The Bloch wave operator: generalizations and applications: II. The time-dependent case

TOPICAL REVIEW

The Bloch wave operator: generalizations and applications: II. The time-dependent case

Georges Jolicard[1] **and John P Killingbeck**[1,2]

[1] Observatoire de Besançon (UMR-CNRS 6091), Université de Franche-Comté, 41 bis,
Avenue de l'Observatoire, 25000 Besançon, France
[2] Mathematics Department, University of Hull, Hull HU6 7RX, UK

Abstract
Part II of the review shows how the stationary Bloch wave operator of part I
can be suitably modified to give a time-dependent wave operator. This operator
makes it possible to use a relatively small active space in order to describe the
dynamical processes which occur in quantum mechanical systems which have
a time-dependent Hamiltonian. A close study is made of the links between
the time-dependent and time-independent wave operators at the adiabatic
limit; the analysis clarifies the way in which the wave operator formalism
allows the time evolution of a system or a wave packet to be described in terms
of a fast evolution inside the active space together with weak transitions out of
this space which can be treated by perturbation methods.

Two alternative wave operator equations of motion are derived and
analysed. The first one is a non-linear differential equation in the usual Hilbert
space; the second one is a differential equation in an extended Hilbert space with
an extra time variable added and becomes equivalent to the usual Bloch equation
when the Floquet Hamiltonian is taken in place of the ordinary Hamiltonian.
A study is made of the close relationships between the time-dependent wave
operator formalism, the Floquet theory and the (t, t') theory. Some original
methods of solution of the two forms of wave operator equation are proposed
and lead to new techniques of integration for the time-dependent Schrödinger
equation (e.g., the generalized Green equation procedure). Mixed procedures
involving both the time-independent and time-dependent wave operators are
shown to be applicable to the internal eigenstate problem for large complex
matrices.

A detailed account is given of the description of inelastic and photoreactive
processes by means of the time-dependent wave operator formalism, with
particular attention to laser-molecule interactions. The emphasis is on
projection operator techniques, with special attention being given to the method
of selection of the active space and to the use of basis set expansions in terms
of instantaneous or generalized Floquet eigenstates. The adiabatic transport
principle and its representation in terms of the wave operator approach are

described, as well as the way in which effective energy trajectories in the complex plan can act as indicators of the degree of adiabaticity or non-adiabaticity of a dynamical process.

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Contents

1. A brief historical review

Part I of this review paper included a description of the Bloch effective Hamiltonian theory, which was developed within nuclear physics in the 1960s to determine the effective interactions between nucleons and in quantum chemistry to overcome some limitations of ab initio and semi-empirical methods. The original wave operators of Møller (1945) were defined within the context of scattering theory, while the later work of Bloch (1958), Des Cloizeaux (1960), Durand (1983) and others developed the theory of the Bloch wave operator, which is more suitable for dealing with bound state problems. Part I of this review (Killingbeck and

Jolicard 2003) made heavy use of the partitioned matrix approach (for the benefit of general readers) and showed how the use of a traditional Rayleigh–Ritz approach to bound state calculations would naturally lead to the construction of the Bloch and related wave operators without any use of the concepts of Møller.

When an attempt is made to extend the Bloch wave operator formalism to treat time-dependent phenomena it is then necessary to deal with the time development operators $U(t, t_o)$ which describe the evolution of a quantum mechanical state; in this context it becomes more natural to explore links with the Møller wave operators, which, although time independent, are usually defined within the context of the time-dependent theory as the limits for $t \rightarrow \pm\infty$ of a simple product $\exp[iHt/\hbar]\exp[-iH_o t/\hbar]$ of time development operators. The book by Roman (1965) described the derivation of the Møller wave operators via time-dependent theory, while the book by Pearson (1988) gave the rigorous mathematical theory for a range of wave operators which have been defined in scattering theory. In the end, however, it turns out (sections 2.2 and 2.3) that the various approximations which need to be made to the Møller operator lead back to what is essentially the Bloch wave operator. Part II of this review looks at how time dependence can be introduced into Bloch wave operator theory (extending the ideas sketched briefly in the appendix of part I) and describes some applications to problems of molecular dynamics, particularly to the theory of the photodissociation of molecules by laser pulses. Several of the techniques described in part I will be seen to be equally useful in the calculation of time-dependent behaviour, the main novel feature being that complex variable forms of the algorithms are needed, since the matrices studied often have complex elements.

Various topics in molecular interaction theory have given rise to both stationary and time-dependent treatments. In scattering theory, for example, the close-coupling formulation and the Lippmann–Schwinger approach use the mathematics of differential and integral equations and proceed by finding solutions of the time-independent Schrödinger equation which have specific energies and which obey the correct asymptotic conditions. By contrast, the wave packet formalism applied to the same problems gives a time-dependent treatment which involves the propagation and the asymptotic analysis of wave packets of finite extent; this approach can be used to treat inelastic or reactive interactions over finite energy ranges corresponding to the energy spectrum of the wave packet. A Gaussian wave packet is usually used for the translational asymptotic degree of freedom because it allows good control of its extent in phase space (Kosloff 1988). For bound asymptotic degrees of freedom an eigenstate is often chosen as the initial wavefunction and the total initial wave packet is constructed as a product of the wave packets of different degrees of freedom.

