

# Response to "Comment on 'Generalization of the multiconfigurational time-dependent Hartree method to nonadiabatic systems'"

[J. Chem. Phys. 109, 349 (1998)]

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(Received 11 March 1997; accepted 27 March 1998)

[S0021-9606(98)02725-1]

As mentioned in the very abstract of Ref. 1, the objective of the paper is to present a completely generalized and compact equation of motion for multiconfiguration time-dependent Hartree method (MCTDH) on *full collision* nonadiabatic systems involving an arbitrary number of surfaces and dimensions. This leads to Eq. (12) in Ref. 1, which is not found in any of the references mentioned by Fang, Meyer, and Worth. However, it is correct that MCTDH has been applied to special nonadiabatic systems before, but the fundamental equations of motion for the single-particle functions are expressed in a different and most of all less general form than the one we present.

Meyer and co-workers<sup>2-4</sup> have extended the original single-surface formulation of MCTDH<sup>5</sup> to multisurface photodissociation (i.e., half-collision) systems by simply using one of the degrees of freedom as a gridless electronic coordinate. This corresponds to using the same single-particle functions on all of the electronic surfaces, which is clearly only justifiable when studying *half collisions* where the single-particle functions on the different surfaces do not occupy the same configurations in time-space. However, when studying the more general full collision dynamics, the formulation of Meyer and co-workers is, in our opinion, less adequate and one has to extend the working equations to include different single-surface functions for the different electronic surfaces. This is exactly what was done in Ref. 1. Special simplified cases of this generalized set of working equations can be found in a series of publications by Fang and Guo. But even the simplified Eqs. (7) and (8) in the Comment by Meyer *et al.* are not found anywhere in the literature. The unitary transformation mentioned in the Comment is, in our opinion, nontrivial. We therefore think that the form which was derived in Ref. 1 is more general and more appropriate for nonadiabatic full collision problems than those derived prior to our paper.

However, we do admit that it would have been appropriate to cite some of the MCTDH references by Fang and co-workers as well as Meyer and co-workers.

In the last part of their comment, they seem to merely cite a private communication with Meyer prior to the submission of the comment. In this communication we emphasized that the text between Eqs. (18) and (19) in Ref. 1 should have read "and we assume the fixed single-particle functions." But the same scheme has in fact been used by Meyer *et al.*<sup>6</sup> in MCTDH papers. However, that the testing system in Ref. 1 was too simplistic to conclusively judge upon the usefulness of the MCTDH method was explicitly pointed out in Ref. 1, and this point therefore does not deserve any more attention. Our point of view is that the MCTDH method is an approximate method which only in the limit of many basis functions becomes exact. It is therefore important to test it against other exact methods. The fact that these other methods cannot be used for some of the systems mentioned by Fang and Meyer cannot be used as an argument for not performing such tests. For example, in our simple case, the resonance might easily have been overlooked if an accurate calculation had not been performed. Furthermore, we have just finished a two-dimensional, two-surface full collision study of H<sub>2</sub>+Cu(100) using our interaction formulation of the nonadiabatic MCTDH presented in Ref. 1. This work, which will be submitted to J. Chem. Phys. shortly, actually repeats the conclusion made for the numerical study of Ref. 1—namely, that the direct exact propagation method here is also much faster than the nonadiabatic MCTDH.

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<sup>6</sup>A. Jäckle and H. D. Meyer, J. Chem. Phys. **102**, 5605 (1995).