The extension of Wave Operator-Floquet formalism to molecular photodissociation processes with short laser pulses.

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Abstract

Photodissociations induced by intense short laser pulses are investigated using a generalized Floquet formulation. This formulation replaces the continuous electric field shape function by a discrete step function. An initial active space is defined by using the Bloch's wave operator theory and the corresponding target spaces, in which the dynamics is confined, are built for each new discrete value of the electric field magnitude. A powerful computational method of calculation of dissociation probabilities is elaborated upon by calculating and storing some basic data at each step of the discretized shape function : the eigenvalues of the target spaces, the overlap matrix between two successive groups of Floquet eigenvectors and finally the projection of the Floquet eigenvectors onto the bound states. The calculation is achieved by exploiting these data in a fast integration of the dynamic projected into the active space. An illustrative example, concerning the photodissociation of H_2^+ reveals that the procedure is particularly suitable for studying the influence of the pulse shape.

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1 Introduction

Over the last few years, multiphoton dissociation of molecules has been intensively studied both theoretically and experimentally. In the case of a cw laser, the Floquet theory takes advantage of the periodicity of the Hamiltonian in order to transform this time-dependent problem into an equivalent time-independent infinite dimensional eigenvalue problem [1]. This Floquet theory can be easily generalized to the complex quasivibrational energy (QVE) formalism [2] to study dissociation processes. The use of a complex rotation or the addition of a complex optical potential authorizes the use of a finite basis set of (L^2) integrable functions, the evaluation of the matrix $\mathcal{H}_F$ being then carried out in practice by using a complex-scaling Fourier-grid Hamiltonian [3]. The difficulties due to the large size of the Floquet matrix in the case of strong fields, can be reduced using the time-dependent complex-coordinate-Floquet method (TDCCFM)[4] or the complex scaled adiabatic switch method (CSASM)[5].

For short laser pulses the situation is quite different. The wave packet treatments, which seem well-adapted, predominate [6]. Nevertheless, such time dependent formulations require long CPU calculation times even when the DVR basis sets and Fast Fourier Transforms (FFT) accelerate the calculations. A part of this time is used to extract a detailed understanding of the dynamical process from the final averaged results. A complementary analysis is for example presented in a recent study of the H_2^+ multiphoton dissociation [7]. This work built in a multimode picture, and based on the concept of dressed molecule explains in detail the proton kinetic spectrum obtained previously in wave packet treatments and confirms the presence of bond softening and stimulated Bremstrahlung effects.

Fortunately the use of a wave packet formulation is not the only way of integrating the time-dependent Schrödinger equation. Peskin and Moiseyev [8] have recently introduced the (t,t') method to resolve this equation with time-dependent Hamiltonians (not necessarily time-periodic). Their algorithm based on the use of the Floquet-type operator in an extended Hilbert space, avoids the introduction of the time ordering operator and enables techniques originally developed for time independent Hamiltonians to be used.

One on the advantages of the Floquet formulation is its consistency with the concept of active spaces (A.S.) and with the projection of the dynamics into these spaces. This is an important point for c.w. laser calculations because the dynamics is then often reduced to small vectorial spaces. There are numerous ways of defining these active spaces in the literature. Quack's quasi resonant approximation [9] and Whaley and Light's rotating frame approximation [10] are A.S. determination techniques specific to some particular Hamiltonian structure. More general solutions have been given by the multitier approach [12] and several artificial intelligence techniques [13, 14, 15]. A recent study has shown that the Bloch wave operator theory is also, in the framework of the complex quasivibrational energy formalism, an effi-

cient tool to select the active space which mainly participates in the dissociation process [16].

The purpose of this paper is to extend this Floquet-type formulation to short pulse perturbations by introducing the concept of an evolutional target space. Section II summarizes briefly the Floquet matrix description and the integration of the Bloch equations and derives the equations relating the photodissociation in the framework of the evolutional target space model. Section III analyses more precisely the adiabaticity concept and the role played by the resonances induced by the field-matter coupling and the diffusion states. The study of the dissociation of H_2^+ with various laser intensities and pulse shapes illustrates the model and confirms some theoretical predictions. Some conclusions are also given.

