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To cite this article: A Ruiz et al 2008 J. Phys.: Conf. Ser. 99 012018

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Quasiresonances in atom-surface collisions

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Abstract. The only global autonomous system in which quasiresonant processes have been previously described is the seminal example of one atom colliding with a diatom molecule. In this work we describe classical quasiresonances in a different context, the grazing angle atom-surface collisions. While in the first system the actions related to the process correspond to the internal vibro-rotational degrees of freedom of the molecule, in this new example they turn to be the two components of the momentum of the atom parallel to the surface. We discuss the range of initial actions where quasiresonant processes arise, and suggest a new method to localize quasiresonance regions using the dwell time of the incoming atom in the vicinity of the surface.

1. Introduction
The concept of quasiresonance was first introduced in state resolved inelastic collisions between vibrotationally excited diatom molecules and one atom to describe some very efficient and specific energy transfer between the molecular internal degrees of freedom [1, 2]. This effect was experimentally observed for certain regions of initial internal molecular states, provided that the collision time was longer than the molecular period. Similar results were reproduced in classical trajectory studies of the collision process [2, 3, 4].

Recently the concept of quasiresonance has been extended to new processes in different systems [5, 6]. It has been shown that this is a common effect which arises from the perturbative transient interaction between quasiresonant, i.e. not necessarily exactly resonant, degrees of freedom of an integrable system. Let us consider a two-dimensional integrable system described by the action variables $J_1$ and $J_2$. The perturbative transient interaction induces a process from an initial state with actions $(J_{1i}, J_{2i})$ to a final state with actions $(J_{1f}, J_{2f})$. If the initial actions nearly satisfy the $M : N$ resonance condition,

$$M\omega_{2i} - N\omega_{1i} \simeq 0,$$

with $\omega_{\alpha}$ ($\alpha = 1, 2$) the frequencies associated with the two degrees of freedom, the classical adiabatic invariance theory and the method of averaging can be used to show that the changes in the action variables, $\Delta J_\alpha = J_{\alpha f} - J_{\alpha i}$, are related by [6]

$$\frac{\Delta J_2}{\Delta J_1} = -\frac{M}{N},$$

with $M$ and $N$ coprime integers.
being $M$ and $N$ small integer values. The hallmark of quasiresonance is this extremely accurate negative rational correlation in the action changes. A quasiresonance region is defined by the interval of initial actions where the condition (1) is satisfied. The exact resonant condition, $M\omega_{2i} - N\omega_{1i} = 0$, localizes the center of each region. We point out that this result is valid only for weak transient interactions in which a perturbative analysis can be applied. Although the equation (2) has been obtained using a classical analysis, it also defines the quasiresonance region when the quantum dynamics is considered. However, classical quasiresonance regions could have no equivalent in the quantum dynamics [4].

A quasiresonant process can arise due to an explicitly time dependent transient interaction or one that occurs autonomously. Examples of quasiresonant processes in non-autonomous systems occur in two oscillators that are transiently coupled by an explicitly time dependent function [6], and the deflection of an atom due to the transient interaction with an optical lattice [5]. An example in a global autonomous system is the inelastic atom-diatom collisions previously mentioned, where the interaction with the external atom is the transient perturbation responsible for the quasiresonant process between the rotational and vibrational molecular degrees of freedom.

In this work we present a new example of quasiresonance in a time-independent system, the grazing angle scattering of one atom from an infinite periodic surface. We consider a classical analysis of the dynamics. In section 2 we describe the model considered for the collision of a structureless particle with an infinite periodic rigid surface. Section 3 explains how the quasiresonance arises in the atom-surface collision process, and which ones are the actions associated with the two degrees of freedom involved in a quasiresonance. In section 4 we illustrate this effect in grazing incidence angle collisions. We also present a new manifestation of the quasiresonance related to the dwell time of the incoming atom in the vicinity of the surface. Finally we summarize the main results.

