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COMMENTS

Comment on "Monte Carlo Evaluation of Real-Time Feynman Path Integrals for Quantal Many-Body Dynamics: Distributed Approximating Functions and Gaussian Sampling"

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In a recent article[1] in *The Journal of Physical Chemistry*, Kouri *et al.* compared the behavior of their Distributed Approximating Function (DAF) propagator[2] (constructed by fitting the free-particle propagator with Hermite functions) to that of the effective Truncated Plane Wave (TPW) propagator that I proposed[3] in 1989 (obtained by projecting onto a truncated basis set of plane waves to filter out high-momentum contributions)—referred to as the "Fourier" propagator in ref 1. That comparison is flawed, as I illustrate in three points below.

Effective system-specific short-time propagators $K_{\rm eff}(x_0,x_f;\Delta t)$ were introduced[3] as well-behaved functions (i.e., devoid of the very rapid oscillations of the full Feynman propagator) suitable for evolving a wave function Ψ according to the relation

$$\Psi(x_f;t+\Delta t) = \int dx_0\, K_{\rm eff}(x_0,x_f;\Delta t)\, \Psi(x_0;t) + \Delta\Psi$$

where $\Delta\Psi$ is an "acceptable" error that arises from replacing the exact propagator by $K_{\rm eff}$ and which can be made arbitrarily small by adjusting the smoothing parameters that define the effective propagator. Clearly, the smoothness of $K_{\rm eff}$ attainable in a particular application is governed by the accuracy desired; typically, increased accuracy requires use of a more oscillatory (i.e., less desirable) effective propagator. Thus, an objective comparison of the smoothness of two propagators should utilize parameters such that both propagators yield equally accurate evolution over equal lengths of time.

As a first point, therefore, the comparison of Kouri *et al.* is not accurate, because the parameters used by these authors in their graphical illustration of the two propagators were not selected with the same accuracy considerations. Instead, the parameters in ref 1 were adjusted arbitrarily to enforce resemblance of the two propagators in the small $|x_f - x_0|$ region. Thus, the DAF propagator in Figure 1 of ref 1, while smoother than the TPW propagator shown in the same figure, produces significant errors in the evolution after less than one vibrational period (see Figure 1 below). (These errors were not observed in ref 1 because the numerical tests reported there covered only *half* a vibration.) By contrast, the TPW propagator yields essentially exact results over many oscillations. If the parameters of the DAF propagator are altered to increase accuracy, it becomes just as nonsmooth as the TPW.

As a second (and perhaps more fundamental) point, the conclusions of ref 1 regarding the expected performance of the two propagators in a Monte Carlo path integral calculation are wrong, because they are based on examination of the smoothness of the *real part* of these propagators. It is clear that the magnitude of the Monte Carlo error (which determines the feasibility of a path integral calculation) is *not* governed by the decay characteristics of the real (or imaginary) part of the effective propagator $K_{\rm eff}(x_{k-1},x_k;\Delta t)$ itself but rather by the behavior of the *product* of two such propagators:[4]

$$K_{\rm eff}(x_{k-1},x_k;\Delta t)\, K_{\rm eff}(x_k,x_{k+1};\Delta t)$$

This is so because each variable x_k appears *twice* in the integrand of the path integral. If this product is examined, the two propagators compared in ref 1 and in Figure 1 of this Comment appear almost indistinguishable. Furthermore, Figure 2 shows the real and imaginary parts of the above propagator product as functions of the path integral variable x_k at fixed values of x_{k-1} and x_{k+1} with parameters chosen such that both propagators produce results of similar accuracy (errors smaller than 1%) when used to propagate the same initial wave function over at least five vibrational periods. It is seen that in contrast to the bare propagators, the above critical product is *better behaved* (i.e., less oscillatory) in the case of the TPW propagator than it is in the case of the DAF propagator.

