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A multiconfiguration time-dependent Hartree approximation based on natural single-particle states

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The time-dependent Schrödinger equation is solved with a multiconfiguration form for the state. It is shown that the use of natural single-particle states results in a minimal number of configurations. The equations of motion of the natural single-particle states are derived by differentiation with respect to time of the defining equations, which are eigenvalue equations of reduced density matrices. The method is tested on a two-dimensional model of H_2 dissociation on a transition metal surface. It is shown that numerically exact solutions can be obtained. Computation times and memory requirements are less than for methods that solve the time-dependent Schrödinger equation directly.

I. INTRODUCTION

Grid methods for solving the time-dependent Schrödinger equation (TDSE) in quantum dynamics have become a good alternative to time-independent methods. This is due to the faster hardware of computers and the development of very efficient algorithms to solve the TDSE. Especially for reactive scattering, the grid methods are easier to use. The grid methods have been used in gas phase reactions, in surfaces reactions, and also in high energy physics (for reviews see Refs. 1–4).

In spite of the advances over the last years^{5–9} a quantum dynamics simulation using grid methods forms still a large computation. As the computation time scales exponentially with the number of degrees of freedom grid methods have mainly been restricted to systems of dimension three or less. It is possible to go to higher dimensions if an approximation of the exact state of the system is made. We mention the Gaussian wave packet method,^{2,10,11} where the coordinate representation of the state is approximated by a Gaussian wave packet, and the time-dependent Hartree (TDH) approximation,^{12–16} where the state is written as a tensor product.

Success of the TDH approximation depends on whether or not there is a strong correlation between the factors of the product. This depends on the coordinates that are used. An obvious extension, to include correlation, is to write the state as a sum of products. This leads to the multiconfiguration time-dependent Hartree (MCTDH) approximation. Recently Manthe *et al.*^{17–19} have generalized initial work,^{12,20–23} and have shown that the MCTDH approximation can be as accurate as solving the TDSE directly at drastically reduced computational cost.

In this paper we would like to present our work on the MCTDH approximation, which differs in two important aspects from previous work. First, to analyze the convergence of the state with respect to the number of configurations natural single-particle states have been used. We construct the configurations directly from these natural single-particle states. This has the advantage that we have a minimal number of configurations, and an additional

analysis of the configurations becomes superfluous. Second, in order to derive the equations of motion of the natural single-particle states we do not use a time-dependent variational principle. It turns out to be much easier to get the equations of motion by differentiation of the eigenvalue equation of the reduced density matrix that defines the natural single-particle states with respect to time. Although our work deals almost exclusively with configurations of two factors, we will show that with this derivation it is almost trivial to derive the equations for three or more factors.

As an example we will show results for simulations of the H_2 dissociation on transition metals modeled by a number of potential energy surfaces (PES's) with barriers in different positions.²⁴ As degrees of freedom we only use the H–H distance and the H_2 -substrate distance. We will primarily focus on the convergence of the simulations with the number of configurations.

II. THEORY

A. The multiconfiguration state

We approximate the exact state $|\Psi\rangle$ with a state of the form

$$|\Psi_{\text{MCTDH}}\rangle = \sum_{n=1}^{N_{\text{conf}}} |\psi_n^{(1)}\psi_n^{(2)}\rangle. \quad (1)$$

Here we have split all degrees of freedom of the system into two groups corresponding to two Hilbert spaces H_1 and H_2 . The Hilbert space of the whole system is $H_1 \otimes H_2$, $|\psi_n^{(1)}\rangle \in H_1$, and $|\psi_n^{(2)}\rangle \in H_2$. We will call each term in Eq. (1) a configuration, and each $|\psi_n^{(1)}\rangle$ and each $|\psi_n^{(2)}\rangle$ a single-particle state. For convenience and without loss of generality we can impose the restrictions

$$\langle \psi_n^{(1)} | \psi_m^{(1)} \rangle = \delta_{nm}, \quad (2)$$

$$\langle \psi_n^{(2)} | \psi_m^{(2)} \rangle = 0 \quad \text{if } n \neq m, \quad (3)$$

and

$$\sum_{n=1}^{N_{\text{conf}}} \langle \psi_n^{(2)} | \psi_n^{(2)} \rangle = 1. \quad (4)$$

The last equation normalizes $|\Psi_{\text{MCTDH}}\rangle$. The inner product $\langle \psi_n^{(2)} | \psi_n^{(2)} \rangle$ gives the fraction that the configuration $|\psi_n^{(1)} \psi_n^{(2)}\rangle$ contributes to $|\Psi_{\text{MCTDH}}\rangle$. There are no other restrictions on the terms in Eq. (4). In particular, $\langle \psi_n^{(2)} | \psi_n^{(2)} \rangle$ may be zero. Equations (2)–(4) still do not unambiguously define the single-particle states. An additional restriction is necessary in the case when $\langle \psi_n^{(2)} | \psi_m^{(2)} \rangle = \langle \psi_m^{(2)} | \psi_n^{(2)} \rangle$ for certain n and m with $n \neq m$. This restriction will be determined, however, by the equations of motion, and will therefore be treated in the next subsection.

