Comment on "Comparison of positive flux operators for transition state theory using a solvable model" [J. Chem. Phys. 104, 7015 (1996)]

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Muga *et al.*[1] have recently revisited the problem of how to define a rigorous and useful quantum mechanical version of transition state theory (QMTST). This is a problem that seems to have eternal interest, perhaps because, among other things, it appears to have no uniquely satisfying solution.

In referring to previous work of mine[2] on the subject (Ref. 13 of Muga *et al.*[1]), these authors imply that a δ-function term in the Weyl version of the positive component of the flux operator was incorrectly omitted in Ref. 2. The purpose of this Comment is to note that this term was omitted because it makes no contribution to the QMTST of Ref. 2.

Thus, the QMTST rate constant as defined in Ref. 2 [cf. Eq. (4.12)] is

$$k = \mathrm{tr}(\hat{\rho}\hat{F}_+), \tag{1}$$

where $\hat{\rho}$ is proportional to the Boltzmann operator, $e^{-\beta\hat{H}}$, for the canonical rate $k(T)$, and to the microcanonical density operator, $\delta(E-\hat{H})$, for the microcanonical rate $k(E)$. Written out explicitly for the one-dimensional case, this becomes

$$k = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx' \langle x'|\hat{\rho}|x\rangle\langle x|\hat{F}_+|x'\rangle, \tag{2}$$

where the Weyl version of the positive component of the flux operator is given by Muga *et al.*[1] [their Eq. (14)] as

$$\langle x|\hat{F}_+|x'\rangle = \frac{\hbar}{2\pi m}\,\delta\left(\frac{x+x'}{2}-x_0\right) \times \frac{\partial}{\partial x}\left[\frac{1}{x-x'} - i\pi\delta(x-x')\right]. \tag{3}$$

With the (trivial) modification $x_0=0$, Eq. (3) is my[2] Eq. (4.16) if the term $-i\pi\delta(x-x')$ is discarded. The reason this term was dropped without comment in Ref. 2 is that, from several points of view, it makes no contribution to Eq. (2) above: (i) it would give an *imaginary* contribution to the rate (because the matrix elements $\langle x'|\hat{\rho}|x\rangle$ are *real*) and there is a "real part of" symbol (explicit or implied) in front of all rate expressions in Ref. 2, and (ii) since $\langle x|\hat{\rho}|x'\rangle$ is even upon the exchange $x\leftrightarrow x'$, and $\delta'(x-x')$ is odd, the integral over x and x' in Eq. (2) involving this term vanishes identically.

There is no dispute that the δ-function term is indeed present in the matrix elements of the positive flux operator, Eq. (3) above; this is evident from its integral representation [Eq. (4.16) of Ref. 2, Eq. (16) of Ref. 1],

$$\begin{aligned}\langle x|\hat{F}_+|x'\rangle &= \delta\left(\frac{x+x'}{2}-x_0\right) \times (2\pi\hbar)^{-1}\int_0^{\infty} dp\,\frac{p}{m}\,e^{ip(x-x'+i\epsilon)/\hbar} \\ &= \delta\left(\frac{x+x'}{2}-x_0\right)\frac{\hbar}{2\pi m}\,\frac{\partial}{\partial x}\,\frac{1}{x-x'+i\epsilon},\end{aligned} \tag{4}$$

where the convergence factor $i\epsilon$ is added in the usual way to regularize the integrand at $p\to\infty$. Furthermore, there may be some situations where it makes a contribution (cf. Appendix A of Ref. 1). The point of this Comment, though, has been to note that it does not do so for the QMTST rate constant as defined in Ref. 2.

[1] J. G. Muga *et al.*, J. Chem. Phys. **104**, 7015 (1996).
[2] W. H. Miller, J. Chem. Phys. **61**, 1823 (1974).

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