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Convergence study of multi-configuration time-dependent Hartree simulations: H₂ scattering from LiF(001)

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The multi-configurational time-dependent Hartree method is compared with close-coupling and close-coupling wave-packet calculations for a four-dimensional model of scattering of H₂ from a LiF(001) surface. Accurate results are obtained for the rotation–diffraction scattering probabilities. An analysis of the accuracy of the simulations as a function of the number of configurations shows that more single-particle functions are needed for the scattering coordinate than for the others to obtain good results. Reasonable results are, however, already obtained with a small number of configurations. © 1996 American Institute of Physics. [S0021-9606(96)00409-6]

I. INTRODUCTION

In recent years wave-packet methods have become used more and more to describe various fundamental quantum dynamics phenomena.^{1–5} This development is due to new efficient methods to propagate the wave packet (split-operator,^{6,7} Chebysev,^{7,8} short-iterative Lanczos^{7,9}), and methods to represent the wave-packet compactly [methods that use a fast-Fourier transform (FFT)¹⁰ and discrete-variable representations (DVR)¹¹]. If the system size increases these time-dependent methods scale somewhat more favorably than time-independent methods. Another advantage is that they can readily provide a visualization of dynamical processes, which makes interpretation of results easier.¹²

One major problem with time-dependent methods is the exponential scaling law of the number of grid points with the number of dimensions D . This leads to exponential scaling with D in computation time and memory too. There is no general method to handle systems with more than three dimensions, and for large systems it is necessary to resort to system-specific techniques and mixed approaches. The multi-configuration time-dependent Hartree (MCTDH) method is an attempt to overcome these difficulties.^{13–15} It is an extension of the time-dependent Hartree (TDH) approximation. In TDH the wave function is written as a product of functions each depending usually on just one coordinate. In this way a D dimensional problem can be reduced to the solution of D coupled one-dimensional problems. The drawback is that only an approximate solution for the time-dependent Schrödinger equation is obtained. In MCTDH correlation effects are taken into account by using more configurations (a configuration is one such product of functions each of which usually depends on only one coordinate). MCTDH can be made as accurate as one wants by increasing the number of configurations. Since its introduction, the method has been applied to a variety of chemical processes.^{14–24}

Still relatively little is known about the performance of

MCTDH; in particular, about the convergence of the number of configurations. In this work we apply the MCTDH method to scattering of H₂ from a LiF(001) surface. This system has been studied previously with time-independent [close-coupling (CC)] and time-dependent [close-coupling wave packet (CCWP)] methods, with a simple model potential and with a more sophisticated one.^{25–28} The results of these studies are very accurate. This fact makes H₂/LiF(001) a good benchmark for MCTDH.

II. THEORY

The CC and CCWP calculations that we use as reference have been described in detail elsewhere.²⁷ We give here a short overview of the MCTDH approximation, as this method is not so well known. More details can be found in Refs. 14 and 15. The exact wave function of a D -dimensional system, is approximated by an expression of the form

$$\Psi_{\text{MCTDH}}(q_1, \dots, q_D; t) = \sum_{n_1 \dots n_D} c_{n_1 \dots n_D}(t) \psi_{n_1}^{(1)}(q_1; t) \dots \psi_{n_D}^{(D)}(q_D; t). \quad (1)$$

From this expression, it is possible to obtain the equations of motion for the one-dimensional functions $\psi_{n_i}^{(i)}(q_i; t)$ and for the correlation coefficients $c_{n_1 \dots n_D}(t)$. Without loss of generality we can choose the $\psi_{n_i}^{(i)}$'s to be natural single-particle functions.¹⁵ They insure that we obtain the best approximation to the exact $\Psi(q_1, \dots, q_D; t)$ for a fixed number of configurations; i.e., they minimize the expression $\langle \Delta | \Delta \rangle$ where

$$\Delta = \Psi - \Psi_{\text{MCTDH}}, \quad (2)$$

and where Ψ is the exact wavefunction. The natural single-particle functions are eigenstates of the reduced density operators.

