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REPLY

Reply to 'Comment on "Semiclassical approximations in phase space with coherent states"'

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Abstract

The Herman–Kluk (HK) formula was shown in (Baranger *et al J. Phys. A: Math. Gen.* **34** 7227) not to be a correct semiclassical limit of an exact quantum mechanical formula. Two previous attempts to derive it using semiclassical arguments contain serious errors. These statements are left totally untouched by Herman and Grossmann's comment. They argue that the formula which we found to be at fault is not the one that should be called the HK formula. However, the formula we criticized is definitely one of the steps, in fact the main step, in these two published derivations of the HK formula. Very recently, a new derivation was published by Miller. It is interesting, but it is not semiclassical.

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1. Summary

In this note of reply to Grossmann and Herman's comment (GH) [Gro02], we sincerely hope that we can clear up the serious misunderstanding that has arisen between us. Perhaps we should begin by acknowledging now, rather than at the end of the paper, the efforts of the referee and the editor of this journal, who insisted that this misunderstanding be aired out.

We see two points of contention between GH and us. One is a fundamental point of physics. The other is a relatively trivial question of interpretation. Our first point is that the Herman–Kluk approximation (HK) [Her84], irrespective of its considerable other virtues, is not a semiclassical approximation in the strict sense of the term. About this we are certain. We have shown it already in our paper [Bar01] in great detail, and we are going to show it again in section 3 in a totally different way. Therefore, every statement by GH about HK being correctly semiclassical is misleading. If the HK approximation is not semiclassical, then what

is it? This is a very interesting question that we shall not fully answer here, but we shall make a beginning. See section 3.

Our second point has to do with the sins of 'misconception' and 'misinterpretation' which are attributed to us in the introduction to the comment. Actually we are not guilty. Our paper [Bar01] shows that we knew and understood all along that the full formula has to contain an integral over initial position and momentum, as written in equation (1) of GH. This is the whole spirit of the IVR and we were entirely familiar with it. Section 4 of [Bar01] is about the IVR, and one of its earliest equations, namely (4.3), is

$$\langle x|\psi(t)\rangle = \int \langle x|K(t)|z'\rangle \frac{\mathrm{d}^2 z'}{\pi} \langle z'|\psi(0)\rangle$$

which says: to get the wavefunction at time t, take your initial wavefunction $\langle x'|\psi(0)\rangle$, transform it to the coherent state representation $\langle z'|\psi(0)\rangle$, then multiply it by the kernel $\langle x|K(t)|z'\rangle$ and integrate over all initial p' and q'. This is identical to GH's equation (7), in which they have chosen $|\psi(0)\rangle$ to be $|z_\alpha\rangle$. It is also identical to equation (1) of [Klu86] with the appropriate kernel. There is no misconception here: we always implied that our equation (4.3) was to be used. What instead is that, later, in section 5 of [Bar01], we labelled the kernel $\langle x|K(t)|z'\rangle$ with the subscript 'HK'. Apparently it is common usage in the chemical physics community to reserve the HK name for the integrated formula, but not the kernel. There are good reasons for this, to which we shall return in section 4. Our labelling by HK of the kernel was simply due to our ignorance of this common usage.

2. What does semiclassical mean?

Any approximation of quantum mechanics by a formula involving classical trajectories could be called semiclassical, no matter how the formula was obtained. When an expression is claimed to be 'semiclassically correct', however, more stringent standards are implied. Such language demands, not only that the formula involve classical trajectories, but that it be 'semiclassically derived'. This means the following. Take an exact quantum mechanical expression. Let $\hbar$ become very small. Realize that, due to multiple interference, most of the contribution comes from the vicinity of classical trajectories. Introduce these classical trajectories explicitly without changing the value of the overall expression. Then neglect whatever can be neglected in the limit $\hbar \to 0$. This is a semiclassical approximation in the strict sense. It is never unique, but it has certain rules, one of which is that all laws of quantum mechanics must be obeyed until the last moment. At that time, the smallness of $\hbar$ allows you to discard certain terms.