Like the methods described above, the wave operator formalism has also evolved; the operators of Bloch and Møller have acquired time-dependent forms which are analysed in the present review. This evolution has been associated with new trends in the experimental and theoretical treatments of molecular dynamics during the last two decades. Two of these trends are particularly important.

- The first is the introduction of finite discrete L^2 representations which are able to reproduce the bound part of the molecular spectrum and also to describe the continuum part. The use of similarity transformations in the complex plane, or of absorbing boundary conditions (sometimes called the optical potential method) makes possible the calculation of resonance states and the treatment of reactive or photoreactive processes using these representations. The discretization approach is appropriate for implementation on digital computers and has been facilitated by recent progress in the area of discrete variable representations (DVRs) (Kosloff and Kosloff 1983, Light *et al* 1985, Bačiç and

Light 1989). It is now possible to perform analytical continuation of the resolvents in the complex plane by operating within these discrete representations. The Møller wave operator and the Lippmann–Schwinger equation, which are both directly related to the resolvent operators, are thus treatable by these modern techniques within the optical potential formalism (see section 2.2). The use of finite discrete L^2 representations to describe dynamical processes leads back to the use of large matrices, i.e. to the context of part I of this review, with the extra feature that the matrices (and part of the spectrum) will be complex. Most of the entities arising in the theory of the time-independent wave operator have an analogue in the theory of the time-dependent wave operator; for example, the static effective Hamiltonian which gives a subset of the energy levels in the static case becomes a time-dependent effective Hamiltonian which drives the dynamical processes in the active space; this space is the analogue of the target space in the static case and is represented in a first approximation by a model space analogous to the A space of part I. This close similarity at the theoretical level means that some computational techniques which were introduced in part I also find applications in part II; the recursive distorted wave approximation (RDWA) and the single cycle method (SCM) are both applicable (in complex variable form) once the time-dependent problem has been converted to a form involving large complex matrices.

The combined introduction of discrete representations and complex asymptotic transformations has helped in improving the treatment of quantum dissipative systems. Some twenty years ago the most commonly used quantum mechanical approach was the stationary coupled channel (CC) approach, which is based on a solution of the stationary scattering equation, and is difficult (or even impossible) to implement for systems in which more than one continuum of final states exists. For such systems the time-dependent quantum mechanical methods based on wave packet propagation have clear advantages. Nevertheless the non-local character of the interactions, which requires a global description of all the molecular phase space, dramatically increases the memory and CPU time requirements in many cases. The wave operator method, which selects reduced model spaces and then studies the associated projected dynamics, is an efficient tool in this area. Its applicability in conjunction with a non-Hermitian description of dissipative systems makes it useful for the new non-Hermitian quantum mechanics of Narevicius and Moiseyev (1998, 2000), which introduces complex adiabatic potential energy surfaces to separate slow and fast motions.

• The second trend is the increasing study of control processes, particularly the selective laser control of molecular dynamical processes, which is one of the major goals of current photophysics and photochemistry. Intense and ultrashort laser pulses induce strong non-linear effects during their time of interaction with a molecule. To describe the associated experiments it is essential to possess an accurate theory of the dynamical processes occurring during the interaction. Formulations which concentrate on asymptotic behaviour, such as the close-coupling treatment, are relatively inefficient for this purpose. In contrast, the time-dependent wave operator theory, which uses generalized Hilbert spaces (with the time as a supplementary variable) and which describes the dynamics using small active spaces, is well adapted to investigate these problems, particularly when many repetitive numerical trials are necessary to select the best group of adiabatically evolving parameters (see section 7.2).

Most of the abbreviations used throughout the text are explained in context but we gather together here a few of the ones which are used fairly frequently: OPM (optical potential model); TDOP (time-dependent optical potential); TDSE (time-dependent Schrodinger

equation); TDWOT (time-dependent wave operator theory), IR, UV (infrared, ultraviolet); fs (femtosecond, i.e. 10^{-15} s); cw (continuous wave, as opposed to pulsed, for a laser).

1.1. Some general references on related themes

When the wave operator theory is applied to perform calculations it will usually need to be combined with various other concepts and techniques which are relevant to the treatment of the time-dependent Schrodinger equation. This means that when describing applications, particularly to laser-molecule interactions, the review has to mention several ancillary techniques which are not the main theme of the paper but which might not be familiar to the general reader. Although the text gives a fairly detailed discussion of some of these techniques, the authors have thought it useful to give a brief overall survey of them. Accordingly this brief literature survey cites some works which will enable the general reader to explore in more detail the context within which the time-dependent wave operator theory has been and is being applied. Several recent review articles have given much information about the modern theory of the interaction of laser pulses with atoms and molecules. The review of Gavrila (2002) dealt with atomic stabilization due to intense laser beams and that of Shapiro and Brumer (2003) treated the control problem. The problem of the control of molecular processes by means of appropriately designed groups of laser pulses is nowadays being widely studied. The very recent review by Guerin and Jauslin (2003) has the double interest of discussing the control problem and of setting out the Floquet theory, which is another of the themes ever-present in modern work on laser-molecule interactions.

