A wave operator description of molecular photodissociation processes using the Floquet formalism

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Abstract

During the last few years the Floquet matrix approach to the theory of intense-field multiphoton dissociation processes has undergone

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a revival of interest which is due to the emergence of new powerful algorithms within the complex quasivibrational energy formalism. The method presented here shows that the Bloch wave operator theory is, in the framework of this theory, an efficient tool to select the active space which principally participates in the dissociation process. An illustrative numerical example reveals that the one dimensional active space model, mainly used to reproduce c.w. laser experimental results fails when the laser is tuned to bound state - bound state transitions.

1 Introduction

Multiphoton dissociation of molecules has been intensively studied by theoreticians and experimentalists [1, 2, 3].Wave packet treatments predominate in the theory of processes involving intense ultrashort laser pulses, for which they are well-adapted. A good specimen process to illustrate this point is the dissociation of H_2^+. In the last few years many works analysing this system have tested various representations, time propagators and asymptotic absorbing methods [4, 5, 6] and have revealed most of the effects which characterize the photodissociation phenomenon in strong laser fields : multiphoton above-threshold dissociation [7], the bond softening effect [8], the stimulated Bremsstrahlung effect [9] and the vibrational trapping mechanism [10]. In the case of a c.w. laser the situation is more intricate. For field intensities above $10^{11} W/cm^2$ the non-linear effects predominate and perturbative solutions cannot be used. By starting from a purely quantum description with $H = H^{mol} + H^{rad} + V$, the time evolution may be obtained by linking the evolution operator to the resolvent operator [11].

$$\exp(-iHt/\hbar) = \frac{1}{2i\pi} \int dE \exp(-iET/\hbar) G^+(E) \tag{1}$$

with

$$G^+(E) = \lim_{\epsilon \to 0^+} (E + i\epsilon - H)^{-1}$$

This equation gives the usual result that the time dependence is dominated by poles of $(z-H)^{-1}$ near the real axis but on higher Riemann sheets. It can be extended by using the Möwer partitioning [12] and the artificial channel model [8],thus transforming the half collision problem into a true collisional problem. Nevertheless this approach requires uncontrolled approximations, such as for instance the neglect of the energy dependence of the transition operator $T(E)$, and it uses a Close Coupling approximation which suffers from severe difficulties when the number of field-matter channels becomes significant. A second general method takes advantage of the periodicity of the Hamiltonian in order to transform this time-dependent approach into an equivalent time-independent infinite dimensional Floquet Hamiltonian eigenvalue problem [13]. This Floquet theory has been generalized to the complex quasivibrational energy (Q.V.E.) formalism [14] by including the complete set of continuum states as well as the bound vibronic states in photodissociation studies. In this case the use of a complex rotation or the addition of a complex optical potential make the $\hat{H}_F$ Floquet matrix non-hermitian and the quasi energies ϵ become complex. The construction of $\hat{H}_F$ can be carried out in practice by using a complex-scaling Fourier-grid Hamiltonian [15]. However in the case of strong fields the large size of the

Floquet matrix, which has a dimension equal to the product of the number of terms in the Fourier series expansion of the quasienergy state and the number of molecular basis functions, presents severe difficulties. As noted by Ben-Tal et al in ref [16] the truncation of $\hat{H}_F$ produces an "edge effect" which makes it hard to isolate the quasienergies which are associated with a single Brillouin zone.

This handicap has been partially overcome in ref. [16] where it is shown that the resonance positions and widths of metastable quasienergy states can be obtained from solutions of the time-dependent Schrödinger equation over the first optical cycle. More recently ref. [17] has reduced the computational effort required by this Time-Dependent-Complex-Coordinate-Floquet-Method (T.D.C.C.F.M.) by proposing the Complex Scaled Adiabatic Switch Method (C.S.A.S.M.) which in some simple cases involves only the propagation of a single vector.

The purpose of the present article is to present a new Floquet matrix approach to photodissociation experiments. Our treatment makes a partitioning of the dynamical space within which the evolution operator acts and also simplifies the relaxation scheme which is deduced from the Schrödinger equation. The choice of the relevant subspaces and construction of the effective Hamiltonians which govern the resultant projected dynamics are both carried out using Bloch wave operator techniques. Section 2 summarizes briefly the Floquet matrix description of molecular photodissociation processes and presents the wave operator formalism for the selection of the active space and the construction of the projected dynamics. A recent procedure for the integration of the non linear Bloch equation, called the single cycle method [18], is presented in the framwork of this application. In section 3 a model Hamiltonian to describe the photodissociation of the HF molecule is introduced. A detailed analysis then determines the minimal size of the active space necessary to achieve a satisfactory convergence of the numerical results. Section 4 contains some conclusions.

