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Comment on: A corrected exponential power series expansion of the position matrix elements of the time evolution operator for a system in the presence of a vector potential

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Recently, Makri and Miller presented a simple exponential power series in the time for the position matrix elements of the time evolution operator (hereafter called "propagator"), first within a semiclassical approximation,[1] and then a fully quantum mechanical version.[2] The resulting recursion relations for the coefficients of the time were readily obtained. The coefficients are solutions of simple first order inhomogeneous differential equations. The method was developed for Hamiltonians which did not contain vector potentials (or velocity dependent potentials in general). The second paper[2] included a section claiming to generalize the procedure to include vector potentials, but this is unfortunately in error. The purpose of this comment is to point this out and discuss how the correct coefficients are related to the exact results for a system which is in the presence of a constant magnetic field.

Suppose we consider a 3D system in the presence of a vector potential **A**. The Hamiltonian is

$$H=\frac{1}{2m}\left(\mathbf{p}-\frac{e}{c}\mathbf{A}(\mathbf{r})\right)^2+V(\mathbf{r}). \tag{1}$$

The propagator is defined as

$$\langle \mathbf{r}t|\mathbf{r}_0o\rangle=\langle \mathbf{r}|e^{-iHt/\hbar}|\mathbf{r}_0\rangle. \tag{2}$$

Makri and Miller expanded $\langle \mathbf{r}t|\mathbf{r}_0o\rangle$ in an exponential power series in time,

$$\langle \mathbf{r}t|\mathbf{r}_0o\rangle\equiv\langle \mathbf{r}t|\mathbf{r}_0o\rangle_0\exp\frac{i}{\hbar}(W_1+W_2t+W_3t^2+\cdots), \tag{3}$$

with

$$\langle \mathbf{r}t|\mathbf{r}_0o\rangle_0=\left(\frac{m}{2\pi i\hbar t}\right)^{3/2}\exp\frac{im(\mathbf{r}-\mathbf{r}_0)^2}{2\hbar t}, \tag{4}$$

the free particle propagator. They then showed that the coefficients W_n satisfy,

$$(n-1)W_n-\frac{i\hbar}{2m}\nabla^2W_{n-1}+\frac{1}{2m}\sum_{n'=0}^{n}\nabla W_{n'}\cdot\nabla W_{n-n'}+\delta_{n2}\left[V(\mathbf{r})+\frac{e^2}{2mc^2}\mathbf{A}^2(\mathbf{r})\right]-\frac{e}{mc}\mathbf{A}\cdot\nabla W_{n-1}=0. \tag{5}$$

The equation for W_1 is particularly important,

$$(\mathbf{r}-\mathbf{r}_0)\cdot\nabla W_1=\frac{e}{c}(\mathbf{r}-\mathbf{r}_0)\cdot\mathbf{A}(\mathbf{r}), \tag{6}$$

a well-known result.[3]

Makri and Miller integrated Eq. (6) to arrive at the usual straight line approximation for a propagator in the presence of a vector potential,[4] namely

$$W_1=\frac{e}{c}\int_{\mathbf{r}_0}^{\mathbf{r}}d\mathbf{l}\cdot\mathbf{A}(\mathbf{l})=\frac{e}{c}\int_0^1 ds(\mathbf{r}-\mathbf{r}_0)\cdot A[\mathbf{r}_0+s(\mathbf{r}-\mathbf{r}_0)]. \tag{7}$$

Their error was in assuming that Eq. (7) is equivalent to[5]

$$\nabla W_1=\frac{e}{c}\mathbf{A}. \tag{8}$$

Equation (8) says that **A** is a gradient of a scalar, which corresponds to a gauge transformation. Thus, the subsequent equations for W_2, W_3, etc., are in error. Their result (after correcting an arithmetic error) is

$$\langle \mathbf{r}t|\mathbf{r}_0o\rangle=\langle \mathbf{r}t|\mathbf{r}_0o\rangle_{\mathbf{A}=0}\exp\left(\frac{ie}{c}\int_{\mathbf{r}_0}^{\mathbf{r}}d\mathbf{l}\cdot\mathbf{A}(\mathbf{l})\right), \tag{9}$$

an expression which is approximately true when $\mathbf{B}=\nabla x\mathbf{A}$, but exactly true when $\mathbf{A}(\mathbf{r})=\nabla\lambda$.