The original mathematical work of Floquet on differential equations with periodic coefficients has had several by-products in physics. When the periodicity is a spatial one the theory leads to the well-known theorems about the periodicity of the wavefunctions of band theory for electrons moving in the periodic potential of a crystal lattice. For an atom or molecule which is acted on by a laser beam of a given frequency the periodicity is in the time variable and the corresponding theory has taken over some of the terminology familiar to solid state physicists; for example, it is common to refer to 'the first Brillouin zone' in discussions of the quasi-energies associated with the Floquet theory. The literature on Floquet theory is vast and so the authors have selected only a few papers which will give a general reader a good survey of the historical development and uses of the theory. The paper by Shirley (1965) treated the theory of a Schrödinger equation with a Hamiltonian which is periodic with a single fixed time period. The work of Sambe (1973) treated the problem in more detail and used the notions both of an extended Hilbert space (with the time variable included) and of the Floquet Hamiltonian; both notions occur throughout the present review. Howland (1974), within a scattering theory context, considered how to construct transformations which would produce a stationary problem for a Hamiltonian with a general (not necessarily periodic) time dependence. Ho *et al* (1983) extended Shirley's work on singly periodic Hamiltonians to the case of a multiperiodic Hamiltonian and Garrison (1999) treated the multimode Floquet theory by a group theoretical approach, with an account of the history of the theory, including the solid state case, which involves a spatial periodicity. Recently, Palma *et al* (2002) gave a novel treatment of the Floquet states of a harmonic oscillator in a single-mode field by using the Bargmann–Segal space. Amongst the many works which have combined theoretical and calculational treatments of Floquet theory we cite only a very few, which themselves gave references to previous works as well as containing some original developments. The works of Chu (1981), Jolicard *et al* (1994) and of Unnikrishnan (1995) described a range of useful techniques (complex coordinate transformations, L^2 discretization, the extended Hilbert

space) while treating the types of transitions produced in a molecule by intense laser fields. The paper by Emmanouilidou and Reichl (2002) treated electron scattering rather than laser-molecule interactions but gave a good account of the relevant Floquet theory. Very recently Daems *et al* (2003) have given a treatment of the theory of pulse-driven systems which uses a sequence of transformations to develop a superconvergent perturbation theory. Their approach represents an extension to quantum mechanics of the KAM perturbation theory of classical mechanics but adds some new features to previous attempts in this direction. In several respects the KAM approach in quantum mechanics resembles the Van Vleck perturbation theory briefly described in part I, but has a different way of solving the equations, as well as being used in the extended Hilbert space rather than in the standard Hilbert space. The R matrix approach to multiphoton processes due to laser-molecule interactions has been developed over many years by the group of P G Burke at Belfast; the detailed paper by Burke *et al* (2000) showed how the R matrix approach can be allied with Floquet theory to give a non-perturbative description of multiphoton processes and it gave some illustrative numerical results.

The (DVR) approach is one of the most widely used methods for producing a large but finite matrix which can give an accurate description of the bound or resonant states of a molecule as well as giving a discretized simulation of the continuous part of the spectrum. The technique has been gradually refined, with various authors having studied specific technical points. Whitnell and Light (1989) developed a three-dimensional DVR to study the H_3^+ ion. Szalay (1993) studied the DVR representation of differential operators. Corey and Tromp (1995) looked at how to endow the DVR with the same variational properties as the simple Rayleigh–Ritz method. Kauppi (1996) calculated vibrational energy levels with a DVR method which avoided the need to obtain an explicit functional form for the potential energy surface, since only the data at the discrete points used by the DVR were employed. Schweizer and Fassbinder (1997) combined DVR and finite element techniques. Tuvi and Band (1997) studied the special methods which must be adopted to produce a DVR matrix which is both Hermitian and has elements which can be calculated analytically. Wei (1997) studied the presence of 'ghost levels' in some DVR calculations and showed how to remove them by modifying the formalism. Chen and Guo (1999) showed how the use of symmetry adaption can reduce the computational effort of DVR calculations; even for molecules with no physical symmetry the inherent symmetry of the kinetic energy operator can be exploited. Weatherford *et al* (2002) described a general approach to the construction of DVR representations, using a method which involves a combination of Lanczos matrix methods and Gaussian integration theory.

Within the context of a Floquet approach in a generalized Hilbert space, the (t, t') approach introduced into quantum mechanics a device which goes back as far as the work of Jacobi in classical mechanics, namely the use of a dummy 'time' variable t', with the 'physical' time being placed on an equal footing with the space variables. The result of this approach is that various problems of time-ordering which appear in a traditional approach to the time-dependent Schrodinger equation are side-stepped, since the problem formally resembles that for a time-independent Hamiltonian (with the new time variable t'). This facilitates the use of the more simple theory of time development associated with a time-independent Hamiltonian. The main problem of interpretation then becomes that of extracting any required quantities from the formalism; this usually involves taking the limiting case $t \rightarrow t'$. The relevant theory, together with some applications, was given in the papers of Peskin and Moiseyev (1993) and Peskin *et al* (1994a, 1994b). Yao and Wyatt (1994) explored in detail the use of the extended Hilbert space, showing how it made possible the application of several techniques which are usually applied to stationary quantum mechanical calculations. Some

of the wave operator approaches described in the present review have a resemblance to the (t, t') theory and so comments on that theory appear at some points throughout the text.