2 Theory

2.1 The quasi energy eigenvalue formulation

Within the framework of a semi-classical treatment of both the electromagnetic field and the matter-field interaction, using the dipole approximation and the length (electric field) gauge interaction term $\mu.E$, the expression for the Hamiltonian of a molecule hit by a laser pulse is :

$$\mathcal{H} = \mathcal{H}_o(q, r) - \mu(q, r)E(t) \tag{2}$$

q denotes the various bound internal vibration-rotation degrees of freedom and r is the inter-fragment axis. The electric field amplitude $E(t)$ is given as the product of a constant amplitude E_o and a real cosine form with a peak frequency ω :

$$E(t) = E_o \cos(\omega t) \tag{3}$$

The field-matter interaction is assumed to be turned on at t=0. By taking advantage of the periodicity of the Hamiltonian in eq.(3), the time-dependent problem with driving term $\mathcal{H}(t)$ (eq.2) can be transformed into an equivalent time-independent infinite dimensional Floquet Hamiltonian eigenvalue problem [13]. In terms of the Floquet-state basis $|n,\alpha>$, where $|\alpha>$ denotes the molecular states and $|n>$ are the Fourier photon indices ranging from $-\infty$ to $+\infty$.

$$\sum_{\beta}\sum_{m} < n,\alpha|\hat{H}_F|m,\beta >< m,\beta|\lambda_\eta >= \epsilon_\eta < n,\alpha|\lambda_\eta > \tag{4}$$

Examples of Floquet matrices corresponding to linearly polarized and rotating radiation fields, to purely monochromatic fields and to polychromatic fields can be found in ref [3]. We shall investigate in the next section the photodissociation of a diatom (modeled by means of a Morse potential) which has a fixed direction in space and which is submitted to a coherent linearly polarized monochromatic field of angular frequency ω. This one dimensional system can be represented using a finite radial range $[r_{min} \leq r \leq r_{max}]$ and with a discrete variable representation, after the addition of an asymptotic optical potential

$$\mathcal{H}(r,t) \rightarrow \mathcal{H}_{tot}(r,t) = \mathcal{H}(r,t) - iV_{opt}(r) \tag{5}$$

On the L^2 basis set the operators $\mathcal{H}$ and $\mathcal{H}^+$, the latter satisfying the adjoint boundary conditions, are identical and it is thus not possible to eliminate the surface term in a generalized version of Green's identity. This difficulty is overcome by using the optical potential, since $\mathcal{H}_{tot}$ becomes artificially complex; moreover this transformation is consistent with the asymptotic behaviour defining the resonance and does not change the resonance eigenvalues.

The relevant complex Floquet matrix is composed of various blocks $(\hat{H}_F)_{n,k}$. The block indices denote the Fourier photon indices; in the present case we have:

$$\begin{aligned}(\hat{H}_F)_{n,n} &= -\frac{\hbar^2}{2m}\nabla^2 + \frac{1}{T}\int_0^T (V_{Morse}(r) - iV_{opt}(r))dt + n\hbar\omega \\ (\hat{H}_F)_{n,k\neq n} &= \frac{1}{T}\int_0^T -\mu(r)E(t)\exp[i\omega(k-n)t]dt \end{aligned} \tag{6}$$

where m is the reduced mass of the fragments and $T = 2\pi/\omega$. The block matrices can be expressed using, for instance, a molecular basis set composed of properly normalized particle-in-a-box eigenfunctions.

$$\Psi_l(r) = \sqrt{\frac{2}{r_{max} - r_{min}}}\sin(l\pi\frac{r - r_{min}}{r_{max} - r_{min}})\ ,\ l = 1\ to\ N \tag{7}$$

The photodissociation dynamics can be easily expressed in this stationary formulation. For instance the transition probability from an initial molecular state $|\alpha >$ and a coherent field state to a final quantum state $|\beta >$,summed over all final field states and then averaged over the initial phases of the field seen by the molecular system, is [3] :

$$P_{\alpha\to\beta}(\Delta t) = \sum_n | < n,\beta|\exp(-i\hat{H}_F\Delta t/\hbar)|0,\alpha > |^2 \tag{8}$$

or equivalently, by using the complete basis set of quasi-energy eigenvectors. (cf eq(4)).

$$P_{\alpha\to\beta}(\Delta t) = \sum_n |\sum_\eta < n,\beta|\lambda_\eta >< \lambda_\eta|0,\alpha > \exp^{-i\epsilon_\eta\Delta t/\hbar}|^2 \tag{9}$$

2.2 Active space and projected dynamics equations

In most cases, the large dimension of $\hat{H}_F$ prevents the use of standard algorithms for diagonalization. Fortunately, not all the quasi energy states

$|\lambda_\eta >$ have the same weight in eq(9). A first simplification arises from the general properties related to quasi energy eigenvector periodicities

$$\begin{aligned} \epsilon_{n,\alpha} &= \epsilon_{0,\alpha} + n\hbar\omega \\ < n+p, \alpha|\lambda_{m+p,\beta} > &= < n, \alpha|\lambda_{m,\beta} > \end{aligned} \tag{10}$$

Secondly, the long-time relaxation behaviour is driven by the quasienergy resonance states whose eigenvalues are near the real axis on higher Riemann sheets. If experiments only determine long-time averaged values or cross sections, the summation in eq(9) can be limited to these resonances. In ref [17] for instance, the high harmonic generation detected in rare gas atom systems in the presence of high-intensity laser fields is studied by considering only the resonance state with the largest life-time. However, it has been shown in ref [19] that such a drastic simplification has direct consequences for the normalization of these resonance states in order to preserve the general norm invariance equation. This approximation also fails to reproduce the behaviour at small times when the electric field changes rapidly or when the matter-field coupling is tuned to bound-bound transitions and mixes the corresponding resonant states.

These features become comprehensible in the framework of the wave operator theory. Let S_o be an active space which is expected to reproduce correctly the dynamic features of the relaxation process (the selection of this space, which includes the initial state $|0, \alpha >$ will be examined in a self consistent manner at the end of this section).

