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The problem of adsorption of rare gas atoms on solids is treated for the case of submonolayer films. An energy spectrum calculation method which is suitable for band structure or heat capacity calculations is discussed. It is particularly useful for adsorbate–substrate systems in the region intermediate between "tight binding" and "plane wave" behavior. The method employs a technique introduced by Kohn and Luttinger of using the eigenfunctions corresponding to a particular point in the Brillouin zone as a basis set. The cases of He and Ne adsorbed on Xe are discussed.

I. INTRODUCTION

The physical adsorption of rare gas atoms on solids is a subject which enjoys current theoretical and experimental interest.[1-9] Recent experimental work has focused upon physically adsorbed films in the submonolayer range. The density of these thin films is low enough to allow the interaction between the adsorbed atoms and substrate to be treated as dominant over the interaction between neighboring atoms in the film. The initial approach to a theoretical study of such films is a treatment of the single particle states of an adsorbed atom.

Two different methods have been used to study this problem. The first is a "tight binding" approach[1-3] which is used for the highly localized case where the adsorbed atom becomes firmly trapped in one adsorption site on the surface and exhibits low mobility. The second is a "plane wave" approach[4-7] which is used for the nonlocalized case where the adsorbed atom exhibits high mobility on the surface. Both of these approaches are quantum mechanical in nature. They share a central theme of a numerical calculation involving a wavefunction expansion in terms of a set of suitable basis functions. The two methods differ in their choice of basis sets. The "tight binding" method uses a basis set (harmonic oscillator eigenfunctions) that is appropriate to the highly localized case. The "plane wave" method uses a basis set (plane waves) that is appropriate to the nonlocalized case. Obviously these methods apply to different adsorbate–substrate systems and further methods are needed for the intermediate regions.[3] In this work we propose such a method.

We focus our attention on a system consisting of the light rare gases, He and Ne, as adsorbate and a heavy rare gas crystal, Xe, as substrate. We consider the (111) face of the Xe crystal as the adsorption surface.

Our approach is a band structure calculation method first proposed by Kohn and Luttinger.[10] As in the above methods, we perform a quantum mechanical calculation which involves expanding the system's wavefunction in a suitable set of basis functions. In the Kohn–Luttinger representation the basis set consists of the eigenfunctions of the system's Hamiltonian at the $k=0$

point in the Brillouin zone. This is the point where band extrema and the ground state occur.

We use the "plane wave" method to calculate the eigenfunctions at $k=0$. Hence our accuracy is limited to that found in the "plane wave" approach. However the "plane wave" method can be made quite accurate, even in localized regime,[6] provided that one is willing to work with sufficiently large basis sets. Large basis sets, however, are unwieldy and impractical for energy spectrum calculations at more than one or two points in reciprocal lattice space because of the large amounts of computer time involved. Hence in the intermediate regime the "plane wave" method is not suitable for band structure or heat capacity calculations, since the energy spectrum has to be calculated at many points in the Brillouin zone; but it is practical for use at just one point, $k=0$, to generate the eigenfunctions. These eigenfunctions can then be used to calculate the energy spectrum at the other points in k space.

II. POTENTIAL ENERGY

The substrate is assumed to be a semi-infinite perfect Xe crystal having at the surface an unrelaxed structure identical to the bulk. Defects, thermal vibrations, and deformation due to the adsorbed atom are neglected. Xe has an fcc lattice structure with lattice constant $a_0 = 6.24$ Å. The (111) face of this crystal contains Xe atoms arranged in a closed hexagonal array. Figure (1a) shows a portion of this surface. The circles represent Xe atoms. The coordinate system is set up with the xy axes lying in the plane of the surface and the z axis normal to the surface. The nearest neighbor distance for atoms in the plane of the surface is $a = a_0/\sqrt{2}$. An adsorption site occurs at the center of each equilateral triangle formed by three neighboring surface atoms. Neighboring adsorption sites are not perfectly identical,[1] but the difference between them is quite small and here we neglect it.

The interaction of the rare gas atom with the substrate can be written as a sum over all Xe atoms of the two-body Lennard-Jones (12–6) potential. Values used for the Lennard-Jones parameters ϵ_0 and ρ_0 were taken from Ricca[3] and are $\epsilon_0 = 66.24 \times 10^{-16}$ erg, $\rho_0 =$
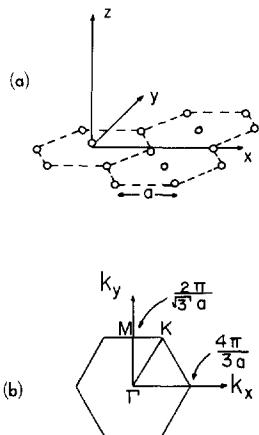
FIG. 1. (a) Orientation of the x–y–z coordinate system on the (111) plane of the Xe crystal. Each circle represents a surface Xe atom. "a" denotes the nearest neighbor separation for atoms in the plane. (b) The Brillouin zone for the Xe lattice.

