PHYSICAL REVIEW B VOLUME 28, NUMBER 12 15 DECEMBER 1983

Simple solution to the Newns-Anderson Hamiltonian of chemisorption

M. Baldo and R. Pucci
*Istituto di Física dell'Università degli Studi di Catania, 57 Corso Italia, I-95129 Catania, Italy
and Centro Siciliano di Física Nucleare e di Struttura della Materia—Unità di Catania,
Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche, I-95129 Catania, Italy
and Sezione di Catania, Istituto Nazionale di Física Nucleare, I-95129 Catania, Italy*

F. Flores
*Departamento de Física del Estado Sólido, Facultad de Ciencias, Universidad Autónoma de Madrid,
Canto Blanco, Madrid 34, Spain*

G. Piccitto
*Istituto di Física dell'Università degli Studi di Catania, 57 Corso Italia, I-95129 Catania, Italy
and Centro Siciliano di Física Nucleare e di Struttura della Materia—Unità di Catania,
Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche, I-95129 Catania, Italy
and Sezione di Catania, Istituto Nazionale di Física Nucleare, I-95129 Catania, Italy*

A. Martin-Rodero
*Departamento de Física del Estado Sólido, Facultad de Ciencias, Universidad Autónoma de Madrid,
Canto Blanco, Madrid 34, Spain*

(Received 21 July 1982; revised manuscript received 29 August 1983)

A new method for solving the Newns-Anderson model of chemisorption is proposed. It is based on the introduction of an adatom self-energy, which is obtained using a surface-molecule viewpoint. This self-energy is calculated by means of elementary group-theoretical techniques. The method, applied to the case of a three-atom chain, shows, besides great simplicity, good accuracy compared both with the exact result and with the most refined methods known in the literature.

I. INTRODUCTION

Chemisorption of hydrogen on transition metals has been the subject of extensive research in recent years. From the theoretical point of view the bulk of the effort has followed the pioneering work of Newns.[1] This author has proposed a type of Anderson Hamiltonian for the chemisorption of simple atoms on metal surfaces giving an approximate solution to this case within the Hartree-Fock (HF) scheme.

Other researchers[2–6] have looked for improved solutions by using different approaches. Special mention must be given to the work of Brenig and Schönhammer,[7] and the work of Schuck[8]—a generalization of Ref. 7 for the asymmetric case—which gives the most accurate solutions to the Newns-Anderson model. Quite recently, Martin-Rodero *et al.*[9] have given a new procedure—a generalization of the one given by Schönhammer[10]—which goes a step further in accuracy.

If one considers the model of an adatom being joined to an end of a chain of three atoms the binding energy of the adatom can be obtained exactly.[2] One can also calculate exactly[11] the electron density of states projected into the valence-electron orbital of an adatom adsorbed on a simple discrete-level substrate. It is therefore desirable that a solution of the Newns-Anderson model for chemisorption reproduces these exact results correctly.

Furthermore, it seems possible that the chain model or the discrete level substrate model have some physical relevance. According to Newns[1] the key property of the surface density of states is its bandwidth, and its detailed shape is relatively unimportant.

It is worthwhile to notice that although the most widely used approximation is the HF approximation, Schrieffer and Gomer[12] raised some doubts on the accuracy of the HF solution in situations where the correlation-energy parameter is large compared with resonance energy of the one-electron part of the Hamiltonian. This problem is particularly relevant for hydrogen chemisorbed on transition metals. In this case the intra-atomic Coulomb repulsion U has an effective value of about 8 eV and the tight-binding hopping parameter T for the substrate is chosen in order to simulate the bandwidth [$T \simeq 1$ eV in the case of Ni (Ref. 1)]. The hopping integral V between the adatom and the substrate is usually treated as a parameter [near 4 eV in the case of Ni (Ref. 10)].

The purpose of this paper is to reconsider the Newns-Anderson Hamiltonian of chemisorption and give a new method—comparable in accuracy to the one given by Martin-Rodero *et al.*[9]—but having the advantage of greater simplicity. Our method is based on the observation that if one considers the crystal levels as degenerate the Newns-Anderson Hamiltonian displays a SO(4) dynamical symmetry and thus is analytically soluble. This is apparent from the fact that the Hamiltonian can be expressed in terms of the generators of the group.

Furthermore, the use of relations (A1) greatly simplifies the calculations of the Green functions, whereas one needs the repeated application of the Hamiltonian operator on the reference states for the evaluation of the effects of the evolution operator.

