Semiclassical Description of Inelastic Atom Scattering by Surfaces

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Inelastic scattering of atoms of moderate energies (say < 5 eV) by solid surfaces is almost entirely due to energy exchange with lattice vibrations. It can give valuable information about the atom-surface interaction potential and the vibrational dynamics at surfaces. Theoretically this process represents a challenging many-body problem, calling for suitable approximation methods. Work in progress (K. Burke, L. D. Chang, and W. Kohn) is described. (1) We have solved a simple model problem in which the normal modes of the lattice are schematized by a single one-dimensional harmonic oscillator, initially in its ground state $(T = 0)$. The classical solution gives a unique energy loss. We have calculated the leading quantum correction and find a Gaussian final energy distribution whose width is proportional to $h^{1/2}$. Our exact results are in general different from the so-called trajectory approximation. (2) We are about to propose a new type of atom–surface scattering experiment, which will provide a direct measure of the quantum corrections to classical scattering.

PREFACE

My friendship with Howard Reiss goes back over a little more than one-half of our lives, to the summer of 1953. I had come to Bell Labs on the first of about a dozen annual summer visits and found Howard in masterly command of the theory of solid solutions of group III and group V atoms (acceptors and donors) and their complexes in Si and Ge. This was, of course, during the heady years of the spectacular transistor revolution, and Howard's work was at the theoretical center of the preparation of the essential *n*- and *p*-doped samples of Si and Ge. As a neophyte in solid state

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physics I was enormously impressed (not to say intimidated) by the breadth of understanding and variety of techniques which Howard had at his command.

In the intervening years we both moved—along quite different paths—into faculty positions at the University of California, and there have been many occasions when I have enjoyed, and frequently profited from, Howard's extraordinary qualities as a scientist. His great originality and outstanding ability to solve—somehow—almost any reasonable problem in physical or solid-state chemistry are truly astonishing.

Howard is equally at home in classical and quantum theory. I hope, therefore, that the following contribution, which is on the borderline between classical and quantum physics (or chemistry) will be to his liking.

1. INTRODUCTION

In many branches of quantum physics a semiclassical description has been the most appropriate and most instructive. Two examples are bound states in atoms and molecules of high quantum numbers n; and the description of crystal electrons in a weak magnetic field H, where the large parameter is the label n of the Landau level (or, in complicated geometries, something similar). Semiclassical treatments of scattering of a particle by a *fixed* external potential are also long familiar and governed by the BWK equation or semiclassical path integral methods.

The problem of *inelastic* scattering of an atom by a surface is conceptually and calculationally much more difficult. If the velocity of the incident atom ("incidon") is sufficiently smaller than typical electronic velocities—and this is true up to ~ 1 keV for H and ~ 100 keV for heavy atoms—the Born–Oppenheimer approximation is valid and the system can be described by a Hamiltonian of the form

$$H = \frac{p^2}{2m} + \left[\sum_j \frac{p_j^2}{2M} + W(r_1, ..., r_N) \right] + \sum V(r; r_1, ..., r_N) \tag{1}$$

where (m, p, r) describe the incidon and (M, p_j, r_j) the N lattice atoms. Thus, electronic degrees of freedom are completely represented by the interaction potentials W and V. I limit the present treatment to this Born–Oppenheimer regime.

Provided that the surface temperature T is much greater than the Debye temperature θ_D and the incident atom has a de Broglie wavelength much shorter than a characteristic length of the surface (say, $\ll 10^{-8}$ cm), a fully classical description evidently is in order. If these conditions are almost, but not quite, satisfied a semiclassical approach is clearly appropriate.

But what if initially the surface temperature T is smaller than the Debye temperature, so that at least the high-lying modes are only weakly excited ($n = 0$ or 1) before the collision; or, a more extreme case, $T = 0$, so that initially *all* modes are in their $n = 0$ ground states? Is the classical (normally $n \gg 1$) limit *at all* an appropriate starting point? And what are the appropriate conditions, if any, on the masses m and M, the incident velocity v, and other parameters, such as interaction strengths and ranges?

A good deal of progress has been made in recent years on semiclassical inelastic scattering theory. It is of great interest not only for atom–surface scattering, but also for scattering of molecules by surfaces, accompanied by internal molecular excitations, and, of course, related to chemical reactions between gaseous molecules. To my mind, the above and other questions have not yet been fully answered and considerable work remains to be done.

