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Comparison of 3D classical and quantum mechanical He scattering on Rh(3 1 1)

E. Balázs [a,b], G. Varga [a,*,1], L. Füstöss [a]

[a] *Budapest University of Technology and Economics, Institute of Physics, Budafoki út 8, H-1111, Budapest, Hungary*
[b] *Laboratory of Theoretical Physics at the Research Institute for Technical Physics and Material Science of HAS, P.O.B. 49, H-1525 Budapest, Hungary*

Abstract

He-clean Rh(3 1 1) scattering has been discussed within the frame of classical and quantum mechanics. These models of thermal energy atomic scattering on solid surfaces are based on the one particle problem. In the classical case the mass point of the He atom is scattered on the interaction potential of He–Rh(3 1 1) system. The classical equation of motion is solved. The scattering has been investigated as a function of impact parameters. Detailed computations show three-dimensional chaotic effects on trajectories, phase diagrams, deflection angle function and dwell time function. In the case of quantum mechanical model the He atomic beam is described as a Gaussian wave packet. Its time propagation is governed by the time dependent Schrödinger equation. Both the classical and quantum models show trapping effect. The classical model shows chaotic scattering and a non-realistic intensity distribution. The more realistic quantum model provides correct intensity distribution but no trace of chaotic scattering. The results underline the idea that many published classical chaotic computations do not describe any real physical system.

Keywords: Noble gases; Atom–solid interactions, scattering, diffraction; Computer simulations; Rhodium; Single crystal surfaces

1. Introduction

The thermal energy atomic scattering (TEAS) from solid surfaces is very useful tool in the energy range of 10–100 meV because the usually applied He probe particles do not penetrate into the surface but provide information about the top layer [1–3]. TEAS provides information about surface structure, disorder and phonon spectra. In addition to these physical properties, TEAS can describe the quantum processes on the solid surface.

First the classical model leading to three-dimensional (3D) chaotic behaviour of He–Rh(3 1 1) is considered. The phenomenon of chaos arises as a chattering region of impact parameter vs deflection angle function, a chattering region of impact parameter vs dwell time function, trapped trajectories of particles or semi-closed curves of real space vs momentum space diagrams.

After that a quantum mechanical model of He–Rh(3 1 1) is applied. The interaction of neutral atoms and solid surface is strictly quantum

* Corresponding author.
E-mail address: vargag@phy.bme.hu (G. Varga).
[1] Home Page: http://goliat.eik.bme.hu/~vargag/.

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mechanical [4]. What does it mean in the picture of quantum mechanics? Since the interaction is generally strong, Ehrenfest's theorem invalidates the picture of the trajectories. If we adhere the purely stochastic (''Heidelberg approach'') discussion of quantum chaos; the dwell time of atoms near the surface has to be determined as a function of appropriate physical parameters [5]. If the dwell time fluctuates the quantum chaos appears.

Section 2 describes the 3D classical TEAS model and the numerical method for solving the appropriate differential equation system. Time dependent quantum mechanical model of TEAS and its numerical solution are presented in Section 3. The interaction potential of He–Rh(3 1 1) system is constructed in Section 4. Classical and quantum mechanical calculations are shown in Sections 5 and 6, respectively. At last the conclusions can be read in Section 7.

