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Perspective

Using classical mechanics in a quantum framework. Perspective on "Semiclassical description of scattering"

Ford KW, Wheeler JA (1959) Ann Phys (NY) 7: 259

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Abstract. Ford and Wheeler's paper on elastic scattering was the first to fully analyze the semiclassical limit of quantum mechanics for a collision process and thus reveal the nature of quantum corrections to classical mechanics therein. This "perspective" discusses the historical setting, the content, and present day implications of this work.

Key words: Semiclassical – Scattering – Quantum effects – Interference – Initial value representation

I have interpreted the invitation to write about an especially influential paper in our field in a very personal way, choosing one that had a particularly strong impact on me at the formative stage of my early graduate school years.

By the early 1960s the development of crossed molecular beam experimental methods had given one the vision of being able to study chemical reactions at a fundamental molecular level, and many of us that were theoretically inclined leapt at the challenges offered by this new field of chemical dynamics. Though it was clear that quantum mechanics was the right theoretical approach – and, indeed, much quantum reactive scattering theory was initiated in that early period and has born fruit up to the present – it also became clear that classical (i.e., Newtonian) mechanics was a useful approximation for describing atomic and molecular dynamics and, most importantly, that it was much easier to carry out classical trajectory calculations for reactive collisions than to solve the corresponding Schrödinger equation. (The pioneering paper of Karplus et al. [1] is thus justly one of these presently being honored as especially influential.) Today, of course, classical molecular dynamics simulations are a major industry, being applied not only to gas-phase reactive scattering but also to molecular processes in liquids, in (or on) solids, and particularly to the description of dynamical processes in large biologically relevant molecules.

One worries, however, about the neglect of quantum effects in these classical simulations, particularly when the motion of hydrogen atoms is involved. For example, the zero-point vibrational energy in CH and OH bonds is enormous (compared to normal thermal energies), and it can cause unphysical behavior in a classical simulation if not treated properly. (In many simulations these bonds are held rigid, in part to avoid any problems with zero-point energy, but this is clearly not always satisfactory, most obviously so if they are involved in chemical reactions.) Tunneling of hydrogen-atom motion can also be a significant correction to purely classical dynamics, and quantum coherence (interference) effects may also survive on the short time scales relevant to the dynamics of chemical reactions.

In seeking a way to include these quantum phenomena, while at the same time retaining the usefulness of classical trajectory approaches, Ford and Wheeler's paper [2] (to which I was introduced in a course given by Dudley Herschbach) was the Rosetta stone: it showed in a beautifully simple way how classical mechanics could be used in the framework of a rigorous quantum theory for the case of elastic scattering. This so-called semiclassical theory combined classical mechanics in a consistent way with the quantum principle of superposition (of probability amplitudes), thereby describing interference effects in the scattering cross section. (Bernstein's 1964 review [3] of semiclassical elastic scattering is still one of the best.) A companion paper by Ford et al. [4] showed how tunneling effects could also be incorporated in this semiclassical theory of elastic scattering, and a third paper [5] described several applications of the theory.

Ford and Wheeler [2] described four approximations to the quantum scattering amplitude that led to what we

would today call the "primitive" semiclassical approximation for the differential scattering cross section (or angular distribution), which has the form

$$\sigma(\theta) = \left| \sum_k \sigma_k(\theta)^{1/2} \exp\left[i\mathrm{S}_k(\theta)/\hbar\right] \right|^2 . \qquad (1)$$

Here the index k denotes different classical trajectories that lead to the same final scattering angle θ; $\sigma_k(\theta)$ is the classical cross section associated with the kth trajectory, and $\mathrm{S}_k(\theta)$ is a classical action integral along it. The only vestige of quantum mechanics in Eq. (1) is that $\hbar$ sets the units for measuring the classical action; everything else is from classical mechanics. Amazingly, however, this theory describes *all* the quantum effects in elastic scattering, at least qualitatively. (Near the rainbow angle – the boundary between a "classically allowed" and a "classically forbidden" region – the primitive version of the theory breaks down and more sophisticated treatments, uniform asymptotic methods, are needed to obtain a quantitative description.)

All of the quantum features seen in Ford and Wheeler's treatment of elastic scattering have found generalizations in inelastic and reactive scattering cross sections and other dynamical quantities. For example there are interference (and rainbow) effects in the rotational/vibrational state distributions following an inelastic/reactive collision (or after photodissociation), and generalized (or "dynamic") tunneling gives rise to "classically forbidden" processes, i.e., those for which there are no purely classical contributions. In these more general situations it has also been found that all quantum effects (also including symmetry-based selection rules and quantization of bounded motion itself) are ultimately a result of the superposition of probability amplitudes and are thus contained (at least qualitatively) in the semiclassical description.

Interestingly, if the fourth approximation in Ford and Wheeler's sequence (the stationary-phase approximation for the partial wave sum/integral) is not made, then one obtains a result for the differential cross section that would nowadays be called an initial value representation,

$$\sigma(\theta) = (2\pi\hbar \sin\theta)^{-1} \times \left| \int_{-\infty}^{\infty} \mathrm{d}b(pb)^{1/2} \exp\{i[S(b) + pb\theta]/\hbar\} \right|^2 , \qquad (2)$$

where

$$p = \sqrt{2mE} .$$

In Eq. (2) b is the initial impact parameter for the classical trajectory, and $S(b)$ the classical action for this trajectory; here there is no sum over multiple trajectories since the initial impact parameter determines a unique trajectory, but there is an integral over all initial impact parameters. Unlike the primitive semiclassical expression in Eq. (1), Eq. (2) provides a quantitative description of quantum effects in the cross section at all scattering angles (except *very* small angles, $\theta \lesssim \hbar/pa$, where a is the length scale of the long-range part of the potential), describing interference effects on the "bright" side of the rainbow angle and (generalized) tunneling behavior on the "dark" side, and also the transition between them. Initial value representations are of great interest today as a practical way of applying semiclassical theory to complex molecular processes and thus describing quantum effects therein.

In summary, Ford and Wheeler's paper was important at the conceptual level, in showing the basic nature of how quantum theory alters the classical description (of elastic scattering), and also at the practical level, in lending credence to the use of classical mechanics for atomic and molecular processes and providing the understanding of where quantum effects are likely to be significant. Semiclassical theory is still useful today in both these contexts, and certain versions of it (e.g., the initial value representation) are leading to practical ways of including quantum effects in classical molecular dynamics simulations of complex processes.

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