The above analysis can be illustrated by the simple example of a system in a constant magnetic field, for which (in the symmetric gauge),

$\mathbf{A}(\mathbf{r})=\frac{1}{2}\mathbf{B}x\mathbf{r}$.

When $V=0$, or V is linear and/or quadratic in **r**, $\langle \mathbf{r}\,t|\mathbf{r}_0o\rangle$ is exactly known. In the case when $V=0$, we have in units of $\hbar=1$, and $m=1$,[6]

$$\langle \mathbf{r}t|\mathbf{r}_0o\rangle=\left(\frac{1}{2\pi it}\right)^{3/2}\frac{\omega t}{\sin\omega t}e^{-iV_0(t)}, \tag{10}$$

where

$$\omega=\frac{eB}{2c}, \tag{11}$$

and

$$V_0(t)=\omega\hat{B}\cdot(\mathbf{r}x\mathbf{r}_0)+\frac{1}{2t}[\hat{B}\cdot(\mathbf{r}-\mathbf{r}_0)]^2+\omega\cot\omega t[\hat{B}x(\mathbf{r}-\mathbf{r}_0)]^2. \tag{12}$$

Note that the first term in $V_0(t)$ is just W_1. By direct expansion one can see that, e.g., W_2, is

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$$W_2 = -\frac{\omega^2}{6}[\hat{B}x(\mathbf{r}-\mathbf{r}_0)]^2. \tag{13}$$

Here it is easy to obtain the explicit forms for W_1 and ∇W_1:

$$W_1 = \frac{e}{2c}\mathbf{r}\cdot(\mathbf{r}_0 x B), \tag{14}$$

and

$$\nabla W_1 = \frac{e}{2c}\mathbf{r}_0 x\mathbf{B}. \tag{14'}$$

Hence, we do have that Eq. (6) is satisfied, because of the cross produce rule, even though **A** is certainly not ∇W_1.

Finally, we point out that Eq. (5) is still valid for short times and correct expressions for W_2, etc., may readily be determined. For example, the correct equation for W_2 is

$$(\mathbf{r}-\mathbf{r}_0)\cdot\nabla W_2 + W_2 = -V(\mathbf{r}) + \frac{i\hbar}{2m}\nabla^2 W_1 - \frac{1}{2m}\left(\nabla W_1 - \frac{e}{c}\mathbf{A}(\mathbf{r})\right)^2. \tag{15}$$

Notice that this equation depends on the difference $(\nabla W_1 - (e/c)\mathbf{A})$, which is gauge invariant. Also, because we have chosen (and used) $\nabla\cdot\mathbf{A} = 0$, then $\nabla^2 W_1 = 0$ for that portion of ∇W_1 which is due to a gauge potential. The equations for the higher W's will also be gauge invariant.

In conclusion, a corrected short time propagator in the spirit of Makri and Miller may certainly be obtained. For homogeneous magnetic fields the method may be unnecessary.[7] For inhomogeneous magnetic fields the chief use of the entire idea may well be to determine "ground state" path integrals, and arrive at density-current functional theories.[7–9] As may readily be shown, W_1 alone gives no contribution to ground state properties when the short time expansion is used without further shredding of the propagator.[8] In many particle Green's functions, W_1 alone has a nonvanishing effect in two particle Green's functions.[3,4]

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[1] N. Makri and W. H. Miller, Chem. Phys. Lett. **151**, 1 (1988).

[2] N. Makri and W. H. Miller, J. Chem. Phys. **90**, 904 (1989).

[3] See, for example, A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw Hill, New York, 1971), pp. 468–469.

[4] See the article by N. R. Werthamer in *Superconductivity*, edited by R. D. Parks (M. C. Dekker, New York, 1969), p. 321.

[5] Equation (3.7) of Ref. 2.

[6] E. H. Sondheimer and A. H. Wilson, Proc. R. Soc. London Ser. A **210**, 173 (1951).

[7] R. A. Harris and J. A. Cina, J. Chem. Phys. **79**, 1381 (1983).

[8] R. A. Harris and L. R. Pratt, J. Chem. Phys. **82**, 5084 (1985).

[9] C. J. Grayce and R. A. Harris, Mol. Phys. **70**, 1 (1990).