FIG. 3. Potential profile for Ne on Xe. Shows $V(\mathbf{r})$ as a function of z for three fixed points in the x–y plane. Also shown are energy level diagrams for the lowest seven $\Gamma(k=0)$ states for Ne.

3.72 Å for He on Xe; and $\epsilon_0 = 123.7 \times 10^{-16}$ erg, $\rho_0 = 3.82$ Å for Ne on Xe. If $V(\mathbf{r})$ is the potential energy of the adsorbed atom with position vector $\mathbf{r}$, and ρ_i is the distance between the adsorbed atom and the ith atom, then

$$V(\mathbf{r}) = \sum_i \epsilon_0[(\rho_0/\rho_i)^{12} - (\rho_0/\rho_i)^6], \qquad (1)$$

where the sum extends over all Xe atoms. The details of the numerical calculation of the potential are given elsewhere.[4]

The behavior of $V(\mathbf{r})$ can be displayed by plotting $V(\mathbf{r})$ as a function of z for fixed positions (x, y) in the surface plane. This has been done for three special points in the plane: (1) at the adsorption site, (2) at a saddle point midway between two Xe atoms, and (3) at a Xe atom site. The results are shown in Fig. 2 for He as adsorbate and in Fig. 3 for Ne as adsorbate.
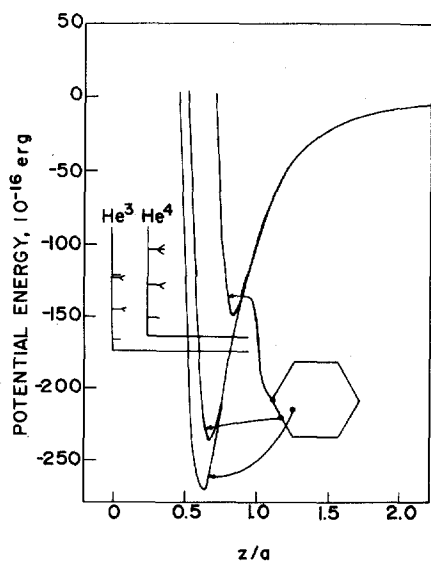
The potential is noticeably nonseparable, i.e., it cannot be written as the sum of a function of x and y and a function of z. This will result in a mixing of motion parallel to the surface with motion perpendicular to the surface. The adsorbed atom will undergo localization in the xy dimension as well as in the z dimension. The minimum values of the potential for our three special points in the plane are given in Table I. These values are all about 2% deeper than the corresponding values found by Ricca.[3]

III. BASIS SET

The Kohn–Luttinger basis functions are the $k=0$ eigenfunctions for the single particle states of the adsorbed atom in the potential field given by Eq. (1). They are found by solving the Schrödinger equation,

$$[-(\hbar^2/2m)\nabla^2 + V(\mathbf{r})]\psi(\mathbf{r}) = E\psi(\mathbf{r}), \qquad (2)$$

where m is the mass of the atom and E is its energy.

The periodicity of the potential allows us to apply Bloch's theorem and decompose the wavefunction into Bloch waves,

$$\Psi(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})u_k(\mathbf{r}), \qquad (3)$$

where $\mathbf{k}$ is a two-dimensional vector lying in the xy plane and u_k is a function which retains the periodicity

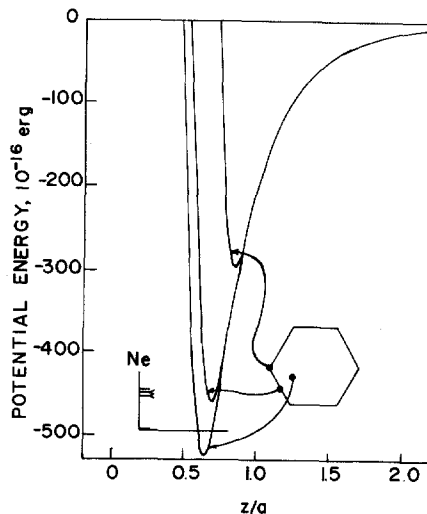

FIG. 2. Potential profile for He on Xe. Shows $V(\mathbf{r})$ as a function of z for three fixed points in the x–y plane. Also shown are energy level diagrams for the lowest seven $\Gamma(k=0)$ states of ^{3}He and ^{4}He.