In their work Manthe *et al.*^{17–19} have pointed out the role of natural single-particle functions. Here we extend their discussion. Suppose $|\Psi\rangle$ is the normalized exact state. What are then the single-particle states with which to approximate $|\Psi\rangle$ best for some fixed number N_{conf} of configurations? We answer this question by minimizing $\langle \Delta | \Delta \rangle$ where

$$|\Delta\rangle \equiv |\Psi\rangle - \sum_{n=1}^{N_{\text{conf}}} |\psi_n^{(1)} \psi_n^{(2)}\rangle, \quad (5)$$

by varying the single-particle states, and using Lagrange multipliers for the restrictions (2)–(4). This leads to

$$\langle \psi_m^{(2)} | \Psi \rangle = \mu \langle \psi_m^{(1)} | \psi_m^{(2)} \rangle \quad (6)$$

and

$$\langle \psi_m^{(1)} | \Psi \rangle = \mu \langle \psi_m^{(2)} | \psi_m^{(1)} \rangle. \quad (7)$$

Here μ , which is real, is the Lagrange multiplier associated with Eq. (4). Note that $\langle \psi_m^{(2)} | \Psi \rangle \in H_1$ in Eq. (6) and $\langle \psi_m^{(1)} | \Psi \rangle \in H_2$ in Eq. (7). Substitution of these equations into the expression for $\langle \Delta | \Delta \rangle$ yields

$$\langle \Delta | \Delta \rangle = 2(1 - \mu). \quad (8)$$

Hence μ indicates the accuracy of our approximation. Elimination of $\langle \psi_m^{(2)} |$ in the left-hand side of Eq. (6) gives us finally an equation for the $|\psi_n^{(1)}\rangle$'s

$$\hat{\rho}_1 |\psi_m^{(1)}\rangle = \nu_m |\psi_m^{(1)}\rangle, \quad (9)$$

with

$$\hat{\rho}_1 = \text{Tr}^{(2)} |\Psi\rangle \langle \Psi|, \quad (10)$$

where the trace is over H_2 , and

$$\nu_m = \mu^2 \langle \psi_m^{(2)} | \psi_m^{(2)} \rangle. \quad (11)$$

Equation (9) is an eigenvalue equation of a reduced density matrix. Hence the single-particle states should be, so-called, natural single-particle states of the exact state $|\Psi\rangle$ (there is a similar equation for the $|\psi_m^{(2)}\rangle$'s). A similar theorem has been known for a long time in the configuration interaction approximation for electrons.²⁵ The natural single-particle states do not depend on the number of configurations N_{conf} . As

$$\sum_{\{n\}} \nu_n = \sum_{\{n\}} \mu^2 \langle \psi_n^{(2)} | \psi_n^{(2)} \rangle = \mu^2, \quad (12)$$

where the summations is over the N_{conf} natural single-particle states that we choose to construct the multiconfiguration state, and because of Eq. (8), we get the following formal procedure to obtain the best multiconfiguration state. Compute the $|\psi_m^{(1)}\rangle$'s from Eq. (9); choose those with the highest eigenvalue; calculate μ using Eq. (12); and compute the $|\psi_m^{(2)}\rangle$'s using Eq. (7). That we should choose the largest eigenvalues follows also from Eq. (7), which yields

$$\sum_{n=1}^{N_{\text{conf}}} \langle \psi_n^{(1)} \psi_n^{(2)} | \Psi \rangle = \mu. \quad (13)$$

Note that $\sum_{\{n\}} \nu_n \leq 1$, where the summation is now over any subset of all eigenvalues, because $|\Psi\rangle$ is normalized. The ν_n 's are non-negative, because the reduced density matrix is semipositive definite.

The derivation above shows that, in approximating the solution of the time-dependent Schrödinger equation by a multiconfiguration state, we would like to obtain the evolution of the natural single-particle states. Except for the initial state, it is not possible to use for this Eq. (9), as it requires the exact state $|\Psi\rangle$. Therefore, we have to look for equations of motion for the natural single-particle states without reference to the exact state.

B. The equations of motion

The usual procedure to derive equations of motion for an approximate state is to use a time-dependent variational principle like the one derived by McLachlan.²⁶ This leads to the same equations of motion that we will derive. However, in such a derivation, the fact that we want to obtain the evolution of natural single-particle states cannot be expressed. Hence we have chosen for a different approach. Additional advantages of this derivation are that it is simpler, and that it can be extended most easily to the case where the degrees of freedom are split into more than two groups as will be shown at the end of the next section.

We assume that we have at a time t the exact state $|\Psi\rangle$ in a multiconfiguration form

$$|\Psi\rangle = \sum_n |\psi_n^{(1)} \psi_n^{(2)}\rangle, \quad (14)$$

where the $|\psi_n^{(1)}\rangle$'s and $|\psi_n^{(2)}\rangle$'s are defined by Eqs. (7) and (9). It is convenient in this derivation to put no bounds on the number of configurations. Later on we will see how to obtain results for a finite number of configurations. Part of that procedure will be simply putting $|\psi_n^{(2)}\rangle = |0\rangle$ for almost all except for a finite number of n 's. One of the consequences of having an infinite number of configurations is that we can put $\mu = 1$ in Eq. (7), because the summation in Eq. (12) becomes the trace of $\hat{\rho}_1$ which equals one. The equations of motion for the $|\psi_n^{(1)}\rangle$'s we find by differentiation of Eq. (9) with respect to time, and application of $\langle \psi_m^{(1)} |$. This gives us

$$\begin{aligned} \langle \psi_m^{(1)} | \frac{d\hat{p}_1}{dt} | \psi_n^{(1)} \rangle + v_m \left\langle \psi_m^{(1)} \left| \frac{d\psi_n^{(1)}}{dt} \right. \right\rangle \\ = \frac{dv_n}{dt} \delta_{mn} + v_n \left\langle \psi_m^{(1)} \left| \frac{d\psi_n^{(1)}}{dt} \right. \right\rangle, \end{aligned} \quad (15)$$

For $n=m$ this becomes

$$\begin{aligned} \frac{dv_n}{dt} &= \langle \psi_n^{(1)} | \frac{d\hat{p}_1}{dt} | \psi_n^{(1)} \rangle \\ &= -i \langle \psi_n^{(1)} | \text{Tr}^{(2)} [\hat{H} | \Psi \rangle \langle \Psi | - | \Psi \rangle \langle \Psi | \hat{H} | \psi_n^{(1)} \rangle \\ &= 2 \text{Im} [\langle \psi_n^{(1)} \psi_n^{(2)} | \hat{H} | \Psi \rangle]. \end{aligned} \quad (16)$$