2. From the Møller wave operator to the time-dependent Bloch wave operator

The theoretical description of many experiments in molecular dynamics is characterized by two special but contrasting features; the sizes of the vector spaces involved are very large as a consequence of the non-local character of the quantum interactions, but the number of eigenvectors effectively contributing to the dynamical processes is often small, especially when suitably adapted representations such as the generalized Floquet eigenstate representation are used (see section 5.2). The aim of the wave operator theory is to condense the dynamics into these small active spaces by using projection techniques and to form the effective Hamiltonians which drive this reduced dynamics. Two features require special attention in formulating such a project: (i) the choice of the representation, especially in the presence of continua (ii) the status of the time variable in the analytical and numerical treatments.

With regard to the status of the time variable t one can distinguish three different cases in an increasing order of difficulty. In the most simple case the Hamiltonian $H(H = H_o + V)$ of the molecular system is an Hermitian and time-independent Hamiltonian used to describe the evolution of a non-dissipative system. The interaction V is assumed to be delocalized in time and the total energy takes a precise and constant value throughout as a consequence of the Heisenberg principle. The quantum scattering theory of inelastic collisions is the typical example of such a situation. This first case is analysed in section 2.1. The second case, corresponding to a time-independent interaction which is turned on suddenly, is analysed in the framework of the stationary wave operator theory in section 2.2. Finally the third case, that of a general time-dependent Hamiltonian, allows us to introduce the time-dependent wave operator concept in section 2.3.

2.1. Quantum scattering theory and the Møller wave operator

The Møller wave operator Ω^+ arises in the context of scattering theory in a form which is independent of an explicit specification of the initial state. We assume here that the total Hamiltonian H which describes the scattering is split into two terms.

$$H = H_o + H_1 \tag{2.1}$$

where H_o is taken to be the Hamiltonian for all the free particles and H_1 includes interactions responsible for collision processes. We also assume that H_o is so simple that all its eigenvalues and eigenvectors are known and, finally, that to each state $|E, n\rangle$ in the continuous part of the H_o spectrum which has an energy E there belongs a corresponding state in the continuum part of the H spectrum which has the same energy. The discrete bound states are supposed to lie lower than any state in the continuum and we exclude for the moment the presence of metastable states embedded in the continuum (although this possibility can be considered in the framework of the Bloch wave operator theory).

Although the standard Møller wave operator is a purely time-independent one, an interesting time-dependent point of view can be adopted towards it (the value of which will be clearer with the introduction of the time-dependent wave operator in section 2.3). By introducing the time evolution operator in an interaction representation, the Møller wave

operators are defined by Roman (1965) and Levine (1969)

$$\Omega^+ = U(0, -\infty) = \lim_{t' \to -\infty} e^{\frac{i}{\hbar} t'(H_o + H_1)} e^{-\frac{i}{\hbar} t' H_o}$$

$$\Omega^- = U(0, +\infty) = \lim_{t' \to +\infty} e^{\frac{i}{\hbar} t'(H_o + H_1)} e^{-\frac{i}{\hbar} t' H_o}. \tag{2.2}$$

By using the integral representation,

$$U(0, -\infty) = \lim_{\epsilon \to 0^+} \epsilon \int_{-\infty}^{0} e^{\epsilon t'} e^{\frac{i}{\hbar} t'(H_o + H_1)} e^{-\frac{i}{\hbar} t' H_o} \, dt' \tag{2.3}$$

and by applying this operator to a stationary eigenvector $|E, n\rangle$ of the unperturbed problem, one obtains the state

$$|E, n^+\rangle = \lim_{\epsilon \to 0^+} \frac{i\epsilon}{E - H + i\epsilon} |E, n\rangle \tag{2.4}$$

which can be identified with the exact incoming state of the time scattering problem and which is a solution of the Lippmann–Schwinger equation.

$$|E, n^+\rangle = |E, n\rangle + \lim_{\epsilon \to 0^+} (E - H_o + i\epsilon)^{-1} H_1 |E, n^+\rangle. \tag{2.5}$$

A similar equation is obtained for $|E, n^-\rangle$ by taking the term $-i\epsilon$ in place of $+i\epsilon$ on the rhs of equation (2.5). From the previous definitions, it appears that $|E, n^+\rangle$ coincides with an unperturbed state of the reference system at an infinitely remote past time: $\lim_{t \to -\infty} |E, n^+\rangle = |E, n\rangle$; similarly $\lim_{t \to +\infty} |E, n^-\rangle = |E, n\rangle$. These identities justify the names *incoming* and *outgoing states* used to specify the states $|E, n^+\rangle$ and $|E, n^-\rangle$, respectively. Thus, $\Omega^\pm$ induces a state-to-state correspondence between the states of H with the continuous energy E and the initial states of H_o with the same energy

$$|E, n^\pm\rangle = \Omega^\pm |E, n\rangle. \tag{2.6}$$

This leads to the formal definition

$$\Omega^\pm = \sum_n \int dE |E, n^\pm\rangle \langle E, n| \tag{2.7}$$

when using the normalization convention: $\langle E', n' | E, n \rangle = \delta(E' - E)\delta_{n'-n}$.