2 Theory

2.1 Discretization of the electric field function

Fig. 1 presents the envelope function $\mathcal{F}(t)$ of a laser pulse versus time.

$$E(t) = \mathcal{F}(t)\cos\omega_o t \tag{1}$$

In our discretization model the whole variation range between $\mathcal{F} = 0$ and the absolute maximum value $\mathcal{F}^{max}$ is divided into N elementary intervals of the same width :

$$\Delta\mathcal{F} = \frac{\mathcal{F}^{max}}{N} \tag{2}$$

For each index $i, 1 \leq i \leq N$ the horizontal line $\mathcal{F}_i = i \times \Delta\mathcal{F}$ cuts out the continuous functions $\mathcal{F}(t)$ in a even number $2p_i$ of points $t_i^{(n)}, n = 1, 2, \ldots, 2p_i$. The continuous function $\mathcal{F}(t)$ is then approximated by the discontinuous function $F(t)$ which takes the constant value $\mathcal{F}(t_i)$ when t is between the two adjacent points t_i and t_{i+1} in an increasing part of the function and the constant value $\mathcal{F}(t_{i+1})$ at the same position but in a decreasing part.

2.2 The evolutional target space concept.

Within the framework of a semiclassical treatment of both the electromagnetic field and the matter field interaction, using the $A.P$ gauge by invoking the dipole approximation and neglecting the $A.A$ term , the expression for the Hamiltonian of a molecule under the action of an electromagnetic field is :

$$\mathcal{H} = \mathcal{H}_o(q,r) - (\frac{V_2(r) - V_1(r)}{\hbar\omega})\mu(q,r)E(t) - iV_{opt}(r) \tag{3}$$

In this expression q denotes the various bound internal vibration-rotation degrees of freedom and r is the interfragment axis. V_1 and V_2 are the ground

and the excited potential energy functions and ω is the laser frequency. The continuous function $E(t)$ (eq.1) is replaced by a discontinuous one as explained in the previous section. An asymptotic optical potential is added in order to eliminate the surface term in a generalized version of Green's identity when an L^2 basis set is used to span a finite radial range. As demonstrated in ref [17] this transformation is consistent with the asymptotic behaviour defining the resonances and does not change significantly their eigenvalues.

N different expressions of $\mathcal{H}$ correspond to the N discrete values of the field magnitude previously defined ($E_j(t) = j\Delta\mathcal{F}\cos\omega_o t$) . The N relevant complex Floquet matrices $H_F^{(j)}$,$j = 1$ to N are composed of various blocks $(H_F^{(j)})_{n,k}$ the indices of which correspond to the Fourier basis function indices. They can be built using the simple rules:

$$(H_F^{(j)})_{n,n} = \frac{1}{T}\int_0^T (\mathcal{H}_o(q,r) - iV_{opt}(r))dt + n\hbar\omega_o$$

$$(H_F^{(j)})_{n,k\neq n} = \frac{1}{T}\int_0^T -(\frac{V_2(r)-V_1(r)}{\hbar\omega})\mu(q,r)E_j(t)\exp^{i\omega_o(k-n)t}\,dt \qquad (4)$$

The main approximation of our treatment can now be introduced. This simplification is expressed in terms of the Floquet-state basis $|n,\alpha>$ where α denotes the molecular states (i.e. the eigenvectors of $\mathcal{H}_o - iV_{opt}$) and where $|n>$ are the Fourier photon indices ranging from $-\infty$ to $+\infty$. The need to use a simplified scheme of relaxation results from the large dimension of the matrix H_F which prevents the exact integration of the dynamics. In ref. [8] this problem was overcome by dividing the propagation time to subsequent identical time intervals. For a sufficiently small time step only a few Fourier basis functions are needed to accurately reproduce the dynamics. This leads to a precise solution since the errors can be diminished by reducing the elementary time intervals.