2. The atom-surface collision model

In the model, the solid surface is assumed to form a perfect, two-dimensional, infinite, periodic lattice. We consider low energy incoming atoms, without internal structure, which do not modify the internal structure of the atoms in the surface, and are unable to penetrate beyond the surface layer. Thus the model describes elastic scattering events only in which an incoming monoenergetic beam of atoms strikes the surface with incident momentum vector $\mathbf{p}_i$ and is diffracted with a range of outgoing momentum vectors $\mathbf{p}_f$.

An incoming atom interacts with the surface through a potential $V_s(\mathbf{r})$ which is a function only of its position $\mathbf{r} = (x, y, z)$. In the following we use a coordinate system in which $x$ and $y$ are in the surface layer and the $z$-direction is the outward normal to the surface. The asymptotic region for the collision corresponds to large positive values of $z$. We consider the following interaction potential

$$V_s(x, y, z) = V_M(z) + v_0 V_z(z) V_{zy}(x, y),$$

a widely used form in atom-surface collision studies. We remark that the quasiresonance effect has been shown to be insensitive to the details of the potential energy in the system [1], and therefore the general results presented below do not depend on the particular form considered to simulate the atom-surface interaction.

Assuming an incident atom of mass $m$ and energy $E$, the Hamiltonian that describes the system can be expressed as

$$H = \frac{1}{2m} \left(p_x^2 + p_y^2 + p_z^2\right) + V_s(x, y, z).$$

We consider a typical process in which the atom starts in the asymptotic region, where it evolves freely with initial momentum $\mathbf{p}_i = (p_{xi}, p_{yi}, p_{zi})$, defined by the incident polar and
azimuthal angles $\theta_i$ and $\varphi_i$. After the atom is scattered off the periodic surface, we follow its time evolution until it reaches the asymptotic region, where it moves freely again with a final momentum $p_f = (p_{xf}, p_{yf}, p_{zf})$.

3. Classical analysis of the quasiresonance

To explore how quasiresonance arises in the atom-surface collision, we can split the Hamiltonian \( (4) \) into three terms [6]. The first one,

\[
H_0(p_x, p_y) = \frac{1}{2m} \left( p_x^2 + p_y^2 \right),
\]

(5)

describes an effective two dimensional atom. The components of the surface projected momentum vector $P = (p_x, p_y)$ are the two actions that are expected to be involved in the quasiresonance effect in this process, \((J_1, J_2) \equiv (p_x, p_y)\).

The second term,

\[
H_k(z, p_z) = \frac{p_z^2}{2m} + V_M(z),
\]

(6)

describes the additional degree of freedom in the total system, corresponding to the translational coordinate $z$ and its conjugated momentum $p_z$.

The third term corresponds to the transient interaction

\[
V(x, y; z) = v_0 V_z(z) V_{xy}(x, y)
\]

(7)

that induces quasiresonance, and which satisfies the condition

\[
\lim_{z \to z_{i,f}} V(x, y; z) = 0,
\]

(8)

with $z_i$ and $z_f$ the initial and final $z$ coordinate of the atom in the asymptotic region.

In this system, the conditions required for a valid perturbative analysis of the transient interaction in the quasiresonance effect imply the collision with a weakly corrugated surface (small \(v_0\) in our model potential), and a slow dependence of the atom-surface interaction on the translational coordinate $z$ (grazing incidence with polar angle \(\theta_i\) slightly above \(\pi/2\)). Under these conditions the described decomposition of our model total Hamiltonian is equivalent to the Hamiltonian decomposition considered in the general theory given in [6].

According to this theory, the quasiresonance effect is expected to arise in the atom-surface scattering process as a correlation between the changes in the two components of the momentum parallel to the surface. The quasiresonance region associated with the rational ratio

\[
\frac{\Delta p_y}{\Delta p_x} = -\frac{M}{N}
\]

(9)

should extend over the interval of initial states (incident directions) that satisfy the approximated $M : N$ resonance condition

\[
M p_{yi} - N p_{xi} \simeq 0,
\]

(10)

since

\[
\omega_\alpha = \frac{\partial H_0}{\partial p_\alpha} = \frac{p_\alpha}{m} \quad (\alpha = x, y).
\]

(11)

The center of this region should be located at the exactly resonant initial state, which implies an incident direction defined by the azimuthal angle $\varphi_i = \arctan(N/M)$.

