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On quantal trajectories and chemical reactivity

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Abstract

Quantal corrections to classical trajectories as brought about by a "quantal force" are shown to be inconsistent, as there is no quantal trajectory.

In a recent paper[1] quantal corrections are atempted to be made to classical trajectories by using Wigner's distribution. It is shown here that such an enterprise is inconsistent.

Wigner's distribution (in one dimension) reads

$$\rho(q,p,t) = \frac{1}{2\pi\hbar} \int dy \cdot \psi^*(q-y/2,t)\psi(q+y/2,t)e^{ipy/\hbar} \ , \tag{1}$$

where $\psi(q,t)$ is the wavefunction. This ditribution has several remarkable properties; first, it is normalized, $\int \rho dq dp = 1$, secondly $\int \rho dp = |\psi(q,t)|^2$ is the position (q) distribution of probability, while $\int \rho dq = |\psi(p,t)|^2$ is the momentum (p) distribution of probability, where $\psi(p,t) = (1/\sqrt{2\pi\hbar}) \int dq \cdot \psi(q,t)e^{ipq/\hbar}$ is the Fourier transform of the wavefunction. In addition, the ρ-average of any physical quantity is also the quantal average of that quantity, which means that we have a faithful representation of the quantal mechanics in terms of the distribution ρ too. A function of q- and p- simultaneously for quantal situations is very tempting to suggest a classical picture, but this is not the case. Indeed, for a general representation

$$\psi(q) = (2\alpha/\pi)^{1/4}e^{-\alpha(q-q_0)^2}e^{-ip_0q/\hbar} \tag{2}$$

of the wavefunction ψ one gets

$$\rho(q,p) = \frac{1}{\pi\hbar}e^{-2\alpha(q-q_0)^2}e^{-(p-p_0)^2/2\alpha\hbar^2} \ , \tag{3}$$

whence one can see that for a well-determined position q_0 ($\alpha \to \infty$) the momentum is not determined, and viceversa, for a well-determined momentum p_0 ($\alpha \to 0$;) the position is not determined; though ρ provides a minimum position-momentum uncertainty $\Delta q \Delta p = \hbar/2$. Originally, the distribution ρ given by (1) has been used in fact for getting quantal corrections to the classical thermodynamics.[2]

The time dependence of ρ can easily be inferred from (1) and Schrodinger's equation for a particle of mass m; it reads

$$\partial\rho/\partial t = -(p/m)\partial\rho/\partial q + \int d\xi \cdot J(q,p-\xi)\rho(q,\xi,t) \ , \tag{4}$$

where

$$J(q,p) = \frac{i}{2\pi\hbar^2} \int dy \cdot [V(q+y/2) - V(q-y/2)]e^{-ipy/\hbar} \quad , \tag{5}$$

which leads to

$$\partial\rho/\partial t = -(p/m)\partial\rho/\partial q - \frac{\partial}{\partial p}(-\rho V' + \frac{\hbar^2}{24}V'''\partial^2\rho/\partial p^2) + ... \tag{6}$$

for a power expansion of the potential $V(q)$. It is tempting to view the $\hbar^2$-term in the *rhs* of (6) as a quantal force superimposed over the remaining classical Liouville equation; however, this leads to an inconsistent picture.

Indeed, equation (6) may be writetn as

$$\partial\rho/\partial t = -f(p)\partial\rho/\partial q - g(q,p)\partial\rho/\partial p \quad , \tag{7}$$

where

$$f(p) = p/m \ , \ g(q,p) = \frac{\partial}{\partial p}(-\rho V' + \frac{\hbar^2}{24}V'''\partial^2\rho/\partial p^2)/(\partial\rho/\partial p) \ ; \tag{8}$$

it is then solved for any function $\rho(q,p,t) = \rho(q - q(t), p - p(t))$, providing

$$\dot{q}(t) = f(p) = p/m \ ,$$

$$\dot{p}(t) = g(q,p) = -V'(q) + \frac{\hbar^2}{24}V'''(q)(\partial^3\rho/\partial p^3)/(\partial\rho/\partial p) \tag{9}$$

which resemble the classical trajectories of motion; indeed, (7) reads then

$$\partial\rho/\partial t = -\dot{q}(t)\partial\rho/\partial q - \dot{p}(t)\partial\rho/\partial p \quad , \tag{10}$$

which is Liouville's equation. However, the velocities $\dot{q}(t)$ and $\dot{p}(t)$ as given by (9) do not originate in a hamiltonian, *i.e.* there is no function H such as $\dot{q}(t) = \partial H/\partial p$ and $\dot{p}(t) = -\partial H/\partial q$, and this because of the quantal $\hbar^2$-term in (9). The existence of a hamiltonian would imply $\partial f(p)/\partial q + \partial g(q,p)/\partial q = 0$, which is not satisfied by the functions f and g given by (9), precisely due to the presence of the quantal correction. Had such an identity be satisfied, and a hamiltonian be granted, the momentum velocity would be given by

$$\dot{p}(t) = -V'(q) + \frac{\hbar^2}{24}V'''(q)(\partial^2\rho/\partial p^2)/\rho \tag{11}$$