Our proposition is quite different, it leads to more coarse grained solutions but gives a considerable economy in C.P.U. time when studying the pulse shape influence. The existence of an active space S_o is assumed. It is exclusively determined by the initial molecular state and the features of the laser pulse : magnitude, width, mean frequency ... For each discretized value of the field magnitude a target space is associated with the active space:

$$S_o \longrightarrow S^{(j)} \qquad (5)$$

All the vectorial space S_o and $S^{(j)}$, $j = 1$ to N have the same dimensions. If $|\eta>$ is the group of vectors which span the free space S_o, $S^{(j)}$ is spaned by the group $|\lambda_\eta>$, each Floquet-eigenvector $|\lambda_\eta>$ being derived from the relevant free vector $|\eta>$ by establishing adiabatically the field-matter interaction. Our simplified relaxation scheme is then defined as follows : within our discretized model the field-matter interaction is a series of discontinuous constant couplings ; it is assumed that at the discontinuity between two adjacent values, namely j and $j+$

1, the wavefunction located in the subspace $S^{(j)}$ is completely projected into the subspace $S^{(j+1)}$, i.e. the projection outside this last subspace is negligible, after the evolution driven by the $(j+1)^{th}$ value of the Floquet matrix is acomplished inside the subspace $S^{(j+1)}$. As a direct consequence the whole evolution is limited to the initial active space S_o and to the N relevant target spaces $S^{(j)}$. Precise expressions concerning this evolution are given in section (2.4).

2.3 Definition of the active space and calculation of the target spaces

It is evident that the validity of the simplified relaxation scheme primarily depends on the definition of the initial active space within which the dynamics is confined. Various approaches for a proper definition of S_o have been proposed in the literature [10, 11, 12, 13, 14, 15]. In a recent publication [16] the wave operator theory was put forward in a self consistent manner to select the active space S_o. The procedure is as follows: let $|i>\equiv|n=0,\alpha>$ designate the initial state of the matter-field space and let Ω_P be the wave operator associated with the trial one-dimensional active space spanned by this vector. The non diagonal part of this operator, namely : X_P, is the solution of the nonlinear equation :

$$Q_o(1-X_P)H_F(1+X_P)P_o=0 \tag{6}$$

where P_o and Q_o are the projectors of the active space and of the complementary space respectively.

By using an iterative method as the Recursive Distorted Wave Approximation (RDWA) [18] or the Single Cycle Algorithm (S.C.A.) [19], eq.(6) is iterated up to a high order and the vectors of the whole space are sorted in the order of decreasing values of the matrix component moduli of the wave operator

$$|<\alpha|X_P|i>|. \tag{7}$$

Then the active space, the dimension N_o of which is imposed, can be built by taking the N_o first vectors $|\alpha>$. Two points must be noted concerning this procedure.

Firstly it could appear inconsistent to use a stationary formulation to select an active dynamical space. A better fashion for defining the active space would be to use the time dependent version of the wave operator theory [20]. This theory describes the evolution arising from the active space S_o by dividing it into two parts :

$$U(t,0;\mathcal{H}(t))P_o=(P_o+X(t,0))U(t,0;\mathcal{H}_{eff}) \tag{8}$$

The first, represented by $U(t,0;\mathcal{H}_{eff})$, with

$$\mathcal{H}_{eff}(t)=P_o\mathcal{H}(t)(P_o+X(t)) \tag{9}$$

is confined in the space S_o. The second, described by the time-dependent wave operator $X(t,0)$, which is itself the solution of a non linear equation :

$$i\hbar\frac{\partial X(t,0)}{\partial t} = Q_o(1-X(t,0))\mathcal{H}(t)(1+X(t,0))P_o \tag{10}$$

represents the transition outside the active space without a reverse path. The existence of a hypothetical active space in which the whole dynamics is confined implies

$$X(t,0) \sim 0 \text{ for any time} \tag{11}$$

The introduction of this identity into the basic equation (10) leads to equation (6) which defines the stationary wave operator. This property justifies, a posteriori, the choice of our stationary selection procedure.