In Sec. II we describe the proposed method of solution. Section III is devoted to the numerical results for different substrate models and comparison with other methods. In the Appendix we give details of the calculations.

II. DESCRIPTION OF THE METHOD

The general Newns-Anderson Hamiltonian reads

$$H=\sum_{k,\sigma} E_k C^\dagger_{k\sigma}C_{k\sigma}+\epsilon_H\sum_{\sigma} A^\dagger_\sigma A_\sigma+\sum_{k,\sigma} V_k(A^\dagger_\sigma C_{k\sigma}+\text{H.c.}) + UA^\dagger_\sigma A_\sigma A^\dagger_{-\sigma}A_{-\sigma}\ , \tag{1}$$

where the E_k's are the substrate-level energies, ϵ_H is the adatom-level energy, the V_k's are the interaction matrix elements between the adatom and the substrate, U is the intra-atomic interaction for the adatom, and σ is the spin variable.

If we assume $E_k=0$, the Hamiltonian can be written

$$H=\epsilon_H\sum_{\sigma} A^\dagger_\sigma A_\sigma+\bar{V}\sum_{\sigma}(A^\dagger_\sigma B_\sigma+\text{H.c.})+UA^\dagger_\sigma A_\sigma A^\dagger_{-\sigma}A_{-\sigma}\ , \tag{2}$$

where

$$\bar{V}=\left[\sum_k V_k^2\right]^{1/2},\quad B^\dagger_\sigma=\frac{1}{\bar{V}}\sum_k V_k B^\dagger_{k\sigma}\ . \tag{3}$$

Hamiltonian equation (2) is formally equivalent to the "molecular limit" of Ref. 2, and thus it is analytically soluble. The solubility is a straightforward consequence of an underlying group symmetry and is not bound to a two-atom surface model. For instance, with the same Hamiltonian [Eq. (2)] we can treat the three-level substrate model of Ref. 11, in which no clustering is assumed and the only simplification is of the band structure of the substrate. The main point is that the assumed degeneracy implies that only a particular single-particle state of the substrate is active, depending on the particular model of the substrate. This will be used as the starting point for a more realistic treatment of the substrate [see Eq. (9)] where the degeneracy assumption is relaxed and the bandwidth of the substrate levels will be treated explicitly.

The Hamiltonian equation (2) can actually be expressed through the following operators:

$$\begin{gathered}I=\sum_{\sigma}(A^\dagger_\sigma A_\sigma+B^\dagger_\sigma B_\sigma),\quad K_1^\sigma=\tfrac{1}{2}i(A^\dagger_\sigma B_\sigma-B^\dagger_\sigma A_\sigma)\ ,\\ K_2^\sigma=\tfrac{1}{2}(A^\dagger_\sigma B_\sigma+B^\dagger_\sigma A_\sigma),\quad K_3^\sigma=\tfrac{1}{2}(A^\dagger_\sigma A_\sigma-B^\dagger_\sigma B_\sigma)\ ,\end{gathered} \tag{4}$$

which form a closed SO(4) Lie algebra,

$$[K_i^\sigma,K_j^{\sigma'}]=i\delta_{\sigma\sigma'}\epsilon_{ijl}K_l^\sigma,\quad [K_i^\sigma,I]=0 \tag{5}$$

where ϵ_{ijl} is the total antisymmetric tensor in three dimensions. The operator I acts as the identity operator. In terms of the generators K_i's and the operator I the Hamiltonian equation (2) can be expressed as

$$H=(\epsilon_H-\tfrac{1}{2}U)(\tfrac{1}{2}I+K_3^+ +K_3^-)+2\bar{V}(K_2^+ +K_2^-) +\tfrac{1}{2}U(\tfrac{1}{2}I+K_3^+ +K_3^-)^2\ . \tag{6}$$

The fact that Hamiltonian (2) displays SO(4) symmetry as shown in Eq. (6) allows us to obtain an analytic solution. We note that the Hamiltonian (6) contains electron-electron correlation, which gives rise to the quadratic term.

