

BAND STRUCTURE OF AN ATOM ADSORBED ON A SURFACE; APPLICATION TO THE He/Cu (113) SYSTEM

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We present a method of exactly calculating the band energies of an atom adsorbed on a surface based on Neumann iteration of the projected transition matrix equations. The band structure calculated for a model of He on a Cu(113) surface shows large shifts and band gaps and differs substantially from the nearly free particle model. Comparison with an approximate calculation shows that the contributions to the energy shifts due to continuum state transitions are nearly negligible except for the higher band levels.

1. Introduction

The technique of atomic beam scattering has evolved recently as a very effective probe of the atom-surface interaction. In particular the region of the attractive adsorption well can be rather precisely determined through observation of resonant scattering with the bound states, historically called selective adsorption [1]. A precise knowledge of this attractive potential is of importance to workers in the field of physical adsorption. For light atoms in the submonolayer regime, the energy band structure of the bound states plays an important role in the calculation of the thermodynamic properties of the film. These effects recently have been very clearly demonstrated by Carlos and Cole for the case of He adsorbed on graphite [2]. They have considered the correct interaction potential given by atom-surface scattering and have calculated several thermodynamics effects in the low coverage regime in which the band structure effects are clearly apparent.

One of the advantages of the He/graphite system is its very weak surface corrugation which allows the band structure to be interpreted to a good approximation in the nearly free particle model. In this article we wish to consider adsorbed He atoms on rough metal surfaces, in particular the stepped

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surfaces of Cu for which many data have recently become available [3-5]. It has been shown that the surface average of the He/Cu interaction is essentially independent of the crystal face and is well represented by a Lennard-Jones type 9-3 potential having bound states at energies of 4.5, 2.2, 0.95 and 0.35 meV. We carry out detailed calculations for a model of the Cu(113) surface given by a Morse corrugated potential where the corrugation is sufficiently strong that the band structure is not at all represented by a nearly free particle picture.

The calculation is based on a method previously developed for scattering calculations in which the transition matrix is determined exactly by Neumann iteration together with an appropriate projection of the band structure states. In this way the effects of the continuum states are correctly included as opposed to previous calculations in which continuum state contributions are completely neglected [2,6,7]. By comparing the two types of calculations we are able to determine the contribution of continuum states to the negative energy band structure and we find that it is rather small for the lower bands, but increasingly important for bands closer to the top of the potential well.

When the total energy is positive it is the complex band structure associated with the outgoing solution to the Schrödinger equation which is important in a calculation of scattering intensities. There the effect of continuum states becomes increasingly important, particularly for the imaginary part of the band structure which gives the width or lifetime of a selective adsorption resonance.

2. Theory

We begin this section by briefly discussing the standard approach to band structure calculations as applied to the surface problem. The wave function $\psi(\mathbf{r})$ of the total interaction potential $V(\mathbf{r})$ is expanded in terms of the eigenstates $\chi_p(\mathbf{r})$ of some conveniently chosen one-dimensional potential $U(z)$. That is, we have

$$[H_0 + U(z)] \chi_p(\mathbf{r}) = E_p \chi_p(\mathbf{r}),$$

where $\chi_p(\mathbf{r})$ is the product of a plane wave in directions parallel to the surface and a bound or continuum eigenstate $\chi_\alpha(z)$ of $U(z)$ in the perpendicular direction. Then the expansion of the wavefunction can be written as

$$\psi(\mathbf{r}) = \sum_{\mathbf{G}} \sum_{\alpha} e^{i(\mathbf{K} + \mathbf{G}) \cdot \mathbf{R}} \chi_{\alpha}(z) C_{\mathbf{G}, \alpha}, \quad (1)$$

where z and \mathbf{R} are position vectors perpendicular and parallel to the surface respectively. Since $\psi(\mathbf{r})$ must have the same periodicity as the surface potential $V(\mathbf{r})$, the sum over directions parallel to the surface is a discrete sum over the

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surface reciprocal lattice vectors \mathbf{G} . The Schrödinger equation for $\psi(\mathbf{r})$ is then

$$[H_0 + U + v] \psi(\mathbf{r}) = E \psi(\mathbf{r}), \quad (2)$$

where $v = V(\mathbf{r}) - U(z)$. Since the potential can be expanded as a Fourier series in the reciprocal lattice vectors,

$$V(\mathbf{r}) = v_0(z) + \sum_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}} v_{\mathbf{G}}(z), \quad (3)$$

an obvious choice for $U(z)$ is the surface averaged potential $v_0(z)$, although for particular calculations other choices may be more convenient. Inserting the expansion for $\psi(\mathbf{r})$ of eq. (1) into eq. (2) and using the orthogonality relations for the eigenstates of $U(z)$ leads to the usual homogeneous equation for the expansion coefficients $C_{\mathbf{G},\alpha}$

$$\sum_q C_q [(E_q - E) \delta_{pq} + v_{qp}] = 0, \quad (4)$$

where in the condensed notation $q = (\mathbf{G}, \alpha)$, and the E_q are

$$E_q = E_{\mathbf{G},\alpha} = (\hbar^2/2m)(\mathbf{K} + \mathbf{G})^2 + \epsilon_{\alpha}. \quad (5)$$