(We use units with $\hbar=1$.) For $n \neq m$ we obtain from Eq. (15)

$$\begin{aligned} i(v_n - v_m) \left\langle \psi_m^{(1)} \left| \frac{d\psi_n^{(1)}}{dt} \right. \right\rangle &= i \langle \psi_m^{(1)} | \frac{d\hat{p}_1}{dt} | \psi_n^{(1)} \rangle \\ &= \langle \psi_m^{(1)} \psi_n^{(2)} | \hat{H} | \Psi \rangle \\ &\quad - \langle \Psi | \hat{H} | \psi_n^{(1)} \psi_m^{(2)} \rangle. \end{aligned} \quad (17)$$

If $v_n \neq v_m$ then this equation gives us $\langle \psi_m^{(1)} | d\psi_n^{(1)}/dt \rangle$. If, however, $v_n = v_m$ then $\langle \psi_m^{(1)} | d\psi_n^{(1)}/dt \rangle$ is undetermined. Moreover, we must have $M_{nm} \equiv \langle \psi_m^{(1)} \psi_n^{(2)} | \hat{H} | \Psi \rangle - \langle \Psi | \hat{H} | \psi_n^{(1)} \psi_m^{(2)} \rangle = 0$ in order for Eq. (17) to hold. As M is an anti-Hermitian matrix this can be accomplished with the transformation

$$| \psi_n^{(1)} \rangle \rightarrow \sum_m | \psi_m^{(1)} \rangle U_{mn}, \quad (18)$$

$$| \psi_n^{(2)} \rangle \rightarrow \sum_m | \psi_m^{(2)} \rangle U_{mn}^*, \quad (19)$$

where U diagonalizes M . This transformation does not change $|\Psi\rangle$ if the indices are restricted to those for which $v_n = v_m$ holds.

We may assume that the $|\psi_n^{(1)}\rangle$'s form a complete basis for Hilbert space H_1 , as we can always add terms with $|\psi_n^{(2)}\rangle=0$ to the sum in Eq. (14). We can therefore rewrite Eq. (17) as

$$i \frac{d}{dt} | \psi_n^{(1)} \rangle = \sum_m A_{nm} | \psi_m^{(1)} \rangle, \quad (20)$$

with

$$A_{nm} = \frac{\langle \psi_m^{(1)} \psi_n^{(2)} | \hat{H} | \Psi \rangle - \langle \Psi | \hat{H} | \psi_n^{(1)} \psi_m^{(2)} \rangle}{\langle \psi_n^{(2)} | \psi_n^{(2)} \rangle - \langle \psi_m^{(2)} | \psi_m^{(2)} \rangle}, \quad (21)$$

if $\langle \psi_n^{(2)} | \psi_n^{(2)} \rangle \neq \langle \psi_m^{(2)} | \psi_m^{(2)} \rangle$. We have used Eq. (11) to eliminate the v 's. We have no restrictions yet on A if the denominator vanishes. We obtain the equations of motion for the $|\psi_n^{(2)}\rangle$'s by differentiation of Eq. (7).

$$i \frac{d}{dt} | \psi_n^{(2)} \rangle = \langle \psi_n^{(1)} | \hat{H} | \Psi \rangle - \sum_m | \psi_m^{(2)} \rangle A_{mn}. \quad (22)$$

We have used

$$A_{nm}^* = A_{mn}. \quad (23)$$

This relation is automatically fulfilled if $\langle \psi_n^{(2)} | \psi_n^{(2)} \rangle \neq \langle \psi_m^{(2)} | \psi_m^{(2)} \rangle$. Equation (23) is also necessary and sufficient for Eqs. (2)–(4) to hold at all times, which can be verified by differentiation of these equations with respect to time, and substitution of Eqs. (20) and (22).

Up till now we have worked with an unbounded number of configurations in Eq. (14). We now assume that we need at most N_{conf} configurations, and that $|\psi_n^{(2)}\rangle=0$ for $n > N_{\text{conf}}$. The number of equations of motion for the $|\psi_n^{(2)}\rangle$'s reduces to N_{conf} , and the number of terms in the summation in Eq. (22) also reduces to N_{conf} . The number of equations of motion for the $|\psi_n^{(1)}\rangle$'s reduces to N_{conf} , because $|\psi_n^{(1)}\rangle$ with $n > N_{\text{conf}}$ is irrelevant as $|\psi_n^{(1)} \psi_n^{(2)}\rangle = |0\rangle$. However, the number of terms on the right-hand side of Eq. (20) does not decrease. We therefore rewrite that equation as

$$\begin{aligned} i \frac{d}{dt} | \psi_n^{(1)} \rangle &= \sum_{m=1}^{N_{\text{conf}}} A_{nm} | \psi_m^{(1)} \rangle + \sum_{m > N_{\text{conf}}} A_{nm} | \psi_m^{(1)} \rangle \\ &= \sum_{m=1}^{N_{\text{conf}}} A_{nm} | \psi_m^{(1)} \rangle + \frac{1}{\langle \psi_n^{(2)} | \psi_n^{(2)} \rangle} \\ &\quad \times \sum_{m > N_{\text{conf}}} | \psi_m^{(1)} \rangle \langle \psi_m^{(1)} \psi_n^{(2)} | \hat{H} | \Psi \rangle \\ &= \sum_{m=1}^{N_{\text{conf}}} A_{nm} | \psi_m^{(1)} \rangle + \frac{1}{\langle \psi_n^{(2)} | \psi_n^{(2)} \rangle} \\ &\quad \times \left[\hat{1} - \sum_{m=1}^{N_{\text{conf}}} | \psi_m^{(1)} \rangle \langle \psi_m^{(1)} | \right] \langle \psi_n^{(2)} | \hat{H} | \Psi \rangle. \end{aligned} \quad (24)$$