In the Appendix we sketch the derivation, from Hamiltonian (6), of the corresponding single-particle Green function $\hat{G}(\omega)$, which satisfies

$$\begin{bmatrix} M_{AA}(\omega)-\omega & \bar{V}\\ \bar{V} & -\omega\end{bmatrix}\underline{\hat{G}}(\omega)=\mathbb{1}\ , \tag{7}$$

where the self-energy M_{AA} can be analytically expressed (for the symmetric case) as

$$M_{AA}=\frac{U^2\omega}{4(\omega^2-9\bar{V}^2)}\ . \tag{8}$$

Of course, the derivation of Eq. (8) is based simply on algebraic manipulations and thus it could also be derived by other standard methods. We found it, however, easier to use systematic commutation relations such as (5), even if other procedures are equally well suited.

Equation (8) is nothing but the self-energy presented in a surface-molecule picture in which the only state of the substrate (defined by the operator $\hat{B}$) which interacts with the adatom is decoupled from the rest of the substrate.

Let us consider now a more realistic model of the substrate by relaxing the degeneracy assumption, i.e., the above-mentioned decoupling. It is easy to show that the full Newns-Anderson Hamiltonian [Eq. (1)] is exactly equivalent to

$$H_{\text{eff}}=\sum_{k,\sigma} E_k C^\dagger_{k\sigma}C_{k\sigma}+[\epsilon_H+M_{AA}(\omega)]\sum_{\sigma} A^\dagger_\sigma A_\sigma +\bar{V}\sum_{\sigma}(A^\dagger_\sigma B_\sigma+\text{H.c.})\ , \tag{9}$$

where $M_{AA}(\omega)$ is the exact self-energy of the adatom. In fact, by using the one-body Hamiltonian [Eq. (9)], one derives the exact set of equations for the single-particle Green function given in Eqs. 2(a)—2(c) and (5) of Ref. 9. The proposed procedure for solving the Newns-Anderson model for chemisorption is to approximate the exact self-energy M_{AA} appearing in Eq. (9) by expression (8) obtained in the degenerate case.

Actually, it can be shown[13] that Eq. (9) corresponds to the first-order term of an exact expansion in the substrate bandwidth of the adsorbate self-energy. However, it is essential to realize that all the self-energy matrix elements derived from Eq. (9), except $M_{AA}(\omega)$, are already the exact ones. The successive approximations modify only $M_{AA}(\omega)$. The meaning of approximation (9) is thus clear: it corresponds to assuming for the adatom-adatom self-energy an average self-energy obtained by adopting a simplified substrate structure. It is expected that this average

TABLE I. Quasiparticle spectrum for the exact and approximate solutions (see text) of an atom chemisorbed on a three-atom chain for $V=1$, $T=1$, and $U=8$ (all in eV).

Exact		This method		Ref. 9		Ref. 7	
Level	Weight	Level	Weight	Level	Weight	Level	Weight
$E_{\text{chem}}=-0.5785$		$E_{\text{chem}}=-0.5836$		$E_{\text{chem}}=-0.5770$		$E_{\text{chem}}=-0.5445$	
						0.3131	0.0921
+0.3397	0.1124						
				0.3470	0.1176		
		0.4027	0.1593				
						1.2171	0.0433
+1.4250	4.1×10^{-3}						
				1.4408	2.67×10^{-3}		
		1.4700	0.0117				
						1.5426	0.0451
+1.7768	0.0341						
				2.2835	0.03394		
3.1806	0.0034						
				3.5641	0.03980		
4.2852	0.0009						
4.5871	0.0040						
				4.7032	0.0844		
4.8361	0.3337						
		5.0672	0.3291				
						5.1030	0.3195
				5.1736	0.2216		
6.2267	0.0102						

self-energy produces the main groups of peaks of the projected adatom density of states and that the successive approximations simply introduce additional structures in each group of peaks. This is confirmed by the numerical applications of the next section.

In the present paper we restrict ourselves to approximations (8) and (9) because they already produce quite good results. Note that $M_{AA}(\omega)$ gives the exact solution to Hamiltonian (2) and that our approximate solution to Hamiltonian (1) consists in taking for this Hamiltonian the same self-energy. With this approximation we automatically recover the exact solutions in the following limits: (i) U going to zero, (ii) V going to zero, and (iii) the bandwidth going to zero.

III. RESULTS AND COMMENTS

In order to check the accuracy of the proposed solution we have chosen to compare our results with some calculations[7,9] based on the chain model and with the exact calculations of Zavadil *et al.*[11]

We have solved the case of an adatom adsorbed on a metal chain of three atoms. We have obtained the exact results for different parameters and the approximate solutions with the method proposed by Brenig and Schönhammer[7] and Martin-Rodero *et al.*[9]

In this model the fundamental parameters are V, the interaction between the adatom and the last atom of the metal, U, the intra-atomic interaction, T, the hopping integral between nearest neighbors in the metal, and ϵ_H, the adatom level. In our calculations we have only considered the symmetric case $\epsilon_H=-U/2$; then, the solutions proposed in Refs. 9 and 10 coincide.