$$\rho_j(q_j, q'_j) = \int dq_1 dq_{j-1} \dots dq_{j+1} \dots dq_D \Psi(q_1 \dots q_{j-1} q_j q_{j+1} \dots q_D) \Psi^*(q_1 \dots q_{j-1} q'_j q_{j+1} \dots q_D). \quad (3)$$

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The equations of motions for the natural single-particle functions can be obtained by differentiation of the eigenvalue equation:

$$\int dq'_j \rho_i(q_j, q'_j) \psi_n^{(i)}(q'_j) = \nu_n^{(i)} \psi_n^{(i)}(q_j). \quad (4)$$

This gives us

$$i\hbar \frac{\partial}{\partial t} \psi_{n_j}^{(j)} = h_j \psi_{n_j}^{(j)} + \sum_{m_j} B_{n_j, m_j}^{(j)} \psi_{m_j}^{(j)} + \frac{\langle \tilde{\psi}_{n_j}^{(j)} | V | \Psi \rangle}{\langle \tilde{\psi}_{n_j}^{(j)} | \tilde{\psi}_{n_j}^{(j)} \rangle} \psi_{n_j}^{(j)} - \sum_{m_j} \frac{\langle \psi_{m_j}^{(j)} \tilde{\psi}_{n_j}^{(j)} | V | \Psi \rangle}{\langle \tilde{\psi}_{n_j}^{(j)} | \tilde{\psi}_{n_j}^{(j)} \rangle} \psi_{m_j}^{(j)}, \quad (5)$$

where

$$B_{n_j, m_j}^{(j)} = \frac{\langle \psi_{m_j}^{(j)} \tilde{\psi}_{n_j}^{(j)} | V | \Psi \rangle - \langle \Psi | V | \psi_{n_j}^{(j)} \tilde{\psi}_{m_j}^{(j)} \rangle}{\langle \tilde{\psi}_{n_j}^{(j)} | \tilde{\psi}_{n_j}^{(j)} \rangle - \langle \tilde{\psi}_{m_j}^{(j)} | \tilde{\psi}_{m_j}^{(j)} \rangle}, \quad (6)$$

and

$$\tilde{\psi}_{n_j}^{(j)} = \sum_{n_1 \dots n_{j-1}} \sum_{n_{j+1} \dots n_D} c_{n_1 \dots n_D} \psi_{n_1}^{(1)} \dots \psi_{n_{j-1}}^{(j-1)} \times \psi_{n_{j+1}}^{(j+1)} \dots \psi_{n_D}^{(D)}, \quad (7)$$

with the Hamiltonian H given by

$$H = \sum_{j=1}^D h_j + V. \quad (8)$$

The equations of motion for the coefficients

$$c_{n_1 \dots n_D} = \langle \psi_{n_1}^{(1)} \dots \psi_{n_D}^{(D)} | \Psi \rangle \quad (9)$$

are again obtained by differentiation.

$$i\hbar \frac{d}{dt} c_{n_1 \dots n_D} = \langle \psi_{n_1}^{(1)} \dots \psi_{n_D}^{(D)} | V | \Psi \rangle - \sum_{j=1}^D c_{n_1 \dots n_{j-1} m_j n_{j+1} \dots n_D} B_{m_j n_j}^{(j)}. \quad (10)$$

Equations (5) and (10) are a particular form of the more general equations obtained from a time-dependent variational principle.¹⁴ They conserve the norm of the wave function and the mean energy of a time-independent Hamiltonian. The resulting system of first-order differential equations, has to be solved with a general-purpose integrator. We used the variable-order variable-step Adams method, as implemented in the NAG library.²⁹ Compared with the CCWP method, the maximum step size allowed during the propagation is quite small; in the optimal case of only one configuration, it turns out to be on average 0.072 fs. For a larger number of configurations, this limit can be approached by carefully choosing the initial natural single-particle functions that do not contribute to the total wave function ($\nu_n^{(i)} = 0$ at $t=0$). The singularities in Eqs. (5), (6), and (10) have been treated numerically by the regularization procedure described in Ref. 15.