We have tacitly assumed that $\langle \psi_n^{(2)} | \psi_n^{(2)} \rangle \neq 0$ for $n \leq N_{\text{conf}}$. This is certainly not always correct. A quite common situation is where the initial state consists of one configuration, whereas we have $N_{\text{conf}} > 1$ after some time. The configurations for which initially $\langle \psi_n^{(2)} | \psi_n^{(2)} \rangle = 0$, but later $\langle \psi_n^{(2)} | \psi_n^{(2)} \rangle \neq 0$ holds, are instances of a more general problem with the definition of A ; its matrix elements are not defined when $\langle \psi_n^{(2)} | \psi_n^{(2)} \rangle = \langle \psi_m^{(2)} | \psi_m^{(2)} \rangle$. The next subsection will show a solution to this problem; for now we will ignore it. Equations (22) and (24) with $n \leq N_{\text{conf}}$ and $|\Psi\rangle$ the finite sum of configurations form then our equations of motion.

C. Computational details

The equations of motion may be brought to a slightly more convenient form by using the specific form of the Hamiltonian. We write the Hamiltonian as

$$\hat{H} = \hat{h}_1 + \hat{h}_2 + \hat{g}, \quad (25)$$

where $\hat{h}_1(\hat{h}_2)$ is an operator working only on the $|\psi_n^{(1)}\rangle$'s ($|\psi_n^{(2)}\rangle$'s), whereas $\hat{g}$ works on both single-particle states. Substitution of this expression into Eq. (21) gives us

$$\begin{aligned} A_{nm} &= \langle \psi_m^{(1)} | \hat{h}_1 | \psi_n^{(1)} \rangle \\ &\quad + \frac{\langle \psi_m^{(1)} \psi_n^{(2)} | \hat{g} | \Psi \rangle - \langle \Psi | \hat{g} | \psi_n^{(1)} \psi_m^{(2)} \rangle}{\langle \psi_n^{(2)} | \psi_n^{(2)} \rangle - \langle \psi_m^{(2)} | \psi_m^{(2)} \rangle}, \end{aligned} \quad (26)$$

if $\langle \psi_n^{(2)} | \psi_n^{(2)} \rangle \neq \langle \psi_m^{(2)} | \psi_m^{(2)} \rangle$. If $\langle \psi_n^{(2)} | \psi_n^{(2)} \rangle = \langle \psi_m^{(2)} | \psi_m^{(2)} \rangle$ a term $\langle \psi_m^{(1)} | \hat{h}_1 | \psi_n^{(1)} \rangle$ can be split off from $\mathbf{A}_{nm}$. This gives us the following equations of motion:

$$i \frac{d}{dt} |\psi_n^{(1)}\rangle = \hat{h}_1 |\psi_n^{(1)}\rangle + \sum_{m=1}^{N_{\text{conf}}} \mathbf{B}_{nm} |\psi_m^{(1)}\rangle + \frac{1}{\langle \psi_n^{(2)} | \psi_n^{(2)} \rangle} \times \left[\hat{1} - \sum_{m=1}^{N_{\text{conf}}} |\psi_m^{(1)}\rangle \langle \psi_m^{(1)}| \right] \langle \psi_n^{(2)} | \hat{g} | \Psi \rangle \quad (27)$$

and

$$i \frac{d}{dt} |\psi_n^{(2)}\rangle = \hat{h}_2 |\psi_n^{(2)}\rangle - \sum_{m=1}^{N_{\text{conf}}} |\psi_m^{(2)}\rangle \mathbf{B}_{mn} + \langle \psi_n^{(1)} | \hat{g} | \Psi \rangle, \quad (28)$$

where

$$\mathbf{B}_{nm} = \frac{\langle \psi_m^{(1)} \psi_n^{(2)} | \hat{g} | \Psi \rangle - \langle \Psi | \hat{g} | \psi_n^{(1)} \psi_m^{(2)} \rangle}{\langle \psi_n^{(2)} | \psi_n^{(2)} \rangle - \langle \psi_m^{(2)} | \psi_m^{(2)} \rangle}, \quad (29)$$

if $\langle \psi_n^{(2)} | \psi_n^{(2)} \rangle \neq \langle \psi_m^{(2)} | \psi_m^{(2)} \rangle$, and otherwise $\mathbf{B}_{nm}$ is arbitrary except for $\mathbf{B}_{nn} = \mathbf{B}_{nn}^*$. Using this procedure it is possible to isolate the kinetic energy operators, which will end up in $\hat{h}_1$ and $\hat{h}_2$.

It is also convenient to rewrite $\hat{g}$ as^{18,19}

$$\hat{g} = \sum_{k=1}^G \hat{g}_1^{(k)} \hat{g}_2^{(k)}, \quad (30)$$

where the $\hat{g}_1^{(k)}$'s [$\hat{g}_2^{(k)}$'s] are operators working on the $|\psi_n^{(1)}\rangle$'s ($|\psi_n^{(2)}\rangle$'s) only. If G is small then this expression can drastically reduce computation times as will be shown in the next section. The reason for this can be seen by writing

$$\langle \psi_n^{(1)} \psi_m^{(2)} | \hat{g} | \Psi \rangle = \sum_{k=1}^G \sum_{l=1}^{N_{\text{conf}}} \langle \psi_n^{(1)} | \hat{g}_1^{(k)} | \psi_l^{(1)} \rangle \times \langle \psi_m^{(2)} | \hat{g}_2^{(k)} | \psi_l^{(2)} \rangle. \quad (31)$$

We see that matrix elements of $H_1 \otimes H_2$ can be expressed in terms of matrix elements of H_1 and H_2 , which will be much easier to evaluate.

