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A test of the accuracy of the partially-separable time-dependent self-consistent-field approach

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The accuracy of the time-dependent self-consistent-field (TDSCF) approach assuming partial factorization of the total wave packet is tested against an exact treatment, when applied to calculate asymptotic properties. The test is carried out in the framework of a three-dimensional simulation of the Ar–HCl UV photodissociation dynamics. All the partially-separable TDSCF ansatzs possible for this problem are investigated. The quality of the TDSCF results is found to be strongly dependent on the specific partially-separable ansatzs applied. In general, the TDSCF predictions are in very good (even quantitative) agreement with the exact ones for magnitudes associated with direct photodissociation dynamics, and are qualitative in the case of indirect photodissociation. The deviation of the TDSCF results from the exact dynamics is interpreted in terms of an error operator defined as the difference between the exact and the TDSCF Hamiltonians. The analysis of this operator also explains the different accuracy of the partially-separable ansatzs investigated. Based on this analysis, a simple procedure is suggested to estimate the relative average quality of the different TDSCF ansatzs. © 1999 American Institute of Physics. [S0021-9606(99)01042-9]

I. INTRODUCTION

The exact solution of the time-dependent Schrödinger equation becomes prohibitively expensive for quantum molecular dynamics problems with several degrees of freedom. At present, typically a maximum of 5–6 degrees of freedom can be treated exactly,^{1–4} and this number reduces when more than one continuum is involved in the problem studied. A drastic reduction in computation time is achieved by using approximate quantum methods based on total or partial decoupling of the system modes. Among these methods, the time-dependent self-consistent-field (TDSCF) approach^{5–8} has been widely applied in molecular dynamics simulations. The main advantage of the TDSCF scheme is that partial interaction and exchange of energy between the separated modes is possible along the dynamical evolution.

A mean-field separable method like TDSCF makes it possible to study problems of which an exact treatment is out of reach.⁹ In those cases where an exact calculation is not feasible, and experimental data are not available, TDSCF becomes most useful as a predicting method. However, the price to pay for the TDSCF efficiency is that the results obtained are only approximate. Therefore, in the absence of either exact or experimental results to compare with, one has to trust the reliability of the TDSCF approach for the particular problem studied. In general it is expected that TDSCF will not provide the same quality of results for different problems. Moreover, there exists the risk of predicting apparently physical effects, which are artificially produced by the approximations of the method. All the above emphasizes the importance of establishing the validity conditions of the TDSCF approach in a wide variety of physical situations, where it is still possible to test its reliability against exact or experimental results.

A few three-dimensional calculations of triatomic sys-

tems with $J=0$ (i.e., three-mode systems) have been reported^{10–13} which tested the TDSCF predictions by comparing with exact simulations or experimental data. These works were concerned with different dynamical processes like the hydrogen transfer reaction¹⁰ in ClHCl^- , the UV photolysis of Ar–HCl,¹¹ and the vibrational predissociation of $\text{I}_2\text{--Ne}$ (Ref. 12) and $\text{Cl}_2\text{--Ne}$.¹³ In the above TDSCF studies the total wave packet was partially factorized, instead of assuming the total separation in one-dimensional functions of the traditional TDSCF scheme. The exact coupling was retained for the two modes considered more relevant to the dynamics of each specific problem, and the third mode was explicitly separated. Encouragingly good (even quantitative) agreement with the exact or experimental results was found for some of the quantities calculated, essentially those depending on the two correlated modes. Poorer results were obtained for properties more strongly related with the mode explicitly factorized.

In this article the partially-separable (PS) TDSCF approach is applied to simulate the ultraviolet photodissociation of the Ar–HCl cluster, and the results are compared with those of an exact calculation. As mentioned above, a previous test of TDSCF against exact results was carried out in Ref. 11 for this photolysis process. In that work a relatively short-time propagation was performed, with the primary focus on comparing the evolution of the TDSCF and exact wave packets. In the present study the process is simulated for a longer time, which allows one to test the TDSCF predictions for asymptotic properties like the product fragment distributions. The TDSCF method is known to be a good short-time approximation, which deteriorates with increasing time. Thus, analyzing the quality of the TDSCF description of asymptotic properties is a demanding test of the method.

Photodissociation of Ar–HCl has been extensively stud-

ied theoretically, using both approximate^{11,14–19} and exact^{11,19–22} methods. It was found that cluster fragmentation may occur following two different dissociation paths. One path involves indirect dissociation of the hydrogen atom, which is temporarily trapped in between Ar and Cl. In this case collisions of the hydrogen with the heavier atoms lead to total fragmentation into H+Ar+Cl. The other path, which is the dominant one, consists of direct dissociation of H, and can produce either total fragmentation or partial fragmentation into H+Ar–Cl radicals. Hence photolysis of Ar–HCl appears as a very suitable problem in order to investigate the effect of different partially-separable schemes of the wave packet on the quality of the TDSCF results.

The paper is organized as follows. In Sec. II the TDSCF method applied is outlined. The TDSCF and the exact results are compared and discussed in Sec. III. Conclusions are given in Sec. IV.

II. THEORETICAL APPROACH

Photolysis of the Ar–HCl cluster occurs upon optical excitation of the HCl molecule from its electronic ground state $^1\Sigma^+$ to the repulsive excited state $^1\Pi$. Only these two states are assumed to be involved in the process. Excitation takes place through an ultrafast Franck–Condon transition. The potential-energy surfaces representing the two electronic states have been described in Ref. 11. The initial state of Ar–HCl corresponds with the vibroelectronic ground state of the cluster, and details on its calculation are given elsewhere.^{11,21}

A. The PS TDSCF equations

In the calculations Jacobi coordinates (r, R, θ) are used to represent the system, where r is the HCl distance, R is the separation between the Ar atom and the HCl center of mass, and θ is the angle between the vectors associated with r and R . The total angular momentum of the cluster is assumed to be zero. For convenience, the total wave packet describing the system is defined as

$$\Psi(r, R, \theta) = \Phi(r, R, \theta)/rR, \quad (1)$$

such that the Hamiltonian for the reduced wave packet $\Phi(r, R, \theta)$ is (for $J=0$),

$$\begin{aligned} \hat{H}(r, R, \theta) = & -\frac{\hbar^2}{2\mu_r} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2\mu_R} \frac{\partial^2}{\partial R^2} \\ & + \left(\frac{1}{2\mu_r r^2} + \frac{1}{2\mu_R R^2} \right) \hat{j}^2 + V_{\text{H-Cl}}(r) \\ & + W(r, R, \theta), \end{aligned} \quad (2)$$

where μ_r and μ_R are the reduced masses associated with the r and R modes, respectively, and the term $W(r, R, \theta)$ represents the interaction of Ar with H and Cl. The photodissociation dynamics of Ar–HCl is simulated by solving the time-dependent Schrödinger equation for $\Phi(r, R, \theta, t)$ in the excited state

$$i\hbar \frac{\partial \Phi(r, R, \theta, t)}{\partial t} = \hat{H}\Phi(r, R, \theta, t). \quad (3)$$

Numerical integration of Eq. (3) provides the exact solution of the dynamical problem (for the given potential surface), with which the TDSCF results will be compared.

In the present TDSCF approximation the partially-separable ansatz used for $\Phi(q_1, q_2, q_3, t)$ is

$$\Phi^{\text{TDSCF}}(q_1, q_2, q_3, t) = \psi(q_1, q_2, t) \phi(q_3, t) e^{i\gamma(t)}, \quad (4)$$

where the Jacobian coordinates have been denoted generically by (q_1, q_2, q_3) , in order to make the theoretical exposition that follows more compact. The phase factor $e^{i\gamma(t)}$ is a coordinate-independent factor which arises as a consequence of factorizing $\Phi(q_1, q_2, q_3, t)$.^{23,24} In this work the three possible schemes of partial factorization are analyzed.