The natural single-particle functions have some minor advantages over other possible choices of single-particle functions. The most important one is that one can directly see from $\langle \tilde{\psi}_n^{(i)} | \tilde{\psi}_n^{(i)} \rangle$ how well Ψ_{MCTDH} approximates the exact wave function. How much a natural single-particle functions contributes to the wave function is given by the eigenvalue $\nu_n^{(i)}$ of the reduced density matrix. In an approximate MCTDH simulation $\langle \tilde{\psi}_n^{(i)} | \tilde{\psi}_n^{(i)} \rangle$ is an approximation for this exact eigenvalue. The natural single-particle functions are also convenient for interpreting the results of a simulation.

III. RESULT AND DISCUSSION

The initial wave function represents an H₂ molecule in the rotational ground state directed towards a LiF(001) surface. We use the same initial condition as in Ref. 27 in order to allow a direct comparison with CC and CCWP calculations previously performed on the same system. The initial wave function is given by

$$\Psi_0(X, Y, Z, \theta) = \psi_{\text{par}}(X, Y) \psi_{\text{perp}}(Z) Y_{00}(\theta) \quad (11)$$

with

$$\psi_{\text{perp}}(Z) = \left(\frac{1}{2\pi\xi^2} \right)^{-1/4} \exp \left[-\frac{(Z-Z_0)^2}{2\xi^2} + ik_Z Z \right] \quad (12)$$

and

$$\psi_{\text{par}}(X, Y) = e^{ik_X X + ik_Y Y}. \quad (13)$$

The coordinates X , Y , and Z , refer to center-of-mass position of H₂; the X - and Y -axis are parallel to the surface, Z is the scattering coordinate perpendicular to the surface. The angle θ defines the orientation of molecular axis with respect to the surface normal. There is no coupling between the azimuthal angle φ and the surface corrugation, so that the orientation of the molecule can be described using spherical harmonics with $m=0$, and we leave out the angle φ as argument of the spherical harmonics. The position of the Gaussian wave packet Z_0 is chosen far from the surface. The width ξ is chosen large to have a small spread in translational energy of H₂. The direction to which the H₂ molecule moves is given by $\mathbf{k} = (k_X, k_Y, k_Z)$. We have looked at normal incidence ($k_X = k_Y = 0, k_Z \neq 0$), and incidence at an angle of 30° with the surface normal ($k_Y = 0, k_X, k_Z \neq 0$). In the latter case the component k_X is incommensurate with the translational symmetry of LiF(001). We have therefore used the Fourier-shift theorem as in the CCWP simulation.²⁷ The translational energy in all cases has been 7.353 mHartree.

The single-particle functions for the center-of-mass coordinates, are represented using an FFT collocation scheme¹⁰ with grids of $N_X = 32$, $N_Y = 32$ and $N_Z = 128$ points for X , Y , and Z , respectively. The grids in X and Y cover one whole unit cell of the LiF(001) surface with cell parameter $a = 5.367$ a.u. The grid in Z includes the region near the surface and extends well into the asymptotic region. For the angular coordinate a DVR based on Legendre polynomials has been employed;^{11,30} four grid points are enough for an accurate representation, which is equivalent to using a basis for θ of Y_{00} , Y_{20} , Y_{40} , and Y_{60} . Parameters are summarized

TABLE I. Parameters for the initial wave function.

Parameter	Interpretation	Value (atomic units)
ξ	width initial wave function in Z	3.0
Z_0	location initial wave function in Z	17.0
N_X, N_Y	number of grid points for X and Y	32
N_Z	number of grid points for Z	128
N_θ	number of DVR points for θ	4
$X_{\min}, Y_{\min}$	lower bound grids in X and Y	-2.59955552
$X_{\max}, Y_{\max}$	upper bound grids in X and Y	+2.59955552
$Z_{\min}$	lower bound grid in Z	1.5
$Z_{\max}$	upper bound grid in Z	33.25
E_T	translation energy of H ₂	$7.353 \cdot 10^{-3}$

in Table I. In order to obtain a full agreement with previous calculations, we use the empirical rotational energies of H₂ for the evaluation of the rotational kinetic operator (see Table I of Ref. 31).