TABLE I. Potential energies of adsorption (measured in units of 10^{-16} erg) for He and Ne on the (111) face of Xe.

Adsorbed atom	Site	Saddle	Atom
He	−274.3	−237.8	−150.8
Ne	−527.4	−462.1	−300.2

of the crystal. We first look at the $k=0$ point in the Brillouin zone and apply the "plane wave" method to calculate the 17 lowest eigenvalues and their corresponding eigenfunctions. This method is described fully by Milford and Novaco[5,6] and is only outlined here. The function $u_k(\mathbf{r})$ is expanded in terms of a set of basis functions. A plane wave or complex exponential Fourier series expansion is used for the xy dependence of $u_k(\mathbf{r})$. The z dependence is expanded as a linear combination of Morse functions. The expansion has the form

$$u_k(\mathbf{r}) = \sum_j \sum_K A_{jK}(\mathbf{k}) M_j(z) \exp(i\mathbf{K}\cdot\mathbf{r}), \qquad (4)$$

where the M's represent the Morse functions and $\mathbf{K}$ represents the two-dimensional wave vector for the plane waves. By the use of Eqs. (3) and (4), Eq. (2) becomes an eigenvalue equation for a matrix whose eigenvalues are the $E(\mathbf{k})$ and whose eigenvectors have
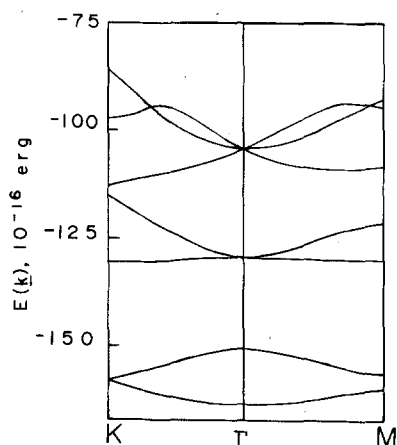

FIG. 4. Energy bands for ^{3}He along the $K\Gamma M$ contour in the Brillouin zone, showing the lowest seven bands.

components given by the A_{jK}. Once all the components of this matrix are calculated the eigenvalues and eigenvectors are found by standard numerical techniques.

Nineteen plane waves and seven Morse functions are used in the calculation making a total of 133 functions in the basis set. This allows the energy levels to be calculated to an accuracy of 1% for Ne adsorbed on Xe and better than 1% for He on Xe.

The resulting ground state energies for ^{3}He, ^{4}He, and Ne adsorbed on Xe are: -163.8×10^{-16} erg, -174.4×10^{-16} erg, and -496×10^{-16} erg, respectively. The seven lowest energy levels for ^{3}He and ^{4}He are shown on Fig. 2 and the corresponding levels for Ne are shown on Fig. 3. The zero point energies for ^{3}He, 111×10^{-16} erg, and ^{4}He, 100×10^{-16} erg, are larger than the minimum energy barrier (difference between the potential minimum above the adsorption site and above a saddle point) of 36×10^{-16} erg that opposes tunneling from site to site, but less than the maximum potential barrier (difference between the potential minimum
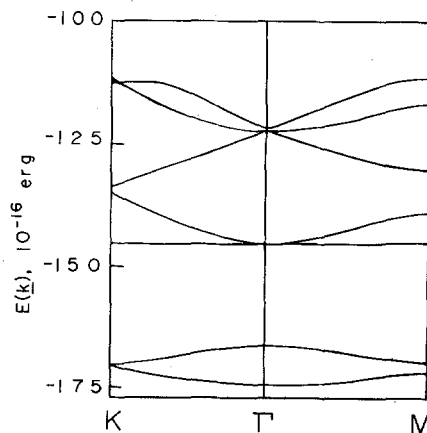

FIG. 5. Energy bands for ^{4}He along the $K\Gamma M$ contour in the Brillouin zone, showing the lowest seven bands.

above the adsorption site and above a Xe atomic site) of 123×10^{-16} erg. Hence ^{3}He and ^{4}He fall into the "plane wave" regime. The effect of the periodic potential will be stronger here than in the case of He adsorbed on graphite[4] but it will not be strong enough to localize the He. The Ne zero point energy 31×10^{-16} erg is less than the minimum potential barrier 65×10^{-16} erg putting it well into the intermediate region.