Regardless the specific identification between the generic coordinates (q_1, q_2, q_3) and the Jacobian coordinates, a TDSCF Hamiltonian corresponding with the separable ansatz of Eq. (4) can be defined as

$$\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t) = \hat{H}_1^{\text{eff}}(q_1, q_2, t) + \hat{H}_2^{\text{eff}}(q_3, t) - \hat{H}_3^{\text{eff}}(t), \quad (5)$$

where $\hat{H}_1^{\text{eff}}(q_1, q_2, t)$, $\hat{H}_2^{\text{eff}}(q_3, t)$, and $\hat{H}_3^{\text{eff}}(t)$ are time-dependent effective mean-field Hamiltonians,

$$\hat{H}_1^{\text{eff}}(q_1, q_2, t) = \langle \phi(q_3, t) | \hat{H}(q_1, q_2, q_3) | \phi(q_3, t) \rangle, \quad (6)$$

$$\hat{H}_2^{\text{eff}}(q_3, t) = \langle \psi(q_1, q_2, t) | \hat{H}(q_1, q_2, q_3) | \psi(q_1, q_2, t) \rangle, \quad (7)$$

$$\begin{aligned} \hat{H}_3^{\text{eff}}(t) = & \langle \psi(q_1, q_2, t) \phi(q_3, t) | \hat{H}(q_1, q_2, q_3) | \\ & \times \psi(q_1, q_2, t) \phi(q_3, t) \rangle, \end{aligned} \quad (8)$$

which govern the time evolution of $\Phi^{\text{TDSCF}}(q_1, q_2, q_3, t)$ through the new equations of motion

$$i\hbar \frac{\partial \psi(q_1, q_2, t)}{\partial t} = \hat{H}_1^{\text{eff}}(q_1, q_2, t) \psi(q_1, q_2, t), \quad (9)$$

$$i\hbar \frac{\partial \phi(q_3, t)}{\partial t} = \hat{H}_2^{\text{eff}}(q_3, t) \phi(q_3, t), \quad (10)$$

$$\gamma(t) = \int_0^t dt' \hat{H}_3^{\text{eff}}(t'). \quad (11)$$

The above TDSCF equations [Eqs. (6)–(11)] are solved in a self-consistent way, making possible energy exchange between the separated modes through the effective Hamiltonians.

It should be noted that the phase factor $e^{i\gamma(t)}$ affects only the calculation of those properties explicitly dependent on the whole phase of $\Phi^{\text{TDSCF}}(q_1, q_2, q_3, t)$, such as the autocorrelation function $a(t) = \langle \Phi^{\text{TDSCF}}(q_1, q_2, q_3, t=0) | \Phi^{\text{TDSCF}}(q_1, q_2, q_3, t) \rangle$ [and therefore the absorption spectrum calculated as the Fourier transform of $a(t)$]. Magnitudes like product distributions which are evaluated as $\langle \Phi^{\text{TDSCF}}(q_1, q_2, q_3, t) | \hat{O} | \Phi^{\text{TDSCF}}(q_1, q_2, q_3, t) \rangle$ when $t \rightarrow \infty$, where $\hat{O}$ is the (time-independent) operator associated with the magnitude of interest, are unaffected by the factor $e^{i\gamma(t)}$. If one is interested only in this latter type of quantities, Eqs. (8) and (11) are unnecessary in the TDSCF calculation.

The TDSCF equations (6)–(11) are general for the type of factorization of the total wave packet applied in Eq. (4).

However, in a practical calculation, slightly different definitions of the effective Hamiltonians than those of Eqs. (6)–(8) are usually employed. One can realize that in the expressions of $\hat{H}_1^{\text{eff}}(q_1, q_2, t)$ and $\hat{H}_2^{\text{eff}}(q_3, t)$ some terms appear which are time-dependent but coordinate-independent ones. Those terms generate coordinate-independent phase factors in the wave packets $\psi(q_1, q_2, t)$ and $\phi(q_3, t)$ when they are propagated with Eqs. (6), (7), (9), and (10). The same coordinate-independent terms appearing in $\hat{H}_1^{\text{eff}}(q_1, q_2, t)$ and $\hat{H}_2^{\text{eff}}(q_3, t)$ are also present in $\hat{H}_3^{\text{eff}}(t)$, so all these terms actually cancel in $\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$ of Eq. (5). Therefore, the three effective Hamiltonians can be redefined by removing all the terms which cancel in $\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$. In this way, new and simpler effective Hamiltonians are obtained, which in the case of $\hat{H}_1^{\text{eff}}(q_1, q_2, t)$ and $\hat{H}_2^{\text{eff}}(q_3, t)$ consist only of coordinate-dependent terms. The calculation of the new effective Hamiltonian $\hat{H}_3^{\text{eff}}(t)$ is now reduced to the Hamiltonian coupling terms between the three modes q_1 , q_2 , and q_3 ,

$$\hat{H}_3^{\text{eff}}(t) = \langle \Phi^{\text{TDSCF}}(q_1, q_2, q_3, t) | \hat{H}_I(q_1, q_2, q_3) | \Phi^{\text{TDSCF}}(q_1, q_2, q_3, t) \rangle, \quad (12)$$

where in the particular case of the Hamiltonian of Eq. (2),

$$\hat{H}_I(r, R, \theta) = \left(\frac{1}{2\mu_r r^2} + \frac{1}{2\mu_R R^2} \right) \hat{j}^2 + W(r, R, \theta). \quad (13)$$

The new effective Hamiltonians are now the ones which are actually applied in Eqs. (9)–(11).

An “error operator” $\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$ of the TDSCF evolution can be defined as

$$\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t) = \hat{H}(q_1, q_2, q_3) - \hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t). \quad (14)$$

This operator involves only those coupling terms of the Hamiltonian [i.e., of $\hat{H}_I(r, R, \theta)$] between the separated modes, and represents the deviation at time t of $\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$ from the true Hamiltonian $\hat{H}(q_1, q_2, q_3)$. It can be easily seen from Eqs. (5)–(8) that

$$\langle \Phi^{\text{TDSCF}}(q_1, q_2, q_3, t) | \Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t) | \Phi^{\text{TDSCF}}(q_1, q_2, q_3, t) \rangle = 0, \forall t, \quad (15)$$

which implies that

$$\begin{aligned} & \langle \Phi^{\text{TDSCF}}(q_1, q_2, q_3, t) | \hat{H}(q_1, q_2, q_3) | \Phi^{\text{TDSCF}}(q_1, q_2, q_3, t) \rangle \\ &= \langle \Phi^{\text{TDSCF}}(q_1, q_2, q_3, t) | \hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t) | \Phi^{\text{TDSCF}}(q_1, q_2, q_3, t) \rangle \\ & \times \langle q_1, q_2, q_3, t | \rangle, \forall t. \end{aligned} \quad (16)$$

Equations (15) and (16) ensure the correct mean total energy conservation of the TDSCF dynamics during the time evolution.

The fact that Eq. (15) holds does not mean that $\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t) = 0$ in the portion of phase space dynamically accessible. Was this the case, the TDSCF treatment would be exact, and that happens only in a few limit-

ing, model cases. In general the situation is that $\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t) \neq 0$, and this is the origin of the error developed by the TDSCF wave packet with respect to the exact one. Actually the TDSCF and the exact dynamics take place at the same total energy [Eq. (16)], but the energy transfer (and therefore the energy partitioning) between the modes is different because of the difference between the $\hat{H}(q_1, q_2, q_3)$ and $\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$ Hamiltonians. It is obvious that minimizing the operator $\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$ implies minimizing the TDSCF error. Efforts have been invested in this direction by investigating the effect of using different coordinate representations on the quality of both static²³ and time-dependent²⁵ SCF methods, assuming a totally-separable ansatz for the wave packet. For a specific problem one can search for a set of coordinates in which the magnitude of the coupling terms involved in $\Delta\hat{H}^{\text{TDSCF}}$ is minimized with respect to other sets of coordinates. Now, for a given coordinate representation, the assumption of partial factorization of the wave packet leads to different operators $\Delta\hat{H}^{\text{TDSCF}}$, depending on how the factorization is designed. As a result, different accuracy is expected from the different PS TDSCF ansatzs, and one of them will be optimal.