The MCTDH wave function is propagated in the same model potential-energy surface as was used in Ref. 27 (see also Ref. 25). It is a Lennard-Jones/Devonshire form, already in a factorized form, so that we do not need any further approximation to reduce the computation of the potential operator to one-dimensional operations. The simulation is performed until the wave packet is far from the surface; i.e., in most simulations for about 400 fs. Figure 1 shows the time evolution of the modulus square of the wave function averaged over Y and θ , and Fig. 2 shows the same averaged over X , Y , and θ . During the scattering the momentum parallel to the surface of the H₂ molecule can change only by multiples of lattice vectors of LiF(001). Part of the initial energy can also be transferred to the rotational degree of freedom (rotationally inelastic scattering). As a result the molecule, after the interaction with the surface, can have only particular translational energy along the scattering coordinate. The wavepacket is strongly deformed during the interaction. The dynamics of the wave packet shows that after a sufficiently long time the initially Gaussian wavefunction splits in two parts. The faster contribution is due to elastic scattering ($j=0$) and the slower to rotationally inelastic scattering ($j \neq 0$). In Fig. 1, the wave packet has been propagated for an extra long time ($t=3000$ fs). This is possible in MCTDH with little increase in computer time. One has to perform the simulation on a very large grid (1024 points for the scattering coordinate), but one does not have to use tricks to handle the fast-spreading wave packet.

The probabilities for scattering into different channels $P(000 \rightarrow mnj)$ have been calculated by projecting the final wave function on different rotational and diffraction states. The momenta of the diffraction states are given by $\mathbf{k} + \mathbf{g}_{mn}$, where $\mathbf{k}$ is as before and $\mathbf{g}_{mn} = (2\pi m/a)\hat{\mathbf{X}} + (2\pi n/a)\hat{\mathbf{Y}}$ is a reciprocal lattice vector. Since the MCTDH scheme includes the exact solution as a limiting case, we can expect accurate results when we use a sufficiently high number of configurations. Tables II–V show the calculated scattering probabilities for normal and non-normal scattering. The MCTDH calculations have been done with $5 \times 5 \times 15 \times 4$ configurations; i.e., there are 5, 5, 15, and

FIG. 1. Contour levels of the modulus square of the wave function at different times averaged over Y and θ . In (a) contour levels are shown for $t=384$ fs; the wave packet has just left the surface, and the elastic and inelastic part are still indistinguishable. In (b) contour levels are shown for $t=1500$ fs (lower contours) and 2700 fs (upper contours) at which times the splitting of the wave packet can clearly be seen.

4 single-particle functions for X , Y , Z , and θ , respectively. Results agree to within 1% of the CC or CCWP reference calculations,^{27,32} for all the diffraction channels in the case of normal scattering. For the non-normal scattering, there are some larger deviations for high-energy diffraction channels of rotationally excited molecules. As in the CCWP method, one problem is that parts of the wave packet remain trapped in the potential well and the simulation has to be performed for a very long time. Looking at the single-particle functions for the scattering coordinate we can see some of them in the interaction region still after 1500 fs. Another problem is that in this case there are very small correlation coefficients present, and we have to integrate the system of differential equations with an accuracy two orders of magnitude better than for the normal scattering. As a consequence, the time step is small and a very long simulation is not feasible. Other integration methods were not successful. This situation will probably need an asymptotic analysis in order to obtain better results.^{27,33}

The results above show that an accurate solution can be obtained. It is now very important to understand the

FIG. 2. The probability distribution for the scattering coordinate Z . Comparison between a converged MCTDH ($5 \times 5 \times 15 \times 4$ configurations), TDH (1 configuration) and two low precision MCTDH (2^4 and 3^4 configurations). The numbers in the legend refer to the number of configurations for the coordinates X , Y , Z , and θ , respectively. The ordinate represents the modulus squared of the wave function averaged over X , Y , and θ .

