi}_{\text{HF}}\rangle \ , \\ |4\rangle &= V\sum_\sigma \psi_{a\sigma}^\dagger \psi_{b\sigma} n_{a-\sigma}|\tilde{\Psi}_{\text{HF}}\rangle \ , \end{aligned} \tag{A1}$$

the overlap matrix S_{ij} can be easily calculated using the fact that all expectation values $\langle\ \ \rangle$ containing more than two field operators can be factorized using the fact that $|\tilde{\Psi}_{\mathrm{HF}}\rangle$ is of the form (2.4). Using the abbreviations $n=\langle n_{a\sigma}\rangle$ and $\rho_{ab}=\langle\psi_a^\dagger\psi_b\rangle$ the *nonzero* elements in the upper right of S_{ij} are given by

$$\begin{aligned} &S_{00}=(1-n)^2, \quad S_{11}=2n(1-n), \quad S_{22}=n^2 , \\ &S_{03}=2V\rho_{ab}(1-n), \quad S_{24}=2V\rho_{ab}n , \\ &S_{33}=2V^2[n(1-n)\langle n_b\rangle+(1+n)\rho_{ab}^2] , \\ &S_{44}=2V^2[n(1-n)(1-\langle n_b\rangle)+(2-n)\rho_{ab}^2] . \end{aligned} \tag{A2}$$

The calculation of the matrix elements H_{ii}, $i=0$, 1, 2 was indicated in Sec. III. We rewrite Eq. (3.3)

$$H_{ii}=\tilde{E}_0+U[(1-2n_0)\delta_{i,2}-n_0\delta_{i,1}]S_{ii}-\langle\tilde{V}P_i\rangle . \tag{A3}$$

The last term yields for $i=0$, 1, 2

$$\begin{aligned} &\langle\tilde{V}P_0\rangle=\langle P_1\tilde{V}P_0\rangle=(\tilde{V}/V)S_{03}=2\tilde{V}\rho_{ab}(1-n) , \\ &\langle\tilde{V}P_2\rangle=\langle P_1\tilde{V}P_2\rangle=(\tilde{V}/V)S_{24}=2\tilde{V}\rho_{ab}n , \\ &\langle\tilde{V}P_1\rangle=(\tilde{V}/V)(S_{03}+S_{24})=2\tilde{V}\rho_{ab} . \end{aligned} \tag{A4}$$

The off-diagonal in the upper right-hand elements for $i, j=0$, 1, 2 are given by

$$H_{01}=\langle P_0VP_1\rangle=S_{03}, \quad H_{02}=0, \quad H_{12}=S_{24} . \tag{A5}$$

For the other nonzero matrix elements one obtains

$$\begin{aligned} &H_{03}=\tilde{E}_0S_{03}-\langle\tilde{V}P_0VP_1\rangle=\tilde{E}_0S_{03}-(\tilde{V}/V)S_{33} , \\ &H_{24}=[\tilde{E}_0+U(1-2n_0)]S_{24}-(\tilde{V}/V)S_{44} , \\ &H_{13}=S_{33}, \quad H_{24}=S_{24} , \end{aligned} \tag{A6}$$

and

$$\begin{aligned} H_{33}&=\langle P_1VH_0P_0VP_1\rangle=\langle H_0P_1VP_0VP_1\rangle \\ &\quad+\langle P_1[V,H_0]P_0VP_1\rangle \\ &=\tilde{E}_0S_{33}-(\tilde{V}/V)\langle V^2P_0VP_1\rangle+\langle[V,H_0]P_0VP_1\rangle , \end{aligned}$$

$$\begin{aligned} H_{44}&=[\tilde{E}_0+U(1-2n_0)]S_{44}-(\tilde{V}/V)\langle V^2P_2VP_1\rangle \\ &\quad+\langle[V,H_0]P_2VP_1\rangle , \end{aligned} \tag{A7}$$