Thus the relaxation issuing from S_o is governed by the operator (cf eq(8) :

$$U_P(t) = \exp(-iH_F t/\hbar)P_o \tag{11}$$

The usual notations P_o, Q_o and P, Q for the projection operators of S_o, S_o^+ and the assiociated target spaces S and S^+ are used. By introducing the wave operators associated with the two complementary spaces S_o and S_o^+ and the corresponding reduced wave operators [20, 21], namely :

$$\begin{aligned} \Omega_P &= P(P_oPP_o)^{-1} = P_o + X_P \\ \Omega_Q &= Q(Q_oQQ_o)^{-1} = Q_o + X_Q \end{aligned} \tag{12}$$

and by constructing the non-unitary transformation :

$$T = 1 + X_P + X_Q \tag{13}$$

which decouples H_F within the two subspaces S_o and S_o^+, the evolution operator $U_P(t)$ can be written.

$$\begin{aligned} U_P(t) &= \Omega_P \exp[-i(P_oH_{eff}P_o)t/\hbar]P_oPP_o \\ &+ \Omega_Q \exp[-i(Q_oH_{eff}Q_o)t/\hbar]Q_oQP_o \end{aligned} \tag{14}$$

with

$$H_{eff} = T^{-1}H_FT \tag{15}$$

The simplification of the active space is achieved by neglecting the relaxation path through the space S_o^+, i.e. by neglecting the second contribution in the r.h.s. of eq.(14) [22]. Eqt (14) can then be rewritten more simply by expanding the term P_oPP_o as:

$$P_oPP_o = (P_o\Lambda P_o) \times (P_o\Lambda P_o)^\dagger \tag{16}$$

where Λ is the matrix composed of the eigenvectors of H_F, and by taking into account some basic relationships between the eigenvectors of H_F and the eigenvectors of H_{eff}. According to the choice made by the Bloch formulation, the eigenvectors of H_{eff} are the projections into the active space of exact eigensolutions of H_F. (i.e. $P_o \Lambda P_o$ is the matrix which diagonalizes H_{eff}), and the wave operator Ω_P transforms these eigenvectors projected into S_o back to the exact eigenvectors.

$$\Lambda P_o = \Omega_P (P_o \Lambda P_o) \tag{17}$$

This leads to:

$$U_P(t) = \Lambda P_o \exp[-i(P_o E P_o)t/\hbar](P_o \Lambda P_o)^\dagger \tag{18}$$

where $P_o E P_o$ describes the eigenvalue spectrum of space S_o

Then using eq(18) and assuming that the initial state is $|0, \alpha>$ one can approximate eq(8) by :

$$P_{\alpha \to \beta}(\Delta t) = \sum_n | < n, \beta | \Lambda P_o \exp[-i(P_o E P_o)\Delta t/\hbar](P_o \Lambda P_o)^\dagger | 0, \alpha > |^2 \tag{19}$$

or, by introducing the eigenvectors of $\hat{H}_F$.

$$P_{\alpha \to \beta}(\Delta t) = \sum_n | \sum_{\eta \in S_o} < n, \beta | \lambda_\eta >< \lambda_\eta | 0, \alpha > \exp^{-i\epsilon_\eta \Delta t/\hbar} |^2 \tag{20}$$

This equation is identical to equation (9) except that the summation $\sum_\eta$ is limited to states of S_o. This proves that the wave operator theory is, within the framework of time-dependent dissociation processes, perfectly compatible with projection methods in active spaces. The Bloch wave operator theory is, in a certain sense, a practical tool to achieve the projection of the dynamics into the active space, and is particularly efficient when strong couplings are present inside S.

2.3 Selection of the active space

The basis formalism of the effective Hamiltonian was developped by Bloch [20] and Des Cloizeaux [23] in the sixties. This theory has been widely used and developed in quantum chemistry, where theoretical or ab initio methods suffered from severe computational drawbacks [24]. Choosing the model space for the eigenvalues problem is generally not difficult, but the situation is quite different in the case of molecular dynamics. The model space is then not the space into which the reduced quantum information is projected but rather an active space within which the dynamics is confined. This makes its definition more intricate.

Various approaches for a proper definition of S_o have been proposed in the literature. They include the Rotating Frame Approximation of Whaley and Light [25], the multitier approach of Sibert, Reinhardt and Hynes [26], the adiabatically reduced coupled equations of Voth and Marcus [27], the low frequency expansion of Nadler and Marcus [28] and various artificial intelligence techniques [29, 30, 31, 32]. However the wave operator theory, used in the preceeding section to build the reduced dynamics, can also be invoked in a self consistent manner to select the active space S_o. The procedure is as follows. Let $|i>$ designate the initial state, previously denoted $|n = 0, \alpha>$, of the matter-field space and let S_o be the trial one dimensional active space spanned by this vector. The associated wave operator Ω_P is the solution of the non-linear equation [21]

$$H_F \Omega_P = \Omega_P H_F \Omega_P \tag{21}$$

This equation can be transformed by considering the wave operator as a part of a non-unitary transformation [34, 35] :

$$Q_o(1 - X_P) H_F (1 + X_P) P_o = 0 \tag{22}$$

Several linear and quadratic iterative methods have been proposed to solve eq. (22) [36, 37, 38, 39, 21]. In ref [40] the recursive distorted wave approximation (R.D.W.A.) leads to the equations

$$\begin{aligned} X &= \lim_{N \to \infty} X^N \\ X^N &= X^{N-1} + \sum_{\beta \in S_o^+} \sum_{i \in S_o} |\beta >< i| \left(\frac{< \beta | H^N | i >}{< i | H^N | i > - < \beta | H^N | \beta >} \right) \end{aligned} \tag{23}$$

with

$$\begin{aligned} X^{N=0} &= 0 \\ H^{N>0} &= (1 - X^{N-1}) H (1 + X^{N-1}) \end{aligned} \tag{24}$$