quality of the approximation for a small number of configurations, and to assess how MCTDH converges to an accurate solution without relying on previously available calculations. Figure 2 shows the probability density for the scattering coordinate after 3000 fs and different numbers of configurations. The simplest case employs only one configuration. This is the well-known time-dependent Hartree approximation (TDH). As expected it is not able to represent the splitting of the wave function; the probability density remains concentrated into the initial non-excited state, and there is no exchange of energy with the rotational degree of freedom. This means that, in the simple one-configuration model, some important correlation effects are missing, and only a description of average properties of the system is possible. On the other hand, diffraction probabilities, averaged over the rotational coordinate, are a reasonable approximation for the sum of the exact rotationally elastic and inelastic probabilities as can be seen in Table VI. As the number of single-

TABLE II. Rotationally elastic diffraction probabilities $P(000 \rightarrow mn0)$ for normal incidence and $E_T = 7.353$ mHartree. Channel energy refers to final translational energy parallel to the surface. Close-coupling (CC) calculations are compared with converged MCTDH.

Diffraction order	m	n	CC	MCTDH	Error (%)	Channel energy (mHartree)
0	0	0	$0.837416 \cdot 10^{-1}$	$0.840856 \cdot 10^{-1}$	0.41	0.000
1	1	0	$0.628858 \cdot 10^{-1}$	$0.629229 \cdot 10^{-1}$	0.06	0.186
2	1	1	$0.452168 \cdot 10^{-1}$	$0.451951 \cdot 10^{-1}$	-0.05	0.373
2	2	0	$0.738213 \cdot 10^{-2}$	$0.737836 \cdot 10^{-2}$	-0.05	0.746
3	2	1	$0.502355 \cdot 10^{-2}$	$0.502336 \cdot 10^{-2}$	0.00	0.932
3	3	0	$0.277121 \cdot 10^{-3}$	$0.276433 \cdot 10^{-3}$	-0.25	1.679
4	2	2	$0.534627 \cdot 10^{-3}$	$0.534168 \cdot 10^{-3}$	-0.09	1.492
4	3	1	$0.175057 \cdot 10^{-3}$	$0.174624 \cdot 10^{-3}$	-0.25	1.865
4	4	0	$3.6741 \cdot 10^{-6}$	$3.69368 \cdot 10^{-6}$	0.53	2.984

TABLE III. Rotationally inelastic diffraction probabilities $P(000 \rightarrow mn2)$ for normal incidence and $E_T = 7.353$ mHartree. Channel energy refers to final translational energy parallel to the surface. Close-coupling (CC) calculations are compared with converged MCTDH.

Diffraction order	m	n	CC	MCTDH	Error (%)	Channel energy (mHartree)
0	0	0	$0.617614 \cdot 10^{-1}$	$0.615216 \cdot 10^{-1}$	-0.39	1.615
1	1	0	$0.442875 \cdot 10^{-1}$	$0.441471 \cdot 10^{-1}$	-0.32	1.801
2	1	1	$0.303089 \cdot 10^{-1}$	$0.303327 \cdot 10^{-1}$	0.08	1.988
2	2	0	$0.484845 \cdot 10^{-2}$	$0.484736 \cdot 10^{-2}$	-0.02	2.361
3	2	1	$0.312524 \cdot 10^{-2}$	$0.314467 \cdot 10^{-2}$	0.62	2.547
3	3	0	$0.158118 \cdot 10^{-3}$	$0.159415 \cdot 10^{-3}$	0.82	3.293
4	2	2	$0.306393 \cdot 10^{-3}$	$0.309255 \cdot 10^{-3}$	0.93	3.107
4	3	1	$9.38195 \cdot 10^{-5}$	$9.49139 \cdot 10^{-5}$	1.17	3.480
4	4	0	$1.58468 \cdot 10^{-6}$	$1.6436 \cdot 10^{-6}$	3.72	4.599

particle functions for each coordinate increases, the contribution to the state $j=2$ increases at expense of the state $j=0$. However, it is not just the number of configurations that is important. One has to know which coordinate needs more single-particle functions than others.