2. Model of classical atom surface scattering

A short description of classical model is shown as follows. The classical model of TEAS is based on the one particle problem. It means that the mass point of the particle is scattered on an appropriately chosen interaction potential. This interaction potential also describes the solid surface. The motion of the particle mass point is governed by Newton's second law in an appropriate inertial frame. Of course, we have to fix the initial conditions outside the interaction region. The initial conditions are given by the position vector and the velocity of the mass point at the initial time. Moreover it is worth to characterise the position vector as a function of the so called impact parameters. The impact parameters ensure that the mass point of the particle may scan different regions of the surface. According to the model description let us prescribe the equations of the classical model [6]: $m(\partial^2\mathbf{r}/\partial t^2) = -\mathrm{grad}\, V(\mathbf{r})$, where m is mass of the atom, $\mathbf{r}$ is the position vector, t is the time and $V(\mathbf{r})$ is the interaction potential. In 3D case the direction x and y are parallel and the direction z is perpendicular to the surface. The initial conditions have been chosen in the following manner: $x_\mathrm{i} = -z_\mathrm{max}\mathrm{tg}\Theta_\mathrm{i}\cos\Phi_\mathrm{i} + c_x a$, $y_\mathrm{i} = -z_\mathrm{max}\mathrm{tg}\Theta_\mathrm{i}\sin\Phi_\mathrm{i} + c_y b$, $z_\mathrm{i} = z_\mathrm{max}$, $v_{x\mathrm{i}} = \sqrt{2E/m}\sin\Theta_\mathrm{i}\cos\Phi_\mathrm{i}$, $v_{y\mathrm{i}} = \sqrt{2E/m}\sin\Theta_\mathrm{i}\sin\Phi_\mathrm{i}$ and $v_{z\mathrm{i}} = -\sqrt{2E/m}\cos\Theta_\mathrm{i}$, where subscript i denotes initial state, z_max is a large enough distance measured from the surface belonging to the asymptotic region of the scattering. Θ_i is the incident and Φ_i is the azimuthal angle. c_x and c_y are the impact parameters in the direction x and y, respectively. The impact parameters are in the interval [0,1]. a and b are lattice constants. $v_{x\mathrm{i}}$, $v_{y\mathrm{i}}$ and $v_{z\mathrm{i}}$ are the initial velocities in the direction x, y and z, respectively. E is the average energy of the incident He particle. Trajectories are calculated until $z \geqslant z_\mathrm{max}$ becomes valid. The crucial point of the above described model is the numerical method to solve the system of differential equations. For example the method based on the explicit Runge–Kutta formula does not lead to correct results [7]. However, it can be considered as the best function of ''first try'' for most problems. For stiff problems – as the present problem is – the variable order solver based on numerical differentiation formulae (NDFs) is recommended. We should recognise that the backward differentiation formulae (also known as Gear's method) are usually less efficient than NDFs [8].

3. Quantum mechanical model

For the description of the problem outlined in the introduction the time dependent Schrödinger equation (TDSE) will be solved. The model assumptions for solving it are: Gaussian wave packet to describe the incoming particle beam and the interaction potential with no restriction of periodicity and time independence. Basically, quantum mechanics is able to describe physical processes of TEAS. In certain conditions – e.g. the probe particles are heavy atoms – semi-classical model approach is appropriate [4]. The particles of atomic beam do not interact with each other, but they have a special velocity and energy distribution. The Gaussian wave packet characterises the atomic beam as a special quantum ensemble of independent particles. 3D Gaussian wave packet has been chosen as an initial wave function:

$$\Psi(x,y,z,t=0) = C\exp(-(x-x_0)^2/2\sigma_1^2 - (y-y_0)^2/2\sigma_2^2 - (z-z_0)^2/2\sigma_3^2) \times \exp(\mathrm{i}\mathbf{kr}), \quad (1)$$

where Ψ is the wave function, (x,y,z) are Cartesian coordinates, t is the time, C is the normalisation constant, (x_0,y_0,z_0) is the average position at $t=0$, σ is the standard deviation, 'i' is the complex unit, $\mathbf{k}$ is the wave number vector and $\mathbf{r}$ is the position vector.

Let us consider the time dependent Schrödinger equation: $\mathrm{i}\hbar(\partial\Psi(\mathbf{r},\mathrm{t})/\partial\mathrm{t}) = H\Psi(\mathbf{r},\mathrm{t})$, where $\hbar$ is the Planck constant divided by 2π and H is the Hamiltonian. A propagation scheme and an application of the Hamilton operator have to be applied. By splitting the Hamilton operator into two parts – the kinetic energy operator A and the potential energy operator B – in the case of time independent potential we can write the exact formal solution: $\Psi(\mathbf{r},t+\Delta t) = \exp[-\mathrm{i}\Delta t(A+B)/\hbar]\Psi(\mathbf{r},t)$. The solution of TDSE demands time propagation at every time step and requires a method to determine the effect of the Hamilton operator on the wave function. We have chosen an efficient splitting operator method with third-order accurate formula in time [9–14] and Fast Fourier transformation (FFT) has been applied to calculate $H\Psi$ at every time step [15].