Hence a quasiresonance region in grazing angle atom-surface collisions implies a domain of incident directions, with initial values $p_{xi}$ and $p_{yi}$ satisfying an approximated resonance condition (10), in which the ratio of the changes in the two components of the momentum parallel to the surface (which are the two actions) is locked to a negative low order rational value.
4. Grazing angle atom-surface collisions

To illustrate the quasiresonance effect in grazing angle atom-surface collisions we now consider a particular form of the interaction term (3). The term $V_M(z)$ is fixed as an standard Morse potential,

$$V_M(z) = D \left(1 - e^{-\alpha z}\right)^2 - D. \quad (12)$$

To simulate the surface we assume an infinite square lattice described by the corrugation term

$$V_{xy}(x, y) = \cos^\eta \left(\frac{\pi x}{a}\right) \cos^\eta \left(\frac{\pi y}{a}\right) \quad (13)$$

with $\eta$ an even integer and $a$ the unit cell constant. This term is damped by the exponential term,

$$V_z(z) = De^{-2\alpha z}. \quad (14)$$

In our numerical simulations we consider an incoming helium atom, $m = 4.0026$ amu, a unit cell constant $a = 2\text{Å}$ and a corrugation term with $\eta = 4$. We fix a potential strength $v_0 = 0.02 \text{meV}$, and the Morse potential parameters $D = 6.35 \text{meV}$ and $\alpha = 1.05\text{Å}$. All the classical trajectories start in the asymptotic region with well defined initial momentum $p_i$. After scattering off the surface the integration is carried on until they reach the asymptotic region again, with final momenta $p_f$. For each fixed energy and incident direction, we present results averaged over a large ensemble of trajectories with initial $x$ and $y$ coordinates randomly chosen within a unit cell. Considering the spatial symmetry of the square lattice, we restrict our analysis with respect to the incident azimuthal angle to the interval $[0, \pi/2]$.

We start our numerical analysis by using classical trajectories with the same modulus of the initial surface projected momentum, $P_i = \sqrt{p_{z_i}^2 + p_{y_i}^2}$, but different incidence polar angle $\theta_i$ (different component $p_{z_i}$). The variables $(x, y)$ can be identified as the "internal" coordinates of the perturbed the system (5), and $z$ as the translational collision coordinate. Thus the change in $p_{z_i}$ for a constant value of $P_i$, can be interpreted as the change in the translational collision energy, $E_k = p_{z_i}^2/2m$, for constant initial internal energy, $E_i = P_i^2/2m$.

Figure 1 shows the ratio of action changes for different initial $z$-component of the momentum $p_{z_i}$ and incident azimuthal angle $\varphi_i$. As $p_{z_i}$ goes from zero to large negative values (large translational energy $E_k$), the incident direction evolves from being parallel to the surface to become normal. In the trajectories with large initial translational energy $E_k$ the ratio of action changes does not present any structure. But as the $p_{z_i}$ approaches to zero there are some intervals of initial azimuthal angles where this ratio stabilizes and takes an accurate negative low order rational value. Such intervals define a staircase structure composed of a series of plateaus, each of them being a quasiresonance region. Moving upstairs in the figure, the main plateaus are localized at the rational ratios $-M/N$ equal to $-2, -1$ and $-1/2$. Some small secondary plateaus associated with higher order non-linear resonances (large integers $M$ and $N$) become only visible at nearly parallel incidence. The interval of small negative $p_{z_i}$ where the quasiresonance plateaus emerge corresponds to the region of initial values that satisfies the grazing incidence angle condition required for a valid perturbative analysis of the atom-surface interaction. Notice that (a) the precise initial value of $p_z$ where a quasiresonance plateau emerges, and (b) the span of the plateau in the initial values of the azimuthal angle (i.e. the initial azimuthal angle interval where the perturbative analysis holds) are different for each quasiresonance domain.

