R-matrix propagation study of He scattering from NaCl(001) and its Kr overlayer

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Abstract

For the first time, we employ the *R*-matrix propagation technique of Stechel et al. to model the diffraction of atomic helium from a bare NaCl(001) surface and also from a NaCl(001) surface with a Kr overlayer. The Kr/NaCl(001) has recently been reported by De Kieviet et al. as the only known commensurate overlayer system with square symmetry. To verify this theoretically, we solve the close-coupling equation. The *R*-matrix propagation technique is used, since it has many computational advantages and will be shown to yield efficient and accurate results for such systems. Once the final *R*-matrix is obtained from this propagation method, scattering information is extracted from the *S*-matrix. We obtain excellent agreement between calculated relative intensities derived from the *S*-matrix elements and experimental relative intensities for the He/NaCl(001) system, and good agreement for the more interesting and complex He–Kr/NaCl(001) system. Corrections for inelastic effects have been attempted using the Debye–Waller factor, resulting in little or no improvement. © 2000 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

In the past 20 years or so, the field of surface science has experienced accelerated growth. One reason for this is the development of new and improved experimental technologies that can be applied to the study of surfaces and surface processes. These technologies have enabled many novel experiments to be carried out, which in turn has spawned a commensurate theoretical interest in studying surface processes. One such class of experiments pertaining to weak physisorption phenomena, such as ordered overlayers on crystal surfaces, has attracted much interest in recent years [1–5]. This paper will present theoretical results for two surface systems that were motivated by these experiments.

Recent experimental success is not the only reason to study overlayer systems, however; in the case of physisorbed noble gas systems, a theoretical model of the interaction potential is better known, and thus can allow for precise theoretical scattering calculations to be performed on these systems. The rare-gas–rare-gas pair potentials are well established from gas-phase experiments [6–8]. The model potential interaction used in this paper is obtained by summing over these two-body rare gas potentials, and adding two-body and three-body interactions with the substrate (Section 3.1).

Apart from experimental and theoretical considerations, overlayer systems are interesting physical systems in their own right. There is a delicate balance between the periodically modulated adsorbate–substrate forces, and the lateral interactions,

that determines the structure and dynamics of such overlayers. Relatively small perturbations to this balance have been found to produce a richness of two-dimensional phases. In most cases, the substrate holds the particles down in a planar layer. We are interested in the symmetry and structure of these adlayers, compared with that of the substrate. By studying such rare-gas overlayer systems, we hope to gain a more general understanding of these kinds of adsorption phenomenon. In fact, knowledge gained by studying overlayer systems is used in many areas of applied science and technology today — perhaps one of the most important of these being the field of epitaxial growth of thin films and layered solids.

In this paper, we examine diffraction for two different systems: He scattering from (1) NaCl(001); and from (2) a Kr overlayer on NaCl(001) [9]. The latter overlayer system is interesting because the Kr atoms adsorb above the Na ions in square symmetry with the same dimensions as the NaCl unit cell. This means the overlayer is commensurate with the substrate in both the X and Y degrees of freedom. This appears to be an unusual phenomenon, since usually in the case of rare-gas overlayers on insulator crystals the adatom–adatom forces dominate over the adatom–substrate forces, and not the other way around. Kr/C(0001) has also been shown to have a sufficiently strong adatom–substrate interaction to compete with the lateral forces within the Kr overlayer. In fact, this system — which was first investigated decades ago [10,66] — is still one of the most frequently researched by surface scientists [11,12].

Essential to an understanding of surface systems is the application of mathematical models to give physical insight into the experimental results. Of the mathematical methods that have already been applied to model atom–surface scattering, quantum methods are preferred over approximate methods (i.e. classical trajectory [13], semiclassical [14,67]). Whereas approximate methods usually allow calculation at high incident energies, or the inclusion of very many open channels, exact quantum methods tend to be more limited. However, in order to model the two systems in this paper accurately, we need to apply an exact quantum method. In the case of highly corrugated surfaces, however, such as overlayer systems, exact methods can be computationally expensive.

In principle, we can calculate the relative peak intensities from a helium diffraction experiment exactly from a given realistic helium–surface potential by using an algorithm to solve the close-coupling equation (see Section 3.2). Specifically, we will evaluate the two systems considered using the R-matrix propagation method of Stechel et al. [15]. This method has been found to have some advantages over other exact quantum methods (see Section 3.3). Also, this method has already been applied to a variety of reactive scattering [16–20] and surface-scattering problems [21–23]. Thus, doing a direct comparison between theory and experiment will further demonstrate the accuracy and applicability of the R-matrix method to these kinds of problems, and also evaluate the adequacy of the potential model. In the next section, we discuss the background leading up to the present theoretical project. In Section 3.1 we describe the potential, and in Section 3.2 we describe the theory behind the R-matrix approach. In Section 3.3 we discuss the advantages of applying the R-matrix method to these kinds of problems. Also, in Section 3.4 we discuss symmetry adaptation as used for these particular systems and in Section 3.5 we describe the theory behind the Debye–Waller factor. In Section 4 we discuss the theoretical results as they compare with actual experimental results by De Kieviet et al. [9], and the resulting implications. Finally, in Section 5 we present concluding remarks.