4. The interaction potential of He–Rh(3 1 1) system

The construction of the interaction potential of He–Rh(3 1 1) system is based on the results of [1]. The chosen Morse potential is completed with a corrugation function resulting from the inverse hard corrugated wall (HCW) model computations [1]. The potential is the following:

$$V(\mathbf{R},z) = D[\exp(-2\alpha(z-\zeta(\mathbf{R}))) - 2\exp(-\alpha(z-\zeta(\mathbf{R})))], \quad (2)$$

where $\zeta(\mathbf{R})$ is the corrugation function, $D = 7.74$ meV, $\alpha = 1.01$ Å^{-1}, $\mathbf{R}$ is parallel and z is perpendicular to the surface. Obviously, Eq. (2) does not provide the effective corrugation function [16]. However, it is a good approach to the interaction potential in first order.

The Fourier representation of the corrugation function of the clean Rh(3 1 1) surface is [1]:

$$\xi(\mathbf{R}) = c_{mn}\sum_{m,n\geqslant 0}\left(a_{mn}\cos\left(m\frac{2\pi}{a}x\right)\cos\left(n\frac{2\pi}{b}y\right) + b_{mn}\sin\left(m\frac{2\pi}{a}x\right)\cos\left(n\frac{2\pi}{b}y\right)\right), \quad (3)$$

where

$c_{mn} = 1$, if $m > 0$ and $n > 0$;
$c_{mn} = \frac{1}{2}$, if m or $n = 0$;
$c_{mn} = 0$, if $m + n =$ odd.

The corrugation parameters in Eq. (2) from Ref. [1]:

$a_{20} = 0.27$ Å, $a_{40} = -0.02$ Å, $b_{40} = 0.02$ Å,
$a_{11} = 0.03$ Å, $b_{11} = -0.02$ Å, $b_{31} = -0.02$ Å.

5. Results of 3D classical scattering computations

The following computations consider out-of-plane scattering, too. Since the corrugation function [1] is two-dimensional (2D) in Eq. (1), the He–Rh(3 1 1) scattering is a 3D problem. The dwell time and deflection angle functions are 2D functions. It is appropriate to demonstrate the chaotic behaviour by contours. That is one of the impact parameters has to be fixed while the other is changing.

Fig. 1A and B refer to 3D trajectories and phase diagrams for $c_y = 0$ and $c_x = 0.54$. Fig. 1C and D show the same curves for $c_y = 0.71$ and $c_x = 0.54$. The regular and irregular (trapped) trajectories can be seen in Fig. 1A and C. Fig. 1B and D render phase diagrams. The semi-closed trajectory in Fig. 1D corresponds to trapping phenomenon.

Fig. 2 shows the dwell time function as a function of impact parameters. The impact parameters are $c_y = 0$ and c_x. c_x varies in the interval [0.2,0.6]. One can see a regular curve in Fig. 2A. Chaotic phenomenon does not arise. If $c_y = 0.7$ a chattering region appears, which is around $c_x = 0.54$