In Tables I—III we give the quasiparticle levels for positive energies (electrons) obtained with the different methods, and their weights on the adatom. The energy of chemisorption is also given.[9]

Results of Tables I—III show that our method gives quite good results, better than the results obtained using Brenig and Schönhammer's procedure, although slightly worse than the ones obtained with the method of Martin-Rodero *et al.*[9] The advantage of the method given here compared with the last one resides in the simplicity of the calculations; this is reflected in the smaller numbers of levels displayed in Tables I—III for the present method and in the simple self-energy (8).

The three levels obtained in the present method mimic very accurately the main levels of the exact solution. On the other hand, the chemisorption energy can be taken as a good measure of the accuracy of each solution. Values given in Tables I—III confirm the accuracy of our method.

It could be worth commenting that for typical chemisorption cases (V ranging from 3 to 5) our simple solution has an accuracy around 99.9%. We note that in this range of V values the rebonded surface-complex picture[2] applies well. However, as already mentioned, our model gives the exact limit for small V.

We have also compared our results with the exact calculations of Zavadil *et al.*[11] These authors have schematized the substrate band with a three-levels substrate.

TABLE II. Same as Table I for $V=3$, $T=1$ and, $U=8$ (all in eV).

Exact		This method		Ref. 9		Ref. 7	
Level	Weight	Level	Weight	Level	Weight	Level	Weight
$E_{\text{chem}}=-3.7583$		$E_{\text{chem}}=-3.7622$		$E_{\text{chem}}=-3.7584$		$E_{\text{chem}}=-3.7481$	
						0.8803	0.0433
0.9301	0.0608						
				0.9302	0.0608		
		0.9322	0.0607				
						1.0431	0.0158
2.7383	0.0804						
				2.7820	0.1089		
		2.9165	0.3426				
2.9173	0.2401						
				2.9225	0.2148		
						2.9488	0.3460
4.4343	0.0106						
				5.1281	0.0120		
				7.5658	0.0286		
8.8880	0.0538						
		9.9310	0.0967				
						9.9720	0.0949
				10.2135	0.0749		
10.5216	0.0401						

With Zavadil *et al.*[11] we assume that the adatom ionization level is 4 eV below the center of the "band" and that $U=8$ eV. If we represent the substrate band with one level [corresponding to SO(4) dynamical symmetry in our model] we predict two localized levels. We report the results for $V=0.5$, 1, and 1.5 in Fig. 1 in comparison with the exact calculations of Zavadil *et al.*[11] Of course, the exact solution[11] is richer than the unperturbed SO(4) solution. However, the two main SO(4) peaks reproduce both the centroids and total strengths of the two main groups of states of the exact calculations very well. This clearly displays the underlying approximate SO(4) symmetry of the Newns-Anderson Hamiltonian. We have also considered in our method the nondegenerate three-level case according to the scheme of the preceding section.

The substrate "conduction band" is assumed to be 2 eV

TABLE III. Same as Table I for $V=5$, $T=1$, and $U=8$ (all in eV).

Exact		This method		Ref. 9		Ref. 7	
Level	Weight	Level	Weight	Level	Weight	Level	Weight
$E_{\text{chem}}=-7.5395$		$E_{\text{chem}}=-7.5410$		$E_{\text{chem}}=-7.5395$		$E_{\text{chem}}=-7.5364$	
						0.9591	0.0143
0.9783	0.0208						
				0.9783	0.0208		
		0.9784	0.0208				
						1.0164	6.4×10^{-3}
2.9346	1.5×10^{-5}						
				2.9395	$<10^{-6}$		
4.8996	0.4323						
				4.9011	0.4331		
		4.9192	0.4386				
						4.9274	0.4390
6.6926	2.1×10^{-3}						
				7.0721	2.26×10^{-3}		
9.6989	0.0029						
				11.2731	8.23×10^{-3}		
13.0748	0.0087						
		15.5835	0.0406				
						15.6131	0.0403
				15.8205	0.0356		
15.9347	0.0321						