The most convenient way to study the behavior of the wave function as a function of the number of configurations is to look at the fraction that each natural single-particle function contributes in the approximate MCTDH representation.^{14,15} In the limiting case of a converged solution, these quantities should be identified with the $\nu_n^{(i)}$'s of Eq. (4). In general we look at $\langle \tilde{\psi}_n^{(i)} | \tilde{\psi}_n^{(i)} \rangle$. The convergence of the MCTDH approximation can be determined by looking at the convergence $\langle \tilde{\psi}_n^{(i)} | \tilde{\psi}_n^{(i)} \rangle \rightarrow \nu_n^{(i)}$. Figure 3 shows the time evolution of the contribution of the natural single-particle functions for each coordinate as obtained from a converged calculation (because of the symmetry of the system, X and Y coordinates are identical). First, we see that the

TABLE IV. Rotationally elastic diffraction probabilities $P(000 \rightarrow mn0)$ for non-normal incidence at an angle of 30° with the surface normal and $E_T = 7.353$ mHartree. Channel energy refers to final translational energy parallel to the surface. Close-coupling wave packet (CCWP) calculations are compared with converged MCTDH.

Diffraction order	m	n	CCWP	MCTDH	Error (%)	Channel energy (mHartree)
0	0	0	0.1888	0.1893	0.26	1.837
1	-1	0	$0.5697 \cdot 10^{-1}$	$0.569 \cdot 10^{-1}$	-0.12	0.853
1	0	± 1	0.1152	0.1152	0.00	2.024
1	1	0	$0.4545 \cdot 10^{-1}$	$0.4532 \cdot 10^{-1}$	-0.28	3.195
2	-1	± 1	$0.3558 \cdot 10^{-1}$	$0.3553 \cdot 10^{-1}$	-0.14	0.242
2	-2	0	$0.5323 \cdot 10^{-2}$	$0.5309 \cdot 10^{-2}$	-0.26	1.040
2	0	± 2	$0.1114 \cdot 10^{-1}$	$0.1112 \cdot 10^{-1}$	-0.17	2.584
2	1	± 1	$0.2456 \cdot 10^{-1}$	$0.2451 \cdot 10^{-1}$	-0.20	3.381
2	2	0	$0.9697 \cdot 10^{-3}$	$0.9701 \cdot 10^{-3}$	0.04	4.925
3	-1	± 2	$0.3489 \cdot 10^{-2}$	$0.3486 \cdot 10^{-2}$	-0.08	0.004
3	-2	± 1	$0.3363 \cdot 10^{-2}$	$0.3357 \cdot 10^{-2}$	0.17	0.428
3	-3	0	$0.2574 \cdot 10^{-3}$	$0.2572 \cdot 10^{-3}$	0.07	1.599
3	0	± 3	$0.3171 \cdot 10^{-3}$	$0.3165 \cdot 10^{-3}$	-0.18	3.516
3	1	± 2	$0.2037 \cdot 10^{-2}$	$0.2037 \cdot 10^{-2}$	0.00	3.941
3	2	± 1	$0.4451 \cdot 10^{-3}$	$0.4485 \cdot 10^{-3}$	0.76	5.112

TABLE V. Rotationally inelastic diffraction probabilities $P(000 \rightarrow mn2)$ for non-normal incidence at an angle of 30° with the surface normal and $E_T = 7.353$ mHartree. Channel energy refers to final translational energy parallel to the surface. Close-coupling wavepacket (CCWP) calculations are compared with converged MCTDH.