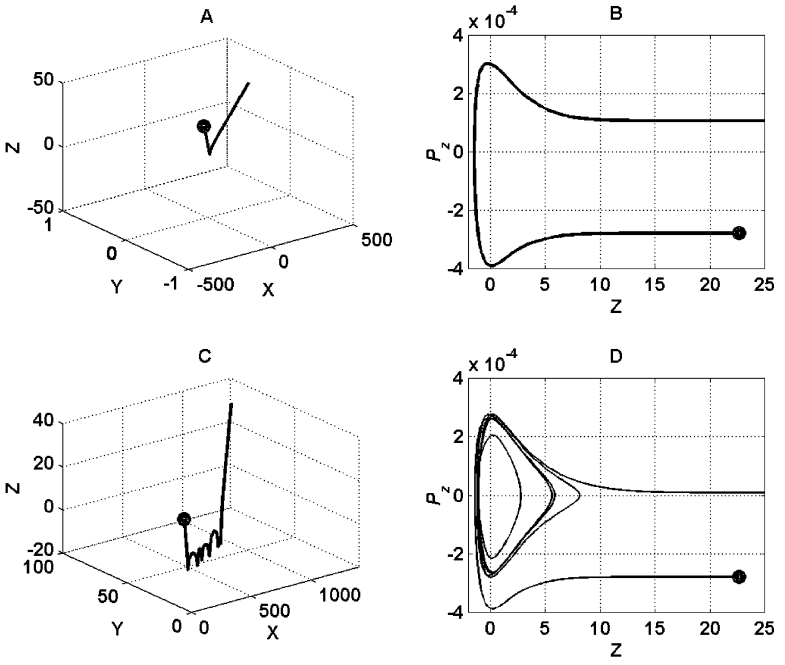

Fig. 1. Trajectories and phase diagrams of classical He–Rh(3 1 1) 3D scattering (atomic units are used). The filled circles denote the beginning of the curves. (A) Regular trajectory can be seen when the impact parameters are: $c_x = 0.54$ and $c_y = 0$. (B) Phase diagram for the direction z-momentum p_z of the case (A). (C) Irregular trajectory can be seen when the impact parameters are: $c_x = 0.54$ and $c_y = 0.7111$. (D) Phase diagram of the direction z-momentum p_z of the case (C).

(Fig. 2B). In Fig. 2C and D $c_y = 0.7$, but near the chattering region the dwell time curve is zoomed in. These figures preserve the property that the curves contain regular and irregular parts. The curves give self-similarity that is a convincing evidence of 3D classical chaotic scattering [17].

6. Results of 3D quantum scattering computations

In Eq. (1) the main input parameters of the He beam are (in atomic units, abbreviation: a.u.): $\sigma = \sqrt{5}$, $x_0 = 9.8644$, $y_0 = 12.681$, $z_0 = 11$ and $\mathbf{k} = (k_x = 0, k_y = 3.0636, k_z = -2.1452)$, $k = 3.74$. The average energy of the He atom is: $\approx$26 meV. The incident angle is: $\Theta_i = 55°$ and the azimuth angle is: $\Phi_i = 0°$. Sample points 32, 96 and 64 are chosen in the direction x, y and z, respectively. In Fig. 3A and B the probability density functions (PDF) are shown in the real and in the momentum space, respectively as the wave-packet approaches the classical turning point ($\langle z \rangle = 2.62$ a.u., '$\langle\ \rangle$' stands for the average). PDF is equal to $|\Psi(\mathbf{r}, t)|^2$. PDF is split into slices parallel to the solid surface since PDF is a function of three variables in space. Fig. 3A and B show the slices at $z = 2.62$ a.u. when $\langle z \rangle = 2.62$ a.u. In that region the interaction is essential. One can see a very important fact, for $|\mathbf{k}| > 3.74$ a.u. the probability significantly differs from zero. This corresponds to a bound state. Fig. 3C and D show PDF after the scattering, beyond the interaction region in the real and in the momentum space, respectively. One can also see in-plane and out-of-plane scattering. The component of the wave number vector $\mathbf{k}$ parallel to the surface is shorter than 3.74 a.u. on the contrary when the He atom is near the top layer of the Rh(3 1 1) surface. The attractive part of the interaction potential leads to longer lifetime near the surface.