The second difficult point of the present application is the existence of several Floquet matrices H_F. Their number is equal in our model to the number of discrete values of the electric field magnitude (typically 250 or 500). Moreover, a correct description of the spectrum of the short laser pulse requires the introduction of several frequencies centered around ω_o. As the field magnitude and the laser frequency are two basic parameters of the Floquet matrix, their multiplicity, must influence the active space selection. To appreciate this influence a multiple-choice procedure (multi-magnitude or multi-frequency) has been conceived. The comparison of the selection corresponding to a single choice (central frequency ω_o and maximum magnitude $\mathcal{F}^{max}$) and to multiple choice (multi-frequency choice and multi-magnitude choice) is made for the photodissociation of H_2^+ using two electronic states $1s\sigma_g$ and $2p\sigma_u$. The calculations are performed with a DVR basis of 150 functions ($j = 1$ to 150) and ten Floquet blocks ($n = -6$ to $+3$). The diagonalisation of the two blocks ($n = 0, n = -1$) gives a complete spectrum $|n,j>$ of respectively 18 bound states and 132 diffusion states for the surface $1s\sigma_g$ and of 150 diffusion states for the surface $2p\sigma_u$. The initial state is the ground vibrational state $|n = 0, j = 1>$, the field magnitude $\mathcal{F}^{max}$, c.f. eq. 2, corresponds to a laser intensity of $I = 25TW/cm^2$ with the central frequency being $\omega_o = 0.40 a.u.$. The multi-frequency choice procedure is carried out using a five value procedure : $I = 25TW/cm^2$; $\omega = 0.400, 0.395, 0.405, 0.390, 0.410$a.u. Five values are also introduced into the multi-magnitude choice procedure : $\omega = 0.40; I = 25., 9., 4., 1.$ and $0.25TW/cm^2$. By imposing the dimension of the active space $N_o = 20$, the three successive procedures give similar results : the three active spaces have in common a group of 18 states, namely :

- 6 bound states belonging to the initial Floquet block, $|0,1>, |0,2>, |0,3>, 0,4>, |0,5>, |0,6>$
- 12 diffusion states of the adjacent block $(n-1)$ spanning an energetical window centered on ω_o.

Thus, only two states differenciate the three active spaces. Similar results, not presented here, have been observed for $\omega_o = 0.214$a.u. and $\omega_o = 0.138$a.u. confirming a relative insensitivity of the active space choice with respect to the selection procedure.

When the active space is selected, the vectors which span the N successive target spaces can be calculated within the framework of the wave operator theory. For this, the various Floquet matrices $H_F^{(j)}$ are considered by increasing order of the electric field magnitude from j = 1 up to j = N. At each step the basic equation (6) is integrated using the Single Cycle Algorithm [19] by introducing at the start of the iteration, as a trial wave operator, the operator $X^{(j-1)}$ determined at the step just before. The eigenvectors of matrix $H_F^{(j)}$ belonging to the jth target space are finally obtained by diagonalizing the effective Hamiltonian :

$$(H_F^{(j)})^{eff} = P_o H_F^{(j)} (P_o + X^{(j)}) \tag{12}$$

and using the well known one-to-one correspondence between the eigenvectors of $(H_F^{(j)})^{eff}$ and those of $H_F^{(j)}$. [21, 22]

$$\Lambda^{(j)} P_o = (P_o + X^{(j)})(P_o \Lambda^{(j)} P_o) \tag{13}$$

$\Lambda^{(j)}$ designates the eigenvector matrix of $H_F^{(j)}$ and the projected matrix into the model space : $P_o \Lambda^{(j)} P_o$ is the eigenvector matrix of $(H_F^{(j)})^{eff}$.