In the notation used above, n designates the quantum numbers of the initial state, generally not conserved during the interaction, and the symbol $\pm$ refers to the boundary conditions. These conditions are introduced in a formal way by working in the complex plane, with $E^\pm = E \pm i\epsilon$ in equation (2.7), where ϵ is real and positive and tends to zero. Equation (2.5) can be obtained in a fairly elementary way by seeking the states $|E, n^+\rangle$ which arise from $|E, n\rangle$ as the interaction H_1 is turned on. If it is supposed that $|E, n\rangle$ is an eigenstate of H_o with energy E while $|E, n^\pm\rangle$ are eigenstates of $H_o + H_1$ with the *same* energy E (which is possible for the continuous spectrum) then the reader will quickly confirm that the formal result (2.5) is obtained, with E in the $E^\pm$ position and, of course, with the problem that $(E - H_o)^{-1}$ is singular. To avoid this problem it is necessary to use a limiting process; the use of $E^\pm = E \pm i\epsilon$ (with $\epsilon \to 0$) leads to states $|E, n^\pm\rangle$ which describe an incoming (+) and an outgoing (−) scattering state, respectively. The lecture notes of Møller (1959) gave a detailed demonstration of this for the case in which $|E, n\rangle$ is an incoming plane wave of energy E.

Equations (2.4)–(2.6) reveal the close relationship between the Møller wave operator and the Green's operator $G(E^+) = (E^+ - H)^{-1}$, namely

$$\Omega(E^+) = I + G(E^+)H_1 \tag{2.8}$$

and also bring to light the links between Ω, the transition operator $T = V\Omega$ and the S matrix $(S = \Omega^{-\dagger}\Omega^+)$, where the symbol $\dagger$ denotes the Hermitian adjoint.

These equations reaffirm that the Møller wave operator is associated with very precise conditions: it is appropriate for a precise energy and for interactions produced by delocalised and time-independent couplings. The limits which the previous equations introduce, namely $\epsilon \to 0$ and $t \to \infty$, are related to these conditions. Moreover, the conservation of energy condition implicitly imposes the need for a rigorous description of the molecular continuum. Such a situation is, for the wave operator theory, a limiting case in which the active space associated with a fixed energy value E of the continuum consists of a single eigenstate $|E, n^+\rangle$ which reduces to the state $|E, n\rangle$ when the molecular interaction vanishes. The simplicity of the active space results partly from the restrictive assumptions, introduced at the begining, that the continuum and the discrete spectra do not overlap and that metastable states are not present. In the next two sections we will be able to loosen these restrictions by adopting a discrete representation of the continuum in place of a rigorous description and by introducing the time-dependent wave operator concept.

2.2. The optical potential approach for an interaction which is turned on rapidly

A slightly more complicated situation appears in cases for which the interaction is turned on suddenly at a precise time (which can be chosen as $t = 0$ without loss of generality). The initial state can be prepared in various ways. One can, for example, imagine that the wavefunction starts as an eigenstate of H_o at $t = -T$ (with $H(t = -T) = H_o$) and is propagated over a finite interval $[-T, 0]$. This propagation leads to a state $\Psi(t = 0)$ different from any eigenstate of $H(t = 0)$. The wavefunction is driven from this instant by a constant Hamiltonian $H = H(t = 0^+)$. The evolution of a molecule submitted to a constant laser field corresponds to this case if the interval $[-T, 0]$ represents the small but finite time duration over which the molecule-field interaction is turned on.

The time integration procedure is relatively simple because of the pure exponential form of the evolution operator.

$$U(t, 0; H) = \exp[-iHt/\hbar] \tag{2.9}$$

but the time localization of the evolution induces a dispersion of the energies, in conformity with the Heisenberg principle. This dispersion is revealed by introducing the operator K, limited to positive values of t;

$$K(t, 0) = \Theta(t)U(t, 0; H). \tag{2.10}$$

K is the solution of a differential equation which contains an inhomogeneous term describing the initial conditions;

$$\left(i\hbar\frac{\partial}{\partial t} - H\right)K(t, 0) = i\hbar\delta(t, 0). \tag{2.11}$$

K is also related to the Green function of equation (2.8) by a Fourier transform;

$$G(E^+) = \frac{1}{i\hbar}\int_{-\infty}^{+\infty} d\tau \exp(iE\tau/\hbar)K(\tau)$$
$$= \lim_{\epsilon \to 0_+} \frac{1}{E - (H - i\epsilon)}. \tag{2.12}$$