An additional plateau at ratio of action changes equals to zero appears for incident azimuthal angles $\varphi_i \simeq \pi/2$. This region corresponds to initial states in the perturbed system with one internal frequency $\omega_z \simeq 0$, $(p_x \simeq 0)$, in which the perturbative analysis of the quasiresonance effect breaks down. Therefore, this plateau region can not be directly associated with a quasiresonant process.
Figure 1. The ratio $\Delta p_y/\Delta p_x$ for trajectories with initial $z$-component of the momentum $p_{zi}$ and incidence azimuthal angle $\varphi_i$. All the trajectories have the same modulus of the initial surface projected momentum, $P_i = \sqrt{p_{xi}^2 + p_{yi}^2} = \sqrt{2mE \sin \theta_0}$, with $E = 30\ meV$ and $\theta_0 = 0.506\pi$. In this figure, a single trajectory is considered for each pair ($p_{zi}$ and $\varphi_i$) of initial values.

To better illustrate the structure of quasiresonance plateaus, figure 2 displays the dependence of the ratio of action changes on the initial azimuthal angle $\varphi_i$ for a particular grazing incidence angle condition (a fixed value of $p_{zi}$). The quasiresonance regions, identified as plateaus in the lower panel, are associated with intervals of $\varphi_i$ where significant changes in both actions, $p_x$ and $p_y$, occur. Inside these regions, even when the trajectories with the same incident azimuthal angle may present quite different changes in the two individual actions, in all of them the ratio of action changes is locked to the same rational value with extremely high accuracy. For example, the quasiresonance region associated with the non-linear resonance condition $M : N = 1 : 1$ extends over initial angles $\varphi$ around $\arctan(N/M) = \pi/4$. The regions associated with the resonance conditions $M : N = 2 : 1, 1 : 2$ are also clearly seen. Besides the main plateaus, there is a staircase structure composed of a series of small plateaus separated by regions of transitions where the ratio of action changes dramatically. These secondary quasiresonances are associated with changes in the actions hardly visible in the figure scale.

In the non-quasiresonance regions between plateaus, very small changes in both actions are found (an approximate adiabatic invariance of each action of the unperturbed system holds), but the ratio of whatever small changes do occur is not locked at rational ratios. Besides, in the region of initial azimuthal angles where $\Delta p_x \approx 0$, extremely large values of the ratio can be obtained.

Considering this analysis of the change in the two components of the momentum parallel to the surface, we can alternatively identify the quasiresonance regions with the intervals of initial conditions where the trajectories with the same initial azimuthal angle show: (a) a large
Figure 2. The change in the actions $p_y$ (upper panel), $p_x$ (middle panel) and ratio $\Delta p_y/\Delta p_x$ (lower panel) for collisions with total energy $E = 30$ meV and grazing incident polar angle $\theta_i = 0.506 \pi$. Each dot corresponds to one of the 20 classical trajectories used at each incident azimuthal angle. The red solid lines give the values averaged over an ensemble of 1500 trajectories for each initial azimuthal angle $\varphi_i$. The red dashed vertical lines localize the exactly $M : N$ resonant incidence directions.

So far, the quasiresonance regions has been identified from the changes in the actions and their correlation. This analysis requires to resolve the initial and final “internal” states of the colliding atom. However, in this model an additional manifestation of the quasiresonant process can be found in a different quantity, the dwell time of the colliding particles in a given region of the space. We define the dwell time $\tau_D$ as the time interval that a particle spends within the space region bounded by the surface and a parallel plane fixed by a reference value $z = z_0$. The dwell time of each classical trajectory can be simply calculated as the time difference between the last outgoing and the first incoming crossings through the reference plane $z = z_0$. To better characterize the dwell time at each given total energy and incident polar angle, we present the dwell time averaged over ensembles of trajectories with the same initial azimuthal angle.