2.4 The simplified dynamical scheme

Our simplified scheme is based on the model of the discretized electric field presented in section 2.1. In the framework of this model the time-dependent Hamiltonian is transformed, whatever the envelope shape may be, into a succession of Floquet matrices $H_F^{(j)}$. Two consecutive matrices in the series correspond to two adjacent values of the discretized field : $j \longrightarrow j+1$ in the increasing parts of the envelope and $j \longrightarrow j-1$ in the decreasing parts (cf. fig. 1). The various target spaces which have been built in the last section are spanned by eigenvectors $|\lambda_\mu>$ of the Floquet matrices. Thus, the evolution operator corresponding to one or the other of the plateau's constituting the discretized shape-function has a diagonal matrix representation. More precisely if the evolution is driven by $H_F^{(j)}$ between t_j and t_{j+1}, then the following is obtained:

$$\begin{aligned} \Psi(t_j) &= \sum_\beta <\lambda_{\beta_j}|\Psi(t_j)> |\lambda_{\beta_j}> \\ \Psi(t_{j+1}) &= \sum_\beta <\lambda_{\beta_j}|\Psi(t_j)> \exp(-\frac{iE_\beta^{(j)}(t_{j+1}-t_j)}{\hbar})|\lambda_{\beta_j}> \end{aligned} \tag{14}$$

At the discontinuities t_{j+1} the evolution is sudden so that :

$$\lim_{\epsilon \to 0} \Psi(t_{j+1} + \epsilon) = \lim_{\epsilon \to 0} \Psi(t_{j+1} - \epsilon) \tag{15}$$

The main approximation of our treatment, except the discretization procedure, is the assumption that the wave function is confined at any time in the target space built from the active space with the electric field magnitude carried out at this instant. This implies that the following can be written at the time of the discontinuity between the values j and $j+1$:

$$\begin{aligned} \Psi(t_{j+1} + \epsilon) &= \sum_{\beta} < \lambda_{\beta_j} | \Psi > | \lambda_{\beta_j} > \\ &= \sum_{\gamma} \sum_{\beta} < \lambda_{\gamma_{j+1}} | \lambda_{\beta_j} > < \lambda_{\beta_j} | \Psi > | \lambda_{\gamma_{j+1}} > \end{aligned} \tag{16}$$

where β and γ are eigenstates of the target spaces $S^{(j)}$ and $S^{(j+1)}$ respectively. Finally the wave function obtained at any time t can be written as follows:

$$\begin{aligned} \Psi(t) &= {\sum_{\gamma}}' | \lambda_{\gamma_n} > \exp \frac{-iE_{\gamma}^{n} \Delta t_n}{\hbar} {\sum_{\beta}}' < \lambda_{\gamma_n} | \lambda_{\beta_{n-1}} > \exp \frac{-iE_{\beta}^{n-1} \Delta t_{n-1}}{\hbar} \\ &\quad \cdots \exp \frac{-iE_{\mu}^{1} \Delta t_1}{\hbar} < \lambda_{\mu_1} | 0, \alpha > \end{aligned} \tag{17}$$

where $|0, \alpha >$ denotes the initial molecular state and $\sum'$ summations limited to the target spaces previously built. By making an average over the differences of phases of the laser field and the molecular system, the dissociation probability is expressed as :

$$P_{diss}(t) = 1 - \sum_{\text{bound states } \beta} \sum_{n} | < n, \beta | \Psi(t) > |^2 \tag{18}$$

An analysis of equations (17) and (18) reveals that fast calculations of dissociation probabilities versus time can be accomplished for any arbitrary pulse shape, insofar as $\mathcal{F}(t)$ is smaller than $\mathcal{F}^{max}$. This only requires that some data have been stored during the building of the target spaces, namely for each discretized value $\mathcal{F}^{(j)}$ of the field :