B. Two-dimensional calculations

In addition to testing the PS TDSCF ansatz of Eq. (4) against an exact 3D calculation, it is interesting to compare the TDSCF results with those of an exact 2D simulation in which the explicitly separated mode q_3 is removed. The PS TDSCF algorithm is computationally more costly and more complex to implement than that of the exact 2D calculation. The goal is to investigate whether the inclusion of the q_3 mode in the PS TDSCF framework improves the quality of the results with respect to the exact 2D model, and whether this improvement justifies the increase in cost and complexity of the calculation. To this purpose the $\psi(q_1, q_2, t)$ wave packet is propagated by solving the equation

$$i\hbar \frac{\partial \psi(q_1, q_2, t)}{\partial t} = \hat{H}^{2D}(q_1, q_2) \psi(q_1, q_2, t), \quad (17)$$

where

$$\hat{H}^{2D}(q_1, q_2) = \langle \phi(q_3, t=0) | \hat{H}(q_1, q_2, q_3) | \phi(q_3, t=0) \rangle. \quad (18)$$

Note that by defining the reduced-dimensionality Hamiltonian $\hat{H}^{2D}(q_1, q_2)$ as in Eq. (18) the 2D calculation is carried out at the same mean total energy as the PS TDSCF and exact calculations, which make all the results comparable. In addition, the computational cost of solving Eqs. (17) and (9) is the same, so the difference in efficiency between the PS TDSCF and the 2D calculations arises from the additional TDSCF equations (6)–(8), (10), and (11). Exact 2D calculations were carried out only in the cases $(q_1, q_2) = (r, \theta)$ and $(q_1, q_2) = (r, R)$, since a 2D calculation with $(q_1, q_2) = (R, \theta)$, freezing the dissociating r mode, does not make any sense.

TABLE I. CPU time spent by the different calculations carried out in this work. In columns second to fourth the correspondence between the Jacobian and the q_1 , q_2 , and q_3 coordinates is indicated by (q_1, q_2, q_3) . The CPU time of the TDSCF calculation with $(q_1, q_2, q_3) = (r, \theta, R)$ has been chosen as the unit of time.

Method	(r, θ, R)	(R, θ, r)	(r, R, θ)
exact 3D	195.5	195.5	195.5
TDSCF	1	0.656	0.703
exact 2D	0.972	...	0.593

C. Computational details

All the wave packets were propagated using the Chebyshev polynomial expansion method.^{26,27} The Hamiltonian operations on the wave packet were carried out using the Fourier method^{27,28} combined with discrete variable representation (DVR) techniques.²⁹ The wave packets are represented on a grid, and the Hamiltonian operations are calculated locally on that grid. A rectangular grid of 450×270 equally-spaced points was used to represent the r and R coordinates, respectively, with $1.3 \text{ a.u.} \leq r \leq 52.0 \text{ a.u.}$ and $6.0 \text{ a.u.} \leq R \leq 14.5 \text{ a.u.}$ In the case of the TDSCF calculation with $q_3 = r$, the R grid consisted of 300 points (instead of 270) in the range $6.0 \text{ a.u.} \leq R \leq 15.4 \text{ a.u.}$ The action of the kinetic-energy operators associated with these coordinates were evaluated by means of fast Fourier transform (FFT). The operations on the wave packets of the Hamiltonian terms involving the angle θ were calculated using a combination of a finite basis representation (FBR) and a DVR. A FBR of 130 Legendre polynomials combined with a grid of 130 points corresponding to a Gauss–Legendre quadrature as a DVR were used to represent the coordinate θ in the range $0 \leq \theta \leq \pi$. In the TDSCF calculations where $q_3 = r$ and $q_3 = \theta$, the FBR and the DVR consisted of 135 Legendre polynomials and 135 Gauss–Legendre quadrature points, respectively. The unitary Legendre transform relates the two representations.³⁰ All the time propagations were carried out up to $t = 80 \text{ fs}$. A time step, $\Delta t_1 = 1 \text{ fs}$ and $\Delta t_2 = 0.25 \text{ fs}$ were employed in the TDSCF simulations to propagate $\psi(q_1, q_2, t)$ and $\phi(q_3, t)$, respectively. In the exact 2D calculations the time step was $\Delta t = 1 \text{ fs}$.

III. RESULTS AND DISCUSSION

In addition to the quality of the results, it is interesting to analyze the computational efficiency of the different calculations carried out in this work. Table I collects all the corresponding CPU times. The unit of time is taken to be the CPU time of the TDSCF calculation with $(q_1, q_2, q_3) = (r, \theta, R)$, which is 70 min in an Alpha station 500/400. On the one hand, it is found that the ratio between the computational efficiency of the exact and the different PS TDSCF calculations ranges from 195.5 [in the case of $(q_1, q_2, q_3) = (r, \theta, R)$] to 298 [for $(q_1, q_2, q_3) = (R, \theta, r)$]. On the other hand, the exact 2D calculations are only slightly more efficient than the corresponding PS TDSCF ones [3% and 16% in the cases $(q_1, q_2) = (r, \theta)$ and $(q_1, q_2) = (r, R)$, respectively].

A. Kinetic-energy distributions

Among the asymptotic properties associated with the Ar–HCl photolysis, the kinetic-energy distributions in the r and R modes (and in particular the r one) have become central quantities in previous calculations.^{19–21} Such distributions are calculated as

$$P(\epsilon_{k_r}) = \int_0^\pi d\theta \sin \theta \int dR \left| \int dr (2\pi\hbar)^{-1/2} e^{-ik_r r} \times \Phi(r, R, \theta, t = \infty) \right|^2, \quad (19)$$

$$P(\epsilon_{k_R}) = \int_0^\pi d\theta \sin \theta \int dr \left| \int dR (2\pi\hbar)^{-1/2} e^{-ik_R R} \times \Phi(r, R, \theta, t = \infty) \right|^2, \quad (20)$$

in the case of the exact wave packet. Similar definitions are applied in the PS TDSCF and exact 2D calculations. Due to the H/Cl mass ratio, the r mode (in which the excitation energy is initially deposited) describes mainly the hydrogen motion. In turn, the Jacobian R mode closely represents the Ar–Cl stretch vibration. Then, the $P(\epsilon_{k_r})$ and $P(\epsilon_{k_R})$ distributions provide information on how the initial excess energy of the hydrogen is transferred to the Ar–Cl stretching mode during the photolysis process.

The two distributions $P(\epsilon_{k_r})$ and $P(\epsilon_{k_R})$ are displayed in Figs. 1 and 2, respectively, for the different calculations carried out. Note that in the definition of Eqs. (19) and (20), $P(\epsilon_{k_r})$ and $P(\epsilon_{k_R})$ are normalized in the momentum domain, but not in the kinetic-energy domain. Normalization of $P(\epsilon_{k_r})$ and $P(\epsilon_{k_R})$ in the energy domain is achieved by multiplying the distributions by the factors $\mu_r/\hbar k_r$ and $\mu_R/\hbar k_R$, respectively. These factors have not been included in order to avoid singularities, since some of the distributions shown in Figs. 1 and 2 present nonzero intensity in the regions around $k_r = 0$ and $k_R = 0$. The exact 3D $P(\epsilon_{k_r})$ distribution consists of a broad, structureless peak mainly associated with direct dissociation of the hydrogen atom,^{21,22} and a tail at low ϵ_{k_r} energies produced by collisions of H with Ar and Cl. Correspondingly, the exact 3D $P(\epsilon_{k_R})$ distribution shows also a main peak at very low ϵ_{k_R} energies (the direct dissociation peak), and a high-energy tail associated with collisional events.