In the present application the summation $\sum_i$ is limited to one element. The R.D.W.A. (eqs 23-24) is iterated up to a high order N_{it} and the vectors of the whole space are sorted in the order of decreasing values of the matrix component moduli of the wave operator.

$$| < \alpha | X | i > | \tag{25}$$

the initial state ($\alpha \equiv i$) being arbitrarily placed in first position. To overcome possible rapidly diverging behaviour, all the partial contributions $X^N_{\beta,i}$

possessing a modulus larger than an upper limit (0.5 for instance) are changed into new values with modulus weaker than this limit, by means of a proper reducing factor. With a sufficiently large iteration order N_{it}, all the states of the whole space are ordered (more precisely, a given state $|\alpha>$ will participate if, at least one path $|i> \rightarrow |\alpha>$ constituted by a sequence of n transitions with $n \leq N_{it}$ exists). The active space, the dimension N_o of which is imposed, can then be built by taking the N_o first vectors. This method is consistent with the dynamical approximations adopted in the preceding section. The states which are not selected in S_o are characterized by small X_P and consequently by small X_Q components, since the matrix H_F is symmetric. This justifies the neglect of the second relaxation path in eq(14) which appears simultaneously proportional to Ω_Q and to Q_oQP_o.

On the other hand this method is simpler than the artificial intelligence methods, since search algorithms and evaluation functions are not required. It has been adopted and successfully applied by Wyatt et al in ref [41] to the overtone relaxation of benzene.

2.4 The single cycle algorithm

The photodissociation relaxation study is completed in the framework of the wave operator theory by evaluating the expression in the truncated eq(14). In this expression the operator Ω_P plays the central role. According to eq(15), $P_oH_{eff}P_o$ is equal to $P_oH\Omega_P$. Moreover the product P_oPP_o is expressed according eq. (16) in terms of $P_o\Lambda P_o$, which is nothing but the matrix composed by the eigenvectors of H_{eff}.

The central problem is thus the calculation of the operator Ω_P. The R.D.W.A., eqs (23-24), is a possible recursive integration scheme. This integration nevertheless presents difficulties when there are strong couplings, principally because of intruder states associated with avoided crossings. The finite L^2 basis set study of photodissociation experiments is, from this point of view, a severe test, but the R.D.W.A. series takes advantage of some efficient specific features, namely :

- It works with general non-hermitian matrices, so the use of an interaction picture produced by a partial prediagonalization can be used in order to reduce the interspace couplings. A wave operator study of vibrational trapping mechanism using a semi-adiabatic basis set is presently in progress [42].
- Any trial operator $X^{N=0}$ can be introduced in the series. Should the trial solution be close to the exact reduced wave operator, the process quickly converges. Coarse grained trial solutions could for instance be deduced from the T.D.C.C.F.M. [16].

The divergence difficulties can also be reduced by introducing an intermediate space which isolates the model space from its complement. This procedure was first introduced by Malrieu et al [33, 43] in the intermediate Hamiltonian theory. A similar procedure breaking the one-to-one correspondence between the model and target spaces and using the concept of a biorthonormal basis, has been recently proposed by Evangelisti et al [44] .

In the present study the calculation is achieved in the framework of the

Bloch wave operator theory by adapting a treatment called the single-cycle method [18] to the (R.D.W.A.) method. This procedure is made in practice in four steps as follows.

- i) The $\hat{H}_F$ matrix is expressed in a finite representation for which the non diagonal terms are expected to be weak. In practice, this is achieved by first expressing the Floquet Hamiltonian on a D.V.R., using for instance the particle-in-a box eigenfunctions (cf. eqt.(7)), and by then diagonalizing the Floquet blocks on the diagonal: $(\hat{H}_F)_{n,n}$ (c.f. eqt.(6)), leading to a basis constituted by eigenvectors of the molecular + field Hamiltonian without matter-field interaction. The advantage of this choice lies in the fact that the initial wave function has in general a simple expansion at $t = 0$, before the field-matter interaction is turned on. Moreover, all the Floquet blocks on the diagonal are diagonalized by the same transformation, which reduce the computational effort.

- ii) As the N_t states of the whole vector space have been ordered around the initial state using the wave operator formulation (see the last section), a main model space S_m of dimension N_m(projection operator P_m) is easily built by taking the N_m first vectors and an intermediate buffer space S_i of dimension N_i(projection operator P_i) by selecting the next N_i states. In the following the notations are:

$$\begin{aligned} S_o &= S_m \oplus S_i \ , \ S_m^+ = S_i \oplus S_o^+ \\ with\ P_o &= P_m + P_i \end{aligned}$$

$$and\ Q_o \;=\; 1 - P_o$$

- iii) After partitioning the Hilbert space into $S_m \oplus S_i \oplus S_o^+$ and assuming that S_o is small enough ($N_o < 10^3$), the block $P_o H_F P_o$ is diagonalized using a standard algorithm

$$T^{-1}(P_o H_F P_o)T = D \tag{26}$$

  and a new space S_m is defined by selecting the N_m vectors which have the greatest projections into the original space S_m.