GH cite four derivations of the HK formula, [Her84, Kay94, Gro98, Mil02]. Of these, [Her84] and [Gro98] are actually derivations of the kernel $\langle x|K(t)|z'\rangle$, which is then introduced into the integrated formula. These are the derivations that claim to be semiclassical, and we shall return to them shortly in this section. The third reference, [Kay94], is not a derivation aiming to approximate an exact quantum mechanical formula, and therefore it cannot be termed semiclassical. It is a 'cooked up' formula, designed especially to agree with Van Vleck when transformed to the coordinate representation. See our section 5.2. Kay demands, arbitrarily, that the mixed propagator $\langle x|K(t)|z\rangle$ be a fixed-width Gaussian wavepacket. Then he demands that, when this is multiplied by $\langle z|x'\rangle$ and integrated over z, it yields the Van Vleck propagator. This eventually leads to HK, but it is not a microscopic semiclassical derivation. The fourth derivation, quite different from the other three, comes from a new paper by Miller [Mil02]. We shall consider it in section 3.

In our work [Bar01] we followed the same approach as in the aforementioned semiclassical derivations [Her84] and [Gro98] which, as we said, are derivations of the kernel. Therefore, we fully expected to find the same result, namely the HK formula. We were very surprised when it did not come out: a different formula came out instead! After checking our work carefully, we began to suspect that, perhaps, the original derivations contained mistakes. Fortunately, we soon realized that there was actually a smoking gun that showed this to be the case. The exact quantum mechanical kernel is unitary for all values of $\hbar$. This is an essential law of quantum mechanics. As $\hbar$ becomes very small the kernel remains unitary and, therefore, since only very small terms may be discarded in this limit, the semiclassical kernel must be unitary. But the kernel in [Her84] and [Gro98] was not unitary, while the one in [Bar01] was. Thus the mistake was in the earlier derivations. We found the mistake in the paper by Grossmann and Xavier [Gro98] (GX), which was the one that most resembled ours. Since such a derivation is a very subtle business in any case, we explained its origin at some length in section 4.1 of [Bar01]. Basically the mistake in GX occurs because the classical trajectory is complex, so that both q and p have a real and an imaginary part, which effectively renders phase space four dimensional in the case of one degree of freedom. They overlooked this fact and tried to define the stationary point with two real equations instead of four. The mistake in [Her84] is different and occurs at the beginning. After their change of variables from p_1, p_2 to q_1, q_2, the quadratic form Φ of the four real variables r_1, r_2, r_i, r_f is not negative definite any more; its exponential blows up in some directions. For instance, it blows up when $r_1 = r_i$. Therefore, the stationary phase approximation is illegal.

The correct semiclassical kernel coming out of the coherent state path integral is equation (4.29) of [Bar01]. There exists another correct semiclassical kernel which comes out of Heller's thawed Gaussian approximation [Hel75]. It is discussed in section 4.3 of [Bar01]. These two kernels are different, but they strongly resemble each other and they are both unitary. In section 5.1 of [Bar01] we made a very simple numerical comparison of our kernel with the kernel that enters the HK formula and with the exact kernel. The result was that our kernel was far superior. We also have some unpublished numerical comparisons involving our kernel and Heller's kernel, which show them to be about equally good.

Obviously it would be very desirable to do some numerical tests with an integrated formula similar to HK's, but involving one of the two correct semiclassical kernels. No one has done this so far except Kay [Her94], who has compared HK with calculations using Heller's thawed Gaussian kernel. We hesitate to trust his results because he allowed himself to change the normalization of the wavefunction whenever he found it to be too different from unity, an arbitrary procedure which is totally without justification. In addition, his calculations were done for a single Hamiltonian and a single energy. Therefore, nothing definitive can be said about the relative merits of the three integrated formulae. This is an interesting point because of the following. If Herman and Kluk had made a semiclassical approximation without the mistake mentioned above, they would have obtained Heller's kernel, as we shall show in a future publication [Agu02]. If Grossmann and Xavier had really done a semiclassical derivation, they would have obtained our kernel, as we showed in [Bar01]. The fact that the HK formula contains a third kernel is a pure accident, an unforeseen random development. Would the HK formula containing one of the semiclassical kernels have been better, worse or about the same as the present HK formula? It is worth finding out.