The most obvious feature of Figs. 1 and 2 is that the three partially-separable TDSCF ansatzs give qualitatively different results, and the same is true for the corresponding exact 2D calculations. Let us begin by analyzing the exact 2D results, which are the short-dashed lines shown in Figs. 1(a) and 1(c), and in Fig. 2(c). The two exact 2D calculations provide a poorer description of $P(\epsilon_{k_r})$ than the corresponding PS TDSCF simulations, as compared with the exact 3D distribution. The same result is found for $P(\epsilon_{k_R})$ in Fig. 2(c). The interesting finding is that the difference between the quality of the $P(\epsilon_{k_r})$ distributions calculated with the exact 2D and the TDSCF methods strongly depends on the

FIG. 1. Kinetic-energy distribution associated with the r mode, calculated with different methods. Panels (a), (b), and (c) correspond with $(q_1, q_2, q_3) = (r, \theta, R)$, $(q_1, q_2, q_3) = (R, \theta, r)$, and $(q_1, q_2, q_3) = (r, R, \theta)$, respectively. Within each panel, the solid, long-dashed, and short-dashed lines correspond with the exact 3D, TDSCF, and exact 2D calculations, respectively.

partially-separable TDSCF ansatz considered. While the exact 2D and TDSCF distributions of Fig. 1(a) are qualitatively similar, those of Fig. 1(c) are remarkably different.

The basic difference between the TDSCF and the exact 2D simulations is that the wave packet $\phi(q_3, t)$ evolves in time in the former case, while it remains as initially ($\phi(q_3, t) = \phi(q_3, t=0)$) in the exact 2D calculation. This difference affects the time evolution of $\psi(q_1, q_2, t)$ in the two types of simulations through the effective Hamiltonians $\hat{H}_1^{\text{TDSCF}}(q_1, q_2, t)$ of Eq. (6) and $\hat{H}^{2D}(q_1, q_2)$ of Eq. (8). The greater is the deviation of $\phi(q_3, t)$ from $\phi(q_3, t=0)$, the

FIG. 2. Same as Fig. 1 for the kinetic-energy distribution associated with the R mode.

greater will be the difference between the exact 2D and TDSCF wave packets $\psi(q_1, q_2, t)$, and their associated properties. The exact 2D distributions $P(\epsilon_{k_r})$ and $P(\epsilon_{k_R})$ of Figs. 1(c) and 2(c) reveal a much more intense hydrogen trapping between the heavier atoms than the corresponding TDSCF distributions. The reason is that the maximum intensity of $\phi(\theta, t=0)$ is located at smaller angles than that of $\phi(\theta, t)$ (see Fig. 5 of Ref. 11 and Fig. 5 of Ref. 21), which favors hydrogen trapping and collisional events in the exact 2D simulation. The above results indicate that, in general, including the dynamical evolution of the mode explicitly separated in the PS TDSCF scheme may have an important effect in the description of the process. The improvement in the quality of the results, along with the small difference in computational efficiency (see Table I) clearly favors the PS

TDSCF approach vs the exact reduced-dimensionality treatment.

As said above, Figs. 1 and 2 show that the three partially-separable TDSCF ansatzs predict different quality distributions $P(\epsilon_{k_r})$ and $P(\epsilon_{k_R})$, as compared with the exact results. The trend is found that the most accurate distributions are produced by the PS TDSCF ansatzs in which the modes mainly associated with the distributions are not explicitly separated. The quality of the TDSCF distributions associated with explicitly separated modes decreases significantly. This is clearly seen in the TDSCF distribution of Fig. 2(a), calculated with a PS TDSCF ansatz where $q_3=R$, which produces the worst quality $P(\epsilon_{k_R})$ distribution of the three TDSCF calculations. This behavior of the partially-separable TDSCF ansatz was expected, and has also been observed in simulations of a different process like the vibrational predissociation of I_2 -Ne and Cl_2 -Ne clusters.^{12,13} Within this apparently general trend, the quality of a specific TDSCF distribution is essentially determined by the intensity of the Hamiltonian couplings which remain unchanged for that PS TDSCF ansatz. In this sense, it is found that the TDSCF distributions of Figs. 1(b) and 1(c) are qualitatively similar, despite the fact that in the TDSCF calculation of Fig. 1(b) the r mode is factorized, and in the case of Fig. 1(c) it is not. In addition, remarkable differences in quality are observed between the TDSCF distributions of Figs. 1(a) and 1(c) [and between those of Figs. 2(b) and 2(c)] despite that the r mode (and the R mode) is not explicitly separated in both TDSCF calculations. Therefore, in order to describe a specific property there is an optimal PS TDSCF ansatz, that retaining the exact representation of the coupling between the two physically most relevant modes for that property. The difference in the accuracy of the calculated property between the optimal PS TDSCF ansatz and the other ones can be substantial.

The above result has two implications. First, if several properties are to be calculated, more than one PS TDSCF ansatz should be applied in order to optimize the TDSCF description (in the sense of increasing the amount of information available). Second, in the general case that an exact treatment is not feasible, a guide is needed to elucidate which PS TDSCF ansatz is optimal for each magnitude, or equivalently, which are the physically most relevant modes associated with the property of interest. For many properties the dependence on one mode is usually clear, like the dependence of $P(\epsilon_{k_r})$ and $P(\epsilon_{k_R})$ on r and R , respectively. Then, what remains to be determined is the other mode (or modes) which should be explicitly coupled to the above one in the TDSCF ansatz. The analysis of the Hamiltonian coupling terms (both kinetic and potential ones) can help in this determination.

In the case of our present problem, the $P(\epsilon_{k_r})$ and $P(\epsilon_{k_R})$ distributions are best described by the PS TDSCF ansatz with $q_3=R$ and $q_3=r$ [Figs. 1(a) and 2(b)], respectively. In order to provide an additional point of view, in Fig. 3 the same TDSCF and exact 3D distributions of Figs. 1(a) and 2(b) are represented in the momentum domain. Note that these are the only TDSCF distributions which present a tail

FIG. 3. Momentum distributions associated with (a) the r mode and (b) the R mode. In both panels the solid line corresponds with the exact 3D calculation, and the dashed line is the TDSCF result for (a) $(q_1, q_2, q_3) = (r, \theta, R)$, and (b) $(q_1, q_2, q_3) = (R, \theta, r)$.

of intensity at low ϵ_{k_r} (or k_r) and high ϵ_{k_R} (or k_R) values, as the exact result. In both TDSCF distributions the broad peaks corresponding to direct dissociation are better reproduced [even at a quantitative level in the case of $P(\epsilon_{k_r})$ or $P(k_R)$] than the tails at low and high energies (or momenta). The structure superimposed on the direct dissociation peak of the TDSCF distributions $P(\epsilon_{k_r})$ and $P(k_r)$ makes their comparison with the exact distributions more qualitative. This structure will be discussed short below. The agreement between the TDSCF and exact results is encouragingly good taking into account that we are dealing with asymptotic properties. Such magnitudes depend on the whole TDSCF time evolution, which gradually deteriorates. In addition, the much greater efficiency of TDSCF as compared with an exact 3D method makes PS TDSCF a very competitive approach.

