Semiclassical Approach to the Scattering of Atomic Beams by a Corrugated Surface Potential: An Approximate Analytical Solution

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An approximate analytic solution to the scattering problem of atoms by a weakly corrugated Morse potential is presented. In the classical limit the resulting scattering amplitude coincides with that given by the Kirchhoff approximation for the corrugated hard-wall model with a corrugation function identical to that of the Morse potential. Quantum mechanical effects appear as deviations from the Kirchhoff formula. For a general potential it is shown that it is the potential corrugation near vanishing potential which dominates the scattering process and not that at the classical turning point.

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The scattering of atomic and molecular beams from a solid surface is a promising tool for investigating structural and dynamical properties of solid surfaces.[1-3] Recent activity in this field has been focused on structural analysis of single-crystal surfaces with use of He diffraction techniques.[1,4-6]

It turns out, however, that even when only the geometry (or topography) of the surface is of interest, simple-minded models like the hard-corrugated-wall (HCW) models sometimes yield significant deviations from theories which use more realistic (i.e., soft) potentials.[4,5] On the other hand, the use of realistic model potentials impairs considerably the simplicity of the analysis, making large-scale numerical computations virtually inevitable. In this Letter we report significant progress in developing an approximate analytical solution to this problem for a realistic model potential, such as the corrugated Morse (CM) potential. Our motivation is twofold: (1) to provide an alternative simple scheme to the widely used HCW model for interpreting experimental data from soft surface potentials, and (2) to develop a simple method, which can be generalized to include inelastic effects,[7] for which the use of numerical analysis would be impractical.

We have discovered a general property of the scattering amplitude in the semiclassical limit which is a major source of simplification in this problem. In this limit the transition amplitude from the incoming momentum $\vec{p}$ to the outgoing momentum $\vec{p}'$ can be written as[8]

$$T(\vec{p},\vec{p}') = |\bar{p}_z|(4\pi^2\Omega)^{-1}\int d^2K\, f(\vec{p};\vec{K}) f^*(\vec{p}';\vec{K})/(p^2-\hbar^2K^2)^{1/2}, \tag{1}$$

where

$$f(\vec{p};\vec{K}) = (M_G/i\hbar p_z)\int d^3r\, V(\vec{r}) A_{\vec{K}}(\vec{r}) \exp\{(i/\hbar)[\vec{p}\cdot\vec{r} - S_{\vec{K}}(\vec{r})]\}, \tag{2}$$

$S_{\vec{K}}(\vec{r})$ is the classical action integral corresponding to the fully distorted incident wave with an asymptotic momentum $\hbar\vec{K}$ parallel to the surface plane, $A_{\vec{K}}(\vec{r})$ is the amplitude of the corresponding semiclassical wave function,[9] $V(\vec{r})$ is the potential, M_G is the particle's mass, $|\bar{p}_z| \equiv \frac{1}{2}|p_z - p_z'|$, and Ω is the illuminated surface area. Note that in computing $f^*(\vec{p};\vec{K})$ from Eq. (2) the appropriate selection for $S_{\vec{K}}(\vec{r})$ is that of the distorted reflected wave. Note also that we use the standard convention that capital letters denote projections of three-dimensional vectors onto the surface plane. Consistent with the semiclassical approximation used above, the stationary phase (SP) method is applied to the three-dimensional integral in Eq. (2). The corresponding stationary point $\vec{r}_0$ satisfies the equation $[\partial S_{\vec{K}}/\partial\vec{r}]_{\vec{r}_0} = \vec{p}$, so that together with the Hamilton-Jacobi equation

$$(\partial S_{\vec{K}}/\partial\vec{r})^2 = 2M_G[E - V(\vec{r})],$$

one finds that the stationary point $\vec{r}_0$ lies on the equipotential surface $V(\vec{r}) = 0$. As we shall see later, this remarkable result leads to a major simplification of the scattering problem. The surprising aspect of this result is that the major contribution to

the matrix element $f(\vec{p};\vec{K})$ originates in a small, *potential-free* regime near the crossover of the potential from attraction to repulsion, *far away from the classical turning point.* This is clearly due to gross cancellation of contributions from regions where the phase $-S_{\vec{K}}(\vec{r})/\hbar$ of the incident wave is strongly distorted by the potential and, as a result, its matching with the free particle incident wave is very poor.