2. Background

There has been a lot of theoretical work done on atoms scattering from overlayers on surfaces. This work has resulted in a better understanding of these systems and a refinement of our theoretical models. The first quantitative model comparing theory and experiment in atomic scattering from overlayers was applied by Ellis et al. [24]. These authors studied the interaction of H atoms with Xe and Kr monolayers physisorbed onto the basal plane of graphite. Good agreement between theoretical intensities calculated via a close coupling algorithm and the experimental data was obtained.

It was also shown that the calculated intensities were very sensitive to the details of the potential used.

Shortly after this, close coupling calculations for the He–Xe/C(0001) system were carried out by Hutson and Schwartz [21]. They concluded that the sensitivity of the data to changes in the potential is strongly dependent on the energy of the incident beam. They found that at higher energies the scattering patterns for slightly different pair potentials gave similar results. However, at low incident energy the predicted intensities for these two potentials showed strong differences.

Also, theoretical calculations were done on He scattering from commensurate Kr overlayers adsorbed on C(0001) by Jónsson and Weare [10,66]. They compared close coupling calculations with the resonant patterns measured [25]. The potential used in these calculations was constructed by summing over the He–Kr pair interactions and the He–graphite interaction. Since the He–Kr pair potential is better known, some of the uncertainty in the evaluation of the nonadditive interactions is removed. Three-body corrections were added calculating not only the triple-dipole interaction but also the correction due to the repulsive exchange interaction. The theoretical many-body correction is considered very good.

Elastic and inelastic studies of ordered noble-gas (Ar, Kr, Xe) overlayers physisorbed on Ag(111) were carried out by Gibson and co-workers [26,28]. Close coupling calculations were done to describe the elastic scattering experiments. It was concluded that three-body terms are needed in the potential interaction and that the He–rare-gas pair potentials may need further refinement.

Kosloff and Cerjan [29] investigated He scattering from a Xe overlayer on Ag, where both the surface and gas are treated quantum mechanically using a type of mean-field approximation for the coupling of the translating particles to the surface. They found that the qualitative features of the gas–surface interaction, such as strong inelastic backscattering and resonant adsorption, can be understood reasonably well by this model. However, the model is very restrictive, as it uses a one-dimensional surface.

Recently, Bittner and Light [30] used a similar mean-field approach to study He scattering from Xe overlayers adsorbed onto Ag substrates. In this study, a stochastic representation of the quantum density matrix is used to study atom–phonon interactions. The wavefunctions for the atomic scattering degrees of freedom were propagated under a mean-field Hamiltonian that included a stochastic, temperature-dependent potential term due to thermal motion of the surface atoms. It was concluded that three-body effects played an important role in this system, and that the phonon-mediated effects also played an important role in the collisional dynamics and need to be included before making a detailed comparison between theory and experiment.

In this paper, we will for the first time do a theoretical study of He scattering from the bare NaCl and the Kr/NaCl system using the *R*-matrix propagation method to solve the close coupling equations [15]. Our intent was to verify the structure of the overlayer, and in the process demonstrate the effectiveness of the *R*-matrix method in solving such complex and highly corrugated overlayer systems. In order to do this, we will directly compare theoretical relative diffraction intensities derived from the calculated *S*-matrix elements with experimental relative intensities.

3. Theory

3.1. Potential model

For both examples considered in this paper the substrate is the NaCl ionic crystal. In these crystals the electrons are well localized near the ions, so that the interaction potential is a strong function of the lateral position above the surface. In general, the surface potential is a periodic function of the surface coordinates; its Fourier expansion in terms of the reciprocal lattice vectors G_{mn} is given as

$$V(\boldsymbol{R}, z) = \sum_{m,n=0,\pm1,\pm2,\ldots} v_{mn}(z)\, \mathrm{e}^{\mathrm{i} G_{mn} \cdot \boldsymbol{R}} \qquad (1)$$

$$v_{mn}(z) = A^{-1} \int_{\mathrm{unit\ cell}} V(\boldsymbol{R}, z)\, \mathrm{e}^{-\mathrm{i} G_{mn} \cdot \boldsymbol{R}}\, \mathrm{d}R, \qquad (2)$$

where $\boldsymbol{R} = (x, y)$ and $\boldsymbol{G}_{mn}$ is defined using the lattice constants (a_x, a_y) as

$$\boldsymbol{G}_{mn} = \left(\frac{2\pi m}{a_x}, \frac{2\pi n}{a_y}\right). \tag{3}$$