- iv) Then a trial wave operator associated with S_m is defined as:

$$\Omega_m = P_m + P_i X P_m + Q_o X P_m \tag{27}$$

  by taking zero Q_o components

$$Q_o X P_m = 0 \tag{28}$$

  and for the P_i components the solutions of the linear system :

$$(P_m T^t P_m) \times (P_m X^t P_i) = P_m T^t P_i \tag{29}$$

  where the index t denotes the transpose of the matrix. This trial operator is obviously the exact one when the two spaces S_o and S_o^+ are not coupled. It is introduced into the single cycle iterative procedure to derive the exact operator.

The single cycle method has been proposed and analysed in conjunction with the Gauss-Seidel approach in ref. [18]. It has been recently adapted to large degenerate active spaces in ref [45]. The starting point is again eq(22) which guarantees that the nonsingular transformation using $1+X$ (the notation X is used instead of X_P), with $(1+X)^{-1} = 1 - X$, preserves the eigenvalues of matrix $\hat{H}_F$. The R.D.W.A. (eqs (23-24)) which is an iterative solution of this equation is based on a series of nonunitary transformations using $(1+\Delta X^N)$ with $\Delta X^N = X^N - X^{N-1}$ which modify the matrix $\hat{H}_F$ until the couplings$(Q_o + P_i)\hat{H}_F P_m$ disappear.

An interesting feature of the R.D.W.A. is the fact that, at every iteration, only partial update of the large matrix H^N is required. Eqt. (23) reveals that only the diagonal matrix elements H^N_{diag} and the block $(Q_o + P_i)H^N P_m$ are involved and a precise analysis of eqt. (24) shows that the C.P.U. time taken by each iteration order is almost fully devoted to forming the matrix-vector product $H_F \times X^{N-1}$. As most of the matrix elements of H_F are equal to zero, H_F can be generated rapidly " on the fly" from other small arrays. The single cycle method sets out to increase the radius of convergence of the R.D.W.A. iterative process without losing this essential feature. For this, each successive transformation $(1+\Delta X^N)$ is expanded as a series of elementary transformations, namely:

$$1 + \Delta X^N = \prod_{i \in S_m} \prod_{\alpha \in S_m^+} [1 + |\alpha><i| \, \Delta X^N_{\alpha,i}] \tag{30}$$

where i is the column index of the wave operator in the main model space S_m and α the line index in the outer space S_m^+. Each partial transformation is denoted by three indices (N, α, i). In the following a generalized index $\mathcal{L}(\equiv (N, \alpha, i))$, incremented after each partial transformation, is introduced. The calculations have been made by incrementing N first, then α and i

but the choice of α in second and i in third position is arbitrary. The improvement of the single cycle method compared to the R.D.W.A. comes from the fact that after each partial transformation the $\hat{H}_F$ elements are modified and used for the next transformation. By using the index $\mathcal{L}$, the basic equations (23-24) must be replaced by:

$$X = \lim_{\mathcal{L}\to\infty} X^{\mathcal{L}} \,; \mathcal{L} \equiv (N, \alpha, i)$$

with

$$\begin{aligned} X^{\mathcal{L}} &= X^{\mathcal{L}-1} + \Delta X^{\mathcal{L}} \\ \Delta X^{\mathcal{L}} &= |\alpha >< i| \frac{< \alpha|H^{\mathcal{L}}|i >}{< i|H^{\mathcal{L}}|i > - < \alpha|H^{\mathcal{L}}|\alpha >} \end{aligned} \tag{31}$$

and

$$H^{\mathcal{L}} = (1 - \Delta X^{\mathcal{L}-1}) H^{\mathcal{L}-1} (1 + \Delta X^{\mathcal{L}-1}) \tag{32}$$

The stucture of this iteration is more complicated compared to (23-24) because it sets up a step by step relationship $H^{\mathcal{L}-1} \to H^{\mathcal{L}}$, contrary to eqt. 24 which sets up a direct relationship $H \to H^{\mathcal{L}}$. Nevertheless the C.P.U. time and the memory size required remain tractable because only a small part of the modified matrix $H^{\mathcal{L}-1}$ must be explicitly calculated at each step $\mathcal{L}$. These modified elements are as follows:

- modified diagonal elements :

$$\begin{aligned} (H^{\mathcal{L}})_{\alpha\alpha} &= (H^{\mathcal{L}-1})_{\alpha\alpha} - \Delta X^{\mathcal{L}-1} H_{i\alpha} \\ (H^{\mathcal{L}})_{ii} &= (H^{\mathcal{L}-1})_{ii} + H_{i\alpha} \Delta X^{\mathcal{L}-1} \end{aligned} \tag{33}$$

- modified $P_m H P_m$ elements:

$$(H^{\mathcal{L}})_{ji,j\neq i} = (H^{\mathcal{L}-1})_{ji} + H_{j\alpha}\Delta X^{\mathcal{L}-1} \tag{34}$$

- modified $(Q_o + P_i)HP_m$ elements :

$$\begin{aligned}
(H^{\mathcal{L}})_{\alpha j,j\neq i} &= (H^{\mathcal{L}-1})_{\alpha j} - \Delta X^{\mathcal{L}-1}(H^{\mathcal{L}-1})_{ij} \\
(H^{\mathcal{L}})_{\beta i,\beta\neq\alpha} &= (H^{\mathcal{L}-1})_{\beta i} + (H_{\beta\alpha} - \sum_l X^{\mathcal{L}-1}_{\beta l} H_{l\alpha})\Delta X^{\mathcal{L}-1} \\
(H^{\mathcal{L}})_{\alpha i} &= (H^{\mathcal{L}-1})_{\alpha i} - \Delta X^{\mathcal{L}-1}(H^{\mathcal{L}})_{ii} + (H^{\mathcal{L}})_{\alpha\alpha}\Delta X^{\mathcal{L}-1}
\end{aligned} \tag{35}$$

The subscripts F in H_F have been omitted for simplicity. The lower indices are row and column indices, latin letters designating states of the main model space S_m and greek letters designating states of the complementary space S_m^+. The various terms which constitute eqts. (33-35) have been defined previously: the generic terms $X^{\mathcal{L}-1}$, $\Delta X^{\mathcal{L}-1}$ and $H^{\mathcal{L}-1}$ in eqns (31) and (32). H without any index designates the initial H matrix.