We could not develop a numerical integration scheme to solve the equations of motion so that Eqs. (2)–(4) would be fulfilled exactly. Instead we found that a one-step predictor–corrector method that is second-order accurate works sufficiently well. The equations of motion Eqs. (27)–(29) still contain singularities. For the numerical integration we regularized them by making the substitution^{18,27}

$$\frac{1}{x} \rightarrow \frac{x}{x^2 + \epsilon^2} \quad (32)$$

with ϵ some small number, for $1/\langle \psi_n^{(2)} | \psi_n^{(2)} \rangle$ in Eq. (27) and $1/(\langle \psi_n^{(2)} | \psi_n^{(2)} \rangle - \langle \psi_m^{(2)} | \psi_m^{(2)} \rangle)$ in Eq. (29). As will be shown in the next section, it is easy to choose ϵ so that the effect of substitution (32) is negligible. The singularities occur when the natural single-particle states become ill-defined. Hence Eqs. (27)–(29) give large changes for them whereas the multiconfiguration state changes only little. Even though the substitution (32) may yield bad natural

single-particle states, the resultant multiconfiguration state is still accurate. The substitution (32) also makes the restriction on Eq. (29) superfluous. Henceforth, Eq. (29) without the restriction, but with Eq. (32), defines $\mathbf{B}$ always.

With substitution (32) Eqs. (2) and (4) still hold. However, for Eq. (3) we find ($n \neq m$)

$$i \frac{d}{dt} \langle \psi_n^{(2)} | \psi_m^{(2)} \rangle = \frac{\epsilon^2 [\langle \psi_m^{(1)} \psi_n^{(2)} | \hat{g} | \Psi \rangle - \langle \Psi | \hat{g} | \psi_n^{(1)} \psi_m^{(2)} \rangle]}{\epsilon^2 + [\langle \psi_n^{(2)} | \psi_n^{(2)} \rangle - \langle \psi_m^{(2)} | \psi_m^{(2)} \rangle]^2} \neq 0. \quad (33)$$

If the norms of the configurations differ much more than ϵ , and ϵ is small, we see that $(d/dt) \langle \psi_n^{(2)} | \psi_m^{(2)} \rangle$ differs only very little from zero. On the other hand, when $\langle \psi_n^{(2)} | \psi_n^{(2)} \rangle = \langle \psi_m^{(2)} | \psi_m^{(2)} \rangle$, then $\langle \psi_m^{(1)} \psi_n^{(2)} | \hat{H} | \Psi \rangle = \langle \Psi | \hat{H} | \psi_n^{(1)} \psi_m^{(2)} \rangle$ should hold, as has been shown following Eq. (17), which implies $\langle \psi_m^{(1)} \psi_n^{(2)} | \hat{g} | \Psi \rangle = \langle \Psi | \hat{g} | \psi_n^{(1)} \psi_m^{(2)} \rangle$, so that $(d/dt) \langle \psi_n^{(2)} | \psi_m^{(2)} \rangle = 0$.

III. RESULTS AND DISCUSSION

We have tested the MCTDH approximation on a generic model of H_2 dissociation on a transition metal surface. There are two degrees of freedom in the model; the distance between the H atoms, and the distance of H_2 to the substrate. We have used three PES's developed by Halstead and Holloway,^{24,28–31} one with a barrier in the entrance channel, one with a barrier in the exit channel, and one with a barrier in between (central barrier). These PES's were not fitted to represent H_2 dissociation on a specific surface, and, disregarding specific parameters like the height of the barrier, they may be considered representative for a whole range of reaction; e.g., collinear reaction of the type $\text{A} + \text{BC} \rightarrow \text{AB} + \text{C}$. We will concentrate mainly on the barriers in the entrance and in the exit channel. The results for the central barrier do not differ essentially from the results for these barriers as far as the test of the MCTDH approximation is concerned.

We did not attempt to reproduce all the results of Halstead and Holloway. Instead, we have chosen initial states with H_2 in its vibrational ground state and a Gaussian wave packet for the centre of mass. The translational energy was 0.566 eV for the barrier in the entrance channel, 0.446 eV for the barrier in the exit channel, and 0.508 eV for the central barrier. These energies correspond to a probability of dissociation of about 0.75.²⁴ However, as we have used a rather narrow wave packet in the coordinate representation, which gives a broad packet in the momentum representation, a much smaller dissociation probability was found. For the MCTDH approximation it is also necessary to specify $|\psi_n^{(1)}\rangle$'s with $n > 1$ even though $|\psi_n^{(2)}\rangle = |0\rangle$ for the same n . It seems natural to use excited state of the H_2 vibration. However, we found out that any choice of states for which Eq. (2) holds give the same results for the simulations, which is consistent with the fact that the initial state does not depend on the $|\psi_n^{(1)}\rangle$'s with $n > 1$.

The PES was written in a form similar to Eq. (30). First, we split off terms depending only on one of the coordinates

$$V(r, R) = v_1(r) + v_2(R) + W(r, R), \quad (34)$$

where V is the total PES, r is the H-H distance, and R is the H₂-substrate distance. The potentials v_1 and v_2 are determined by minimizing

$$\int_{r_{\min}}^{r_{\max}} dr \int_{R_{\min}}^{R_{\max}} dR [V(r, R) - v_1(r) - v_2(R)]^2, \quad (35)$$

where $r_{\min}$, $r_{\max}$, $R_{\min}$, and $R_{\max}$ determine the area for which we want to use the PES. The result is

$$v_1(r) = \frac{1}{R_{\max} - R_{\min}} \int_{R_{\min}}^{R_{\max}} dR V(r, R) + c \quad (36)$$

and

$$v_2(R) = \frac{1}{r_{\max} - r_{\min}} \int_{r_{\min}}^{r_{\max}} dr V(r, R) - c - \frac{1}{(R_{\max} - R_{\min})(r_{\max} - r_{\min})} \times \int_{r_{\min}}^{r_{\max}} dr \int_{R_{\min}}^{R_{\max}} dR V(r, R), \quad (37)$$

where c is some arbitrary constant, which can be used to minimize the variations of the phase factors of the natural single-particle states. The potentials v_1 and v_2 form, together with the kinetic energy terms, the operators $\hat{h}_1$ and $\hat{h}_2$ of Eq. (25). Without the W term in Eq. (34) the equations of motion become separable.