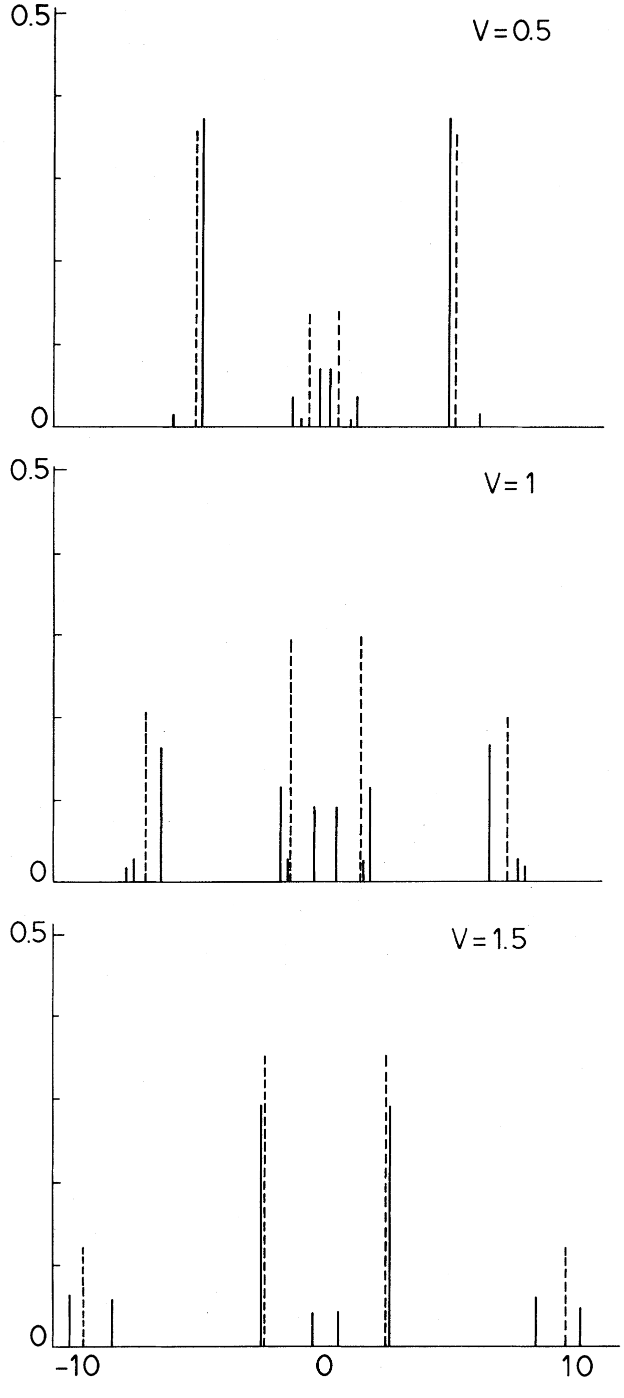

FIG. 1. Density of states in the adatom of the SO(4) approximation (dotted lines) according to the Newns-Anderson Hamiltonian compared with the exact calculation (solid line). Abscissae are in eV. Values of the parameters are $U=8$ eV and $V=0.5$, 1, and 1.5 eV. Splitting of the schematic crystal levels in the exact calculation is 1 eV.