In this case the active space is not composed of a unique eigenstate as it was for the exact quantum scattering theory. There is not, as in equation (2.6), a state-to-state correspondence ($|E, n^+\rangle \leftrightarrow |E, n\rangle$). The wavefunction spreads out over various eigenstates of H and the

role of the wave operator theory is to select these states and to formulate a correct dynamical description using this reduced space. The analysis of the evolution equation

$$\left(i\hbar \frac{\partial}{\partial t} - H \right) \Psi(t) = \delta(t, 0)\Psi(t = 0) \tag{2.13}$$

directly derived from the operator equation (2.11), reveals that the active space is composed of the set of eigenvectors $\{|\phi_n\rangle, n = 1, N\}$ of H which contribute significantly to the expansion of $|\Psi(t = 0)\rangle$. The dimension N of this space is more or less large, depending on the initial conditions and on the required precision; the wave operator approach requires N to be finite in any case and is naturally allied to a discretized description of the molecular continua. This discretization can be obtained by using the optical potential model (Jolicard and Austin 1985, 1986), i.e. by taking a finite asymptotic complex potential $-iV_{\text{opt}}(r)$ along the spatial radial axis in place of the term $-i\epsilon$ in the energy-based definition of the Green function (Durand and Paidarovà 1996). The schematic correspondence involved (relating 'energy' and 'space' limiting processes) is of the form

$$\lim_{\epsilon \to 0^+} \frac{1}{E - (H - i\epsilon)} \Rightarrow \frac{1}{E - (H - iV_{\text{opt}}(r))}. \tag{2.14}$$

This is a coarse grained procedure which destroys the exact representation of the continuum; all the scattering states are strongly modified and their spectrum is rotated in the complex plane. Nevertheless, these distortions do not have any crucial negative consequences for the description of dynamical effects; the procedure is consistent with the use of dynamical treatments using contracted L^2 basis sets because some important fundamental features are preserved. The optical potential transformation, for example, assures the analytical continuation of the Green function through the cut constituted by the real axis, with $G_\alpha(z) = \langle \alpha | \frac{1}{z-H} | \alpha \rangle = (G_\alpha(z^*))^*$. It can be introduced to explore the second Riemann sheet, thus revealing the complex nature of the resonance states without contributing directly to their eigenvalues. It can also be used to determine the resonance spectrum of a quantum system (Jolicard *et al* 1988) or to investigate photoreactive processes which are dominated by the influence of field-matter resonances (Jolicard and Atabek 1992). In numerical work the imaginary potentials make possible the use of finite L^2 representations for the continua. One can then expand the wavefunction $\Psi(t = 0)$ in equation (2.13) on a finite basis set $\{|\phi\rangle_n, n = 1, N\}$ of eigenvectors of $(H - iV_{\text{opt}})$.

Similar concepts have been used in the variational treatment of reactive scattering. The conversion of the multiarrangement channel (MAC) problem into a single arrangement channel (AC) problem is achieved by employing a selected set of negative imaginary potentials which absorb the fluxes leaking from a single retained AC (Neuhauser and Baer 1990, Neuhauser *et al* 1990). By extending the principle from the reagents AC to the product AC, it is possible to find state-to-state reactive probabilities by treating one AC at a time (Last and Baer 1992, 1994)

In the context of the wave operator theory the introduction of negative imaginary absorbing potentials and of large but finite L^2 basis sets is necessary not only for conceptual and numerical reasons but also has an intuitive physical significance. The schema (2.14) describes the correspondence between the energy limit ($\epsilon \to 0^\pm$) present in (2.12) and the spatial asymptotic conditions imposed on the solution. A negative imaginary potential, corresponding to the $(-i\epsilon)$ case, absorbs the outgoing plane waves and, by eliminating as much as possible any reflections, makes the incoming parts vanish. A positive imaginary potential, corresponding to the $(+i\epsilon)$ case, has an opposite effect.

The generalization of the wave operator concept and more particularly the possibility of constructing active spaces including scattering states, molecular resonances and bound states is thus closely related to the use of the OPM. By giving a similar status to these various

types of state the OPM removes the restrictions of Møller's theory and makes it possible to use relatively small active spaces to describe processes such as scatterings with temporary trappings or half collisions induced by electromagnetic field-matter interactions. One can then generalize the definition given by equation (2.7) to include the case of a finite-dimensional model space. Following the notation used by Wyatt and Iung (1996), we define S as the subspace generated by the set of N eigenvectors $|\phi_n\rangle$ which play an important role in our problem (the crucial selection of this subspace will be analysed latter). We will now define S_o as the model space generated by the zero-order description of the states $|\phi_n\rangle$. These states $|\phi_n\rangle^o$, which are eigenvectors of $(H_o - iV_{opt})$, form a biorthonormal basis set characterized by the projection operator P_o. We can then define a third basis set $\{|n\rangle_o, n = 1, N\}$ formed by the projection into the model space of the eigenvectors $|\phi_n\rangle$:

$$|n\rangle_o = P_o|\phi_n\rangle \tag{2.15}$$

where the associated biorthogonal basis set functions $|\bar{m}\rangle$ satisfy

$$_o\langle\bar{m}|n\rangle_o = \delta_{nm} \quad \text{and} \quad P_o = \sum_{n=1}^{N} |n\rangle_{oo}\langle\bar{n}|. \tag{2.16}$$

