

## EFFECTS OF ISOLATED IMPURITIES ON ATOM SCATTERING FROM CRYSTALLINE SURFACES—EXACT QUANTUM-MECHANICAL CALCULATIONS

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A recent method for time-dependent wavepacket scattering calculations is applied to He scattering from a Cu surface with isolated Ar impurities. Several effects are found. (i) broad tails superimposed on each diffraction spike; (ii) shallow impurity rainbow maxima; (iii) impurity—surface interference peaks. A sudden approximation is applied to the interpretation of the newly found features.

### 1. Introduction

Molecular beam scattering, in particular of He atoms, has emerged in recent years as one of the most powerful probes of the structure of crystalline surfaces [1,2]. Essential in this development has been the progress in calculations of diffraction intensities from the atom—surface interaction potential [2–6]. The complexity of such calculations can be considerable when the number of diffraction channels is large [4], but within the rigid surface assumption the basic scattering theory is well understood for the crystalline case, and the available calculation methods are effective [2–6]. In comparison with this, atom scattering from disordered or impure surface is a *tara incognita*. The same reasons that render He an extremely useful probe of crystalline surfaces hold also for disordered systems: Adequate de Broglie wavelength, lack of penetration beyond the surface layer, etc. [1]. However, adequate tools of interpretation and calculation for such systems are not yet available. All the numerical methods treating scattering from crystalline surfaces use the discreteness of the set of diffraction states [2]. When surface periodicity breaks down, the corresponding set of states forms a continuum. We treat here atom scat-

tering from surfaces with adsorbed impurities, using a method that avoids the continuum basis difficulty. The method involves numerical solution of the time-dependent Schrödinger equation for wavepacket scattering. In addition to demonstration of the method, a major aim of this letter is to determine the main impurity effects on the intensity pattern. Previous studies on effects of disorder or impurities on scattering from surfaces [7–10] were confined by method to very special cases, e.g., step disorder [9,10], using approximations that may be uncertain. A recent study [9] examined the scattering pattern for several model types of disorder, but was limited to the sudden approximation.

### 2. Method and model system

Wavepacket calculations do not involve expansion in a diffraction-state basis, which avoids difficulties due to continuum of such states for impure surfaces. In solving the time-dependent Schrödinger equation  $i\hbar\partial\psi(r, t)/\partial t = [-(\hbar^2/2m)\nabla^2 + V(r)]\psi(r, t)$  by time-propagation from a suitable initial value  $\psi(r, t_0)$ , the main difficulty is to compute  $\nabla^2\psi(r, t)$  accurately and efficiently for every point  $r$  at each time step. We employ the Fourier-transform method for

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this purpose [11]: a fast-Fourier-transform (FFT) algorithm is used to transform  $\psi(\mathbf{r})$  to  $k$  space. The transform  $\tilde{\psi}(\mathbf{k})$  is multiplied by  $-k^2$ , representing the action of  $\nabla^2$  in  $k$  space, and the result is back-transformed by FFT to yield  $\nabla^2\psi(\mathbf{r}, t)$  in  $\mathbf{r}$  space. Calculations of  $H\psi(\mathbf{r}, t)$  in this method increase with the number of  $N$  of grid points in  $\mathbf{r}$  space only as  $O(N \ln N)$ . The time integration is carried out by conventional second-order differences. Details of the method, and applications to molecular collisions [12] and scattering from crystalline surfaces [13] are found elsewhere [11–13]. The impure surface for which the calculations were done is a model of Ar at low coverages on Cu. The isolated impurity limit was used with the wavepacket scattered from a single Ar on an extended segment of the surface. A one-dimensional model surface was used, the corrugation chosen to represent that of a corresponding line on the Cu surface. The collision dynamics of the incoming atom is then confined to a single plane ( $z, x$ ),  $z$  denoting the distance from the surface and  $x$  the coordinate along the surface. The interaction between He and the impure surface was taken as:

$$V(z, x) = V_{\text{ps}}(z, x) + V_{\text{A}}(z, x) \quad (1)$$

where  $V_{\text{A}}([z - z_1]^2 + [x - x_1]^2)^{1/2}$  is the He–Ar potential taken from gas-phase data [14].  $x_1, z_1$  give the site of the Ar atom on the surface. Calculations for several sites were carried out to examine the scattering sensitivity to the impurity location.  $V_{\text{ps}}(z, x)$  is the interaction between He and the pure Cu surface, modelled in the Lennard-Jones–Devonshire form [1]:

$$V_{\text{ps}}(z, x) = V_0(z) + \beta V_1(z) \cos(2\pi x/a), \quad (2)$$

where  $V_0(z) = D[\exp(-2\alpha z) - 2 \exp(-\alpha z)]$ ,  $V_1(z) = D \exp(-2\alpha z)$ , with parameter values (in atomic units)  $D = 0.000234$ ,  $\alpha = 0.6$ ,  $a = 4.8378$  [6]. The corrugation parameter was taken as  $\beta = 0.05$ . The initial wavepacket was taken as  $\psi(z, x, t_0) = \exp(ik_x x) \times \exp[ik_z(z - z_0)] \exp[-A(z - z_0)^2]$ , i.e. an extended wave in the  $x$  direction and a localized packet in  $z$ . In principle, the results obtained with this need to be transformed to correspond to the usual plane-wave incoming condition. In fact,  $A$  was taken small ( $\frac{1}{7}$  bohr $^{-2}$ ), the  $z$  dependence was almost that of a delocalized wave, and it was tested and shown that transformation of the results is unnecessary. Integration proceeded from  $t_0 \rightarrow -\infty$  ( $z_0$  outside the interaction range) to

$t \rightarrow -\infty$  when the scattered wave has left the range of the potential. Computing time on VAX 750/11 was  $\approx 100$  min per collision event, but is only  $\approx 8$  min on the FPS 1

### 3. Results

Calculations were carried out over a range of incidence energies and angles, and for several site locations of the impurity. We show here only results for normal incidence, collision energy 0.000315 au, and impurity site  $x_1 = \frac{1}{2}a$  ("between" two surface atoms). More extensive results will be published elsewhere [15]. Fig. 1 shows the calculated scattering intensities as a function of  $\Delta k_x$ , the momentum transfer parallel to the surface. The observed features were interpreted by examination of the numerically obtained wavepackets, and also by qualitative insight from the sudden approximation [16,17]. This high-energy approximation offers a simple expression for the scattering intensities. It was applied to scattering from crystalline surfaces [16,17] and, recently, also from disordered surfaces [9]. At the relatively low energies of the calculations here the sudden should only be applied qualitatively. The sudden scattering intensities are

$$I(k_x \rightarrow k'_x) = \left| \frac{1}{2L} \int_{-L}^L \exp(i\Delta k_x x) \exp[2i\eta(x)] dx \right|^2, \quad (3)$$

with  $L \rightarrow \infty$ .  $\hbar k_x, \hbar k'_x$  are the initial and final momenta

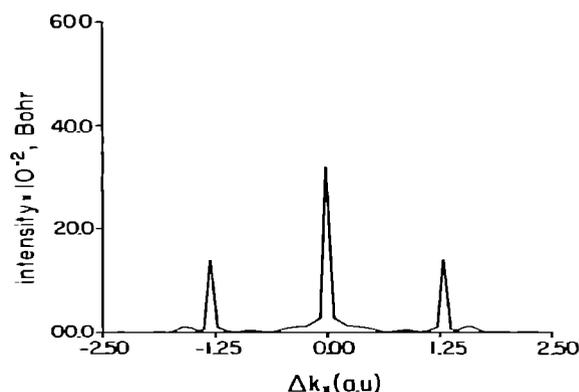


Fig. 1. Scattering intensity versus momentum transfer  $\Delta k_x$ : Results are for He scattered from a (corrugated) Cu surface with an Ar impurity. Collision energy is 0.000315 hartree.

in the  $x$  directions,  $\Delta k_x = k'_x - k_x$   $\eta(x)$  is given by

$$\eta(x) = \int_{z_t}^{\infty} \{ [k_z^2 - (2m/\hbar^2)V(z, x)]^{1/2} - k_z \} dz - k_z z_t \quad (4)$$

$\hbar k_z$  is the initial  $z$ -direction momentum,  $z_t$  the classical turning point. Interpretation involves stationary phase evaluation of (3), but details will not be given here. The main effects seen in fig. 1 and their interpretations are. (1) The diffraction and specular spikes of the pure surface prevail, but a broad shallow background peak is superimposed on each diffraction line. (The width of the diffraction spikes in fig. 1 is numerical, due to the finite sampling grid. The grid can be refined as desired, but this was not of major importance for the purposes of the present study.) It is instructive to compare fig. 1 with fig. 2 showing the scattering intensities for the corresponding case of an impurity free Cu surface. Diffraction is due to the periodic part of the potential  $V_{ps}$  which yields constructive interference between scattering from some equivalent points on the surface and destructive interference otherwise. The impurity produces a localized corrugation  $V_A(x, z)$  causing scattering that interferes with some contributions from regions on neighbouring sites and gives rise to the hump. Stationary phase evaluation of (3) shows that intensity at  $\Delta k_x$  is due to scattering from points  $x_j$  such that  $\Delta k_x = -(\partial\eta/\partial x)_{x=x_j}$ . For a periodic po-