For scattering by a one-dimensional (1D) potential, $f(p_z;0)$ (which is just the reflection coefficient) can be easily calculated by transforming the spatial variable of integration z in Eq. (2) to a new variable $u = V(z)/D$, where D is the potential well depth, and then using the SP method. Consequently, one obtains

$$f(p_z;0) = \exp\{(i/h)[p_z z(0) - S(0)]\} 2i\lambda \int_{-1}^{\infty} u \exp(i\lambda u^2) du, \tag{3}$$

where $\lambda = (M_G D/2\hbar p_z \chi)$, $\chi \equiv (du/dz)_{u=0}$, and $z(0)$ and $S(0)$ are the respective values of z and S at $u = 0$. The interesting aspect of Eq. (3) is that despite the use of the semiclassical approximation, the reflection coefficient $|f|^2$ obtained from Eq. (3) is identical to the exact result (i.e., 1). This is obviously due to the fact that in the semiclassical limit (i.e., where $\hbar\chi << p_z$) the important region of integration (i.e., $u \leq 1/\sqrt{\lambda}$) is far away from the classical turning point [i.e., at $u = (1/\lambda)p_z/4\chi\hbar >> 1/\lambda$].

The extreme simplicity of our approach for a 1D potential indicates that it can be used to derive an analytic solution for a weakly corrugated three-dimensional potential. We have worked out such a solution for a CM potential defined by

$$V(\vec{R},z) = D\mu^2 - 2D\mu, \quad \mu(\vec{R},z) \equiv e^{\chi[z-\zeta(\vec{R})]}, \tag{4}$$

where $\zeta(\vec{R})$ is the corrugation function and χ is the softness parameter. We assume weak corrugation [i.e., $(\partial\zeta/\partial\vec{R})^2 << 1$ almost everywhere] and solve the Hamilton-Jacobi equation for $S_{\vec{K}}(\vec{R},\mu)$ iteratively in the small parameter $\nabla\zeta(\vec{R})$ ($\nabla \equiv \partial/\partial\vec{R}$). To second order in $\nabla\zeta$ (but neglecting higher derivatives) we obtain

$$S_{\vec{K}}(\vec{R},\mu) = \hbar\vec{K}\cdot\vec{R} + (\hbar\vec{K}\cdot\nabla\zeta)\ln\mu/\chi \pm \{[1 - \tfrac{1}{2}(\nabla\zeta)^2]\cdot\tilde{S}(\mu) + \hbar(\vec{K}\cdot\nabla\zeta)^2 \ln[2\mu/(1 + W(\mu) + \gamma\mu)]/2k_z\chi\}, \tag{5}$$

where $\tilde{S}(\mu)$ (Ref. 8) is the classical action for a particle with energy $\hbar^2k_z^2/2M_G = E - \hbar^2K^2/2M_G$ in a 1D Morse potential $V(\mu) = D\mu^2 - 2D\mu$, $W(\mu) = (1 + 2\gamma\mu - \gamma\mu^2)^{1/2}$, and $\gamma = 2M_G D/\hbar^2 k_z^2$. In Eq. (5) the plus corresponds to the incident wave while the minus corresponds to the reflected wave. Using Eq. (5) we have derived the following expansion for the T matrix.

$$T(\vec{p},\vec{p}') = i(|\bar{p}_z|/|p_z p_z'|)\Omega^{-1} \int d^2R\, BB'\hbar k_{z,0} \exp\{i[(\vec{P} - \vec{P}')\cdot\vec{R} + (p_z - p_z')\zeta(\vec{R})]/\hbar\}, \tag{6}$$

where U is a shortened notation for

$$U_{p_z}(\vec{R}) = \{[1 + \tfrac{1}{2}(\nabla\zeta)^2]p_z - \hbar\vec{K}_0\cdot\nabla\zeta - \hbar(\vec{K}_0\cdot\nabla\zeta)^2/2k_{z,0}\}/\hbar k_{z,0}, \tag{7}$$

$$\hbar k_{z,0} = (p^2 - \hbar^2K_0^2)^{1/2}, \quad \hbar\vec{K}_0 = [(\vec{P} + \vec{P}') + (p_z + p_z')\nabla\zeta]/2,$$

$$B = (k_{z,0}\gamma/2i\chi\sqrt{U}) \int_0^{\infty} d\mu(\mu - 2)\exp[ik_{z,0}f(\mu)/\chi], \tag{8}$$

where $f(\mu) = U\ln\mu - \chi\tilde{S}(\mu)/\hbar k_{z,0}$, and B' is obtained by replacing U by U' in Eq. (8). U' is obtained from Eq. (7) by replacing p_z with P_z' and the minus in front of the last term within the curly brackets with a plus. Equation (6) has been derived consistently with the approximations used in the derivation of Eq. (5), namely the integrals have been computed by the SP method and any expansion in $\nabla\zeta$ has been kept to second order. The classical limit of the scattering amplitude, given by Eq. (6), is obtained when the integrals over μ [Eq. (8)] and over $\vec{R}$ [Eq. (6)] are performed by the SP method. The stationary point for the former integral is given by $\mu_0 = 1 + [1 + (1 - U^2)/\gamma]^{1/2}$ while the stationary point $\vec{R}_0$ for the latter integral is, to second order in $\nabla\zeta$, given by