Figure 3 shows the dependence of the averaged dwell time on the initial azimuthal angle. The non-quasiresonance regions can be identified with intervals that present a common nearly constant value of $\tau_D$, determined mainly by the Morse potential term $V_M(z)$ (see the line corresponding to $v_0 = 0$ in the figure). Meanwhile, the quasiresonance regions correspond to intervals of significant variations in the dwell time. The differences in the value of $\tau_D$ can

averaged change in both actions; (b) a large variance for both action changes; (c) a precise ratio of the action changes (d) a small variance of this ratio. The option (c) is the most appealing and convenient since it is also the only one that can be used to identify the precise rational ratio that characterizes each quasiresonance region.
Figure 3. In the upper panel: Classical averaged dwell time $\tau_D$ versus the initial azimuthal angle $\varphi_i$ for $z_0 = 60\, \text{Å}$. The constant solid red line is the dwell time $\tau_{DM}$ given by the Morse interaction term $V_M(z)$, ($v_0 = 0$). The dwell time units are $\text{ps}$. In the lower panel: $\Delta p_z$ for each trajectory (dots) and averaged value for the same $\varphi_i$ (solid red line). The averages include 1500 trajectories for each initial angle $\varphi_i$. The total collision energy $E$ and the incidence polar angle $\theta_i$ are given in figure 2. The red dashed vertical lines localize the exactly $M:N$ resonant incidence directions.

be attributed to two contributions: (1) the time interval that the particle spends in the spatial region close to the surface; and (2) the different escape times due to the change in the asymptotic velocities after the collision, as the global process is elastic and the large changes in the actions $p_x$ and $p_y$ can induce an important change in the final $p_z$, as shown in the figure. At small values of $z_0$, the first contribution is the most important. Numerical tests show that the trajectories included in the quasiresonance regions can have a complicated evolution with several bounces on the surface, increasing $\tau_D$, or on the contrary, can be scattered off the surface very rapidly, lowering $\tau_D$ (both effects can be found inside a given quasiresonance region). At intermediate values of $z_0$, as the one shown in the figure, both contributions are important. At large values $z_0$, the second contribution becomes more important (as it increases linearly with $z_0$), and the variations of $\tau_D$ in the quasiresonance regions will resemble the dependence on the change in $z$-component of the momentum. Notice that this analysis of the classical dwell time allows to localize the quasiresonance regions, without having to resolve the initial and final internal states of the perturbed system. Such state resolution would be required later in order to identify the specific rational change ratio that characterizes each region.

In summary, we have shown how quasiresonant processes arise in collisions of a structureless particle (atom) with an infinite periodic potential (surface). We have described which ones are the quasiresonant actions in this system, the components of the momentum parallel to the...
surface, and the grazing incidence angle conditions required for this effect to appear. Two alternative methods to identify the quasiresonance regions have been suggested: one related to the asymptotic change of the actions and their correlation, whose experimental implantation would require to resolve the initial and final internal state of the incoming atom. The second method analyzes the dwell time of the classical trajectories inside the interaction region. We show that the quasiresonance regions are associated with significant changes in the dwell time, in contrast to a nearly constant common value for all non-quasiresonance ones. We expect that this dwell time analysis would be also applied to identify quasiresonances in other processes where there is an important transfer of energy between the “internal” quasiresonant degrees of freedom and the translational coordinate, as does occur in the atom-diatom collision seminal example.

Acknowledgments
A.R. thanks D. Alonso and S.R. Hain for fruitful discussions. A.R. and J.P. acknowledge financial support from Spanish MCT (FIS2004-05687, FIS2005-02886, FIS2007-64018) and Gobierno de Canarias (PI2004/025). The authors would like to thank the Wilhelm und Else Heraeus Foundation for its financial support for the 395th WE-Heraeus Seminar, “Time Dependent Phenomena in Quantum Mechanics”. We thank the organizers of this conference for their hospitality.

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