Diffraction order	m	n	CCWP	MCTDH	Error (%)	Channel energy (mHartree)
0	0	0	$0.9234 \cdot 10^{-1}$	$0.9207 \cdot 10^{-1}$	-0.29	3.452
1	-1	0	$0.2860 \cdot 10^{-1}$	$0.2858 \cdot 10^{-1}$	0.07	2.468
1	0	± 1	$0.5162 \cdot 10^{-1}$	$0.5155 \cdot 10^{-1}$	-0.14	3.639
1	1	0	$0.1534 \cdot 10^{-1}$	$0.1536 \cdot 10^{-1}$	0.13	4.809
2	-1	± 1	$0.1651 \cdot 10^{-1}$	$0.1657 \cdot 10^{-1}$	0.36	1.856
2	-2	0	$0.2935 \cdot 10^{-2}$	$0.2940 \cdot 10^{-2}$	0.17	2.654
2	0	± 2	$0.4416 \cdot 10^{-2}$	$0.4426 \cdot 10^{-2}$	0.22	4.198
2	1	± 1	$0.7459 \cdot 10^{-2}$	$0.7539 \cdot 10^{-2}$	1.07	4.996
2	2	0	$0.1644 \cdot 10^{-3}$	$0.1721 \cdot 10^{-3}$	4.68	6.540
3	-1	± 2	$0.1443 \cdot 10^{-2}$	$0.1458 \cdot 10^{-2}$	1.03	1.618
3	-2	± 1	$0.1733 \cdot 10^{-2}$	$0.1745 \cdot 10^{-2}$	0.69	2.043
3	-3	0	$0.1567 \cdot 10^{-3}$	$0.1580 \cdot 10^{-3}$	0.83	3.214
3	0	± 3	$0.0991 \cdot 10^{-3}$	$0.1006 \cdot 10^{-3}$	1.51	5.131
3	1	± 2	$0.5219 \cdot 10^{-3}$	$0.5369 \cdot 10^{-3}$	2.87	5.556
3	2	± 1	$6.792 \cdot 10^{-5}$	$6.93 \cdot 10^{-5}$	2.03	6.726

contribution of the configuration with initial contribution equal to one changes slowly and in a rather smooth way. The problem is well suited for a MCTDH calculation, as one configuration is already able to represent about 80% of the total wave function. This is not the same as that the TDH wave function has this overlap with a exact wave function, because these 80% are obtained using a converged MCTDH wave function in the propagation, whereas TDH also propagates with just one configuration. As the wave function approaches the surface, the interaction between the configurations increases the contributions of the other single-particle functions. After the H₂ molecule has left the surface the contributions reach a constant value corresponding to a free propagation. From the figures it is possible to get an idea about the duration of the interaction. The most important changes happen between 150 and 250 fs. Single-particle functions that contribute less are responsible for correlation effects on a longer time scale.

Figure 4 shows the effect of adding configurations. The contributions of single-particle functions converge quickly and monotonically. The fifth natural single-particle function produce almost no changes in the contribution of the previous functions. Different coordinates do not play the same

TABLE VI. Sum of rotationally elastic ($j=0$) and inelastic ($j=2$) diffraction probabilities for different diffraction channels (m, n). Time-dependent Hartree (one configuration; TDH) is compared with close-coupling (CC) reference calculations. There are no contributions to channels with $j > 2$.

m	n	CC	TDH
0	0	0.145	0.148
1	0	0.107	0.108
1	1	$0.755 \cdot 10^{-1}$	$0.795 \cdot 10^{-1}$
2	0	$0.122 \cdot 10^{-1}$	$0.094 \cdot 10^{-1}$
2	1	$0.814 \cdot 10^{-2}$	$0.691 \cdot 10^{-2}$

FIG. 3. Evolution of the contributions of natural single-particle functions as obtained from a converged simulation: (a), (b), and (c) refer to X , Z , and θ , respectively. Contributions are approximated by $\langle \tilde{\psi}_n^{(i)} | \tilde{\psi}_n^{(i)} \rangle$, which for the converged simulation equals $\nu_n^{(i)}$.

role in approximating the wave function. Fixing the number of natural single-particle functions to seven for the scattering coordinate Z , the convergence with respect to the other coordinates is faster and results in a considerable saving for the total number of configurations. With $3 \times 3 \times 7 \times 3 = 189$ configurations 99.8% of the converged wave function is repro-