$$(\vec{P} - \vec{P}') + (p_z - p_z')\nabla\zeta(\vec{R}_0) = 0. \tag{9}$$

To the same order,

$$U_{p_z}(\vec{R}_0) = -U'_{p_z}(\vec{R}_0) = 1, \quad B(\vec{R}_0) = B'(\vec{R}_0) = \exp[ik_{z,0}f(2)/\chi],$$

and both $\mu_0 - 2$ and $\mu_0' - 2$ vanish at $\vec{R}_0$. This result is consistent with the exact theorem, which we have proved above, stating that the stationary point always lies on the surface $V(\vec{r}) = 0$. The resulting expression for the T matrix in the classical limit is thus given by

$$T_{\text{classical}}(\vec{P}, \vec{P}') = i|\bar{p}_z|^2\{1 + [(\vec{P} - \vec{P}')^2 - (p_z + p_z')^2]/8|\bar{p}_z|^2\} \times \frac{1}{\Omega}\int_{\text{Stat. phase}} d^2R \exp\{i[(\vec{P} - \vec{P}')\cdot\vec{R} + (p_z - p_z')\zeta(\vec{R})]/\hbar\} \quad (10)$$

where all irrelevant phase factors have been dropped. This is essentially the classical limit of the Kirchhoff approximation[10,11] for the scattering by a HCW with a corrugation function $\zeta(\vec{R})$.

To restore quantum mechanical (QM) effects, the integral over μ in Eq. (8) and the lateral integral in Eq. (6) should be computed by a more accurate method than the SP method (this is crucially important near a caustic, where a rainbow singularity is generated in the classical limit[11]) Such a method would emphasize regions located away from the stationary point more than the SP method so that the resulting scattering amplitude would deviate from the QM version of the Kirchhoff approximation. Such deviations may be quite significant, especially for high incident energies, since the amplitude B is sensitive to deviations of U^2 from its value at the stationary point (i.e., 1) for small values of γ [see the expression for μ_0 below Eq. (8)].

The conditions under which Eq. (6) is valid can be summarized as follows: (1) The incident velocity should be sufficiently high such that $k_{z,0} >> \chi$ (the semiclassical limit). (2) The effect of the attractive well should be negligible. This condition is satisfied where $\lambda \equiv k_{z,0}\gamma/4\chi << 1$ [see Eq. (3)]. (3) The corrugation should be weak, i.e., $|\nabla\zeta|^2 << 1$. (4) $(\chi a)^2 >> [\nabla\zeta + \vec{P}/|\vec{P}_z|]^2$, where a is the size of the surface unit cell. This condition guarantees that the lateral distance between the points of intersection of the atom's trajectory with the surface $V(\vec{r}) = 0$ is much smaller than a. Classically it means that multiple-hit events are negligible, as indicated by the Kirchhoff-type form of Eq. (10). Thus provided that condition (1) is fulfilled, our theory works better for harder potentials (i.e., larger χ), weaker corrugation, and for incoming beams closer to normal incidence ($\vec{P} = 0$).

It is instructive to discuss some or our basic conclusions in comparison with the relevant literature. In attempting to interpret He-diffraction data from complex surface structures[1,6,12] most researchers have used the HCW model with the intuitively appealing assumption that the best corrugation function corresponds to the classical turning surface. Quite surprisingly we have found that a better definition for the corrugation function should be the equipotential surface $V(\vec{r}) = 0$, which usually leads to a weaker corrugation. This conclusion seems to agree with a remark which appears frequently[10,12,13] in the literature, indicating that the use of the HCW model to fit the scattering data leads to a corrugation weaker than that expected from the actual soft potential at the classical turning surface. Surface charge density calculations for Ni(110) (Ref. 12) indicate, for example, that the corrugation amplitude at electron density, $\rho = 10^{-4}$ a.u. is more than two times larger than that at $\rho = 10^{-5}$ a.u. With use of the Esbjerg-Nørskov relation[14] for the repulsive part $-V_{\text{rep}}$ of the He-surface potential, the above-mentioned values of ρ correspond to the values of 7.5 and 75 meV of V_{rep}, respectively. Thus, since the attractive potential well is of the order of several millielectronvolts, the potential corrugation near $V = 0$ is about a factor of two smaller than that at $V \simeq 70$ meV. This is comparable to the ratio between the experimentally fitted corrugation amplitude, obtained by Rieder and Garcia[13] by using the HCW model, and the theoretical corrugation amplitude, computed by Haman[12] at the classical turning surface for $E_{iz} \simeq 50$ meV. Note that in this case the experimentally fitted values of $\zeta(01)$ (Ref. 13) are almost constant in the range of $E_{iz} = 12.8$–105.7 meV, in agreement with our basic conclusion.