- the N_o eigenvalues of the states constituting the basis set of the space $S^{(j)}$: E_{γ}^{j}
- the overlap matrix of basis sets corresponding to two consecutive target spaces : $< \lambda_{\gamma_{j+1}} | \lambda_{\beta_j} >$
- the projection of the Floquet eigenvectors on the bound states in the various Floquet blocks : $< n, \beta | \lambda_{\beta_n} >$

The calculation are very fast since they only imply products of overlap matrices of small dimension ($N_o \times N_o$) . Moreover, all the dissociation probability calculations from the same initial state $|0, \alpha >$ and implying the same frequency ω_o use the same data (see above).The advantages inherent in this method are obvious by comparison with other techniques of direct integration of the time-dependent Schrödinger equation using F.F.T. methods. Usually the continuous wave laser experiments are solved using the time-independent Floquet theory and the short pulse laser field experiments using a time-dependent wave-packet formulation. Unfortunately, these different treatments make it difficult to compare the physical effects in the two situations. In this paper a new unitary formulation is proposed which works in both cases and which, from a pedagogical point of view, allows us to understand the optical non-linear effects appearing with strong laser fields, in terms of resonance states induced by the matter-field interactions. A second advantage is a significant reduction of the CPU time: For example an interesting study of the trapping in intense laser pulses has been recently proposed by Yao and Chu [23]. However, the detailed study of the influence of the shape of the field envelope on the trapping effects requires the repetition of many wave packet propagations. In our formulation the dynamics is concentrated in a reduced active space and the subsequent target spaces. This requires a large amount work to generate the basis sets which span these spaces, but the data which are stored at the end of this first step can be used to carry out fast dynamical calculations whatever the envelope shape may be. The larger the number of calculations is, the larger the CPU time saving. Cases which are particularly convenient are the pulse envelopes which exhibit a large plateau since the propagation along this plateau only uses one step (see Figs. 3 and 5).

3 Illustrative numerical example

3.1 The photodissociation of H_2^+

The multiphoton dissociation of H_2^+ in a laser field with a power range from 1 to 100 TW/cm^2 has recently been examined by means of time dependent scattering calculations [24] with results which were confirmed by experiment [25]. This application considers once again the two electronic states system $(1s\sigma_g)\Sigma_g^+$ and $(2p\sigma_u)\Sigma_u^+$ by taking the Morse type potentials and the transition dipole moment from ref [26]. The calculations are performed using a Floquet-state basis $|n, \alpha >$ composed of 10 Floquet blocks ($n = -6\ to\ +3$) centered around the initial block ($n = 0$) and 150 radial eigenfunctions distributed on the radial interval $R_{min} = 0 a.u., R_{max} = 10 a.u.$. Among the 150 functions spanning the ground electronic state (i.e. for even n values) 18 are bound states with real eigenvalues, the 132 others and the 150 functions corresponding to the dissociating state are diffusion states with complex eigenvalues. They constitute

a discretization of the two continua.The internuclear distance $R = 0$ to $10a.u.$ is relatively small. Generally one would expect that at least up to $15a.u.$ should be considered to obtain reasonable accuracy. On this interval the optical potential was erected asymptotically using the expression:

$$V_{opt} = V_o(\frac{R - R_{min}}{R_{max} - R_{min}})^{16} \tag{19}$$

This small internuclear distance generates mistakes in the calculation of the eigenvectors which span the electronic states. For example, among the 18 bound states of the ground electronic state, the last 4 near the continuum posses a spurious imaginary eigenvalue component of about $10^{-6}a.u.$ This slightly disturbs the stabilisation procedure in the calculation of the resonance states. Nevertheless, the present calculations do not imply the projection of the total wavefunction onto highly excited bound states and our tests made by increasing the optical potential amplitude reveal that these mistakes do not significantly perturb the final results.