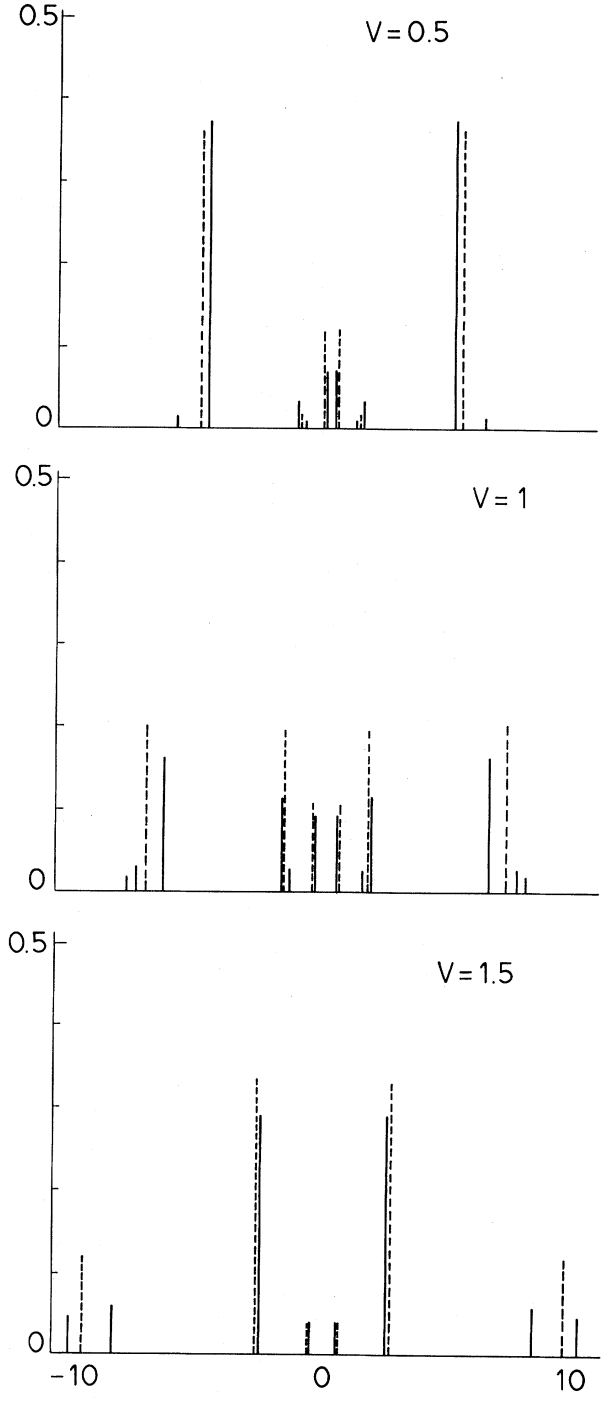

FIG. 2. Density of states in the adatom of the perturbated SO(4) approximation (dotted lines) according to the scheme described in the text compared with the exact calculation (solid lines). Abscissae are in eV. Values of the parameters are $U=8$ eV, $\Delta\epsilon=1$ eV, and $V=0.5$, 1, and 1.5 eV.

wide. The results for $V=0.5$, 1, and 1.5 are reported in Fig. 2, again in comparison with the exact calculations of Zavadil *et al.*[11]. Our solution gives three localized levels which resemble in an impressive way the exact results. We stress again that the model is still completely analytical. The simplicity of our method and its accuracy give some hope that it can be used for typical three-dimensional chemisorption problems with confidence.

ACKNOWLEDGMENT

One of us (F.F.) wishes to acknowledge the kind invitation of the Instituto di Fisica dell'Università degli Studi di Catania where part of this work was performed.

APPENDIX

The commutation relations of the K operators introduced in Eq. (4) with the operators A_σ and B_σ are

$$[K_3^\sigma,A_{\sigma'}]=-\tfrac{1}{2}\delta_{\sigma\sigma'}A_\sigma,\ \ [K_3^\sigma,B_{\sigma'}]=\tfrac{1}{2}\delta_{\sigma\sigma'}B_\sigma\ ,$$
$$[K_2^\sigma,A_{\sigma'}]=-\tfrac{1}{2}\delta_{\sigma\sigma'}B_\sigma,\ \ [K_2^\sigma,B_{\sigma'}]=-\tfrac{1}{2}\delta_{\sigma\sigma'}A_\sigma\ , \tag{A1}$$
$$[I,A_\sigma]=-A_\sigma,\ \ [I,B_\sigma]=-B_\sigma$$

Thus one easily gets

$$[H,A_\sigma]=-(\epsilon_H-\tfrac{1}{2}U)A_\sigma-\bar{V}B_\sigma-\tfrac{1}{2}U[(\tfrac{1}{2}I+K_3^++K_3^-)A_\sigma+A_\sigma(\tfrac{1}{2}I+K_3^++K_3^-)],\ \ [H,B_\sigma]=-\bar{V}A_\sigma\ . \tag{A2}$$

From Eq. (A2) it follows that the two Green's functions,

$$G_{AA}(t,t')=-i\langle T[A(t)A^\dagger(t')]\rangle\ ,$$
$$G_{BA}(t,t')=-i\langle T[B(t)A^\dagger(t')]\rangle\ , \tag{A3}$$

satisfy a closed set of equations of motion whose frequency Fourier transform can be written in matrix form according to Eq. (7) where $\mathbb{1}\equiv(1,0)$.

The remaining Green functions involving the other substrate one-electron states orthogonal to the B state satisfy an independent trivial set of equations of motion. Of course, in the SO(4) limit, the ground state $|\psi_0\rangle$ is degenerate [the one-electron states orthogonal to B do not appear explicitly in the SO(4) Hamiltonian equation (6)].