FIG. 4. Convergence and stability of natural single-particle functions, as new configurations are added. The same number of configurations is used for each coordinate. The ordinate represents $\langle \tilde{\psi}_n^{(i)} | \tilde{\psi}_n^{(i)} \rangle$. In (a) the contributions of the scattering coordinate Z are shown, and in (b) the contributions of X .

duced. This result is comparable with $5 \times 5 \times 5 \times 4 = 500$ configurations that reproduce 99.6%. From Table VII it appears that the first case gives also a better approximation for the scattering probabilities. A closer look at single-particle functions reveals that the convergence of single-particle functions to the exact natural single-particle functions is already good for $2 \times 2 \times 7 \times 3$ configurations. Adding more configurations improves the accuracy of scattering probabilities by the same order of magnitude that these additional configuration contribute to the total wave function. This means that these additional configurations are only important for the very small scattering probabilities. It is, however, very important not to have too few single-particle functions for the scattering coordinate Z . In Fig. 3 we can see this fact reflected by the larger number of single-particle functions for Z contributing to the converged wave function.

IV. CONCLUSIONS

In this work we have applied the MCTDH to a four-dimensional surface scattering problem to study the applicability and the characteristics of the MCTDH method. The system H₂/LiF(001) has been chosen because it was previously employed in CC and CCWP calculations. The availability of accurate results makes this system a benchmark for new numerical methods. We have shown that MCTDH is able to calculate diffraction probabilities accurately. For normal incidence the accuracy is comparable to the accuracy of the CC calculations, whereas for non-normal incidence the accuracy is slightly less than the accuracy of the CCWP calculations. For non-normal incidence it is more difficult to obtain good results for some highly energetic diffraction channels than for normal incidence, because part of the wave function is trapped in the potential well. This necessitates

TABLE VII. Scattering probabilities calculated with different numbers of configurations in MCTDH ($n_X \times n_Y \times n_Z \times n_\theta$ means n_X single-particle functions for X , etc.). Errors are relative to close-coupling calculations. Diffraction channels are grouped by order of magnitude of their probabilities.

Magnitude scattering probabilities	j	m	n	Error (%)			
				$2 \times 2 \times 7 \times 3$ (= 84)	$3 \times 3 \times 7 \times 3$ (= 189)	$4 \times 4 \times 7 \times 3$ (= 336)	$5 \times 5 \times 5 \times 4$ (= 500)
10^{-2}	0	0	0	5.95	0.40	1.22	6.82
	0	1	0	-1.70	1.34	0.78	2.21
	0	1	1	-2.70	-0.12	-0.46	1.03
	2	0	0	2.65	-2.51	-1.29	-5.30
	2	1	0	-2.00	-0.69	-1.31	-3.14
	2	1	1	-0.43	0.95	0.64	-1.79
10^{-3}	0	2	0	23.95	0.70	0.57	2.91
	0	2	1	-0.87	-2.37	-0.21	-5.25
	2	2	0	16.54	-0.90	-1.11	-10.15
	2	2	1	-3.49	-1.34	1.07	11.51
10^{-4}	0	2	2		-11.22	-4.75	-23.58
	0	3	0		-9.99	-0.45	1.09
	0	3	1		-19.28	-3.47	-11.12
	2	2	2		6.54	17.76	73.84
	2	3	0		-15.31	0.59	-16.97

more configurations than in the case of normal incidence, which is computationally expensive, or an asymptotic analysis.

The contributions of natural single-particle functions to the total wave function show how long H₂ interacts with the surface, and the convergence of the MCTDH wave function. The number of natural single-particle functions of a coordinate reflects the importance of that coordinate in approximating the total wave function. In the present case the scattering coordinate turned out to be the most important one, and only with more than seven single-particle functions for that coordinate the convergence for the calculated probabilities is reached. For the other coordinates as few as two single-particle functions suffice.

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