In the NaCl case, the periodic potential is highly 'corrugated'; placing an overlayer on top of this substrate only exacerbates this corrugation. In order to describe such a potential, the interactions between the scattering atom and the surface atoms are normally represented as an expansion over progressively higher-order interactions, consisting of a sum over pair potentials plus a sum over three-body potential functions and so on. In the case of the inert gases, with which we are concerned here, this expansion can often be quickly truncated. Using only the sums of pair potentials and the Axilrod–Teller–Muto triple-dipole interaction [31], the properties of the He–rare gas monolayer interaction can be reasonably explained. However, the interaction of He with the NaCl substrate must also be considered. Again, the interaction can be represented as a sum over two-body pair potential terms plus a McLachlan multibody interaction term [32] (see Gibson and Sibener [26,33]).

To first order, the interaction potential is given by a pairwise additive model, i.e.

$$V(R, z) = \sum_i U(r - R_i). \tag{4}$$

$V(R, z)$ is the sum of the He–rare gas or He–substrate pair potentials $U(r)$, for all the atoms in the overlayer or substrate, at positions R_i.

The method used for determining the Fourier components $V_G(z)$ for the superposition of pair potentials is described by Steele [34]. The result is

$$V_G(z) = \frac{2\pi}{a_c} \sum_\alpha \int_0^\infty \{J_0(Gt) U[(z_\alpha^2 + t^2)^{1/2}]\} t \, dt, \tag{5}$$

where a_c is the area of the unit cell, J_0 is the zero-order Bessel function, U is the pair-potential and z_α is the height of the He atom from the surface layer α. We used Eq. (5) to calculate the pair potential interactions for both the overlayer and the substrate.

Depending on the level of accuracy desired, one could choose any of a number of commonly used pair potentials (i.e. Lennard–Jones, Morse,

Yukawa, etc.). However, since the outcome of a scattering event may depend very sensitively on the exact form and value of the interaction potential, especially at low incident energies, we will consider slightly more sophisticated potential interaction models, such as the Hartree–Fock plus damped dispersion (HFD) [6–8] for the He–rare-gas overlayer interaction, and the simplified Fowler Hutson (SFH) [27] potential for the He–NaCl interaction. The HFD pair potential is parametrized as follows:

$$V_{HFD}(r) = V_{HF}(r) + F(r) V_D(r)$$

$$V_{HF}(r) = A \exp(-\alpha r)$$

$$V_D(r) = -\sum_{n=0}^{4} C_{2n+6} r^{-(2n+6)}$$

$$F(r) = \exp[-(Dr_m r^{-1} - 1)^2] \quad r \leq Dr_m$$

$$F(r) = 1 \quad r \geq Dr_m. \tag{6}$$

The damping parameter D is held fixed at 1.28. To fit the pair potential, the adjustable parameters r_m and C_8 were obtained from multiproperty fits to experimental data by Keil and co-workers [35,36].

A simplified version of the potential neglects higher-order dispersion terms, which result in cancellation of the Axilrod–Teller potential. This version, the SFH potential [27], can be written as

$$V(r) = \sum_{js} v_{surf}^{(s)}(r - R_j - S_{ls}) + \sum_{l \geq 2}^{jls} v_{bulk}^{(s)}(r - R_j - S_{ls})$$
$$- \frac{1}{2} \alpha |E(r)|^2, \tag{7}$$

where the index j labels the surface unit cells, and R is the center of the jth surface unit cell. The indices l and s mark the layer ($l = 1, 2, 3, \ldots l = 1$ denoting the first surface layer) and the ion sort ($s = 1, 2$). Here the third term is the dipole interaction with the electric field E caused by the lattice of ions and the He dipole polarizability α.

The first term is the sum of the pair potentials over the ions of the first surface layer ($l = 1$) only with

$$v_{surf}^{(s)}(r) = A^{(s)} e^{-b^{(s)}r}$$

$$- \sum_{n=3}^{5} \left\{ 1 - \sum_{k=0}^{2n} \frac{[b^{(s)}r]^k k!}{e^{-b^{(s)}r}} \right\} \frac{C_{2n,surf}^{(s)}}{r^{2n}}. \tag{8}$$

The second term is the sum of pair potentials between the He atom and the ions in the deeper layers with

$$v_{\text{bulk}}^{(s)}(r) = -\sum_{n=3}^{5} \frac{C_{2n,\text{bulk}}^{(s)}}{r^{2n}}. \qquad (9)$$

The Eq. (9) contribution need only be known for relatively large distances r, since the distance of approach of the incident He atom is several angströms above the plane of the substrate. Thus the damping is not significant and can be neglected. The parameters used for the He–NaCl case were proposed by Eichenauer and Toennies [37].