The ϵ_{α} are discrete and negative for the bound states and continuous and positive for the continuum states. The existence of solutions for eq. (4) implies that the secular determinant must vanish

$$\det[(E_q - E) \delta_{pq} + v_{qp}] = 0, \quad (6)$$

and this gives the allowed band energies as a function of parallel wave vector $E = E_{\alpha}(\mathbf{K})$ in terms of the matrix elements v_{pq} .

To avoid the difficulties involved with the continuum states in (4) and (6), the usual approximation is to ignore them, leaving the infinite but discrete set associated with the bound states. This is further truncated to a finite set involving only the states of lowest energy. This procedure gives quite acceptable results for the band structure [2], even in situations where the surface is relatively rough [6,7].

The method we wish to present in this paper is similar to the one given above, but the wavefunction $\psi(\mathbf{r})$ is expanded in a finite sum of functions $\Lambda_p(\mathbf{r})$ instead of the infinite set of eq. (1). These functions $\Lambda_p(\mathbf{r})$ contain implicitly all interactions with the continuum states and the band energies are then given by a determinant similar to eq. (6) but of strictly finite dimension.

The wave function $\psi_i(\mathbf{r})$ is written in integral form as

$$\psi_i = \chi_i + G^+ v \psi_i = \chi_i + G^+ P_1 v \psi_i + G^+ P_2 v \psi_i, \quad (7)$$

where in the right-hand side we have introduced the projection operator $P = P_1 + P_2$, where P_2 contains the state or states for which we wish to determine the band structure shifts. If we define the intermediate function

$\Lambda_l(r)$ by

$$(1 - G^+ P_1 v)^{-1} \chi_l = \Lambda_l, \quad (8)$$

a few simple manipulations produce ψ_l as an expansion in the Λ_n :

$$\psi_l = \Lambda_l + \sum_b' \Lambda_b \frac{1}{E_l - E_b} t_{bl} = \sum_n \Lambda_n \tilde{C}_{ln}, \quad (9)$$

where t_{bl} is the transition matrix

$$t_{bl} = (\chi_b, v\psi_l), (\chi_b, t\chi_l), \quad (10)$$

and the sum over b runs over only the finite number of states projected in P_2 .

We note in passing that eq. (8) is equivalent to the differential equation

$$[H_0 + U + P_1 v] \Lambda_l = E_l \Lambda_l, \quad (11)$$

i.e. the Λ_l obey a Schrödinger type equation with the non-local periodic potential $P_1 v$. Similarly one can write from eq. (8) an integral equation for the projected transition matrix $h_{jl} = (\chi_j, v\Lambda_l)$

$$h_{jl} = v_{jl} + \sum_q' v_{jq} \frac{1}{E_l - E_q + i\epsilon} h_{ql}, \quad (12)$$

where the summation runs over all continuum and bound states except those projected out by P_2 .

Eq. (9) shows that the total wave function can be expanded in a finite sum of $\Lambda_l(r)$, and inserting this expansion in eq. (2) for $\psi_l(r)$, and using the easily obtained orthogonality relations between χ_l and Λ_p , leads to a finite matrix equation

$$\sum_n \tilde{C}_{ln} [(E_n - E) \delta_{nm} + h_{nm}] = 0, \quad (13)$$

which gives the band energies corresponding to the projected states through the determinant

$$\det[(E_n - E) \delta_{nm} + h_{nm}] = 0. \quad (14)$$

A few simple examples illustrate the usefulness of this formalism. If only one state is projected, we have

$$E = E_n + h_{nn}, \quad (15)$$

the exact expression for the energy shift of an isolated level. If two states, denoted by n and m , are projected we arrive at the expression usually associated with the splitting of two degenerate levels:

$$(E - E_m - h_{mm})(E - E_n - h_{nn}) = h_{nm}^2. \quad (16)$$

Of course, if the h_{pq} are calculated exactly, eqs. (15) and (16) give the same results for a given energy shift. Using the first order expansion from eq. (12),

$h_{ff} = v_{ff}$, both eqs. (15) and (16) reduce to the familiar expressions from perturbation theory.

Thus the exact determination of the band energies is reduced to a problem of determining the projected t -matrix h_{ff} . This is accomplished by repeated Neumann iteration of the integral equation (12) until convergence is obtained and it is the same method used previously for the scattering equations [8,9]. The crossing of two or more levels in the free particle band structure is a resonance which gives a vanishing denominator in eq. (12). Thus, in order to obtain convergence of the iterative solution, all band crossings and near crossings in the region of a particular energy and parallel wave vector must be projected out by P_2 . For the calculations reported below for He on Cu(113), convergence was rapidly obtained in 5 to 10 iterations with the projection of 2 to 5 states.