Another point of interest in this context concerns the effect of the attractive potential well; it is again very natural to assume that for incident energies of several tens of millielectronvolts a well depth of a few millielectronvolts should not have a big effect. As shown by Perreau and Lapujonlade,[5] however, who compared Armand and Manson's exact numerical results[5] for a CM potential with those for a purely repulsive corrugated exponential potential, the effect of the attractive well on the scattering from a soft potential is important even for $\gamma \equiv D/E \approx 0.1$. This seems to agree with our conclusion that the effect of the attractive well may not be neglected if $\lambda \sim 1$. For example, in the case studied in Ref. 5 (i.e., with $E = 63$ meV, $D = 6.3$ meV, and $\chi \approx 1$ Å^{-1}) $0.5 < \lambda < 0.25$ while $\gamma \approx 0.1$. Generally speaking, the fact discovered in the present work, that the dominant scattering am-

plitudes are generated away from the classical turning point, down the wall in the vicinity of the attractive well, clearly indicates the important effect of the attractive well on the scattering process even for relatively high energies. A more quantitative test of our approach would be to compare it with an exact QM calculation for the model potential considered in this paper [Eq. (4)]. To the best of our knowledge this model potential has not been considered in the past. Exact close-coupling calculations have been applied[15] to a closely related model potential such as a Morse potential corrugated only in its repulsive part.

A comparison between results obtained by such an exact method for this version of the CM potential and the corresponding results obtained for the HCW, both applied to He diffraction from LiF(100), shows that the two methods are in best agreement with each other when the corrugation amplitude of the HCW is about twice that of the CM used. Furthermore, Armand and Manson's exact numerical results for a similar model potential have shown[5] a similar behavior in the case where $E = 21$ meV (but not for $E = 63$ meV). It can be readily verified[16] that for this version of the CM potential the corrugation amplitude of the equipotential surface $V = 0$ is twice the corrugation amplitude of the equipotential surface $V = E$ for E much larger than the potential well depth D. This finding is thus consistent with our basic conclusion regarding the importance of the potential corrugation near vanishing potential in the scattering process.

These preliminary tests of the proposed scheme are very encouraging. More elaborate quantitative tests are, of course, necessary to establish its usefulness as a simple method for analyzing complex diffraction data or as a tractable scheme for investigating the far more complicated problem of inelastic scattering.

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[1]T. Engel and K. H. Rieder, *Structural Studies of Surfaces* (Springer-Verlag, Berlin, 1982).

[2]V. Celli, in *Proceedings of the Twelfth International Symposium on Rarefied Gas Dynamics, Charlottesville, Virginia, 1980,* edited by Sam S. Fisher (American Institute of Aeronautics and Astronautics, New York, 1980), pp. 129–149.

[3]J. C. Tully, Annu. Rev. Phys. Chem. **31**, 319 (1980).

[4]R. B. Laughlin, Phys. Rev. B **25**, 2222 (1982).

[5]J. Perreau and J. Lapujoulade, Surf. Sci. **119**, L292 (1982); G. Armand and J. R. Manson, Surf. Sci. **119**, L299 (1982).

[6]M. J. Cardillo, G. E. Becker, D. R. Hamann, J. A. Serri, L. Whitman, and L. F. Mattheiss, Phys. Rev. B **28**, 494 (1983).

[7]T. Maniv and Morrel H. Cohen, Phys. Rev. B **19**, 4883 (1979).

[8]T. Maniv and Morrel H. Cohen, unpublished results.

[9]W. H. Miller, Adv. Chem. Phys. **25**, 69 (1974).

[10]R. I. Masel, R. P. Merrill, and W. H. Miller, J. Chem. Phys. **65**, 2690 (1976).

[11]M. V. Berry, J. Phys. A **8**, 566 (1975).

[12]D. R. Haman, Phys. Rev. Lett. **46**, 1227 (1981).

[13]K. H. Rieder and N. Garcia, Phys. Rev. Lett. **49**, 43 (1982).

[14]N. Esbjerg and J. Nørskov, Phys. Rev. Lett. **45**, 807 (1980).

[15]G. Wolker, Jr., J. Chem. Phys. **58**, 3047 (1973).

[16]H. Hoinkes, Rev. Mod. Phys. **52**, 933 (1980).