The three-body terms (1) between He–adsorbate–adsorbate and (2) He–adsorbate–substrate were included in our potential model. Although it was found that the three-body terms are rather small, these terms can have a noticeable effect for some surface systems, as stated in Section 2 [31,32].

3.2. R-matrix methodology

We now apply the R-matrix propagation method [15] to the surface scattering problem of elastic atom diffraction from perfectly periodic surfaces. The R-matrix approach has been successfully applied in the past to reactive scattering problems [16–20]. However, to do atom–surface scattering, we must use an extension of the R-matrix methodology to inelastic problems, as first applied by Stechel and co-workers [15,38]. Since we are dealing with elastic scattering, one has energy exchange between perpendicular and parallel atom translational degrees of freedom. The channels are labeled by the outgoing parallel momentum or the indices of the reciprocal lattice vectors. Thus, in this sense, the elastic atom–surface scattering problem is formally like an inelastic gas-phase scattering problem.

In the inelastic formalism of Stechel et al. [15] the R-matrix propagation method is applicable to any system of coupled second-order linear differential equations of the matrix form

$$\frac{\partial^2}{\partial z^2} G_n(z) = \sum_{n'=1}^{N} W_{nn'}(z) G_{n'}(z). \qquad (10)$$

As one can see, the close coupling equation obeys this form. Here, the functions $G(z)$ are the translational scattering functions and W, the coupling matrix, is given in the particular case of atom–surface scattering (i.e. elastic model) as

$$W_{nn'}(z) = \frac{2m}{\hbar^2} V_{n'-n}(z) - \delta_{n,n'} k_z^2. \qquad (11)$$

Here, the total wavefunction is expanded in an orthonormal basis of Bloch functions, which results in a real symmetric coupling matrix.

In this R-matrix propagation scheme the propagation of the solution vector from an initial to a final value has been accomplished by dividing the entire integration range into suitably short intervals called 'sectors', where the center of the sector is $z(i)$ and its width is $h(i)$. By diagonalizing the coupling matrix at the center of each sector, we transform from the Fourier basis to a new representation called the 'F representation'. We assume the coupling matrix W is constant ($W' = 0$) over the width of sector (i). The sector-dependent (but, within a sector, coordinate independent) transformation eliminates all coupling in the differential equations.

Within a given sector (i), we adopt the following notation for the values of the translational functions at the right and left boundaries of the sector:

$$F_{\text{L}}(i) = F^{(i)}(z_i - \tfrac{1}{2}h_i) \quad F_{\text{R}}(i) = F^{(i)}(z_i + \tfrac{1}{2}h_i). \qquad (12)$$

The sector R matrix $r(i)$ for sector (i) in the locally diagonal representation is

$$\begin{bmatrix} F_{\text{L}}(i) \\ F_{\text{R}}(i) \end{bmatrix} = \begin{bmatrix} r_1^{(i)} & r_2^{(i)} \\ r_3^{(i)} & r_4^{(i)} \end{bmatrix} \begin{bmatrix} -F_{\text{L}}'(i) \\ F_{\text{R}}'(i) \end{bmatrix}. \qquad (13)$$

To ensure the continuity of the total wavefunction and its normal derivative at each sector boundary, we transform from the $F(i-1)$ representation to the Fourier basis and back to the $F(i)$ representation. We have

$$F_{\text{R}}(i=1) = Q(i-1, i)F_{\text{L}}(i)$$

$$F_{\text{R}}'(i-1) = Q(i-1, i)F_{\text{L}}'(i)$$

$$Q(i-1, i) = \tilde{T}^{(i-1)} T^{(i)}. \qquad (14)$$

Note that the transformation matrices T are orthogonal, implying that Q is also orthogonal. The R matrix propagation scheme assembles the sector R

matrices defined in Eq. (13) recursively, starting near the origin and working outwards towards asymptotic configurations. At each iteration, a new global R matrix is obtained by assembling a new sector R matrix with the old global R matrix [39].

$$R^{(i)} = r_4^{(i)} - r_3^{(i)} z^{(i)} r_2^{(i)} \tag{15}$$

$$z^{(i)} = [r_1^{(i)} + \tilde{Q}(i-1, i)R^{(i-1)}Q(i-1, i)]^{-1},$$

where $Q(i-1, i)$ is the transformation matrix that takes the diagonal basis in sector $(i-1)$ to that in sector (i).