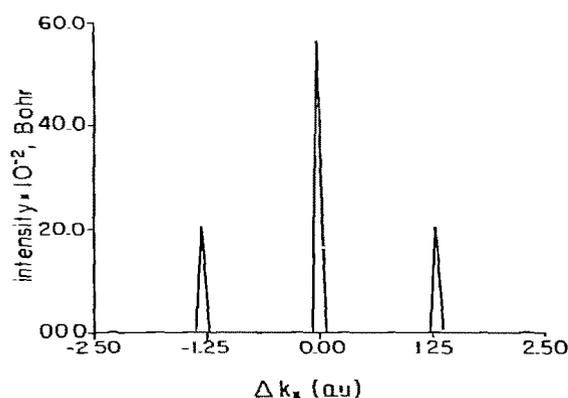


Fig. 2. Scattering intensity versus momentum transfer  $\Delta k_x$ : Results for He scattered from a pure, corrugated Cu surface. Collision energy is 0.000315 hartree. An unperturbed diffraction pattern is seen.

tential one can show that  $k_x = m2\pi/a$ ,  $m$  integer. Due to the localized impurity corrugation, constructive interference arises also for  $\Delta k_x = (m + q) 2\pi/a$ ,  $|q| < 1$ . The stationary phase result shows that the width of the hump around the diffraction line is directly related to the  $x$  dependence of  $V_A(x, z)$ . An impurity of weak local corrugation cannot contribute to large  $\Delta k_x$  so the width of the tails around the diffractions falls off with diffraction order. (2) Intensity peaks are produced at large  $\Delta k_x$  ( $\approx \pm 1.625$  bohr $^{-1}$ ). Comparison with calculations of an impurity on a flat Cu surface [ $\beta = 0$  in (1)], in fig. 3 show *these peaks are independent of surface corrugation*. The peaks are due to the scattering from the localized impurity corrugation. In the classical limit of the sudden such peaks are rainbows produced by the most corrugated  $x$  point around the impurity. Their weakness is due to the fact that only a single impurity is present. For  $\Delta k_x$  values for which no interference occur, a stationary phase analysis of (3) yields:

$$I(k_x \rightarrow k'_x) \propto |\partial^2 \eta / \partial x_r^2|^{-1},$$

where  $x_r$  obeys the stationary phase condition for  $\Delta k_x$ . The impurity rainbow occurs when the above intensity expression is *singular* (which holds only in the classical limit of the sudden). Quantum interference, greatly smooths the "singularities" to yield moderate maxima. (3) There are maxima between the specular and diffraction peaks ( $\Delta k_x = \pm 0.875$  bohr $^{-1}$ ). Calculations have shown that these shallow peaks are insensitive to pure surface corrugation. These peaks are due to interference

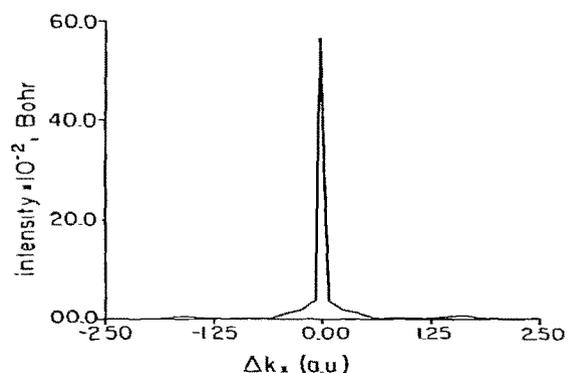


Fig. 3. Scattering intensity versus momentum transfer  $\Delta k_x$ : Results are for He scattered from a flat ( $\beta = 0$ ) Cu surface with an Ar impurity. Collision energy is 0.000315 hartree.

between reflection from the surface and scattering from the impurity. A detailed analysis will be given elsewhere [15]. Features (1) and (3) depend on impurity location with respect to the surface, (3) is sensitive to its distance  $z_1$  from the surface, (1) is sensitive to  $x_1$  mainly. *Scattering intensities thus contain useful, detailed information on impurity location.*

#### 4. Conclusion

Wavepacket calculations were shown to be a powerful tool in the study of atom scattering from impure surfaces. Several important impurity effects on the scattering were determined. The most interesting newly found features are the impurity-induced maxima, interpreted as rainbows, and as surface-impurity interference maxima. The exact calculations should be useful for testing approximations, but are also sufficiently efficient to be used directly in the analysis of experimental data. The fact that the calculations reported here are confined to a one-dimensional surface model may appear a serious limitation in this respect. However, preliminary results from the sudden approximation suggest that for the intensity distributions in the collision plane, a 1D surface model gives reasonable results, for systems of the type considered here. Extension of the "exact" calculations to a 2D surface model appears to us, nevertheless desirable, is feasible, and will be pursued soon. All this calls for experimental-theoretical collaboration in the near future.

We note that from a comment in a most recent article [18] we learned of unpublished work in progress by the authors on wavepacket scattering from impure surfaces.

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