We also calculated the ground state energy of Ne on Xe using a smaller basis set to compare the results with a "tight binding" calculation done with a basis set of similar size. Using a basis set containing 57 functions (19 plane waves and 3 Morse functions) we found a ground state energy of $E_0 = -447\times10^{-16}$ erg. This compares with a "tight binding" result[3] of $E_0 = -454.1\times10^{-16}$ erg done with a 36 function basis set (nine harmonic xy functions and four Morse functions). Hence for Ne on Xe the "tight binding" method gives slightly better results than the "plane wave" method when basis sets of similar size are used. However the "plane wave" method gives the more accurate result when the 133 function basis is used.
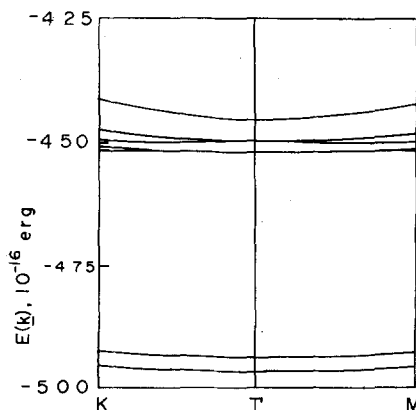

FIG. 6. Energy bands for Ne along the $K\Gamma M$ contour in the Brillouin zone, showing the lowest seven bands.

IV. BAND STRUCTURE

The eigenfunctions from Sec. III are used as a new basis set for the band structure calculation. Let $\phi_n(\mathbf{r})$ denote the nth eigenfunction for the problem at $k=0$. Then Eq. (3) can be written

$$\psi(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r}) \sum_n B_n \phi_n(\mathbf{r}), \qquad (5)$$

where the B's represent the new expansion coefficients. The energy spectrum is then calculated for various points in the Brillouin zone using the same numerical methods as before except that the $k=0$ eigenfunctions form the basis set rather than the plane waves, i.e., Eq. (5) is used rather than Eq. (4).

The accuracy of the Kohn–Luttinger method is tested by comparing its resulting energy levels with those of the "plane wave" method at several points in the Brillouin zone. The maximum difference between the two results is found to be about two orders of magnitude less than the error introduced into the problem by the use of a truncated rather than an infinite basis set in the original "plane wave" calculation of the Kohn–Luttinger eigenfunctions. Hence this method introduces no further error into the calculation beyond that already found in the "plane wave" method.

Our real space unit cell is a rhombus consisting of four neighboring Xe atoms. The rhombus has an edge of length "a." The corresponding Brillouin zone is a hexagon with an edge of length $4\pi/3a$. This is shown in Fig. 1(b). In the conventional manner the points of high symmetry are labeled Γ, M, and K. The band structure is calculated along the $K\Gamma M$ contour.

Figure 4 shows the band structure for ^{3}He, and Fig. 5 shows it for ^{4}He. The noticeable features of the band structure are wide bands and a large gap between the lowest two bands and the rest of the band structure. The large widths of the lower bands indicate that the adsorbed He atom will enjoy considerable mobility on the surface. These band structures are very similar to those found for He adsorbed on Xe-plated graphite.[7] This indicates that most of the effect of the crystal periodicity is coming from the first layer of surface atoms. The ground state energies reported for He on Xe-plated graphite lie significantly higher than those

given here for He on pure Xe. This can be attributed to the fact that the Lennard-Jones parameters used in the Xe-plated graphite calculations came from molecular beam data and differ from those used here which came from virial coefficient data.

Figure 6 shows the band structure for Ne along the $K\Gamma M$ contour. It is noticeably different from the case of He. Here we find narrower bands accompanied by larger band gaps. The Ne atom will have a relatively low mobility and will become localized.

V. CONCLUSION

The Kohn–Luttinger band structure method is shown to be a useful approach to the energy spectrum problem in the physical adsorption of rare gas atoms. It is especially useful in the region intermediate between "plane wave" behavior and "tight binding" behavior. It has been used to calculate band structures for the cases of He and Ne adsorbed on the (111) face of solid Xe. The basis set used in the calculation consisted of the 17 lowest $k=0$ eigenfunctions. The main advantage of this method is that it allows the numerical calculations to be done with a small basis set and hence uses a relatively small amount of computer core and time. Its accuracy is the same as a "plane wave" calculation using a large basis set.

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