We now describe how the S-matrix is obtained from the R-matrix. The R-matrix is defined as the asymptotic wavefunction divided by the derivative of the asymptotic wavefunction:

$$R = \frac{\psi}{\psi'} = \frac{(I - OS)}{(I' - O'S)}, \tag{16}$$

where the diagonal matrices I and O are the incoming and outgoing flux normalized plane waves:

$$I = \frac{1}{\sqrt{k_z}}\, e^{-ik_z z}, \quad O = \frac{1}{\sqrt{k_z}}\, e^{ik_z z}, \tag{17}$$

where k_z is the incident wavevector normal to the surface. S is the appropriate S-matrix element for that channel.

With some manipulation of the above equations one obtains [40]

$$S = a - 2ib^{\dagger}(R - c)^{-1}b, \tag{18}$$

where

$$a = I'O'^{-1} \tag{19}$$

$$b = O'^{-1} \tag{20}$$

$$c = OO'^{-1}. \tag{21}$$

3.3. Advantages of the R-matrix methodology

In this section, the R-matrix approach is compared with other exact quantum methods. Both time-independent and time-dependent quantum methods have previously been employed to atomic scattering from overlayer-covered surfaces [10,21,24,26,28–30,66]. Considering only time-

independent methods for the moment, we find that there are two main types: basis set and propagation methods. Compared with basis set methods (e.g. S-matrix KVP [41], log-derivative KVP [40]) for solving the time-independent Schrödinger equation, propagation methods are more efficient when scattering results are needed at a single energy. Thus the CPU time scales as $N_x^3 N_y^3 N_z$ for a propagation method, and $N_x^3 N_y^3 N_z^3$ for the basis set methods — although basis set methods may be more effective when results for multiple collision energies are desired.

The development of suitable time-dependent methods has seemed to lag behind other techniques for particle scattering. For systems in which only a relatively small number of channel states is involved, such as the case where we have low incident energies, the time-independent close coupling method is definitely more efficient computationally than time-dependent propagation of a wavepacket. Moreover, one loses some of the dynamical insight and control that can be obtained by using coupled channel (CC) treatments. This presumed extra efficiency and effectiveness of the CC method for diffractive scattering at a single energy is well established [42]. However, the cost of obtaining probabilities for an additional collision energy using the CC method is substantial, whereas the cost for wavepacket propagation is almost negligible.

Considering only methods for solving the CC equations, there is a variety of methods to choose from. The following methods have been employed to find scattering information for overlayer systems: log-derivative method [43], variable-interval–variable step integrator of Parker et al. [44], homogeneous integral solution method [45], Numerov method [46] and the R-matrix method [15]. Of these methods, the R-matrix method has been extensively used in applications that involve scattering systems [16–23].

In the following work we use the R-matrix propagation method, since it has several inherent advantages that allow it to be an ideal method for solving problems that involve scattering from overlayers. Besides having the efficiency scaling of a propagation method, the R-matrix method is a potential-following method, and thus has an advantage in the region where the potential does

not vary greatly over the boundaries of the scattering coordinate. Consequently, very few steps are required by this methodology, resulting in a significant saving in computation time. Also, this method involves only real multiplications and diagonalizations because we can use a representation in which the coupling matrix is real symmetric. This can be a significant saving in computational time over other close-coupling methods. Besides these inherent advantages, we also have an added advantage in this case of symmetry adaptation. We discuss the use of symmetry adaptation in the Section 3.4.

3.4. Symmetry adaptation

We now describe how we applied symmetry adaptation to our scattering formalism. In our case, symmetry adaptation is possible because the incident beam is along the X axis, so that we can exploit the reflection symmetry along the Y axis. Basically, we transformed from the Fourier basis in Y to a symmetric basis. Since the Hamiltonian in this basis is block diagonal, the R-matrix is also block diagonal since the R-matrix is derived from the eigenvectors of the Hamiltonian. The following is a representation of the symmetry-adapted R-matrix:

$$R^{cs} = \begin{pmatrix} R^c & 0 \\ 0 & R^s \end{pmatrix}, \tag{22}$$

where 'cs' indicates cosine–sine basis, and 'f' indicates Fourier basis. It should be noted that only the column of the S-matrix with an asymptotic incoming state labeled zero has physical significance for our class of problems. Thus, instead of using b on the right-hand side of Eq. (18), we use the following vector:

$$b_o = \begin{pmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{pmatrix} \frac{-i}{\sqrt{k}} \, e^{ikz}, \tag{23}$$

where the '1' is placed in the $g_x = 0$ and $g_y = 0$ position, since this is the reciprocal lattice vector

of the physically relevant incident beam. In order to use symmetry adaptation with Eq. (18) we must insert the unit matrix made up of the transformation matrix and its adjoint on both sides to transform the matrices involved from the Fourier basis to the cosine–sine basis. The final result is

$$S_{n,0} = a = 2ib^{\dagger f} T^{f,cs} (R^c - c^c)^{-1} b_o. \tag{24}$$

Since only the $(0, 0)$ column of the S-matrix is computed, we find that only the cosine part multiplies the b_o vector to obtain a nonzero answer. Thus, we have reduced the problem involved to include only the cosine part of the R-matrix to find the S-matrix. If only the cosine basis is used in the propagation, CPU time is reduced by a factor of almost eight and we reduce the number of elements of the R-matrix by approximately four.