Two points must be noted concerning this iteration. First, the successive elementary transformations change the large block matrix $(Q_o + P_i)H(Q_o + P_i)$. Fortunately the recurrence does not require us to explicitly calculate these transformations, which are only present through the term $\sum_l X^{\mathcal{L}-1}_{\beta l}$ in eqt. (35). Second, eqt. (35) makes use of the elements $(H^{\mathcal{L}})_{ii}$ and $(H^{\mathcal{L}})_{\alpha\alpha}$ and this requires a specific order of use of the recurrence; calculations with eqt. (33) must be performed before using eqt. (35).

2.5 From the wave operator theory to the photodissociation probability

It has been demonstrated in the two last sections that the Bloch wave operator theory is an efficient tool to select the active space in which the relaxation dynamics take place and also to elaborate the projected equations into this space. Starting from the eigenvectors of the active space one can built up an approximate expression for the wave function

$$|\Psi_{app}(t)>= \sum_{\lambda_{n,j}\in S_m} <\lambda_{n,j}|0,\alpha> \ \exp(-iE_{\lambda_{n,j}}t/\hbar)\,|\lambda_{n,j}> \tag{36}$$

by assuming that the field-matter interaction is turned on at t=0. The dissociation probability can then be approximated by:

$$P_{diss}(t) = 1 - \sum_{bound\ states\ \beta} \sum_{n} | <n,\beta|\Psi_{app}(t)> |^2 \tag{37}$$

3 Application to the dissociation of the HF molecule

This section analyses the application of the Bloch-Floquet formulation to the photodissociation of a diatomic molecule under a c.w. laser field. The goal of this study is to answer some basic questions.

- What is the efficiency of this procedure as compared to different artificial intelligence methods [29, 30, 31]? Within the framework of this theory, can an elaborated analysis of photodissociation experiments be achieved?, i.e. can the kinetic energy spectrum of the fragments be calculated?

- Can photodissociation processes of small molecules be described in small vector subspaces? If this is the case, what is the composition of these subspaces? Need only the resonances induced by the electromagnetic field be taken into account, or the scattering states also be considered when direct excitations of the continua are possible [46]? Can the photodissociation be approximately reproduced by taking only the resonance deduced adiabatically from the initial state as in the C.S.A.S.M. [17]?

The system investigated is a model, but this is not really a handicap in the present case. Our goal was not to derive results which can be compared with experiment but to prove that the wave operator theory is an efficient tool for describing photodissociation. As it is well adapted to large vector spaces, it should not suffer from the increase of the basis size which would arise in treating more realistic systems. Thus the present example, which involves a strong laser field, is a significant test.

3.1 Presentation of the system

The hamiltonian of this one dimensional system is (cf. eq(2)) :

$$\mathcal{H} = \mathcal{H}_o(r) - \mu(r) E_o \cos(\omega t) \tag{38}$$

with

$$\begin{aligned} \mathcal{H}_o(r) &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + D(\exp[-\alpha(r - r_e)] - 1)^2 - D \\ \mu(r) &= A r \exp(-\xi r^4) \end{aligned} \tag{39}$$

The parameters selected in eq(39) are those of a modified Stine and Noid hydrogen fluoride Morse function [47] which supports only six bound states and which has been used previously by Leforestier and Wyatt [48]. The field intensity is I=1TW/cm^2. The calculations are performed for a box [1.a.u. , 17. a.u.] using a D.V.R. of 150 functions and adding the optical potential $V_{opt} = -iD \times (\frac{r-r_{min}}{r_{max}-r_{min}})^{16}$. Ten Floquet blocks ($n = -6$ to $n = 3$) are used to build up the complete basis set. The diagonalization of $\mathcal{H} - iV_{opt}$ in the block n=0, gives a complete spectrum consisting of 6 real eigenvalues (in a.u.) :

$$E_o = -0.05256, \quad E_1 = -0.03654, \quad E_2 = -0.02342$$

$$E_3 = -0.01321, \quad E_4 = -0.005899, \quad E_5 = -0.001497$$

and 144 complex eigenvalues discretizing the continuum.