as assumed in Ref. 1; but this is not the case, and the velocity (11) employed in Ref. 1 is consequently wrong. However, neither the momentum velocity given by (9) does better, again because of the presence of the quantal correction. Indeed, equations (9) make sense only by identifying p with $p(t)$ and q with $q(t)$; this implies $\rho(q,p,t) = \rho(q - q(t), p - p(t)) = \delta(q - q(t))\delta(p - p(t))$, as noted in Ref. 1, and in faithful agreement with a classical dynamics; however, in this case the quantal correction $\sim (\partial^3\rho/\partial p^3)/(\partial\rho/\partial p)$ in (9) vanishes, and we are indeed left with the pure classical dynamics of the problem. Moreover, Wigner's distribution given by (3) becomes the classical distribution $\delta(q - q_0))\delta(p - p_0)$ in the classical limit $\hbar \to 0$ and $\alpha \to \infty$, and q_0 and p_0 can be identified with the classical trajectory $q(t)$ and $p(t)$, respectively; this is the clasical limit of the quantal mechanics; $\hbar \to 0$ means $\hbar$ much smaller than the classical action $p_0 q_0$. Using a smoothed gaussian distribution instead of $\delta(q - q(t))\delta(p - p(t))$, as done in Ref. 1, it is either arbitrary or of the form (3); in the latter case it is not sufficiently smooth simultaneously in q and p in order to ensure a corrective contribution to classical trajectories; consequently, the attempt made in Ref. 1 is inconsistent. In fact, with a gaussian of the form $e^{-\beta(p-p_0)^2}$ for ρ the

quantal correction in (9) is $\sim \hbar^2 \beta$, and for Wigner's distribution $\beta \sim 1/\hbar^2$, so that the quantal correction is no quantal at all; in fact, it is proportional to $1/\alpha$ in (3), which means that it is arbitrary. This proves again that the quantal correction to (9) is inconsistent, and, in fact, it does not exist at all, as shown above.

It would seem that the authors of Ref. 1 make a case from equation (11) satisfying the Ehrenfest theorem $\overline{\dot{p}(t)} = -\overline{V'(q)}$, in contrast with (9) which does not; however, (11) does not satisfy the "classical Ehrenfest theorem", *i.e.* Newton's law; indeed, (11) can also be written as $\dot{p}_0 = -V'(q_0) - (1/4\alpha)V'''(q_0)$ for $\rho \sim e^{-\alpha(q-q_0)^2}e^{-\beta(p-p_0)^2}$, or, since $\beta = 1/\alpha\hbar^2$, a "quantal force" $(-\beta\hbar^2/4)V'''(q_0)$ would appear; which however, is different from the "quantal force" $(-\beta\hbar^2/6)V'''(q_0)$ appearing in (9); which shows again the inconsistency of such forces.

It seems that a quantal correction to classical trajectories in Ref. 1 is motivated by the chemical reactivity

$$R = \int_{q_1} dq \cdot |\psi(q,t)|^2 \quad, \tag{12}$$

which is the probability of finding the particle beyond a certain position q_1 where a potential barrier is supposed to be present. This is a quantal tunneling from a quasi-bound state near the origin, and, as such, is far away of being a correction to classical trajectories. Indeed, the reactivity R is given by

$$R = \sum_{kk'} c_k^* c_{k'} \int_{q_1} dq \cdot \varphi_k^*(q)\varphi_{k'}(q)e^{i(\varepsilon_k-\varepsilon_{k'})t/\hbar} \quad, \tag{13}$$

where $\varphi_k(q)$ are the eigenfunctions of the hamiltonian and the energies ε_k are the corresponding eigenvalues; for a wavepacket centered on some energy one obtains

$$R = \frac{1}{2\pi} \int_{q_1} dq \cdot \int dk \cdot e^{i(q-vt)k} = \int_{q_1} dq \cdot \delta(q-vt) \quad, \tag{14}$$

which vanishes for $t < q_1/v$ and is unity for $t > q_1/v$, the velocity $v = \partial\varepsilon/\hbar\partial k$ being the group velocity of that packet. Actually it is spread over $\Delta t \sim \Delta q/v \sim \hbar/\Delta V$, where Δq is approximately the extent of the barrier around q_1 and ΔV measures the deviation of the barrier from a constant potential. For finite temperatures $T = 1/\beta$ the reactivity is given by

$$R = \frac{1}{Z}\sum_{kk'} c_k^* c_{k'} \int_{q_1} dq \cdot \varphi_k^*(q)\varphi_{k'}(q)e^{i(\varepsilon_k-\varepsilon_{k'})t/\hbar}.$$
$$\cdot e^{-\beta\varepsilon_{k'}} + h.c. \tag{15}$$

where Z denotes the partiton function; similarly, for a wavepacket, we get

$$R = \frac{1}{2\pi} \int_{q_1} dq \cdot \int dk \cdot e^{i(q-vt)k}e^{-\beta\hbar vk} + h.c. \quad, \tag{16}$$

i.e.

$$R = \frac{1}{2} - \frac{1}{\pi}\arctan\frac{q_1-vt}{\beta\hbar v} \quad; \tag{17}$$

it exhibits the same more-or-less pronounced rise toward long times, where it goes like $R \sim 1 - \beta\hbar/\pi t$; the survival probability $1 - R$ goes therefore like $\beta\hbar/\pi t$, which can be approximated by $e^{-\pi t/\beta\hbar}$ for long times; it follows that the well-known reaction constant $k = \pi/\beta\hbar$ has a purely quantal origin, as expected. It is worth noting that it is independent of reaction, and states, in fact, the thermal equilibrium $kt \sim Tt/\hbar \gg 1$; $\hbar/T$ is the fluctuating time. Actually, the exponential rate of decay is valid for moderate times where the rate constant is given by a smaller $k \sim v/q_1$. It is worth noting in this connection that the velocity v may, in fact, depend slightly on position, as given by $v = \sqrt{2(\varepsilon - V)/m}$, and the integrals in (14) and (16) must be performed accordingly; in addition, the time of passing through barrier is zero.

References

[1] A. Donoso and C. C. Martens, Phys. Rev. Lett. **87** 223202-1 (2001).

[2] E. Wigner, Phys. Rev. **40** 749 (1932).