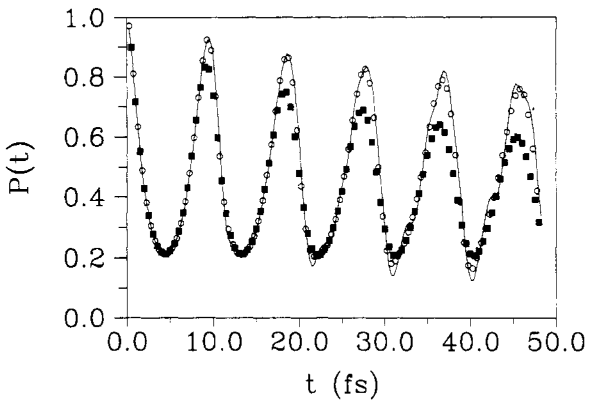

Figure 1. Survival probability over about five vibrational periods for the model problem considered in ref 1. Solid line: exact results, obtained by the split propagator method. The points are results obtained with the DAF and TPW propagators, with the particular parameters employed by Kouri *et al.* (cf. Figure 1 of ref 1). Solid squares: evolution using the DAF propagator with $M = 14$, $\sigma(0) = 0.3$. Open circles: evolution using the TPW propagator with $p_{\rm max} = 12$.

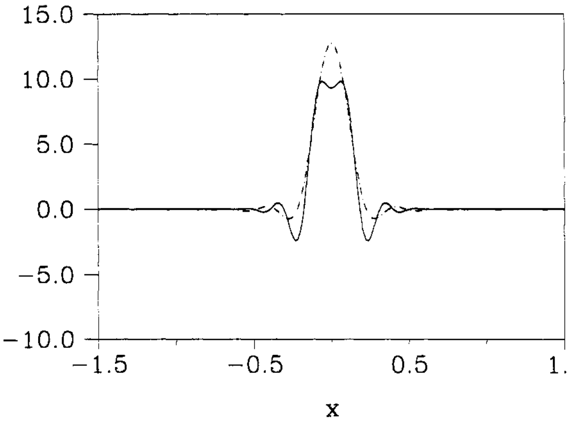

Figure 2. Real part of the critical propagator product

$$K_{\rm eff}(x_1,x;\Delta t)\, K_{\rm eff}(x,x_2;\Delta t)$$

as a function of x for $x_1 = x_2 = 0$ for the DAF and TPW propagators (the potential part is not included). The parameters were chosen such that both propagators yield time evolution accurate to within 1% for the model problem of ref 1 over five vibrational periods. Solid line: DAF propagator ($M = 14$, $\sigma(0) = 0.23$). Chain-dotted line: TPW propagator ($p_{\rm max} = 13$).

Third, Kouri *et al.* incorrectly state[1] that the sampling function I used in the Monte Carlo evaluation of the path integral in ref

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3 produces an exponentially growing integrand, thus causing inefficient sampling. Such pathological behavior was avoided in ref 3 by realizing that Monte Carlo steps of length larger than some Δx can rigorously be excluded. Choosing the sampling function to roughly fit the propagator within the relevant range of Δx and truncating the integrand outside that interval guarantees a stable Monte Carlo scheme, for the integrand is of order unity within the sampled region and *zero* (as opposed to exponentially large) elsewhere.

As a final remark, it should be noted that small differences in the smoothness of various effective propagators have little effect on the achievable number of time steps because the latter increases only logarithmically with numerical effort when the integrand is oscillatory.[4] In that regard, the convergence of Monte Carlo path integral calculations at long time can be dramatically improved by the construction of propagators which—while sufficiently smooth—are valid for significantly longer time increments compared to the Trotter-type DAF or TPW propagators, and we have recently focused our efforts in that direction.[5]

References and Notes

(1) Kouri, D. J.; Zhu, W.; Ma, X.; Pettitt, B. M.; Hoffman, D. K. *J. Phys. Chem.* **1992**, *96*, 9622.

(2) Hoffman, D. K.; Nayar, N.; Sharafeddin, O. A.; Kouri, D. J. *J. Phys. Chem.* **1991**, *95*, 8299. Hoffman, D. K.; Kouri, D. J. *J. Phys. Chem.* **1992**, *96*, 1179. Hoffman, D. K.; Arnold, M.; Kouri, D. J. *J. Phys. Chem.* **1992**, *96*, 6539.

(3) Makri, N. *Chem. Phys. Lett.* **1989**, *159*, 489. Makri, N. *Comp. Phys. Comm.* **1991**, *63*, 389.

(4) Makri, N. *J. Phys. Chem.* **1993**, *97*, 2417.

(5) Makri, N. *Chem. Phys. Lett.* **1992**, *193*, 435. Makri, N. In *Time-Dependent Quantum Molecular Dynamics*; Broeckhove, J., Lathouwers, L., Eds.; Plenum Press, 1992; p 209. Topaler, M.; Makri, N. *J. Chem. Phys.* **1992**, *97*, 9001.