A comment is due on the structure of peaks superimposed on both the TDSCF and exact 2D $P(\epsilon_{k_r})$ distributions of Fig. 1(a). Such a structure is not predicted either by the exact 3D result nor by the other two TDSCF calculations. A similar structure was found in previous hybrid simulations based on the PS TDSCF scheme, where the hydrogen modes were treated quantum mechanically, and the modes of Ar and Cl were described classically¹⁵ or semiclassically.^{16,17(a)} Those calculations were carried out in Cartesian coordinates, and the system was restricted to move on a plane. The two Cartesian hydrogen modes (which remained coupled in the hybrid simulations) nearly corresponded with the Jacobian modes r and θ . Thus, the previous hybrid calculations assumed an equivalent PS TDSCF ansatz to that of the present TDSCF simulation with $(q_1, q_2, q_3) = (r, \theta, R)$. The basic difference is that the present TDSCF approach is full dimensional, while the hybrid simulation was a reduced-dimensionality one. The structure of peaks in the kinetic-energy distribution was assigned in the earlier works to the spectrum of resonance states of the hydrogen moving inside the Ar–Cl cage. Actually, the resonance states do exist,^{21,22,31} but their signature should not appear in the form of this structure on $P(\epsilon_{k_r})$, as shown by the exact result.

The appearance of the structure seems to be related with the reduction of the dimensionality of the problem, by specifically removing the R mode. The TDSCF evolution of $\psi(r, \theta, t)$ (which determines the $P(\epsilon_{k_r})$ distribution) occurs under the action of an effective Hamiltonian $\hat{H}_1^{\text{TDSCF}}(r, \theta, t)$ where the R mode has been removed by an averaging procedure [Eq. (6)]. Due to the action of $\hat{H}_1^{\text{TDSCF}}(r, \theta, t)$, the wave packet $\psi(r, \theta, t)$ develops a structure which is reflected in the $P(\epsilon_{k_r})$ distribution of Fig. 1(a). An explanation is that the broad resonances present in the fully-coupled 3D space²² become narrower when the coupling with the R mode is neglected (as in the 2D exact calculation), or only partially considered (as in the PS TDSCF calculation). The narrower resonances would originate the structured distributions. When the R mode is fully coupled to the other modes, as in the exact wave packet $\Phi(r, \theta, R, t)$, interference between the broad 3D resonances washes out the structure, producing the plain exact $P(\epsilon_{k_r})$ distribution.

Actually, the effect of averaging $\hat{H}(r, \theta, R)$ over $|\phi(R, t)|^2$ to calculate $\hat{H}_1^{\text{TDSCF}}(r, \theta, t)$ (or $\hat{H}^{2D}(r, \theta)$ if $t=0$) is roughly equivalent to reduce drastically the width of $\phi(R, t)$. As a consequence, the evolving $\psi(r, \theta, t)$ wave packet sees in practice a narrow $\phi(R, t)$ packet concentrated around the maximum of the true one. The resonances associated with this reduced-dimensionality situation are narrower than the actual 3D ones. The basic difference between the exact 2D and the TDSCF calculations is that in the latter $\hat{H}_1^{\text{TDSCF}}(r, \theta, t)$ is recalculated every time step, following the evolution of $\phi(R, t)$. The result is that the TDSCF calculation incorporates both some more coupling to the R mode, and some delocalization in this mode, due to the motion of $\phi(R, t)$ toward larger distances. This is why the TDSCF distribution of Fig. 1(a) shows a less pronounced structure than the exact 2D distribution. The kinetic-energy distributions

predicted by the hybrid TDSCF calculations were much more structured than those of Fig. 1(a). This can be attributed to the larger reduction of the system dimensionality to a plane, as well as to additional approximations like the classical or semiclassical description of the Ar and Cl modes.

The structure discussed above is a clear example of an artificial TDSCF prediction of an effect caused by the approximations of the method. The separable nature of the TDSCF approach may favor the enhancement of structures and effects which would be washed out in an exact calculation. However, it should be noted, on the one hand, that the hydrogen resonances actually exist, and the PS TDSCF ansatz with $(q_1, q_2, q_3) = (r, \theta, R)$ only overestimates their signature in the $P(\epsilon_{k_r})$ distribution. On the other hand, the other two PS TDSCF ansatzs do not predict such a structure. In this sense, the calculation of a specific property using different PS TDSCF ansatzs may help to contrast the information obtained with each TDSCF simulation.

B. Free-rotor state distributions

The picture of energy transfer in the Ar–HCl photolysis process is complemented by the distribution of the expansion coefficients of the wave packet in free-rotor states (which in the case of $J=0$ are Legendre polynomials). Such an asymptotic magnitude gives information on the energy flow into the angular mode θ . In the case of the exact simulation this distribution is defined as

$$P(j) = \int dr \int dR \left| \int_0^\pi d\theta \sin \theta P_j(\cos \theta) \times \Phi(r, R, \theta, t=\infty) \right|^2, \quad (21)$$

where $P_j(\cos \theta)$ is a normalized Legendre polynomial. Similar definitions are applied in the TDSCF and exact 2D calculations. The distributions calculated with the different methods are plotted in Fig. 4. All the distributions reproduce the same qualitative pattern. Most of the intensity is located at low and relatively low j values (probably produced by direct photodissociation), and there is a long tail populating very high j states.

Same as with the $P(\epsilon_{k_r})$ and $P(\epsilon_{k_R})$ distributions, the worst description of $P(j)$ corresponds with the PS TDSCF ansatz where the angular mode is explicitly separated [Fig. 4(c)]. Even in this case, however, the pattern of the exact distribution is qualitatively reproduced. The other two distributions are in very good agreement with the exact result, and in particular the distribution of Fig. 4(a), which is practically indistinguishable from the exact one. The only exact 2D distribution of Fig. 4, that of Fig. 4(a), provides also an excellent description of $P(j)$. Again, similarly as with the TDSCF distributions of Figs. 1–3, the TDSCF $P(j)$ distributions (and also the exact 2D one) of Fig. 4 reproduce best the exact result at low j values, the part of $P(j)$ associated with direct photodissociation. As the PS TDSCF description of the angular modes improves, the agreement between the TDSCF and exact 3D distributions extends to higher j states.

FIG. 4. Same as Fig. 1 for the square of the expansion coefficients of the wave packet in free-rotor states [Legendre polynomials $P_j(\cos \theta)$].

C. Spectroscopic properties

Each of the asymptotic properties discussed so far depend mainly on one specific mode of the system. It is interesting to analyze the TDSCF description of a global magnitude as the total-energy distribution, which depends on all the modes of the cluster. The total-energy distributions are calculated as

$$P(E) = \frac{1}{2\pi\hbar} \times 2\mathcal{R} \left[\int_0^\infty dt \langle \Phi(r, R, \theta, t=0) | \Phi(r, R, \theta, t) \rangle e^{iEt/\hbar} \right], \quad (22)$$

FIG. 5. Probability distribution vs the total energy of the cluster. In the three panels the solid lines represent the exact 3D results, and the dashed lines correspond with the TDSCF results (the correspondence between panels and TDSCF calculations is the same as in Fig. 1).

where $\Phi(r, R, \theta, t)$ denotes either the exact or the TDSCF wave packet. The $P(E)$ distribution is closely related to the Ar-HCl absorption spectrum, which is obtained by multiplying $P(E)$ by the excitation photon energy (and the proper normalization factor). In Fig. 5 the three PS TDSCF distributions are compared with the exact one.