2. A SIMPLE MODEL AND A CHECK ON THE TRAJECTORY APPROXIMATION

In recent work by our group we have critically examined a simple model in which the atoms of the surface are schematized as a single one-dimensional harmonic oscillator. Our Hamiltonian is

$$H = \frac{p^2}{2m} + \left(\frac{P^2}{2M} + \frac{K}{2} X^2 \right) + e^{-(X-x)/a} \tag{2}$$

By a simple change of variable, $x \rightarrow x + b$, we have set, without loss of generality, the interaction amplitude equal to unity. Similar models have been studied extensively in the past from various points of view.[1] Our objectives have been twofold. (1) We start with the harmonic oscillator in the ground state and calculate the energy loss spectrum of the incidon *exactly* up to and including the leading quantum mechanical correction, $O(h^{1/2})$. (2) We compare these results with those of the so-called trajectory approximation[2] (which has semiclassical features) to determine under which conditions if any that approximation is valid.

In our model there are two dimensionless classical parameters: $\mu_1 \equiv m/M$ and $\mu_2 \equiv \omega\tau$, where ω is the frequency of the oscillator ($\omega = K^{1/2} M^{-1/2}$) and τ is the time taken by the incidon of energy E to traverse the distance a [$\tau = am^{1/2}(2E)^{-1/2}$].

Our method of solution is to develop a singular limiting solution of the Heller wavepacket equations.[3] Heller's method starts with the

oscillator in its Gaussian ground state and the incidon described by a distant, incoming Gaussian wave packet of the form

$$\psi(x, t) = A \int dp \, \exp[-(p-p_0)^2/h\alpha] \, \exp\{(i/\hbar)[p(x-x_0) - E(p)\,t]\} \qquad (3)$$

Here p_0 and x_0 are the initial mean momentum and position; $E(p) \equiv p^2/2m$; $(h\alpha)^{1/2}$ is the momentum width of the incident wave packet; and A is the appropriate normalization constant.

The following heuristic argument suggests (correctly, as we have confirmed) that the momentum (and energy) distribution of the reflected particle will have a width $\propto h^{1/2}$ for $h \to 0$: The target oscillator has a zero-point momentum distribution of width $\Delta P \sim (h\omega M)^{1/2}$, which, using classical mechanics, leads to a distribution of reflection momenta of $\Delta p \sim \Delta P \propto h^{1/2}$. To distinguish this real quantum spread from the artificial momentum spread of the incident wave packet, we must make the latter relatively negligible, i.e.,

$$(h\alpha)^{1/2} \ll f(\mu_1, \mu_2)(h\omega M)^{1/2}$$

or

$$\alpha \ll (M\omega)^{1/2} f(\mu_1, \mu_2) \qquad (4)$$

where f is some as yet unknown function of the dimensional parameters μ_1 and μ_2. Heller's equations become singular in the limit $\alpha \to 0$ and had to be solved with great care by an expansion in powers of α. The result is that, up to order $h^{1/2}$, the center of the reflected energy distribution is equal to the classical reflection energy, and the width is given by

$$\Delta E = F(\mu_1, \mu_2)(h\omega)^{1/2} \qquad (5)$$

where $F(\mu_1, \mu_2)$ is a function of the dimensionless variables μ_1 and μ_2, which we have calculated for various values of μ_1 and μ_2 from our expansion of Heller's equations.

We have compared these results with those of the so-called trajectory approximation, and for any finite values of μ_1 and μ_2, find quantitative disagreements, from a few percent to factors of the order of 2. Thus, we conclude that, while the trajectory approximation provides a useful orientation concerning the magnitude of quantum effects, it is not quantitatively correct.

3. SPECIFIC QUANTUM EFFECTS IN ATOM–SURFACE SCATTERING EXPERIMENTS

If an atom is incident on a perfect surface at temperature T with a definite momentum $\mathbf{p}_i$, its reflected momentum $\mathbf{p}_f$ will have a spread in both direction and magnitude. Classically this spread is due to the different points of impact and to the different initial states of the target in the temperature ensemble. In addition, quantum mechanically, even for a given initial state of the target there are many possible final target states and corresponding final momenta $\mathbf{p}_f$. To isolate this last, specific quantum mechanical effect we are proposing the following experiment: The target should be at temperature $T \approx 0$, so that variations of the initial target state are negligible. Second, the reflected incidon is to be observed in a definite direction θ_f. Classically, one expects exactly two sharp reflection energies $E_1(\theta_f)$ and $E_2(\theta_f)$ corresponding to precisely two inequivalent impact points leading to scattering in the chosen direction θ_f. (This effect is due to the warping of the surface.) If the quantum corrections are small, each of these two sharp peaks will become a Gaussian line of finite width $\propto h^{1/2}$.

We are currently studying which surfaces, incident atom energies, and directions of incidence promise to show this predicted quantum phenomenon most clearly.

ACKNOWLEDGMENTS

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