3.2 Selection of an active space

The Bloch selection procedure is illustrated by Figs 1 and 2. In both cases, the initial state $|0, \alpha >$ is the ground vibrational state ($v = 0$) of the initial Floquet block ($n = 0$ photon), the laser intensity is $1TW/cm^2$ and the active space dimension is arbitrary taken equal to 12. In fig(1) the laser frequency ($\omega = 0.060$) is large enough to produce a direct transition from the ground state to the continuum. In Fig.(2) the laser frequency is tuned to the frequency of the bound-bound transition ($v = 0 \rightarrow v = 2$). On these Figures the potential surfaces belonging to various Floquet blocks are represented in the scale of the total energy (field + matter). The negative index values

($n = -1$ to $n = -6$) correspond to absorbed photons and the positive index values ($n = 1$ to $n = 3$) correspond to emitted photons. The two figures reveal that only the adjacent blocks($n = -2$ to $n = 1$) are involved in this reduced subspace. Moreover the Bloch selection procedure selects in priority i) the states of the continuum which are in near resonance with the initial state and ii) various bound states. This last choice is understandable, because the photodissociation process principally takes place in the potential well where the bound states mainly suffice for basis completeness. A more detailed analysis of the two figures allows us to roughly understand the mechanism. In the case of Fig. 1 the dissociation proceeds from a direct one photon process, the final states being the pseudo continuum states in near resonance with the initial state. In the case of Fig. 2 this is a sequential two photon process which involves the intermediate state $|n = -1, v = 2>$ which is in resonance with the initial state.

3.3 A detailed understanding of the dissociation process

To apprehend the exact role of the resonances induced by the electromagnetic field it is necessary, according to eqs.(35-36), to detail the complex eigenenergies of the states which participate in the active space and the overlapping of these states with the initial state. This is done in tables I, II and III and in Fig III on a large frequency range. Fig IV presents, on the same range, the dissociation spectrum calculated at $t = 10^9 a.u.$. The analysis of these results reveals the following points :

- The dissociation is principally a one state process involving the resonance state $|\lambda_{n=0,v=0}>$ induced from the initial state $|n=0, v=0>$ by the electromagnetic field, except near some frequencies for which the laser is tuned to a bound-bound transition. In this case the initial state overlaps significantly with the two dressed states in near resonance and the corresponding resonances mix, inducing a significant increase of the width of $|\lambda_{n=0,v=0}>$. These two states have to be selected in eq(35) to reproduce correctly the dissociation process.

- The dissociation is low despite the large value of the field amplitude and the large life time of the pulse; this result is consistent with previous observations [49]. Our results attribute this behaviour to the negligible overlapping of the resonance states with the pseudo continuum states. This is a direct consequence of the weak couplings in H_F between the bound states and the pseudocontinuum states: $< n, v(boundstate)|H_F|n \pm 1, v(continuum) >$. For instance, one can see in the three tables that any pseudocontinuum state is present in the six first states whose overlapping with $|\lambda_{0,0}>$ is the largest. As the widths of the resonances are proportional to these overlap coefficients and to the imaginary parts of the continuum eigenvalues. (these artificial imaginary parts are direct contributions of the optical potential), one can easily understand the weak widths of the resonance states and consequently the low efficiency of the dissociation process.

On the largest part of the spectrum the width $\Gamma(= 2Aimag(E))$ is less than 10^{-12} (cf Fig 3) and the corresponding dissociation probability consequently negligible at $t = 10^9$. To overcome this difficulty the resonance $|\lambda_{0,0}>$ should mix with other resonances possessing a largest width. This is the case in Fig 3 when the laser in tuned to the bound-bound transitions ($0 \rightarrow 2$), ($0 \rightarrow 3$) and ($0 \rightarrow 4$). This features explains the three peaks which compose the dissociation spectrum. It is also interesting to note that Fig 3 reveals the presence of multiphoton processes between bound states for instance $(0, 0 \rightarrow -2, 4)$ and $(0, 0 \rightarrow -2, 5)$ which were previously observed by Leforestier and Wyatt [48] at higher intensities. Nevertheless in the present case the corresponding widths remain smaller than 10^{-12} and the overlapping with $|\lambda_{0,0}>$ negligible so that these multiphoton processes do not introduce supplementary structures in the dissociation spectrum..

4 Conclusion

The simple model analysed here reveals that the dissociation of diatomic molecules under continuous electric fields of medium intensities are molecular processes which can be described using small subspaces within the framework of the Floquet approach. Often only one resonance state induced by the field-matter coupling is needed to describe the dissociative process adequately. In the case where the laser is tuned to transitions between bound states, all the quasibound states which are in near resonance, must be retained. One can presume that with the dense spectrum of polyatomic molecules, many accidental near resonances can appear involving one or many photons, thus inducing a larger active space.

The stationary wave operator formulation would appear to be an efficient tool for selecting these active subspaces. This method is valid insofar as the dimension of the active space remains small with regard to that of the whole space. Numerous improvements can be added. The single cycle method, which is used here to integrate the non-linear Bloch equation, is just one example among others. The elaboration of a new treatment using the C.S.A.S.M. and the Bloch theory is in progress. The intermediate Hamiltonian theory [33, 43] or similar theoretical concepts [44] are other interesting possibilities.

In the treatment of photodissociation dynamics, this formalism is particulary suitable when detailed results are required (e.g. kinetic energy spectrum of fragments, branching ratios and numbers of photons involved) because the theory provides the eigenvectors which compose the active space. These precise results are deduced from the projections of these eigenvectors into each Floquet block or from a quantum flux analysis.Studies being carried out currently, show that it is possible to work, within the framework of this formalism, on phenomena involving above-threshold dissociation and laser-induced avoided crossing between the dressed molecular potentials appearing under strong laser fields and on harmonic generation in ionizing systems. With respect to these projects the main useful feature of the wave operator treatment is its ability to work in very large vector spaces. This feature has been analysed in detail in the last section by studying the recursive rules of the R.D.W.A. and of the single cyle model.