A new operator can then be defined by analogy with the Møller operator (equation (2.7)), but now for a case in which the continuum is discretized using a large basis set and a model space of dimension N has been selected. The appropriate definition modelled on (2.7) is

$$\Omega = \sum_{n=1}^{N} |\phi_n\rangle_o\langle\bar{n}|. \tag{2.17}$$

This operator can be applied to the evolution operator (equation (2.9)) in order to isolate the active space and to confine the dynamics to it. A crucial point of this operation is the selection of the model space S_o; this and other questions will be analysed in more details in section 3, where the problem of a rigid rotator subjected to a strong laser field will be used as an example.

Before proceeding further with the theoretical development, it is perhaps worthwhile to take stock of the consequences of the reasoning which has been used in the preceding discussion. The first step was to express the traditional Møller wave operator (which was originally used in scattering theory) in a spectral sum form which involves the use of biorthogonal basis functions. The second step was to study systems which can have bound states below their continuous spectrum and to introduce the use of finite representations which, when conjoined with the use of optical potentials, could give a reasonable representation of the full spectrum of systems which have both discrete and continuous spectra, as well as possible resonances. This second step reduces the theoretical apparatus employed to that associated with the theory of large matrices with elements which are complex numbers. When the spectral sums appearing in the Møller wave operator are replaced by those related to the finite representations and when the finite basis is further partitioned (as described above) in a manner which is based on that used in part I of this review, then the nature of the spectral sums is changed to such an extent that the resulting modified wave operator is essentially one of the Bloch type which was studied in part I, except that the matrices to be treated are complex rather than real. Thus, although the use of the concepts of Moller provides a useful guide, it turns out that (just as for the stationary case treated in part I) they are not totally indispensable in the construction of the theoretical tools required. As the discussion proceeds it will also emerge that the use of the Floquet theory and of other mathematical procedures often permits the use of a static theory to describe a dynamical system; this means that the resemblance of the computational methods used to those described in part I becomes even more marked.

2.3. The general case of a time-dependent Hamiltonian

Many interesting experiments in molecular dynamics are described by using explicitly time-dependent Hamiltonians. This is the case for the theory of the field-matter interactions produced by intense laser pulses, for mixed quantum-classical treatments in which some of the coordinates are described by classical mechanics, or more simply whenever interaction representations are introduced to treat purely quantum mechanical systems.

For such cases the stationary wave operator theory is inappropriate and the introduction of a new concept is necessary to project the dynamics into a reduced space. This can be achieved in two different ways, both of which take into account the finite dimension of the model space and the finite duration of the interaction (and consequently its non-adiabatic character). The first way is to introduce into the Møller formalism, the states belonging to the model space S_o in place of the single state $|E, n\rangle$ and to use the evolution operator $U(t, 0)$ operating on a finite interval in place of its adiabatic limit $U(0, -\infty)$ (cf equations (2.3), (2.4)). The second way is to take this same operator $U(t, 0)$ in place of the projector P onto the target space in the stationary Bloch expression $\Omega = P(P_o P P_o)^{-1}$ (which was discussed in section 2.4 of part I of this review). The two procedures lead to the same expression;

$$\Omega(t, 0) = U(t, 0; H) \times (P_o U(t, 0; H) P_o)^{-1}. \tag{2.18}$$

This time-dependent wave operator was presented in the framework of an adiabatic theorem approach in the paper of Jolicard and Grosjean (1985) and four years later in the form (2.18) by Jolicard (1989). More detailed and pedagogical presentations can be found in Jolicard (1995) and Jolicard and Killingbeck (1995a).

The analysis of the time-dependent wave operator Ω defined by equation (2.18) and its application to describe the evolution of quantum systems require the derivation of a differential equation satisfied by Ω. Because of the use of a finite (although large) L^2 representation of H, this derivation essentially takes a matrix form. Moreover, the introduction of the projection operators P_o for the model space and Q_o for the complementary space represents each matrix A of the full space as the sum of four components: $P_o A P_o$, $P_o A Q_o$, $Q_o A P_o$, $Q_o A Q_o$. For example, the matrix $P_o U(t, 0; H) P_o$ in equation (2.18) is *a priori* an $N_o \times N_o$ matrix with an $N_o \times N_o$ inverse. This inverse, when augmented by three zero blocks to form an $N \times N$ matrix in the full space, is denoted by $(P_o U(t, 0; H) P_o)^{-1}$ in a slight abuse of the usual conventions (as was discussed in section 2.4 of part I of this review). By using the basic properties of the projection operators, (e.g., $P_o P_o = P_o$, $P_o Q_o = 0$), one can finally transform equation (2.18) into:

$$U(t, 0; H)(P_o U(t, 0; H) P_o)^{-1} = P_o + Q_o U(t, 0; H) P_o (P_o U(t, 0; H) P_o)^{-1} \tag{2.19}$$