An excellent, quantitative agreement is found between the exact $P(E)$ and all the TDSCF distributions, which are practically indistinguishable. This is apparently in contrast with the difference in quality provided by the different TDSCF ansatzs for the asymptotic distributions of Figs. 1–4. The explanation is that the $P(E)$ magnitude, dominated by the fast direct photodissociation, is determined by the very

FIG. 6. Probability distribution vs the total energy of the cluster calculated (a) with the PS TDSCF method with $(q_1, q_2, q_3) = (r, \theta, R)$, and (b) with the exact 2D model with $(q_1, q_2) = (r, \theta)$.

short-time dynamics [first 4–5 fs; see Fig. 7 of Ref. 11 for a plot of the exact and PS TDSCF autocorrelation function $|\langle \Phi(r, R, \theta, t=0) | \Phi(r, R, \theta, t) \rangle|$ vs time]. In this short-time regime the three PS TDSCF ansatzs work very well and give equivalent results for $P(E)$. It is in the further time evolution when the three TDSCF calculations deviate from one another. Such a good agreement between all the TSCF distributions, and between these distributions and the exact one is not expected if the effect of the indirect photodissociation dynamics would be stronger.

Interestingly, while the TDSCF distributions of Figs. 5(b) and 5(c) are structureless [as well as the exact $P(E)$], the TDSCF distribution of Fig. 5(a) presents a diffuse structure of very weak undulations in the region of the maximum. For the sake of clarity, the TDSCF distribution of Fig. 5(a) is shown alone in Fig. 6(a). A similar weak structure is found in the Ar–HCl photoabsorption spectrum simulated with a time-independent complex coordinate method (Fig. 4 of Ref. 31). In this case the same initial state as in the present work

was used, except that the width of the nearly-Gaussian function describing the Ar–Cl coordinate was reduced by a factor 13. The similarity between the weak structure of $P(E)$ in Fig. 6(a) and that of the spectrum of Fig. 4 of Ref. 31 is not surprising. As discussed above, the calculation of $\hat{H}_1^{\text{TDSCF}}(r, \theta, t)$ by averaging $\hat{H}(r, \theta, R)$ over $|\phi(R, t)|^2$ involves the reduction of the width of $\phi(R, t)$ which is felt in practice by the other wave packet $\psi(r, \theta, t)$. This explains the similar structure of both the distribution of Fig. 6(a) and the spectrum of Ref. 31. Actually, the structure appearing in the distributions of Fig. 6(a) and Fig. 1(a) have the same origin in the narrower resonances associated with the reduced-dimensionality space produced by the decoupling of the R mode. The structure is more intense in $P(\epsilon_k)$ because this quantity is more sensitive to the hydrogen resonances (the r mode is essentially a hydrogen mode) than the global magnitude $P(E)$ (where the resonance structure washes out to a large extent).

Reducing the width of the initial state in the R (or Ar–Cl) mode is equivalent to localize the vibrational amplitude of this van der Waals mode. As it has been discussed previously,^{21,22} localization of the amplitude of the van der Waals motions in the initial state favors the hydrogen trapping, and therefore the manifestation of the resonance signature in the observable magnitudes. The time-independent results of Ref. 31, and the TDSCF results of Figs. 1(a) and 6 of this work (the structure of $P(E)$ was also found in Ref. 11) confirm this prediction.

The $P(E)$ distribution associated with the exact 2D wave packet $\psi(r, \theta, t)$ is shown in Fig. 6(b) in order to compare with the 3D TDSCF one of Fig. 6(a). The 2D distribution presents a far more pronounced structure than the TDSCF result. This structure is originated by recurrences appearing in the autocorrelation function associated with the exact 2D wave packet. In fact, similar recurrences are also found in the autocorrelation function corresponding to the TDSCF wave packet $\psi(r, \theta, t)$. However, the TDSCF distribution $P(E)$ is calculated by Fourier transform of the autocorrelation function of the total TDSCF wave packet [Eq. (22)], which involves the product of the autocorrelation functions associated with the $\psi(r, \theta, t)$ and $\phi(R, t)$ wave packets. The autocorrelation function of $\phi(R, t)$ is a monotonically decreasing function with time, which kills almost completely the recurrences of the autocorrelation function of $\psi(r, \theta, t)$. As a result, only very weak recurrences survive in the total autocorrelation function, which are responsible of the weak structure in the distribution of Fig. 6(a). A similar result was found in the hybrid calculation of Ref. 16 (see Fig. 4 of that work). The implication is that, for the present problem, the calculation of $P(E)$ assuming an exact reduced-dimensionality model provides a poorer agreement with the exact 3D result than the 3D TDSCF method, which involves the full dimensionality of the system. This represents an additional advantage of the 3D TDSCF approach vs the exact 2D one.

As commented above, a remarkable agreement between the TDSCF and the exact results is observed for properties like $P(E)$, and those parts of the distributions of Figs. 1–4 which depend on the fast direct photodissociation dynamics.

The good performance of the TDSCF approach for short times, and its progressive deterioration is a well known result. From Eqs. (5) and (14) we have seen that the TDSCF deterioration is caused by the error operator $\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$. Thus, the analysis of the intensity of this operator both in coordinate space and in time domain can help understand the reasons of the TDSCF deviation from the exact dynamics. Actually, the distribution of the operator intensity is not homogeneous in coordinate space for different times. Using the definition of the interaction Hamiltonian $\hat{H}_I$ of Eq. (13), one can give a definition of $\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$ valid for the three PS TDSCF ansatzs applied in this work, by rewriting Eq. (14) as

$$\begin{aligned}\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t) &= \hat{H}_I(q_1, q_2, q_3) - \langle \phi(q_3, t) | \hat{H}_I(q_1, q_2, q_3) | \phi(q_3, t) \rangle \\ &\quad - \langle \psi(q_1, q_2, t) | \hat{H}_I(q_1, q_2, q_3) | \psi(q_1, q_2, t) \rangle \\ &\quad + \langle \psi(q_1, q_2, t) \phi(q_3, t) | \hat{H}_I(q_1, q_2, q_3) | \psi(q_1, q_2, t) \\ &\quad \times \phi(q_3, t) \rangle.\end{aligned}\quad (23)$$

It is obvious from Eq. (23) that the intensity of $\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$ will be smaller in those coordinate-time regions where the averages of $\hat{H}_I(q_1, q_2, q_3)$ over the functions $\psi(q_1, q_2, t)$ and $\phi(q_3, t)$ represent a good approximation of the fully-coupled Hamiltonian $\hat{H}_I(q_1, q_2, q_3)$, and vice versa.

It is possible to distinguish four regions of $\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$ in coordinate space, three of them inside the interaction region, the fourth one being the asymptotic region. Region I consists of the area (or hyper-area) around the maximum of the initial state, in which most of the initial wave packet intensity is localized (for simplicity, in this analysis we shall restrict ourselves to nodeless initial states). In this region the intensity of $\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$ is small, increasing as we get away from the equilibrium configuration of the initial state. In addition, the more localized is the initial state, the smaller becomes $\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$ in Region I. Region II corresponds with the repulsive wall of the potential (and centrifugal) terms of $\hat{H}_I(q_1, q_2, q_3)$ at short distances. In this region the intensity of the operator raises. However, in some dissociative problems, this repulsive region is visited only by the small-intensity tail of the wave packet. Region III includes the remaining portion of the interaction region, for distances and angles (depending on the angular symmetry) larger than those of the equilibrium configuration. In general, when potential wells are involved in $\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$, this region corresponds with the rising wall of the potential towards the asymptote. When all the terms of $\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$ are purely repulsive, Region III does not exist. The dissociating wave packet currently visits this region, and here the intensity of the error operator again increases. Region III is where most of the TDSCF deviation is originated. Finally, Region IV coincides with the

asymptotic region, where all or most of the coupling terms vanish. In Region IV $\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$ approaches zero, but when the TDSCF wave packet reaches this region it is already affected by the deviation accumulated in Region III.