Two series of calculations are performed. The first, with $\omega_o = 0.40a.u.$ favorizes a direct one photon transition from the ground to the dissociating surfaces. The second, made with $\omega_o = 0.214$a.u. implies a priority of two photon processes with small probabilities of dissociation. In both cases an active space of 20 states is built with a multi-magnitude procedure. With $\omega_o = 0.40$a.u., six bound states, namely $(0,1),(0,2),(0,3),(0,4),(0,5),(0,6)$ are selected among the 20 and only two, namely : $(0,1),(0,2)$ for $\omega_o = 0.214$. The other states are diffusion states of the adjacent Floquet block $n = -1$.

The results for various envelope shapes are presented in figures 2-5. In each case, four calculations are performed. Three correspond to target spaces of increasing size : a one dimensional space built on the resonance induced from the initial bound state $(n = 0, v = 1)$ by the field-matter coupling, a space built on the resonances issued from the bound states selected in the active spaces (6 states for $\omega_o = 0.40$ and 2 for $\omega_o = 0.214$ respectively) and finally the target space from the whole active space. The last calculation is quite different since it simply represents the dissociation probability deduced from the norm of the nuclear wave function :

$$P_{diss}(t) = 1 - ||\Psi(t)||^2 \tag{20}$$

3.2 Analysis of the results

Tests made by varying the size of the active space reveal that the results presented are correctly converged. The first important result of our study is thus the weakness of the size of the evolutive target space needed to give correct results. In the present case the dimension $N_o = 20$ is in actual fact negligible compared with the dimension $N_{tot} = 1500$ of the full space. As direct consequence, there is a large C.P.U. time saving economy. For instance each

experiment requires between 1 and 2 minutes on an IBM-RISC/6000/550 workstation, the major part of this time being devoted to the reading of the stored data. The second important result shown by the figures, is the weak role of the diffusion states in the dissociation probability result. In each case investigated the results obtained with a reduced active space spanned by the selected bound states (6 and 2 states respectively) coincide perfectly with the full calculation, making it difficult to distinguish them. This lack of importance of other states can be understood in the following way. When the electric field varies smoothly, the evolution is adiabatic and the wave function is confined in a small vectorial space spanned by one or more resonance states. If the electric field suddenly exhibits a rapid variation ($\mathcal{F}^{(j)} \rightarrow \mathcal{F}^{(j+1)}$) the resonances states of space $S^{(j)}$ have non negligible projections on some diffusion states of space $S^{(j+1)}$. Such projections are omitted when the calculation is confined in the reduced target spaces, but the consequences are not so important as could be expected. The resonant states have, as the diffusion states, complex eigenvalues. For a resonant state the imaginary part of the eigenvalue is relevant to the intrinsic complex nature of this state. However this is only a mathematical artifact produced by the optical potential in the case of a diffusion state. Then the lifetime of the diffusion states can be arbitrarily reduced by increasing the optical potential. Thus, by neglecting the projection on the diffusion states, expressions are generated that are identical to those that would be obtained by approximating the weak lifetime of these states by zero (the part of the wave function projected onto the diffusion states contributes instantaneously to the dissociation probability).

The last important feature of our treatment is its ability to reveal the basic mechanisms of the dissociation process, contrary to other "black box" treatments. The coarse grained calculations corresponding to one dimensional target spaces induce errors of some per cent (see figs 2,4,5). Nevertheless, the dissociation is essentially a purely adiabatic process derived from a single state. In this framework it is possible to understand the two major behaviors exhibited by the dissociation probability versus time: this function appears as a purely increasing function in figures 2 and 3. However the shape of this function is similar to that of the electric field envelope with an increasing and a decreasing part in figures 4 and 5 (a similar behavior was observed in ref [27]). By introducing this coarse grained approximation in equations (17) and (18) :

$$|\Psi(t)> \sim \exp\{\frac{1}{i\hbar}\int_o^t E_\alpha(t')dt'\}|\lambda_\alpha(t)> \qquad (21)$$

so that

$$P_{diss}(t) = 1 - \sum_{\text{bound states}\beta} \sum_n \exp^{-\int_o^t \Gamma_\alpha(t')/\hbar dt'} |<n,\beta|\lambda_\alpha(t)>|^2 \qquad (22)$$