3.5. Inelasticity: Debye–Waller factor

In reality the surface is not rigid, as is assumed in the elastic model. Realistically, the projectile and target exchange some energy, and thus there is error introduced by the elastic model. To date, however, the complete treatment of the complex problem of inelasticity is still far from applicable to realistic cases [47,48]. In the simplest practical case, we consider the reduction of elastic intensities from a static potential model caused by many phonon contributions. A thermal attenuation of coherent elastic diffraction peaks is qualitatively explained by introducing the Debye–Waller factor. This theoretical correction is well known in X-ray and neutron diffraction, where the Debye–Waller factor relates the diffraction intensities at $T = 0$ and $T = T'$ by [49]

$$I_G^{T'} = I_G^0 \, e^{-2W}, \tag{25}$$

where

$$2W = (\Delta k_z)^2 \langle U_z^2 \rangle. \tag{26}$$

Here, Δk_z is the momentum transfer perpendicular to the surface:

$$\Delta k_z = \left(k_i^2 \cos^2 \theta_i + \frac{2m\epsilon}{\hbar^2} \right)^{1/2}$$

$$+ \left(k_i^2 \cos^2 \theta_f + \frac{2m\epsilon}{\hbar^2} \right)^{1/2}. \tag{27}$$

This formula, which was derived by Beeby [50], takes into account the presence of the attractive well, where ϵ is the average well depth of the atom surface potential and m is the mass of the incident atom. Also, using the Debye crystal model we obtain the effective vibrational amplitude as

$$\langle U_z^2 \rangle = \frac{3\hbar^2}{k_B M \theta_s} f\left(\frac{\theta_s}{T_s}\right), \tag{28}$$

where k_B is the Boltzmann constant, M the mass of the surface atom, θ_s the Debye surface temperature, T_s the temperature of the surface, and $f(\theta_s/T_s)$ is defined by

$$f\left(\frac{\theta_s}{T_s}\right) = \frac{T_s}{\theta_s}\left(\frac{T_s}{\theta_s}\int_0^{\theta_s/T_s} \frac{t\,dt}{e^t - 1} + \frac{1}{4}\frac{\theta_s}{T_s}\right). \tag{29}$$

which approaches $\frac{1}{4}$ and T_s/θ_s for $T_s \ll \theta_s$ and $T_s \gg \theta_s$ respectively. It has been shown by Coulomb et al. [51] that higher-order corrections to Eq. (25) contribute less than 1% to the total. This Debye–Waller factor was applied to both the He/NaCl and He–Kr/NaCl systems.

4. Results and discussion

Results are obtained for two systems: (1) He/NaCl and (2) He–Kr/NaCl. The following results were all calculated at an incident energy of 17.1 meV and at an angle of 50° from the normal with direction $\langle 110 \rangle$. Since this is a low energy calculation, the results are more sensitive to the fine details of the surface interaction potential. Although the rare-gas overlayer systems are generally more difficult to model than the simple He/NaCl system, in comparison with other possible atom–surface scattering problems, the rare-gas overlayer potential models might be better known since the pair potential interactions are well known from gas-phase experiments. It can be concluded that the results will show up the inadequacies of the potential model defined in Section 3.1. Also, the close-coupling calculations needed to obtain diffraction data are less expensive at low incident energies, since fewer channels are needed to obtain convergence. Besides this, the

incident direction was chosen for symmetry reasons, allowing us to reduce the size of the calculation further. Therefore, the results will allow us an easy and quick demonstration of the effectiveness of the *R*-matrix method in obtaining fast and accurate results for our chosen scattering problems. Finally, low incident energy gives rise to substantially less inelastic scattering, so we may expect that the inelasticity can be reliably taken care of by the Debye–Waller factor.

The He/NaCl system is historically an interesting system since the alkali halides were the first single crystals from which atomic diffraction was observed. In more recent times the He/NaCl system has been extensively studied by numerous groups [52–55]. We have studied this system since it is, theoretically, the simpler of the two systems, and it will serve as an excellent test to determine whether the part of the theory used to calculate the *S*-matrix is programmed correctly. The added complexity in the potential of the overlayer system induces other complications into the results.