At short times the TDSCF wave packet remains approximately localized in region I or nearby, where $\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$ is small. In the particular case of direct photodissociation (governed by purely repulsive Hamiltonian terms), the TDSCF wave packet moves directly from Region I to the asymptotic region. This explains the good agreement between the TDSCF and the exact dynamics found in this work for direct dissociation. In a more general situation, properties which mostly depend on the potential (or Hamiltonian) details of Region I, are also well reproduced by TDSCF, even for longer times. This is the case of the vibrational predissociation lifetimes of systems like $\text{I}_2\text{-Ne}$ (Ref. 12) and $\text{Cl}_2\text{-Ne}$.¹³ This lifetime is determined by the pumping of intensity from the initial quasibound vibrational state to a lower vibrational state of the system, and this pumping occurs mainly in Region I. For longer times the wave packet populates Region III, and here the TDSCF description is poorer. Correspondingly, the TDSCF predictions for properties more sensitive to the Hamiltonian details of this region become more qualitative. This is the case of the low- and high-energy tails of $P(\epsilon_k)$ and $P(\epsilon_{k_R})$, respectively, and the tail at high j values of $P(j)$, which depend upon collisional events of the hydrogen with the heavier atoms. It appears, thus, that the quality of the TDSCF result depends on the region of $\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$ visited by the wave packet components which determine a specific property, rather than on the amount of time that the wave packet is propagated. The above analysis of the TDSCF performance based on the intensity of the operator $\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$ is valid regardless the ansatz applied (either partially or fully separable).

D. An estimate of the quality of the different TDSCF ansatzs

By comparing the TDSCF distributions of Figs. 1–5 with the exact ones, it is possible to assess the level of accuracy of the different PS TDSCF ansatzs. The following sequence can be established from higher to lower accuracy: $(q_1, q_2, q_3) = (r, \theta, R) > (q_1, q_2, q_3) = (R, \theta, r) > (q_1, q_2, q_3) = (r, R, \theta)$. This sequence is based on a criterion of global quality of the dynamical description, and it does not mean that the best PS TDSCF ansatz gives the best description of all the system properties. As already stated, a property depending on the mode explicitly factorized in the best PS TDSCF ansatz, is likely to be reproduced better by other PS TDSCF ansatz where this mode is not separated. The TDSCF distribution $P(\epsilon_{k_R})$ of Fig. 2(b) is an example. For our particular problem, it is found that the TDSCF calculation with $(q_1, q_2, q_3) = (r, R, \theta)$ does not contribute with any new information of quality to that provided by the other two PS TDSCF ansatzs. Therefore, combining the information obtained with the two best TDSCF calculations provides a

FIG. 7. Evolution of the quantity $\alpha^{\text{TDSCF}}(t)$ vs time for the PS TDSCF calculations with $(q_1, q_2, q_3) = (r, \theta, R)$ (solid line), $(q_1, q_2, q_3) = (R, \theta, r)$ (long-dashed line), and $(q_1, q_2, q_3) = (r, R, \theta)$ (short-dashed line).

good approximation to the exact dynamics, if one is interested in the global picture of the process. In this case we stress that the computational cost of these two TDSCF calculations is 1.656 time units vs the 195.5 time units of the exact calculation (see Table I). Of course, if the purpose is to calculate, e.g., partial cross sections of indirect photodissociation,²² even the best PS TDSCF calculation may not be quantitative enough. In this case, a possible alternative is to apply a method going beyond the separability assumption of the single-configuration TDSCF, like the multiconfiguration TDSCF (Refs. 32, 33) (MC-TDSCF).

For those problems where an exact calculation is not possible, it is interesting to design a means of assessing the reliability of the different TDSCF ansatzs. Such a means should involve the operator $\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$ in some way, since it is the origin of the TDSCF error. Taking into account that the specific form of $\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$ is different for each PS TDSCF ansatz, a simple way to estimate the intensity of each operator consists of defining the function

$$\chi^{\text{TDSCF}}(q_1, q_2, q_3, t) = \Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t) \times \Phi^{\text{TDSCF}}(q_1, q_2, q_3, t), \quad (24)$$

and then integrate the square modulus of $\chi^{\text{TDSCF}}(q_1, q_2, q_3, t)$ over the spatial coordinates,

$$\alpha^{\text{TDSCF}}(t) = \langle \chi^{\text{TDSCF}}(q_1, q_2, q_3, t) | \chi^{\text{TDSCF}}(q_1, q_2, q_3, t) \rangle. \quad (25)$$

The quantity $\alpha^{\text{TDSCF}}(t)$ provides an estimate of the relative intensities of the $\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$ operators associated with the different TDSCF ansatzs, and therefore of the relative quality of the TDSCF calculations vs time.

In Fig. 7 $\alpha^{\text{TDSCF}}(t)$ is shown for the three PS TDSCF ansatzs investigated in this work. The three curves present a similar pattern. The intensity is concentrated at intermediate times, being zero at very short and long times. This pattern is consistent with the spatial regions of $\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$ discussed above. At very short and long times most of the

TDSCF wave packet is localized in Regions I and IV, respectively, where $\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$ is small. At intermediate times the wave packet visits Regions II and III, where the intensity of $\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$ reaches maximum values. The interpretation of the specific shape of the $\alpha^{\text{TDSCF}}(t)$ curves, consisting of two main peaks, is a more delicate point. This shape is probably related to the behavior of the wave packet components associated with indirect photodissociation, i.e., with the successive hydrogen collisions with Ar (Region III) and Cl (Region II).

The most interesting feature of the three curves $\alpha^{\text{TDSCF}}(t)$ is that they predict the same sequence for the quality of the PS TDSCF ansatzs as that found by comparison with the exact calculation. This result, far from being a coincidence, is a consequence of the coupling terms involved in each $\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$ operator. In the case of the PS TDSCF ansatz with $(q_1, q_2, q_3) = (r, R, \theta)$, the three coupling terms of $\hat{H}_I$ [Eq. (13)] contribute to $\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$, while in the other two TDSCF calculations only two types of coupling terms ($W(r, R, \theta)$ and one centrifugal term) appear in the error operator. The fact that all the coupling terms are approximately represented explains the worst performance of the TDSCF ansatz with $(q_1, q_2, q_3) = (r, R, \theta)$. Now, in addition to the approximate representation of the interaction potential $W(r, R, \theta)$, the centrifugal coupling term which is exactly represented makes a difference between the two best PS TDSCF ansatzs. The centrifugal terms become important since high j states are populated in the photodissociation process. Because of the difference in the reduced masses μ_r and μ_R , the term $\hat{j}^2/2\mu_r r^2$ contributes more to the intensity of $\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$ than $\hat{j}^2/2\mu_R R^2$. Therefore, the exact representation of the coupling term $\hat{j}^2/2\mu_r r^2$ makes the PS TDSCF ansatz with $(q_1, q_2, q_3) = (r, \theta, R)$ the most accurate one. Note that the result of Fig. 7 could have been qualitatively anticipated just by analyzing the contribution of the Hamiltonian coupling terms to the different operators $\Delta\hat{H}^{\text{TDSCF}}(q_1, q_2, q_3, t)$.

The simple procedure of Eqs. (24) and (25) appears as a useful tool to estimate the relative accuracy of different TDSCF ansatzs. We stress, however, that $\alpha^{\text{TDSCF}}(t)$ only provides an estimate of the global (or average) accuracy of the TDSCF results. Some properties may deviate (towards both higher or lower accuracy) from this estimate. The design of a quantitative method to estimate the quality of different TDSCF ansatzs for specific magnitudes remains to be investigated in future studies.

IV. CONCLUSIONS

The level of accuracy of the TDSCF approach assuming partial factorization of the total wave packet is investigated when applied to the calculation of asymptotic properties. An application of the method to a 3D simulation of the ultraviolet photodissociation of the Ar–HCl cluster is presented. This process is dominated by direct dissociation of the hydrogen, although indirect photodissociation due to trapping

of the light atom in between Ar and Cl also plays a role to a lesser extent. The three partially-separable TDSCF ansatzs possible in this three-mode problem are tested against an exact wave packet calculation. In addition, exact 2D calculations are carried out in order to check whether they are competitive in efficiency and quality with the corresponding PS TDSCF simulations. The results of the reduced-dimensionality models are found less accurate than the TDSCF ones, with a similar computational efficiency, which makes the TDSCF approach more competitive.