The determination of the escaping directions requires detailed scanning of transient probability over the solid angle. These should contain the diffraction peaks, the selective adsorption and

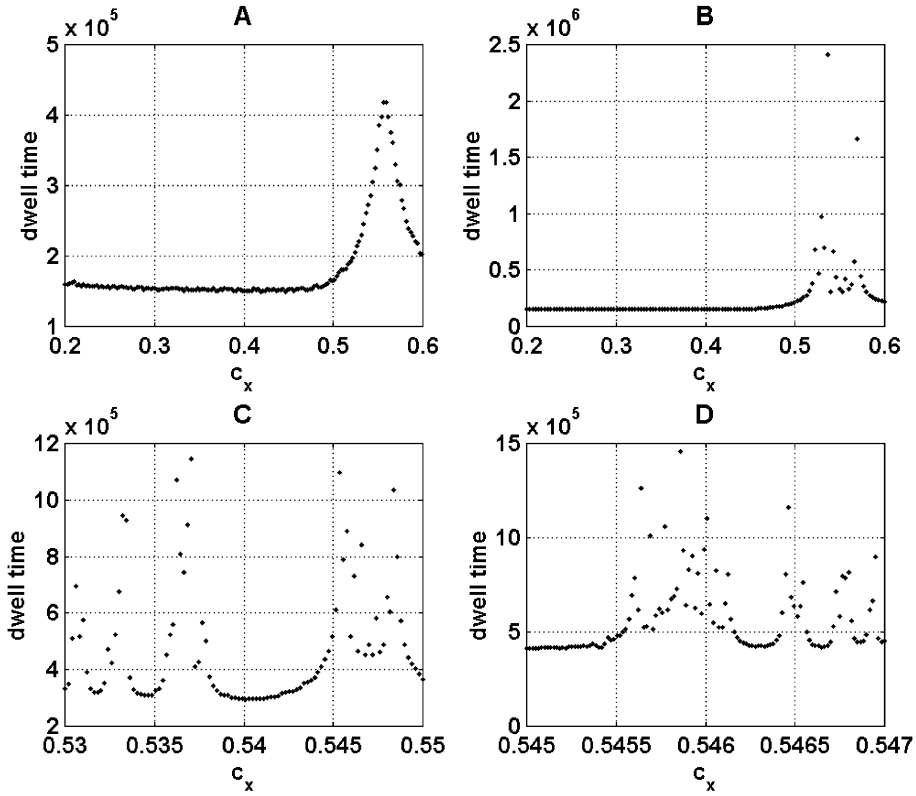

Fig. 2. Impact parameters vs dwell time curves of classical He–Rh(3 1 1) 3D scattering (atomic units are used). c_x and c_y are the impact parameters in the direction x and y, respectively. (A) Regular curve when $c_y = 0$ and (B) Irregular curve when $c_y = 0.7$. Around $c_x \approx 0.54$, a chattering region appears in the curve. (C) and (D) are the same cases as (B), except the curve is zoomed in. Regular and irregular parts of the curves occur.

chaotic effect. In the case of quantum chaos the PDF should show chattering region. Unfortunately, in the case of He–Rh(3 1 1) system quantum chaotic effects could not be found.

He scattering on Rh(3 1 1) surface shows chaotic scattering within the frame of classical mechanical model. The classical chaos does not imply quantum chaos by all means [18]. The quantum mechanical model washes out the "trajectories" since the trajectories do not exist by Ehrenfest's theorem when the interaction is quantum mechanical. The classical chaos is thought to be caused by the strong interaction (quantum mechanical interaction) of He atom–Rh(3 1 1) system. Further investigations are needed to clarify the physical phenomena of He–Rh(3 1 1) scattering. A convincing quantum mechanical method has to determine the dwell time of He atoms near the surface as a function of energy [5] or as a function of measurement time. The measurement time is defined as a time interval of experimental process. When the dwell time function provides chaotic (stochastic) behaviour, the He–Rh(3 1 1) scattering also shows quantum chaos. This is the real physical picture of the scattering. Experimentally, flight time measurement is able to realise this idea. Namely, flight-time measurement gives the function of intensity vs flight time. When the graph is stochastic the probability of the occupied states at the interaction region fluctuates, because the intensity distribution is always related to the probability of the current state. The fluctuating occupied states show a small change of the scattering He beam energy or of the geometrical