3. Results and discussion

As a model for the interaction between He and the Cu(113) stepped surface, we have chosen a Morse corrugated potential

$$V(\mathbf{r}) = D\{\exp(2\kappa[\phi(x) - z])/v_0 - 2\exp(-\kappa z)\}, \quad (17)$$

with $\kappa = 1.05 \text{ \AA}^{-1}$, $D = 6.35 \text{ meV}$ and v_0 the surface average of $\exp(2\kappa\phi)$. The steps are represented by a one-dimensional corrugation function

$$\phi(x) = ha \cos(2\pi x/a)$$

where $h = 0.02$ and $a = 4.227 \text{ \AA}$ is the spacing between steps. The surface average of eq. (17) is a Morse potential and we have chosen this as our distorted potential $U(z)$. The Fourier components of eq. (3) are

$$v_G(z) = I_g(\kappa ha) e^{-2\kappa z} / I_0(\kappa ha), \quad (18)$$

where the integer g is defined through $G = 2\pi g/a$, and $I_g(z)$ is the modified Bessel function of the first kind.

This form of the potential was chosen because it gives excellent agreement with experiment for the diffraction intensities in scattering experiments [3], and all relevant matrix elements v_{pq} can be determined analytically. The surface averaged potential $U(z)$ contains only three bound states at energies 4.58, 1.90 and 0.39 meV which differ somewhat from the experimental results quoted above, coming from observations of selective adsorption. However, even though the potential is somewhat approximate in the region of the well (notably it does not have the $-C_3/z^3$ long range Van Der Waals behavior), the results obtained for the band structure are quite general and do not depend strongly on small variations in potential shape.

Fig. 1 shows the band energies as a function of parallel momentum calcu-

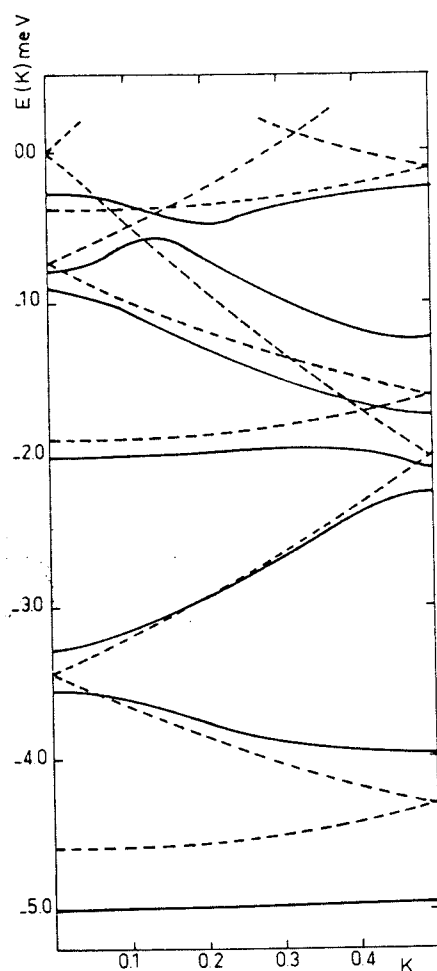


Fig. 1. Band energies of the He/Cu(113) system. The solid lines are the energies calculated from eq. (14). The dashed lines are the energies of a particle in the surface averaged potential. The parallel momentum K is measured in units of $2\pi/a$.

lated from eq. (14) using the potential of eq. (17). For comparison, the energy parabolas of an atom in the distorted potential $U(z)$ are also shown. It is clear that the band energies resemble very little the energy which would be predicted by a nearly free particle picture. Both the energy shifts and the band gaps are quite large. At $K = 0$ the bands corresponding to the three unperturbed energy levels are shifted by -0.41 , -0.11 and $+0.12$ meV, respectively.

Table 1 gives a list of the band gaps at the edge and center of the Brillouin zone compared to the value $2v_{nm}$ predicted by the nearly free particle model.