In Table 1 the probabilities for the in-plane channels were normalized by taking the probability for a particular channel and dividing by the sum of all the in-plane channel probabilities. If one looks at these He/NaCl ratios one finds that they all compare reasonably with experimental ratios. This suggests that the program is in fact working and that the potential surface routine for this system is reasonable. To check whether inelastic effects were significant, we included a Debye–Waller factor. Here, we corrected each channel with its appropriate Debye–Waller factor and

Table 1
Normalized scattering intensities for channels along the *X*-axis for He/NaCl. Comparison is made between the theoretical probabilities, the Debye–Waller (D–W) corrected theoretical probabilities and the experimental values by De Kieviet et al. [9]

Channel	Experimental	Theoretical	D–W corrected
(0, 0)	0.28	0.28	0.30
(−1, 0)	0.36	0.37	0.37
(−2, 0)	0.24	0.24	0.22
(−3, 0)	0.080	0.081	0.077
(−4, 0)	0.032	0.031	0.029
(−5, 0)	0.0019	0.0023	0.0024

added up the results of all the channels. Then the individual corrected channels were divided by the total sum of the corrected channels, just as was done to obtain the normalized channel probabilities. The procedure allows some of the resulting Debye–Waller-corrected channels to have values greater than their uncorrected values. We observe in Table 1 that, for the He/NaCl system, the Debye–Waller factor really has no effect. We conclude that the theory was successful in describing the He/NaCl system.

We now consider the Kr/NaCl system. The growth of the Kr overlayers on various substrates has been investigated previously. Most of these efforts focus on a Kr adsorption pattern with triangular symmetry. Examples are Kr on Pt(111) [56], Ge(111) [57] and the previously mentioned Kr/C(0001) [10,66]. Only a few reports exist on the physisorption of Kr adlayers on top of square substrates. For He scattering on square metal surfaces we have found only Cu(110) and Cu(100) [58,59,68] in the literature. Camillone et al. [60] studied the case of Kr on LiF(001). The lattice spacing and corrugation of this alkali halide appear to be of little importance to this noble gas. In this case the adsorbate–substrate interaction is not sufficient to establish orientational order. Finally, we mention Jordan et al. [61], who wanted to grow a Kr overlayer that was square and commensurate with the symmetry of the bulk. They chose MgO, which has (1) square symmetry, (2) available adsorption sites with a next nearest neighbor separation that matches the Kr—Kr distances in the bulk solid fairly well, and (3) a large corrugation that may introduce enough of an energy barrier to 'pin' down the adatoms at these adsorption sites. Even with these properties the overlayer structure in this case is triangular and incommensurate. Given the fact that krypton does not form a square overlayer on MgO, could it be expected that Kr/NaCl(001) has a square structure?

It was found by De Kieviet et al. [9] that Kr was not only commensurate on NaCl, but that this physisorbed noble gas structure has square symmetry! In this case, the Kr atoms are adsorbed exactly above the Na ions. It has also been determined experimentally by De Kieviet et al. [9] that there is a 1.65% increase over the corresponding values of the lattice constant for the bare crystal. Domains of Kr atoms commensurate with the NaCl therefore form due to this small misfit. In fact, these domains have approximately a diameter of 30 unit cells of NaCl. Because of the Kr being adsorbed commensurate with the NaCl, we find that the Kr overlayer gives Bragg peaks at nearly the same positions as the substrate does, and no extra diffraction peaks.

However, this system is more complex than the bare NaCl system since there is an overlayer added symmetrically to the bare NaCl system, which involves a more complicated potential. Getting accurate results for this He–Kr/NaCl system would give us reason to believe that the potential model is sufficiently able to describe reasonably the complicated interactions involved with these overlayer systems. In Table 2 we show the normalized probabilities for the He–Kr/NaCl. In this particular case the two probabilities [i.e. the $(-1, 0)$ and the $(-5, 0)$] do not compare as well with experiment. Generally speaking, there is good enough correspondence between theoretical and experimental results to conclude that we are theoretically describing the He–Kr/NaCl system correctly.

These discrepancies are probably the result of inaccuracies in the potential model. In fact, it can be shown that there are 'holes' in the potential. There are two large holes per unit cell (i.e. $\frac{1}{2}$ hole per side) that are the result of the Kr atoms being on top of the Na ions. Between the Kr atoms the contour lines of the potential dip far inwards, even below the Na ion level. As a result, our potential

Table 2
Normalized scattering intensities for channels along the X-axis for He–Kr/NaCl. Comparison is made between the theoretical probabilities, the Debye–Waller (D–W) corrected theoretical probabilities and the experimental values by De Kieviet et al. [9]

Channel	Experimental	Theoretical	D–W corrected
$(0, 0)$	0.095	0.10	0.15
$(-1, 0)$	0.30	0.18	0.19
$(-2, 0)$	0.30	0.33	0.28
$(-3, 0)$	0.15	0.18	0.15
$(-4, 0)$	0.091	0.090	0.082
$(-5, 0)$	0.061	0.12	0.14

model is seemingly inadequate for describing these holes. In fact, our potential channels open up far into the classically forbidden region of the laterally averaged potential, which is, in fact, unphysical. We have attempted to fix this problem artificially by adjusting the size of the off-diagonal Fourier components of the Hamiltonian in the repulsive region. Although it appears that these holes play an influential role in the discrepancies found in our results, our attempt gave minimal improvement to the scattering probabilities.