Two regimes can thus be distinguish in equation (21). If

$$\int_o^T \Gamma_\alpha(t)dt \ll 1 \tag{23}$$

where T is the lifetime of the laser pulse, then, the behavior is imposed by the term $< n,\beta|\lambda_\alpha(t) >$ which initially is equal to 1

$$\sum_\beta \sum_n | < n,\beta|\lambda_\alpha(t=0 > |^2 = | < 0,\alpha|\lambda_\alpha(t=0) > |^2 = 1 \tag{24}$$

and is after that a decreasing function of the matter-field interaction, leading to the behavior exhibited in figs 4 and 5. As expected the dissociation probability deduced from the norm is different and only asymptotically gives the same value. If, on the contrary, the resonance width satisfies :

$$\int_o^T \Gamma_\alpha(t)dt \gg 1 \tag{25}$$

the behavior is imposed by the term $\exp(-\int_o^t \Gamma_\alpha/\hbar dt)$ leading to figures 2 and 3.

In summary this simple application shows the ability of this new Wave Operator-Floquet formalism to apprehend the dissociation induced by short laser pulses. Among the more interesting points revealed by this study are the precise results obtained by working in reduced spaces limited to some resonant states. It would appear that this formulation due to its large time saving economy and its clear pedagogical picture could be a good tool for studies requiring repeated calculations as for instance the study of the influence of the envelope shape in photodissociation. The results presented here are the dissociation probabilities. However, our formulation accedes to the total wavefunction (see eq. 17) and through this quantity to a large variety of results. By storing the outgoing wave function at each time step and at a fixed asymptotic position, using for example a time dependent Fast Fourier Transform, the kinetic spectrum of the fragments can be obtained [28]. This calculation is being carried out. The treatment can also be easily modified to calculate the dissociation rate versus the laser frequency because the iterative nature of the calculations permits the introduction of adjustable parameters into the Hamiltonian. In the present case the parameter associated with the pulse envelope is the electric field amplitude but other parameters (for example the laser frequency) can be used.

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Caption to Figures

Fig 1:
Representation of the envelope of the electric field versus time: $\mathcal{F}(t)$ and discretization of this function by steps of constant magnitudes $\Delta\mathcal{F}$. The parameters: $\mathcal{F}^{max}$ and $\Delta\mathcal{F}$ appear in the text in eqs. 1 and 2.

Fig 2:
Probability for dissociation of H_2^+ from the ground vibrational state as a function of time. The frequency of the laser is $\omega_o = 0.40 a.u.$ and the intensity at the top of the electric field envelope is $I = 2.5\ 10^{13} W/cm^2$. The full curve at the bottom represents the envelope of the field. The dashed, dotted and full lines refer to target spaces of increasing size built from three different active spaces, respectively a one dimensional space constituted by the initial bound state, a space of dimension $N_o = 6$ built on the 6 selected bound states and the full initial space of dimension $N_o = 20$ selected by the wave operator procedure. The dashed-dotted line represents the dissociation probability deduced from the norm of the wave function (eq. 20). These results often coincide, making it difficult to distinguish them.

Fig 3:
Same as figure 2 but for a longer laser pulse. The intensity at the top of the electric field envelope is $I = 10^{12} W/cm^2$.

Fig 4:
Same as figure 2 but with a laser frequency $\omega_o = 0.214 a.u.$. The target spaces built on the selected bound states have a dimension equal to 2.

Fig 5:
Same as figure 4 but for a longer laser pulse. The intensity at the top of the electric field envelope is $I = 10^{12} W/cm^2$.

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