Let us introduce the ground-state wave function $|\psi_0\rangle$,

$$|\psi_0\rangle=[\alpha_1A_+^\dagger A_-^\dagger+\alpha_2(A_+^\dagger B_-^\dagger-A_-^\dagger B_+^\dagger)+\alpha_3B_+^\dagger B_-^\dagger]\,|0\rangle\ , \tag{A4}$$

with $|0\rangle$ the vacuum state. With the aid of relations (A1) and (A4) one can easily obtain the effect of the application of the Hamiltonian on the states $A^\dagger|\psi_0\rangle$ and $B^\dagger|\psi_0\rangle$.

For instance, we have

$$\begin{aligned}(\tfrac{1}{2}I+K_3^++K_3^-)B_+^\dagger\,|\psi_0\rangle\\ &=2\alpha_1(\gamma_1A_+^\dagger\,|\psi_0\rangle+\gamma_2B_+^\dagger\,|\psi_0\rangle)\\ &\quad-\frac{\alpha_2}{\sqrt{2}}(\delta_1A_+^\dagger\,|\psi_0\rangle+\gamma_1B_+^\dagger\,|\psi_0\rangle)\ ,\end{aligned} \tag{A5}$$

where γ_1, γ_2, and δ_1 are readily obtainable in terms of α_1, α_2, and α_3.

Equation (A5), together with all the similar equations allows us to construct two 2×2 matrices, $\hat{C}$ and $\hat{D}$, which describe the action of the Hamiltonian on the two subsets of states,

$$|\hat{\phi}\rangle\equiv(A^\dagger|\psi_0\rangle,\ B^\dagger|\psi_0\rangle),\ \ |\hat{\phi}\,'\rangle\equiv(A\,|\psi_0\rangle,\ B\,|\psi_0\rangle)\ , \tag{A6}$$

respectively.

By repeated applications of the matrices $\hat{C}$ and $\hat{D}$, one gets for the evolution operator U_t applied to $|\hat{\phi}\rangle$,

$$U_t\,|\hat{\phi}\rangle\equiv\exp(-iHt)\,|\hat{\phi}\rangle=\exp[(-\tfrac{1}{2}iat)\hat{I}][\cos(\beta t)\hat{I}-i\hat{n}\cdot\vec{\sigma}\sin(\beta t)]\,|\hat{\phi}\rangle\ , \tag{A7}$$

where $\vec{\sigma}$ are the Pauli matrices and

$$a=C_{11}+C_{22},\ \ \beta=[\tfrac{1}{4}(C_{11}-C_{22})^2+C_{12}C_{21}]^{1/2},\ \ \hat{n}\equiv\left[\frac{1}{2\beta}(C_{12}+C_{21}),\frac{i}{2\beta}(C_{12}-C_{21}),\frac{1}{2\beta}(C_{11}-C_{22})\right]\ , \tag{A8}$$

where C_{11}, C_{12}, C_{21}, and C_{22} are matrix elements of the $\hat{C}$ matrix. A similar expression holds for $U_t\,|\hat{\phi}\,'\rangle$.

Equation (A7) allows us to determine all the Green-function matrix elements. For instance

$$\begin{aligned}\langle A_+U_tA_+^\dagger\rangle=\exp\left[-\frac{i}{2}at\right]\Bigg\{\tfrac{1}{2}\exp(i\beta t)\left[\left[\alpha_3^2+\frac{\alpha_2^2}{2}\right]\left[1-\frac{1}{2\beta}(C_{11}-C_{22})\right]-\frac{\alpha_2}{\sqrt{2}}(\alpha_1+\alpha_3)\left[-\frac{C_{12}}{\beta}\right]\right]\\ +\tfrac{1}{2}\exp(-i\beta t)\left[\left[\alpha_3^2+\frac{\alpha_2^2}{2}\right]\left[1+\frac{1}{2\beta}(C_{11}-C_{22})\right]-\frac{\alpha_2}{\sqrt{2}}(\alpha_1+\alpha_3)\left[\frac{C_{12}}{\beta}\right]\right]\Bigg\}\ .\end{aligned} \tag{A9}$$

By Fourier-transforming Eq. (A9) and similar equations one can obtain the explicit expressions of the Green function $G(\omega)$ in terms of U, V, α_1, α_2, and α_3.