Second, we approximate the rest term of Eq. (34) as

$$W(r, R) = \sum_{k=1}^{N_{\text{pot}}} w_1^{(k)}(r) w_2^{(k)}(R). \quad (38)$$

The problem of finding the $w_1^{(k)}$'s and $w_2^{(k)}$'s is identical to the one of finding the best multiconfiguration state [see Eq. (5) ff.]. The $w_1^{(k)}$'s are determined by the eigenvalue equation

$$\int_{r_{\min}}^{r_{\max}} dr' \left[\int_{R_{\min}}^{R_{\max}} dR W(r, R) W(r', R) \right] w_1^{(k)}(r') = \lambda_k w_1^{(k)}(r), \quad (39)$$

and the $w_2^{(k)}$'s by

$$w_2^{(k)}(R) = \int_{r_{\min}}^{r_{\max}} dr W(r, R) w_1^{(k)}(r). \quad (40)$$

The best approximation for W is obtained by taking $w_1^{(k)}$'s with the largest eigenvalue in Eq. (39).

It can be shown that with a different choice of the potentials v_1 and v_2 the root-mean-square deviation for a given number of terms in Eq. (38) becomes larger. In our simulations we used $r_{\min} = R_{\min} = -1$, $r_{\max} = 10.475$, $R_{\max} = 6.65$ (atomic units are used throughout), and $N_{\text{pot}} = 3$. The root-mean-square deviation was 7.5×10^{-4} , and the maximum deviation was 1.3×10^{-2} for all positions of the

FIG. 1. The fractions that the configurations contribute to the total state [i.e., the v_m 's in Eq. (9)], as a function of time (in atomic units) for the PES with the barrier in the entrance channel (a), in the exit channel (b), and in between (central barrier) (c). The initial state consists of a single configuration.

barrier. These deviations were determined using a 256×256 grid. The same grid was used for the simulations. The larger differences between the potentials of Halstead and Holloway and their approximations are found at positions where the probability of finding the system is always small. Numerically exact simulations (see below) showed only very slight differences between the exact potentials and the approximations. Note that $r=0$ and $R=0$ correspond to the minimum of the PES in the entrance and the exit channel, respectively.

To assess the quality of the MCTDH approximation we performed numerically exact simulations for comparison. We used the split time propagator scheme based on the Trotter equation, and used fast Fourier transform to calculate the effect of the kinetic energy.^{2,5} The system was simulated for a time of 3000 a.u. (≈ 75 fs). This was long enough for the dissociation to occur, and for the system to leave the region around the barrier. Using Eqs. (9) and (10) we have calculated the natural single-particle states, and the fractions v_m that the configurations contribute to the total state. Figure 1 shows how these contributions change with time. For the barrier in the entrance channel and the central barrier there is an almost monotonous change in these fractions. Some forbidden crossings can be seen at the lower part of Fig. 1(a). More variations can be seen in the figure with the barrier in the exit channel. For the barrier in the entrance channel Fig. 1 shows that there are at least five configurations necessary to describe the dissociation, and for the barrier in the exit channel and the central barrier at least four. We can also see that with a single configuration (the TDH approximation) only 62%

FIG. 2. The most important natural single-particle states at the end of the simulation ($t=3000$ a.u.) with the barrier in the entrance channel. The $|\psi_n^{(1)}\rangle$'s are on the left, the $|\psi_n^{(2)}\rangle$'s on the right, and, from top to bottom, $n=1, 2, 3$, and 4. The abscissas depict the H-H distance and the H_2 -substrate distance. Zero corresponds to the minimum of the PES in the entrance and exit channel, respectively. All states have been normalized. The solid lines show the real parts, and the dashed lines the imaginary parts of the states. The numbers on the right are the fractions that the configurations contribute to the total state. Configurations that contribute less than 0.02 are not shown. The states $|\psi_1^{(1)}\rangle$, $|\psi_2^{(2)}\rangle$, $|\psi_3^{(2)}\rangle$, and $|\psi_4^{(2)}\rangle$ are vibrational eigenstates.

of the final state (at $t=3000$ a.u.) with the barrier in the entrance channel, 59% of the final state with the barrier in the exit channel, and 43% of the final state with the central barrier can be represented. Actually, as will be shown, the TDH approximation does much worse.

The natural single-particle states of the final state are shown in Figs. 2 and 3. For the barrier in the entrance channel the dominant configuration corresponds to elastic scattering of the H_2 molecule. The largest configuration describing dissociation corresponds to the first excited state of the H_2 vibration with respect to the surface. This agrees with the results of Halstead and Holloway.²⁴ There is no inelastic scattering. For the barrier in the exit channel too the dominant configuration corresponds to elastic scattering of the H_2 molecule. The largest configuration describing dissociation corresponds, however, to the ground state of the H_2 vibration with respect to the surface. Similar plots were also obtained for the central barrier. It is very remarkable that the natural single-particle states describing vibrations are eigenstates of the Hamiltonian for the vibration. This implies that the MCTDH approximation may not only be an efficient way to solve the TDSE, but also provides a nice analysis of the solutions.