Different levels of quality of the TDSCF results are obtained depending on the specific partial-factorization ansatz applied. In general, the dynamical properties associated with direct photodissociation are well reproduced (even quantitatively in some cases) by the TDSCF calculations, while the description of the indirect photodissociation dynamics is rather qualitative. The quality of the TDSCF prediction for a specific magnitude which is mainly associated with one of the modes, decreases significantly if that mode is explicitly factorized in the PS TDSCF ansatz. Consequently, even the best-quality PS TDSCF ansatz is not able to provide a good description of all the system properties. However, magnitudes which are worst described by one TDSCF ansatz, are better reproduced by the other TDSCF ansatzs. Then, combining all the information obtained with the different PS TDSCF calculations provides a good description of the main dynamical features. In addition, the PS TDSCF is found to be computationally much more efficient (between 200 and 300 times faster) than the exact calculation.

An interpretation of the PS TDSCF error is given based on the analysis of a time-dependent error operator, defined as the difference between the exact and the TDSCF Hamiltonian governing the evolution of the TDSCF wave packet. This interpretation is valid for any partially- or fully-separable TDSCF ansatz. A nonhomogeneous distribution of the intensity of the error operator is found in coordinate space, where several regions can be identified. As a consequence, the operator behaves nonhomogeneously also in the time domain. The fact that the TDSCF approach is a good short-time approximation which deteriorates gradually with time is interpreted in terms of the intensity distribution of this operator in time and space. The analysis of the intensity of the error operator also helps to elucidate which properties are expected to be better described by a TDSCF calculation, depending on the spatial regions visited by the wave packet during the dynamics. A simple procedure is proposed to estimate the relative intensity of the error operators associated with the different PS TDSCF ansatzs. This estimate gives a measure of the relative average quality of the three TDSCF ansatzs. The sequence of quality found in this way coincides with that derived from direct comparison of the TDSCF results with the exact ones. Thus, in the absence of an exact simulation to compare with, we envision a great utility of such an estimate.

The results of this work indicate that the optimal PS TDSCF ansatz is dependent on the intensity of the intermode couplings present in the system of interest, and more specifically, of those couplings governing the energy flow during

the dynamics. These more relevant couplings are associated with the mode or modes which are excited in the initial state, where the energy is initially deposited. In general, therefore, the optimal PS TDSCF ansatz is expected to be that retaining an exact representation of such couplings, or equivalently, that which explicitly correlates the excited modes connected through those couplings. The optimal PS TDSCF ansatz thus becomes state-dependent, since for different states of the system the modes that get excited, and then the most relevant couplings, may change.

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- ¹(a) D. H. Zhang and J. Z. H. Zhang, *J. Chem. Phys.* **99**, 5615 (1993); (b) **100**, 2697 (1994).
- ²J. Dai and J. C. Light, *J. Chem. Phys.* **107**, 1676 (1997).
- ³W. Zhu, J. Z. H. Zhang, and D. H. Zhang, *Chem. Phys. Lett.* **292**, 46 (1998).
- ⁴D. H. Zhang and S.-Y. Lee, *J. Chem. Phys.* **109**, 2708 (1998).
- ⁵P. A. M. Dirac, *Proc. Cambridge Philos. Soc.* **26**, 376 (1930).
- ⁶R. B. Gerber, V. Buch, and M. A. Ratner, *J. Chem. Phys.* **77**, 3022 (1982).
- ⁷R. Bisseling, R. Kosloff, R. B. Gerber, M. A. Ratner, L. Gibson, and C. Cerjan, *J. Chem. Phys.* **87**, 2760 (1987).
- ⁸R. Alimi, R. B. Gerber, A. D. Hammerich, R. Kosloff, and M. A. Ratner, *J. Chem. Phys.* **93**, 6484 (1990).
- ⁹P. Jungwirth, E. Fredj, and R. B. Gerber, *J. Chem. Phys.* **104**, 9332 (1996).
- ¹⁰A. B. McCoy, R. B. Gerber, and M. A. Ratner, *J. Chem. Phys.* **101**, 1975 (1994).
- ¹¹A. García-Vela and R. B. Gerber, *J. Chem. Phys.* **103**, 3463 (1995).
- ¹²A. García-Vela, *J. Chem. Phys.* **104**, 1047 (1996).
- ¹³A. García-Vela, *Chem. Phys. Lett.* **290**, 155 (1998).
- ¹⁴(a) A. García-Vela, R. B. Gerber, and J. J. Valentini, *Chem. Phys. Lett.* **186**, 223 (1991); (b) *J. Chem. Phys.* **97**, 3297 (1992).
- ¹⁵A. García-Vela, R. B. Gerber, and D. G. Imre, *J. Chem. Phys.* **97**, 7242 (1992).
- ¹⁶A. García-Vela and R. B. Gerber, *J. Chem. Phys.* **98**, 427 (1993).
- ¹⁷(a) A. García-Vela, R. B. Gerber, D. G. Imre, and J. J. Valentini, *Chem. Phys. Lett.* **202**, 473 (1993); (b) *Phys. Rev. Lett.* **71**, 931 (1993).
- ¹⁸A. García-Vela, R. B. Gerber, and U. Buck, *J. Phys. Chem.* **98**, 3518 (1994).
- ¹⁹T. Schröder, R. Schinke, M. Mandziuk, and Z. Bačić, *J. Chem. Phys.* **100**, 7239 (1994).
- ²⁰T. Schröder, R. Schinke, and Z. Bačić, *Chem. Phys. Lett.* **235**, 316 (1995).
- ²¹A. García-Vela, *J. Chem. Phys.* **108**, 5755 (1998).
- ²²J. C. Juanes-Marcos and A. García-Vela, *J. Chem. Phys.* **111**, 2606 (1999).
- ²³R. B. Gerber and M. A. Ratner, *Adv. Chem. Phys.* **70**, 97 (1988).
- ²⁴R. D. Coalson, *Chem. Phys. Lett.* **165**, 443 (1990).
- ²⁵P. Jungwirth, M. Roeselová, and R. B. Gerber, *J. Chem. Phys.* **110**, 9833 (1999).
- ²⁶H. Tal-Ezer and R. Kosloff, *J. Chem. Phys.* **81**, 3967 (1984).
- ²⁷R. Kosloff, *J. Phys. Chem.* **92**, 2087 (1988).
- ²⁸(a) D. Kosloff and R. Kosloff, *J. Comput. Phys.* **52**, 35 (1983); (b) R. Kosloff and D. Kosloff, *ibid.* **63**, 363 (1986).
- ²⁹(a) J. V. Lill, G. A. Parker, and J. C. Light, *Chem. Phys. Lett.* **89**, 483 (1982); (b) J. C. Light, I. P. Hamilton, and J. V. Lill, *J. Chem. Phys.* **82**, 1400 (1985).
- ³⁰F. Le Quéré and C. Leforestier, *J. Chem. Phys.* **94**, 1118 (1991).
- ³¹E. Narevicius and N. Moiseyev, *Chem. Phys. Lett.* **287**, 250 (1998).
- ³²N. Makri and W. H. Miller, *J. Chem. Phys.* **87**, 5781 (1987).
- ³³(a) H.-D. Meyer, U. Manthe, and L. S. Cederbaum, *Chem. Phys. Lett.* **165**, 73 (1990); (b) U. Manthe, H.-D. Meyer, and L. S. Cederbaum, *J. Chem. Phys.* **97**, 9062 (1992).