3. And what about Miller?

We shall begin by quoting a passage from Miller's very interesting review article about IVR's [Mil01], obviously the result of a lifetime involvement with the subject. In the paragraph

containing his equations (4.5) to (4.7), Miller discusses the 'modified Filinov filtering'. This is a way of evaluating an oscillatory integral, such as

$$I = \int \mathrm{d}x\, A(x)\, \mathrm{e}^{\mathrm{i}S(x)}$$

in the case where the stationary phase approximation is not good enough, but the full numerical evaluation of I is unreliable because of the oscillations of the integrand. The method consists in modifying the formula for I by introducing two extra factors containing a parameter c, which could also be a matrix, and then integrating numerically. The extra factors have the effect of concentrating the regions of integration around the points of stationary phase, without going as far as making a true stationary phase approximation. Thus the method is a kind of interpolation between the exact I and its stationary phase approximation. We quote or paraphrase Miller now: in the limit $c \to 0$, the modified formula reverts to the original integral I. In the limit $c \to \infty$, the modified formula yields exactly the stationary phase approximation. Thus the strategy is to evaluate the modified formula for finite c, extrapolating to values small enough that the $c \approx 0$ limit can be determined.

We switch now to Miller's recent paper [Mil02]. In it Miller derives the HK formula by applying modified Filinov filtering to the Van Vleck propagator, which is semiclassical. The quantity calculated is the matrix element of this propagator between two arbitrary states $\langle \Psi_f |$ and $|\Psi_i\rangle$, which has the form

$$J = \int\int \langle \Psi_f | q_1 \rangle \, \mathrm{d}q_1 \langle q_1 | K(t) | q_0 \rangle_{\text{Van Vleck}} \, \mathrm{d}q_0 \langle q_0 | \Psi_i \rangle .$$

For $\langle \Psi_f |$ and $|\Psi_i\rangle$, Miller chooses two coherent states. This simplifies the argument and the coherent states seem to disappear at the end. Apart from this modified Filinov filtering, and apart from the fact that this is the Van Vleck propagator, and not the exact one, there are no other approximations. What comes out at the end is exactly the HK formula. This is where one realizes, however, that the coherent states have not completely disappeared. They have left a trace of themselves in the parameter γ which enters in the HK formula. This is important and we shall return to it.

Before going on, we point out some danger of confusion. The parameter c appearing in this paper of Miller, which we call c_{2002}, is not the same as the c appearing in the section of his review article mentioned earlier, which would be c_{2001}. The relation between them is

$$c_{2002} = \hbar c_{2001}.$$

In the following, whenever we use c, we mean c_{2001}, which has the dimension of length squared. Miller shows that, in order to get the HK formula, one must set c equal to the mean square deviation, or variance, or squared width, of the coordinate probability distribution for the coherent states. But one does not necessarily want to calculate the matrix element J for two coherent states. It would be more useful if one could substitute for $\langle \Psi_f |$ and $|\Psi_i\rangle$ some relevant atomic or molecular wavefunctions. Miller does not mention this, but our guess is that one should use for c something like the squared width of the probability distribution for the wavefunctions $\langle x | \Psi_f \rangle$ or $\langle x | \Psi_i \rangle$. And in the HK formula one should use the corresponding value for γ, which is $1/2c$. We note that γ is also the quantity that is called $1/b^2$ in [Bar01].

To check whether Miller's result is semiclassical, we can now imagine that $\hbar$ tends toward 0. For this we go back to Miller's review article quoted in the first paragraph of this section. If c were close to 0, we could say that integral J has been evaluated exactly. This would be a semiclassical approximation since Van Vleck is one. If c were very large, we could say that J has been calculated by stationary phase, which would generally be a poor approximation for arbitrary $\langle \Psi_f |$ and $|\Psi_i\rangle$. But c is neither of these extremes. It is just the

squared width of the initial or final wavefunctions. In fact, c_{2001} does not depend on $\hbar$ at all. It is some typical length squared of the molecular system under study. Hence Miller's work shows that the HK formula is not semiclassical. What is it then? It is one particular interpolation between the exact integral (with Van Vleck propagator) and its stationary phase approximation, which is not expected to be good in most cases. There are thousands of possible interpolations. HK is just one of them, possibly a very clever one. But unless some justification is given, the presumption must be that the Filinov modification changes the value of J in some unknown way. We have found a different Filinov interpolation which happens to give the integrated formula with Heller's kernel, as given in [Bar01].

4. Conclusion

The point we are trying to make is that the justification for HK is not that it is 'the' semiclassical formula. And it is too weak a justification simply to say that 'it works'. The justification must be sought in an appropriate, approximate but correct, derivation from exact quantum mechanics. It is quite possible that the integration over the trajectories arising from the multiple initial values manages, somehow, to compensate for the individual errors and to produce a very good result. But this cannot be just stated. It has to be studied thoroughly and understood. And if such a compensation occurs, there is no reason why some similar compensation could not occur also with the two semiclassical kernels.

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