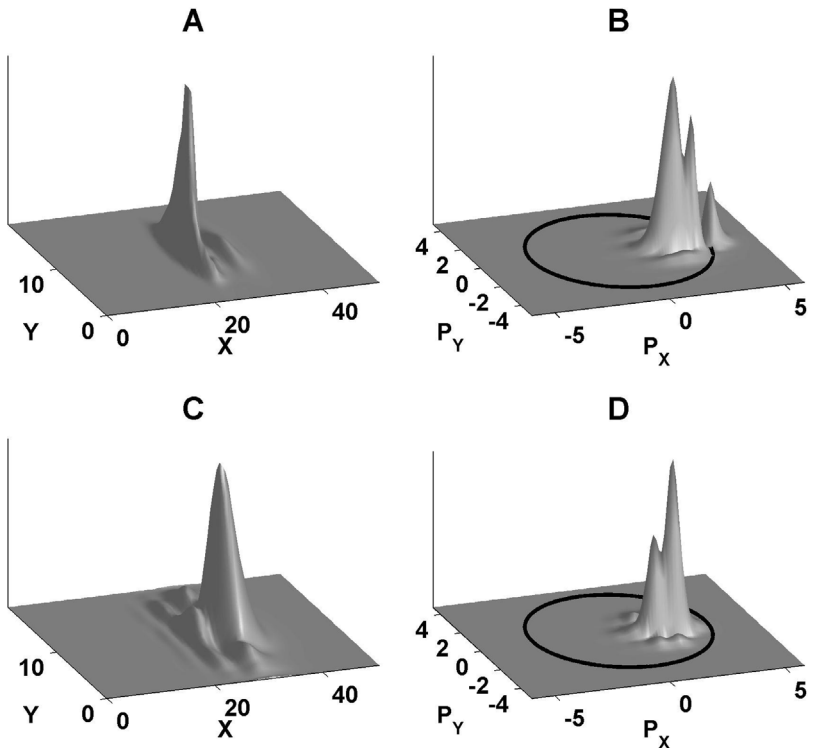

Fig. 3. Illustration of quantum mechanically modelled He–Rh(3 1 1) scattering (atomic units are used). PDF split into slices parallel to the solid surface. P_x and P_y are the moment in the direction x and y, respectively. (A) and (B) PDF is shown in the real space and in the momentum space, respectively when the wave packet is near the classical turning point ($\langle z\rangle = 2.62$ a.u., $z = 2.62$). The radius of the circle in the origin is 3.74 a.u. (C) and (D) PDF is shown in the real and the momentum space when the wave packet is at the detector region. The radius of the circle in the origin is 3.74 a.u.

arrangement which lead to discrete steps of the He atom state.

Let us define the dwell time based on [5] as follows:

$$P(t) = \int_{t_0}^{t} \int_{V_0} |\Psi(\mathbf{r}, t)|^2 \, \mathrm{d}V \, \mathrm{d}t, \tag{4}$$

where t_0 is the time when the measurement is started, and $t \geqslant t_0$ is the measurement time. V_0 is the investigated volume. $P(t)$ is a fraction of $(t - t_0)$. $P(t)$ gives the time spent on average by the He atom of the beam in the volume V_0. Namely, the He atom beam is a quantum mechanical ensemble of independent He particles. If the graph of $P(t)$ behaves stochastically the wave function of He atom beam changes stochastically in V_0 since the region where the particle can be found, is relevant to the state of the He beam.

$P(t)$ has been calculated by four-dimensional trapezoidal numerical integration. The wave function has been computed by time dependent Schrödinger equation with time step short enough. Different volumes V_0 in the physical space have been chosen. Unfortunately, either by this method no stochastic behaviour could be found. The solid angle has been scanned systematically, however chaos has not been found.

7. Conclusions

He–Rh(3 1 1) system has been investigated by classical and quantum mechanical model. The computations underlined the effect of He atoms trapping in the case of classical and quantum mechanical model, respectively. Quantum model

provides more realistic intensity distribution than classical model. Relevant difference can be found in the description of chaos. Classical and quantum models demand absolutely different theory and method to explore the chaos. Classical model computations show chaotic phenomena as against quantum model computations.

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