FIGURE CAPTIONS

Fig1 : Schematic representation in the dressed picture of the potential surface involved in the dissociation process of the HF molecule under a monochromatic laser field. The field intensity is $I = 1TW/cm^2$ and the frequency $\omega = 0.060a.u.$. The surface number n=0 belongs to the initial Floquet block. The surfaces$n = -1$ and $n = 1$ are the dressed surfaces associated with the absorption and emission of one photon. The bound and continuum states constituting the model space $S_o(N_o = 12)$ and retained by the wave operator selection algorithm are included.

Fig2 : The same as Fig 1 but for a laser frequency equal to $\omega = 0.02914$.

Fig3 : Upper panel: non-negligible overlap integral $| < \lambda_{n',v'}|0,0 > |^2$ between the initial state $|n = 0, v = 0 >$ and eigenvectors $|\lambda_{n',v'} > of H_F$. Lower panel: imaginary part of the eigenvalues of the states whose overlap with the initial state is non negligible. Some peaks correspond to particular field-matter transitions $(n,v) \rightarrow (n',v')$.

Fig4 : Dissociation spectrum of the HF molecule in the frequency range [0.015 a.u., 0.048 a.u.] calculated at $t = 10^9 a.u.$ for a c.w. laser of intensity $I = 1TW/cm^2$.

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Table 1: Complex eigenvalues and overlapping with the initial state for the six first eigenvectors $|\lambda_{n,v}>$ ordered by the wave operator selection algorithm. The upper part corresponds to the laser tuned to the bound-bound transition $v = 0 \rightarrow v = 2$. Lower part: a shift destroys the perfect resonance, $\omega = 0.0285368$ instead of $\omega = 0.0291400$

$\omega = 0.0291400$		
state n, v	eigenvalue	$\vert < n, v \vert \lambda_{0,0} > \vert^2$
0,0	-0.0525774 - i 0.8255(-7)	0.5294
-1,2	-0.0525424 -i 0.9420(-7)	0.4644
1,0	-0.0234374 -i 0.8255(-7)	0.164(-2)
0,2	-0.0234024 -i 0.9420(-7)	0.144(-2)
-1,0	-0.0817174 -i 0.8255(-7)	0.164(-2)
-2,2	-0.0816824 -i 09420 (-7)	0.144 (-2)
$\omega = 0.0285366$		
0,0	-0.0525616 -i 0.1417(-9)	0.9927
-1.2	-0.0519550 -i 0.1790(-6)	0.8225(-3)
1,0	-0.0240248 -i 0.1417(-9)	0.3218 (-2)
0,2	- 0.0234183 -i 0.1790(-6)	0.2626(-5)
-1,0	-0.0810983 -i 0.1417(-9)	0.3218(-2)
-2,2	-0.0804918 -i 0.1790(-6)	0.2693(-5)

Table 2: same as table 1 but the upper part corresponds to the laser tuned to the bound bound transition : $v = 0 \to v = 3$. Lower part $\omega = 0.0387468$ insteead of $\omega = 0.0393500$.

$\omega = 0.0393500$		
state n, v	eigenvalue	$\mid < n, v \mid \lambda_{0,0} > \mid^2$
0,0	-0.0525687 -i 0.3071(-7)	0.6199
-1,3	-0.0525484 -i 0.5044(-7)	0.3766
-1,0	-0.0919187 -i 0.3071(-7)	0.1055(-2)
-2,3	-0.0918984 -i 0.05044(-7)	0.6411(-3)
1,0	-0.0132187 -i 0.03071(-7)	0.1055(-2)
0,3	-0.0131984 -i 0.5044(-7)	0.6409(-3)
$\omega = 0.0387468$		
0,0	-0.0525612 -i 0.2348(-10)	0.9962
-1.3	-0.0519527 -i 0.8619(-7)	0.2617(-3)
-1,0	-0.0913080 -i 0.2348(-10)	0.1749(-2)
-2,3	-0.0906995 -i 0.8619(-7)	0.4574(-6)
1,0	-0.0138144 -i 0.2348(-10)	0.1449(-2)
0,3	-0.0132059 -i 0.8619(-7)	0.4507(-6)

Table 3: same as table 1 but the upper part correspondant to the laser tuned to the bound-bound transition :$v = 0 \rightarrow v = 4$. Lower part $\omega = 0.04726$ instead of $\omega = 0.04666$

$\omega = 0.04666$		
state n, v	eigenvalue	$\mid < n, v \mid \lambda_{0,0} > \mid^2$
0,0	-0.0525653 -i 0.1181(-7)	0.5997
-1,4	-0.0525546 -i 0.1777(-7)	0.3978
-1,0	-0.0992253 -i 0.1181(-7)	0.7258(-3)
-2,4	-0.0992146 -i 0.1777(-7)	0.4814(-3)
1,0	-0.0059053 -i 0.1181(-7)	0.7259(-3)
0,4	-0.0058946 -i 0.1777(-7)	0.4813(-3)
$\omega = 0.04726$		
0,0	-0.0525610 -i 0.1727(-11)	0.9975
-1,4	-0.0531622 -i 0.2767(-7)	0.7573(-4)
-1,0	-0.0998242 -i 0.1727(-11)	0.1176(-2)
-2,4	-0.100425 -i 0.2767(-7)	0.8986(-7)
1,0	-0.0052977 -i 0.1727(-11)	0.1176(-2)
0,4	-0.0058989 -i 0.2767(-7)	0.9090(-7)