In order to determine α_1, α_2, and α_3, we must solve, in the symmetric case ($\epsilon_H=-\tfrac{1}{2}U$), the set of equations

$$-\lambda\alpha_1+\sqrt{2}V\alpha_2=0,\ \sqrt{2}V\alpha_2-\lambda\alpha_3=0,\ \ \alpha_1^2+\alpha_2^2+\alpha_3^2=1\ , \tag{A10}$$

where λ is the ground-state energy determined by the secular equation

$$\det \begin{vmatrix} -\lambda & \sqrt{2}V & 0 \\ \sqrt{2}V & \epsilon_H-\lambda & \sqrt{2}V \\ 0 & \sqrt{2}V & -\lambda \end{vmatrix} = 0 . \tag{A11}$$

In this case we obtain

$$\alpha_1 \equiv \alpha_3 = \frac{\sqrt{2}V}{(E_0^2+4V^2)^{1/2}} \equiv \alpha, \quad \alpha_2 = \frac{E_0}{(E_0^2+4V^2)^{1/2}} , \tag{A12}$$

where E_0 is the lowest solution of Eq. (A11),[2]

$$E_0 = -\frac{U}{4} - \left[\frac{U^2}{16} + 4V^2 \right]^{1/2} . \tag{A13}$$

For the symmetric case the matrix elements of the $\hat{C}$ and $\hat{D}$ matrices are

$$\begin{aligned} &C_{11} \equiv D_{11} = -bU, \quad C_{12} \equiv -D_{12} = -\frac{1}{2}\frac{E_0}{V} bU - V , \\ &C_{21} \equiv -D_{21} = \frac{1}{2}\frac{E_0}{V} bU - V, \quad C_{22} \equiv D_{22} = -\tfrac{1}{2}U + bU \end{aligned} \tag{A14}$$

where

$$b = \alpha^2/(4\alpha^2-1) .$$

More general expressions, also valid for the asymmetric case, are given in Ref. 13.

Equations (A14) allow us to determine the four poles of G_{AA} as

$$\omega_i = \pm \left[\frac{U^2}{16} + 4V^2 \right]^{1/2} \pm \left[\frac{U^2}{16} + V^2 \right]^{1/2} , \quad i = 1-4 \tag{A15}$$

and the corresponding residues,

$$R_1 = R_3, \quad R_2 = R_4 , \tag{A16}$$

$$R_1 + R_2 = \tfrac{1}{2} , \tag{A17}$$

$$R_1 - R_2 = (-\tfrac{1}{32}U^2 + V^2) \left[\frac{U^2}{16} + 4V^2 \right]^{-1/2} \times \left[\frac{U^2}{16} + V^2 \right]^{-1/2} . \tag{A18}$$

By using Eqs. (A15)—(A18) we obtain the explicit expression

$$G_{AA}(\omega) = \frac{\omega(\omega^2 - 9V^2)}{\omega^4 - [(U^2/4) + 10V^2]\omega^2 + 9V^4} . \tag{A19}$$

By comparing Eq. (A19) with Eq. (7) we obtain Eq. (8) of the text.

---

[1] D. M. Newns, Phys. Rev. 178, 1123 (1969).
[2] T. L. Einstein, Phys. Rev. B 11, 577 (1975).
[3] B. Bell and A. Madhukar, Phys. Rev. B 14, 4281 (1976).
[4] H. Kranz and A. Griffin, Phys. Rev. B 21, 2309 (1980).
[5] S. K. Lyo and R. Gomer, Phys. Rev. B 10, 4161 (1974).
[6] J. Hertz and D. Handler, Phys. Rev. B 15, 4667 (1977).
[7] W. Brenig and K. Schönhammer, Z. Phys. 267, 201 (1974).
[8] P. Schuck, Phys. Rev. B 13, 5225 (1976).
[9] A. Martin-Rodero, M. Baldo, F. Flores, and R. Pucci, Solid State Commun. 44, 911 (1982).
[10] K. Schönhammer, Solid State Commun. 22, 51 (1977).
[11] J. Zavadil, Z. Sroubek, K. Zdansky, and F. Kubec, Phys. Rev. B 18, 5433 (1978).
[12] J. R. Schrieffer and R. Gomer, Surf. Sci. 25, 315 (1971).
[13] M. Baldo, R. Pucci, F. Flores, G. Piccitto, and A. Martin-Rodero, Surf. Sci. 128, 237 (1983).