

A Century of Semiclassics - Tunneling and Quantization

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Abstract: Two quantum effects have had a big impact on Chemistry. Arguably the most important one is the quantization of vib-rotational energy levels, an effect which challenges classical mechanics computations of molecular dynamics and is at the basis of molecular spectroscopy. The second is quantum tunneling which is especially important when considering light atom transfer, especially hydrogen atoms and proton transfer. Tunneling was reported for the first time by Hund in 1927 in his paper which was submitted on Nov. 19, 1926. The quantization of energy levels was one of the major building blocks of the new quantum theory, the semiclassical quantization condition was formulated in the summer of 1927 by Brillouin, Wentzel and Kramers. In retrospect, a century later, we have learned much about the two effects, yet surprisingly, the giants who discovered and formulated the relevant semiclassical theories left us with some challenges. Some of these have been answered during the past five years and these are the main emphasis of this review, which is not a review of 100 years of semiclassics, a project which calls for books, rather than short review articles. At the same time, we point out some remaining challenges which have not been answered, and which demonstrate, that there is always something new to learn even when considering well established theories.

Key words: tunneling, semiclassical, rate theory, quantization.

1. Introduction

One hundred years ago, Brillouin [1], Wentzel [2] and Kramers [3] derived the well known semiclassical quantization rule for energy levels in one dimensional systems

$$S(E_n) = \oint dq \sqrt{2M[E_n - V(q)]} = 2\pi\hbar \left(n + \frac{1}{2} \right). \quad (1)$$

Here $S(E)$ denotes the action for a system with mass M governed by the Hamiltonian

$$H = \frac{p^2}{2M} + V(q) \quad (2)$$

with potential $V(q)$. n is a nonnegative integer. To be more precise, Brillouin and Wentzel's quantization condition was the old Bohr-Sommerfeld quantization rule of $2\pi\hbar n$, the important added factor of $\frac{1}{2}$ was derived by Kramers only. This famous semiclassical result has mostly been referred to as WKB theory, or JWKB theory when adding the earlier (1924) result of Jeffreys [4] obtained in his study of asymptotic expansions. Historically, Kemble [5] in his paper of 1935 refers to the theory correctly as BWK theory, reflecting the historical development. In retrospect, the really new aspect was that of Kramers, and it is this formula which has been used in innumerable contexts during the past century. Henceforth we will refer to the quantization rule of Eq. (1) as Kramers' quantization rule.

The quantization rule has been used extensively to extend the semiclassical result to multi-dimensional systems. The essential idea is that one may approximate the N dimensional Hamiltonian as being classically integrable, so that $H = H(J_1, J_2, \dots, J_N)$ and each action J_k is quantized as in Kramers' one dimensional result. This is known as Einstein [6], Brillouin [7], Kramers [8] (EBK) quantization. In the EBK method, Kramers' $\frac{1}{2}$ term is replaced by an appropriate Maslov index [9] which in the usual case follows the number of turning points of the relevant underlying orbit. This methodology can be in principle applied on the fly using appropriate Fourier transformation of classical trajectories, as presented for example in Refs. [10,11]. It has also been used in the context of perturbation theory [12].

The second aspect of this subjective review is that of tunneling. A description of the early history was given in a review article by Merzbacher, titled "The Early History of Quantum Tunneling" [13]. Briefly, Hund [14], in a paper submitted on November 19, 1926, discovered tunneling splitting of levels in symmetric molecules. A very short time later, Nordheim [15] solved the transmission and reflection probabilities for scattering on square barriers. Gamow, considered in 1928 α -particle decay of nuclei [16]. He was the first to write down the decay time in terms of the imaginary action integral for motion on the upside down potential barrier. A seminal analytic model was presented in Eckart's 1930 paper [17] where he solved analytically the energy dependent transmission and reflection probabilities through what is now termed as the Eckart barrier. This model potential played an important role in understanding quantum tunneling effects, especially within the Chemistry literature.