The quantities $\langle \psi_m^{(2)} | \psi_m^{(2)} \rangle$ in a MCTDH simulation should be a good approximation to the fractions v_m shown

FIG. 3. The most important natural single-particle states at the end of the simulation ($t=3000$ a.u.) with the barrier in the exit channel. The $|\psi_n^{(1)}\rangle$'s are on the left, the $|\psi_n^{(2)}\rangle$'s on the right, and, from top to bottom, $n=1$ and 2. The abscissas depict the H-H distance and the H_2 -substrate distance. Zero corresponds to the minimum of the PES in the entrance and exit channel, respectively. All states have been normalized. The solid lines show the real parts, and the dashed lines the imaginary parts of the states. The numbers on the right are the fractions that the configurations contribute to the total state. Configurations that contribute less than 0.02 are not shown. The states $|\psi_1^{(1)}\rangle$ and $|\psi_2^{(2)}\rangle$ are vibrational eigenstates.

in Fig. 1. Indeed, with six configurations there is no visual difference between Fig. 1 and a figure of the $\langle \psi_m^{(2)} | \psi_m^{(2)} \rangle$'s obtained from an MCTDH simulation. The largest difference for the final state is only 0.0047 for the fourth largest configuration with the barrier in the entrance channel. Even the subtle forbidden crossings in Fig. 1(a) are found with high accuracy. We also calculated the overlap of the states obtained with the MCTDH approximation and the numerically exact ones. The results are shown in Fig. 4. It is seen that with six configurations the MCTDH approximation becomes numerically almost exact; the overlap for the final states is 0.9973, 0.9993, and 0.9992 for the barrier in the entrance channel, the barrier in the exit channel, and the central barrier, respectively. The results depend hardly on the value of ϵ in substitution (32). We varied ϵ over six orders of magnitude (from 10^{-10} to 10^{-4}), and found only somewhat larger differences between the exact and the MCTDH results with $\epsilon=10^{-4}$. All the results quoted here were obtained with $\epsilon=10^{-6}$.

Figure 4 also shows the overlap for TDH simulations and MCTDH simulations with various numbers of configurations. The sums of the largest eigenvalues are also shown. They form upper bounds to the overlaps. The overlaps, however, remain only close to these upper bounds in the beginning of the simulation if not enough configurations are used. The reason for this is that the exact state is needed to obtain the reduced density matrix so as to follow the upper bounds. The TDH approximation performs very poorly once more configurations become important. We have to point out, however, that this in general depends on the coordinates that have been chosen. We have not investigated other coordinate systems.

Sometimes fewer configurations may be used than are necessary to give an accurate description of the total state. For example, Fig. 5 shows the dissociation probability as a

FIG. 4. The overlap $|\langle \Psi_{\text{exact}} | \Psi_{\text{MCTDH}} \rangle|^2$ (open dots) and the sums of the largest N_{conf} eigenvalues of Eq. (9) (solid lines) for number of configurations N_{conf} ranging from 1 (the TDH approximation) to 6. The sum of the largest N_{conf} eigenvalues is an upper bound for the overlap with N_{conf} configurations in $|\Psi_{\text{MCTDH}}\rangle$. Except in the beginning of the simulations the overlaps are well below these upper bounds. Shown are simulations with the barrier of the PES in the entrance (a) and the exit channel (b).

function of the number of configurations. We see that even two configurations give a reasonable result. One configuration describes then the elastic scattering, the other the dissociation. This reduction of the number of configurations, however, depends strongly on the quantity of interest and the system.

One might wonder if the small number of configurations needed is not due to the way the single-particle states

FIG. 5. The H_2 -dissociation probability for the PES with the barrier in the entrance (open squares) and in the exit channel (solid squares) as a functions of the number of configurations.

are chosen, but to the absence of much correlation. Especially as the entrance and the exit channel are (nearly) separable (but not the reaction zone). However, earlier calculations on a more realistic PES to model the H_2 dissociation on a Cu surface³² also only needed six configurations.³³ Also the two-dimensional calculations of Meyer *et al.*¹⁷ showed a rapid convergence in the number of natural single-particle states. One can get an alternative measure for the correlation directly from the PES. Without the W term in Eq. (34) the Hamiltonian would be separable. As we have minimized this term, in the sense of expression (35), its size is indicative for the correlation. We have found that the W term contributes for all PES's on the grid that we have used on average 0.13 and maximally 3.9 to the total PES. The largest contributions are to the repulsive part of the PES (small r or small R ; especially the part that forms the elbow of the PES), but, more important, almost everywhere in the reaction zone the contribution is much larger than the height of the barrier. Hence we conclude that the correlation is appreciable.

The results above have shown that the MCTDH approximation can yield numerically accurate results. What about its efficiency? We will assume that we have an even number of degrees of freedom D , that H_1 and H_2 each correspond to $D/2$ of these degrees of freedom, and that for each degree of freedom we have N_{grid} grid points. There are of course other cases, but our conclusions will qualitatively remain the same. The memory requirement of a method to solve the TDSE directly scales as N_{grid}^D , compared to $(N_{\text{conf}} + N_{\text{pot}})N_{\text{grid}}^{D/2}$ for the MCTDH approximation. Already for $D=2$ this differs easily by an order of magnitude. The computation time per time step scales as N_{grid}^D for methods to solve the TDSE directly (there is an extra factor $\log N_{\text{grid}}$ if a fast Fourier-transform is used). For the MCTDH approximation this is $N_{\text{grid}}^{D/2}N_{\text{conf}}^2N_{\text{pot}}$. The difference here is less advantageous as for the memory. However, for $D > 2$ a speed-up of several orders of magnitude can probably be achieved. For the methods to solve the TDSE directly we do not include the calculation of the natural single-particle states, which scales as $N_{\text{grid}}^{3D/2}$. The main drawback of the MCTDH approximation is that there is as yet no good method to solve the equations of motion. Consequently, with our predictor-corrector method, the time steps are smaller than for the methods that solve the TDSE directly. Just to give a rough impression of the computation times we find for our implementations for the H_2 dissociation ($D=2$) the following timings. With six configurations and applying the corrector only once, we had a speed-up of four per time step, but had to do ten times as many steps. We could increase the time step by applying the corrector two or three times. The net result was that the MCTDH simulation with six configurations took about as long as the one where the TDSE was solved directly. However, with fewer configurations the MCTDH simulation was up to about an order of magnitude faster, as the computation time scales quadratically with the number of configurations.

