

## Reply to "Comment on 'Optimization of approximate solutions to the time-dependent Schrödinger equation'"

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A method for determining optimal approximate solutions of the time-dependent Schrödinger equation was previously presented by Weglein [Phys. Rev. A 17, 1810 (1978)]. Maidagan and Piacentini have written a comment (preceding Comment) on that work. Their conclusion is simply incorrect. We show precisely where the error in their reasoning occurred.

Equations (1)–(9) and the first equality of Eq. (10) of Ref. 1 are contained in the original Refs. 2 and 3. However, the second equality of Eq. (10) is a new and interesting insight which deserves some attention. Both portions of Eq. (10) are correct. Unfortunately, the conclusions that these authors draw from it are not. These authors argue that since  $\dot{N}(t)$  is zero at the final time  $t_f$  [since  $P^*(t_f)$  is zero] then a zero wave function will be obtained at  $t_f$ . Their error occurs in not distinguishing the difference between the derivative of a function vanishing at a point, and the function itself vanishing at a point. The only valid conclusion in this case is that  $N(t)$  approaches a constant. Since  $\dot{N}(t)$  is always negative and  $N(t_i)$  equals one, the value of  $N(t)$  is bounded by zero and one.

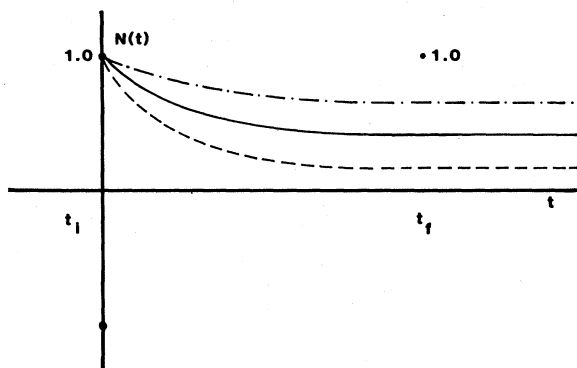


FIG. 1. Three functions  $N(t)$  which satisfy Eqs. (1)–(10) of Ref. 1.

In Fig. 1 we illustrate three possible normalizations which satisfy the negative  $\dot{N}$  criteria, but do not give a zero wave function at  $t_f$ . The particular realization of  $N(t)$  obviously depends on the magnitude of  $\dot{N}$ . The magnitude of  $N$  depends on the difference between the trial function and the exact wave function. If the portion of Hilbert space spanned by the trial function is a good approximation to the exact solution, then the value of the error will be small, and the value of  $N$  at  $t_f$  will be close to one. However, if a significant portion of the exact solution is outside the part of Hilbert space spanned by the trial solution, then the rate of diminution of  $N(t)$  is greater and the norm of the trial function, at large times, could be significantly less than one. This is exactly what we would expect, and it again points out the difference between the usual close-coupled equations and this method. The usual close-coupled equations [Eq. (103) of Ref. 3] give  $N(t) = 1$  for all  $t$  independently of how well the trial function approximates the exact solution. The extra freedom which results from the method of Ref. 2 not only gives optimal transition probabilities, in an error minimization sense, but also provides an indication of how well a trial solution approximates the exact solution. This adds an extra practical value to the method in that the final value of the norm is an indication of the adequacy of the trial solution.

In conclusion, the interesting new point that these authors make is that the trial solution in the method of Ref. 2 has an *always* diminishing norm. The error in their reasoning is the assumption that this means that the limit of the large time norm is zero. Rather than demonstrating the lack of physical reasonability of the work in Ref. 2, these authors have inadvertently added to its significance.

<sup>1</sup>J. M. Maidagan and R. D. Piacentini, preceding Comment, Phys. Rev. A 31, 4023 (1985).

<sup>2</sup>A. B. Weglein, Phys. Rev. A 17, 1810 (1978).

<sup>3</sup>A. B. Weglein and D. Rapp, in *Gas Phase Ion Chemistry*, edited by M. T. Bowers (Academic, New York, 1979), Vol. 2.