Such problems with the overlayer system interaction potential are the result of assumptions associated with its calculation. First, as stated earlier, the nonadditive three-body or many-body terms can have a significant effect on the potential. It is believed that the elastic scattering of He from ordered rare gas surfaces could yield information about the nature of the multibody expansion of the He–surface potential; i.e. which higher-order terms should be included in the potential expansion, and about the magnitude of these terms. However, we have not carried out a systematic study of the sensitivity of resonance spectra to the potential parameters, but this may be a possible next step. For further details of how such a study may be done, see papers by Hutson and co-workers [21,62–65,69]. Next, there is still some question about estimating the overlayer height above the substrate. This may not be as straightforward as stated in the paper by De Kieviet et al. [9]. Finally, there is the crucial question about the remaining uncertainties in the currently accepted He–Kr pair potential. Since the sum over pair potentials is the most significant part of the total He–surface potential, even fairly small errors in them can cause noticeable errors in our calculated results.

Another possible reason for the discrepancies, as mentioned earlier, is that experimentally there are domains, rather than an infinite overlayer surface. This can cause small changes in the final intensities. In fact, the resulting intensities will be shifted towards those of the bare NaCl. This is because there will be scattering off the bare NaCl substrate between the Kr overlayer domains, which will add to the 'NaCl peaks' and subtract from the other parts of the Kr/NaCl spectrum. Also,

depending on the growth conditions, the overlayer structure may not be as perfect as the substrate.

Another possibility is that, in the case of a physisorbed system like Kr/NaCl, both the inter- and the intra-layer bonds are much weaker than that of the ionic crystal and thus are subject to more inelastic effects. Again, we attempted to use the Debye–Waller factor. The Debye–Waller factor of a physisorbed overlayer (i.e. Kr/NaCl) should be larger than that of the ionic crystal NaCl. We observe in Table 2 that the Debye–Waller correction does not appreciably improve the results, and for some channels actually makes the results worse. Since it appears that the Debye–Waller factor did not improve the results, it may be inappropriate for these two systems. However, the Debye–Waller factor correction may not work for a variety of reasons. For example, He atom scattering from surfaces usually has a long interaction time, where there is interaction with many atoms simultaneously. Since the surface vibrational amplitude is averaged over the interaction time we may expect a lower value for W if it is calculated correctly. A lower W means more resemblance to elastic scattering using the Debye–Waller correction and thus less reduction in intensities.

5. Conclusion

The main goal of this paper was to obtain theoretical results on some interesting atom–surface scattering applications. We have, in fact, obtained results on two systems of current interest to surface scientists. Certainly our results for He–Kr/NaCl are reasonable enough to conclude that it does in fact have square symmetry. It is the uniqueness of this system's structure that makes it so interesting. Also, in the process of obtaining these results we have demonstrated the effectiveness of the R-matrix method by Stechel et al. [15] in being able to obtain an accurate and efficient solution to these problems. We have demonstrated that the R-matrix method is accurate since we obtained excellent agreement for the He/NaCl system when compared with experiment. Also, the R-matrix method is very fast for calculating single-energy problems: the He–Kr/NaCl prob-

lem, which involves ~ 100 channels, was calculated in ~ 20 min on an SGXL8000 Challenger.

Besides accessing the effectiveness of the *R*-matrix method, this work also allows us to make judgement about the 'realism' of the elastic model (i.e. CC representation) that we used in order to simplify the application and save computational effort. In this particular case we expect the elastic model to be a reasonable approximation. This is because good crystalline surfaces can be made experimentally that allow a perfectly periodic surface approximation to be good. Also, in our case the problems were done at low incident energy and low temperature, so that, typically, surface phonon vibrations are not excited. Thus the approximation of a rigid surface may be reasonable. However, it should be stated that, in the case of overlayer systems, inelastic effects are more prominent and may be too significant to neglect. Thus we applied the Debye–Waller factor to our results.

If the *R*-matrix method is accurate and the elastic model is appropriate in these particular cases, then it can be concluded that most of the resulting error is probably due to the potential model as stated in Section 4. Nonetheless, if one considers the results overall, it is evident that there has been great progress in developing numerically 'exact' mathematical models necessary to describe the physics and chemistry behind these complicated systems. This is evidenced by the fact that our models can very accurately describe some real physical systems, like He/NaCl. However, since our model is not 'reality', there is always room for improvement, especially with the more complex systems such as He–Kr/NaCl.

Acknowledgements

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