We finally want to present an extension of the MCTDH approximation in which the degrees of freedom

are split into more than two groups. As has been shown by Manthe *et al.*¹⁷⁻¹⁹ there will be no longer a one-to-one correspondence between the $|\psi_n^{(i)}\rangle$'s with the same n but different i . Suppose we have M groups. We then write as an approximation for the exact normalized state

$$|\Psi\rangle = \sum_{n_1=1}^{N_1} \cdots \sum_{n_M=1}^{N_M} c_{n_1 \dots n_M} |\psi_{n_1}^{(1)} \dots \psi_{n_M}^{(M)}\rangle, \quad (41)$$

where the $c_{n_1 \dots n_M}$'s are coefficients. We define the single-particle states to be normalized natural single-particle states; i.e.,

$$\hat{\rho}_i |\psi_n^{(i)}\rangle = \nu_n^{(i)} |\psi_n^{(i)}\rangle \quad (42)$$

with

$$\hat{\rho}_i = \text{Tr}^{(\neq i)} |\Psi\rangle \langle \Psi|. \quad (43)$$

The trace is over all H_j with $j=1, \dots, i-1, i+1, \dots, M$. Looking at the derivation in the previous section we can immediately write down the equations of motion

$$i \frac{d}{dt} |\psi_n^{(i)}\rangle = \sum_{m=1}^{N_i} \mathbf{A}_{nm}^{(i)} |\psi_m^{(i)}\rangle + \frac{1}{\langle \tilde{\psi}_n^{(i)} | \tilde{\psi}_n^{(i)} \rangle} \times \left[\hat{1} - \sum_{m=1}^{N_i} |\psi_m^{(i)}\rangle \langle \psi_m^{(i)}| \right] \langle \tilde{\psi}_n^{(i)} | \hat{H} | \Psi \rangle \quad (44)$$

with

$$\mathbf{A}_{nm}^{(i)} = \frac{\langle \psi_m^{(i)} \tilde{\psi}_n^{(i)} | \hat{H} | \Psi \rangle - \langle \Psi | \hat{H} | \psi_n^{(i)} \tilde{\psi}_m^{(i)} \rangle}{\langle \tilde{\psi}_n^{(i)} | \tilde{\psi}_n^{(i)} \rangle - \langle \tilde{\psi}_m^{(i)} | \tilde{\psi}_m^{(i)} \rangle} \quad (45)$$

and

$$|\tilde{\psi}_n^{(i)}\rangle \equiv \langle \psi_n^{(i)} | \Psi \rangle. \quad (46)$$

Only for the coefficients we have to derive separately equations of motion. Differentiation of

$$c_{n_1 \dots n_M} = \langle \psi_{n_1}^{(1)} \dots \psi_{n_M}^{(M)} | \Psi \rangle \quad (47)$$

yields

$$i \frac{d}{dt} c_{n_1 \dots n_M} = \langle \psi_{n_1}^{(1)} \dots \psi_{n_M}^{(M)} | \hat{H} | \Psi \rangle - \sum_{k=1}^M \sum_{m_k=1}^{N_k} c_{n_1 \dots n_{k-1} m_k n_{k+1} \dots n_M} A_{m_k n_k}^{(k)}, \quad (48)$$

which is similar to Eq. (22). For $M=2$ we can prove the one-to-one correspondence between the $|\psi_n^{(1)}\rangle$'s and $|\psi_n^{(2)}\rangle$'s by substitution of Eq. (41) in Eq. (43) and using Eq. (42). Using equations similar to Eqs. (25) and (30) for $M>2$ yields more or less the same results as for $M=2$.

IV. CONCLUSIONS

We have developed a multiconfiguration time-dependent Hartree approximation based on natural single-particle states. This means that a minimal number of configurations is used to describe the total state. The equations

of motion have been derived using the eigenvalue equation of a reduced density matrix. Singularities in the equations of motion could be easily regularized introducing a small parameter ϵ . Numerical integration of the equations of motion with a predictor-corrector scheme showed negligible ϵ dependence. The potential energy surface was also written as a sum of products. This changed the dependence of computation time on the number of grid points N_{grid} per degree of freedom from N_{grid}^D to $N_{\text{grid}}^{D/2}$, where D is the (even) number of degrees of freedom. The multiconfiguration time-dependent Hartree approximation has been found to be as accurate as methods that solve the time-dependent Schrödinger equation directly. It may, however, be much more efficient. The computation time depends quadratically on the number of configurations.

The multiconfiguration time-dependent Hartree approximation was tested on three two-dimensional model potential energy surfaces for H_2 dissociation on a transition metal. With six configurations we found results identical to the ones obtained using the split time propagator method for solving the two-dimensional Schrödinger equation. In this case the natural single-particle states corresponding to bound motions evolved into vibrational eigenstates. Thus it seems that the multiconfiguration time-dependent Hartree approximation makes an implicit analysis of the total state in terms of eigenstates when, in the limit $t \rightarrow \infty$, the Hamiltonian can be considered separable. Upper bounds were calculated for the overlap of the exact state and up to six configurations. Integration of the equations of motion of the natural single-particle states showed that the overlap remained well below these upper bounds when too few configurations were used. In particular, the time-dependent Hartree approximation was found to do very bad for the potential energy surface with the barrier in the exit channel.

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