Table 1
Energy shifts
the reciprocal
column
approximate

(a) Unperturbed

Zone center

$(\frac{1}{0}) - (\frac{1}{0})$
 $(\frac{1}{0}) - (\frac{1}{0})$

Zone boundary

$(\frac{0}{0}) - (\frac{1}{0})$
 $(\frac{1}{0}) - (\frac{1}{0})$
 $(\frac{0}{1}) - (\frac{1}{0})$
 $(\frac{0}{2}) - (\frac{1}{0})$

The unperturbed
and n values
the two
approximate
gaps are

It is
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The
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Table 2
Comparison
 $K = 0.01$
exact results

(a) Unperturbed

$(\frac{0}{0})$
 $(\frac{1}{0}), (\frac{1}{0})$

$(\frac{0}{0})$
 $(\frac{1}{0}), (\frac{1}{0})$

$(\frac{0}{2})$

Table 1

Energy splittings of the lowest lying gaps at the zone center and zone boundary; column (a) labels the reciprocal lattice vectors and bound state levels of the corresponding unperturbed states, column (b) gives the exact gap energy in meV and column (c) gives the nearly free particle approximation $2v_{nm}$

(a) Unperturbed states	(b) Gap energy (meV)	(c) $2v_{nm}$ (meV)
<i>Zone center, $K = 0$</i>		
$\begin{pmatrix} -1 \\ 0 \end{pmatrix} - \begin{pmatrix} 1 \\ 0 \end{pmatrix}$	0.243	0.0421
$\begin{pmatrix} -1 \\ 1 \end{pmatrix} - \begin{pmatrix} 1 \\ 1 \end{pmatrix}$	0.064	0.027
<i>Zone boundary, $K = \pi/a$</i>		
$\begin{pmatrix} 0 \\ 0 \end{pmatrix} - \begin{pmatrix} -1 \\ 0 \end{pmatrix}$	0.965	0.954
$\begin{pmatrix} 1 \\ 0 \end{pmatrix} - \begin{pmatrix} -2 \\ 0 \end{pmatrix}$	0.150	0.001
$\begin{pmatrix} 0 \\ 1 \end{pmatrix} - \begin{pmatrix} -1 \\ 1 \end{pmatrix}$	0.486	0.616
$\begin{pmatrix} 0 \\ 2 \end{pmatrix} - \begin{pmatrix} -1 \\ 2 \end{pmatrix}$	0.264	0.277

The unperturbed free particle band is denoted by $\begin{pmatrix} g \\ n \end{pmatrix}$ where g is defined above and n is the bound state quantum number. Curiously, the large gap between the two lowest bands, $\begin{pmatrix} 0 \\ 0 \end{pmatrix} - \begin{pmatrix} -1 \\ 0 \end{pmatrix}$, at the zone boundary is reasonably well approximated by $2v_{nm}$ and similarly for the two other $\begin{pmatrix} 0 \\ n \end{pmatrix} - \begin{pmatrix} -1 \\ n \end{pmatrix}$. All the other gaps are substantially larger than the nearly free particle value.

It is also noticed that gaps arise wherever two or more unperturbed bands cross inside the zone. In one dimension the symmetry is so restricted that line crossings are virtually always split, unlike the situation in two or three dimensions where many crossings in high symmetry directions may not be split.

The flattening of the lowest bands is very apparent, implying that the helium atoms are not very mobile on the surface. For the lowest band the effective mass is $1.79m$, but such a description is not very appropriate since the

Table 2

Comparison of exact and approximate calculations of band energies near the zone center, $K = 0.01(2\pi/a)$; column (a) labels the corresponding unperturbed states, column (b) gives the exact results from eq. (14), and column (c) gives the results of the approximation of eq. (6)

(a) Unperturbed states	(b) Exact (meV)	(c) Approximate (meV)
$\begin{pmatrix} 0 \\ 0 \end{pmatrix}$	-4.99	-4.95
$\begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} -1 \\ 0 \end{pmatrix}$	-3.54	-3.53
	-3.29	-3.26
$\begin{pmatrix} 0 \\ 1 \end{pmatrix}$	-2.03	-1.99
$\begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} -1 \\ 0 \end{pmatrix}$	-0.90	-0.88
	-0.85	-0.81
$\begin{pmatrix} 0 \\ 2 \end{pmatrix}$	-0.31	-0.29

band is non-parabolic. For higher bands the deviation from a parabolic form is so strong that an effective mass approach has very little validity.

In order to estimate the effects of continuum states we have carried out a calculation using the matrix element equation (4) truncated to the 14 lowest lying bound states. The band structure obtained in this manner is very similar to that given in fig. 1 with the lowest lying bands shifted up by only one or two percent. Table 2 gives a comparison between the values of the exact and approximate calculation near the zone center and it is seen that the differences become noticeable only for the higher bands.

In conclusion we have demonstrated that an exact calculation of the band structure can be carried out using methods based on Neumann iteration of a projected transition matrix equation that have been successful in scattering calculations. For our model corresponding to the He/Cu(113) system, the band structure is not at all free particle-like. The lowest bands are flattened with large gaps, implying that the adsorbed atoms are significantly less mobile than an atom on a smooth surface. Comparison with the standard approximate calculation based on diagonalization of the matrix form of the Schrödinger equation shows that the effects of interactions with the continuum states is nearly negligible for the lowest lying bands but increasingly important for the higher bands.

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