with

$$\begin{aligned} \langle V^2P_0VP_1\rangle&=2V^3\rho_{ab}\{(1-n)+\langle n_b\rangle(1-n) \\ &\quad+\rho_{ab}^2+2[n(1-\langle n_b\rangle)+\rho_{ab}^2]\} , \\ \langle V^2P_2VP_1\rangle&=2V^3\rho_{ab}\{n+n(1-\langle n_b\rangle) \\ &\quad+\rho_{ab}^2+2[(1-n)\langle n_b\rangle+\rho_{ab}^2]\} , \end{aligned} \tag{A8}$$

and

$$\begin{aligned} \langle[V,H_0]P_0VP_1\rangle&=2\sum_{k,k'}V_{ak}(\epsilon_k-\epsilon_a)V_{ak'} \\ &\quad\times[n(1-n)\langle\psi_k\psi_{k'}^\dagger\rangle+(2-n)\langle\psi_a^\dagger\psi_k\rangle\langle\psi_{k'}^\dagger\psi_a\rangle] , \\ \langle[V,H_0]P_2VP_1\rangle&=-2\sum_{k,k'}V_{ak}(\epsilon_k-\epsilon_a)V_{ak'} \\ &\quad\times[n(1-n)\langle\psi_k^\dagger\psi_{k'}\rangle+(1+n)\langle\psi_a^\dagger\psi_{k'}\rangle\langle\psi_k^\dagger\psi_a\rangle] . \end{aligned} \tag{A9}$$

Using the special form of one-particle Green's function for the Anderson Hamiltonian for the case $U=0$[2] the expectation values in (A8) and (A9) can be expressed in terms of the adatom Green's function only as in (3.6).

$$\begin{aligned} \langle n_b\rangle&=\tilde{V}^{-2}\sum_{k,k'}\tilde{V}_{ak}\langle\psi_k^\dagger\psi_{k'}\rangle\tilde{V}_{k'a} \\ &=\tilde{V}^{-2}\int_{-\infty}^{\epsilon_F}[\epsilon-(\epsilon_a+Un_0)]^2\rho_a(\epsilon)\,d\epsilon , \\ \sum_k\tilde{V}_{ak}\epsilon_k\langle\psi_a^\dagger\psi_k\rangle&=\int_{-\infty}^{\epsilon_F}\epsilon[\epsilon-(\epsilon_a+Un_0)]\rho_a(\epsilon)\,d\epsilon-n\tilde{V}^2 , \\ \sum_k\tilde{V}_{ak}\epsilon_k\langle\psi_b^\dagger\psi_k\rangle&=\tilde{V}^{-1}\int_{-\infty}^{\epsilon_F}\{\epsilon[\epsilon-(\epsilon_a+Un_0)]^2 \\ &\quad-\tilde{V}^2[\epsilon-(\epsilon_a+Un_0)]\}\rho_a(\epsilon)\,d\epsilon . \end{aligned} \tag{A10}$$

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[1] K. Schönhammer, Z. Phys. B 21, 389 (1975).

[2] P. W. Anderson, Phys. Rev. 124, 41 (1961).

[3] D. M. Newns, Phys. Rev. 178, 1123 (1969).

[4] W. Brenig and K. Schönhammer, Z. Phys. 267, 201 (1974).

[5] T. L. Einstein, Phys. Rev. B 11, 577 (1975).

[6] K. Schönhammer, V. Hartung, and W. Brenig, Z. Phys. B 22, 143 (1975).

[7] B. Coqblin and G. Toulouse, J. Phys. Chem. Solids 29, 463 (1968). In the early papers on the local moment problem (Ref. 2) people were looking for magnetic solutions of the type $\langle n_{a\sigma}\rangle\neq\langle n_{a-\sigma}\rangle$. It is now well known that such solutions with a broken spin symmetry do not occur if correlation effects are correctly included in the ground state. This is also confirmed by our work.

[8] D. N. Zubarev, Usp. Fiz. Nauk 71, 71 (1960) [Sov. Phys.-Ushpeki 3, 320 (1960)].