on remembering that in the full space P_o is represented by a unit $N_o \times N_o$ matrix plus three appropriate zero blocks. Starting from equations (2.18) and (2.19), one can write, in conformity with the stationary Bloch wave operator formalism of part I,

$$\Omega(t, 0) = P_o + X(t, 0) \tag{2.20}$$

where Ω induces transitions from the model space to the full space and the off-diagonal part $(X \equiv Q_o \Omega P_o)$ (called the reduced wave operator) induces transitions to the complementary space exclusively. The analogy with the stationary formalism can be used to derive the equation which defines Ω. The principal aim of the Bloch theory in the eigenvalue problem is to generate a matrix transformation which suppresses the couplings between the model space and its complementary part and which transforms H in S_o into a more tractable effective Hamiltonian H^{eff}. A matrix form of this approach has been applied to matrix eigenvalue problems by Coope (1970) and Killingbeck and Jolicard (1992) and was described in

section 2.4 of part I of this review. In the time-dependent case the couplings are changing with time and a single transformation will not serve to decouple the two spaces permanently. It turns out that in principle one can construct a sequence of transformations which will keep on maintaining this decoupling and will involve a time-dependent effective Hamiltonian $H^{\text{eff}}(t)$. In other words, we presume the existence of an $N_o \times N_o$ effective Hamiltonian, such that at each time we have

$$P_o U(t + \mathrm{d}t, t; H) P_o = U(t + \mathrm{d}t, t; H^{\text{eff}}). \tag{2.21}$$

To derive this last expression one can use an interaction representation, based on the identity

$$H = \left(H - \mathrm{i}\hbar \frac{\partial X}{\partial t} \right) + \mathrm{i}\hbar \frac{\partial X}{\partial t}. \tag{2.22}$$

This representation with respect to $\mathrm{i}\hbar \frac{\partial X}{\partial t}$ is clearly non-trivial, since X is the unknown quantity in the problem. Because of the particular block form of $\partial X/\partial t$, the Dyson expansion of the associated evolution operator has a very simple form. The second and higher order terms are equal to zero, owing to the presence of products such as $P_o Q_o$. Thus we have

$$U(t, 0; \mathrm{i}\hbar \partial X/\partial t) = 1 + X(t, 0) \tag{2.23}$$

so that the basic equation of the interaction representation formulation leads to

$$U(t, 0; H) P_o = (1 + X(t, 0)) U(t, 0; H^{\text{eff}}) P_o$$

with

$$H^{\text{eff}}(t) = (1 - X(t, 0)) \left(H - \mathrm{i}\hbar \frac{\partial X}{\partial t} \right) (1 + X(t, 0)). \tag{2.24}$$

Finally, the condition $Q_o H^{\text{eff}} P_o = 0$, which specifies the unknown term X, expresses the evolution issuing from the subspace S_o as a product of two successive evolutions

$$U(t, 0; H) P_o = \Omega(t, 0) U(t, 0; H^{\text{eff}}) = (P_o + X(t, 0)) U(t, 0, H^{\text{eff}})$$

with

$$H^{\text{eff}}(t) = P_o H(t) \Omega(t, 0) \tag{2.25}$$

and leads to the non-linear differential equation which is obeyed by the time-dependent wave operator (Jolicard 1989).

$$\mathrm{i}\hbar \frac{\partial X(t, 0)}{\partial t} = Q_o (1 - X(t, 0)) H(t) (1 + X(t, 0)) P_o. \tag{2.26}$$

Thus the term on the right, which is zero for the stationary case (see part I), plays the role of a driving term in the time-dependent case. The derivation of the equation of motion given above using the intermediate representation generalizes the elementary one given in the appendix of part I of this review for the case of a one-dimensional model space.

Definition (2.18) of $\Omega(t, 0)$, based on the evolution operator, involves a purely time-dependent point of view. Alternative expressions can be derived using an extended Hilbert space formalism which introduces the time as a supplementary variable. These different aspects of the theory and their applications to the description of inelastic and photoreactive interactions are analysed in sections 4–8.

3. The partitioning technique and its application to inelastic and photoreactive processes

Section 2.2 has presented as a possible application of the Bloch wave operator theory the integration of the equations of motion for a quantum system which is driven by a

time-independent Hamiltonian and which has a well-specified initial state $\Psi(t = 0)$ (cf equation (2.13)). For these applications, the efficiency of the effective Hamiltonian theory directly depends both on the nature of the investigated system and on the representation which is used. The Møller wave operator, the definition of which involves the exact scattering solution, would suffice to describe the dynamics with a one-dimensional active space if one identifies this scattering wavefunction with an element of a non-orthogonal basis set, but one cannot expect the same simplicity for a system which is localized in time and which is described on a zeroth-order basis set of large dimension. We will thus analyse in this section how the stationary Bloch operator can be used to reproduce this localized dynamics. The theoretical developments are illustrated by specimen calculations describing photodissociation and inelastic transitions due to intense cw laser fields. An introduction first explains how the theory can take advantage of the periodicity of the field-matter coupling and so transform the semi-classical time-dependent problem into an equivalent time-independent problem.

3.1. The field-matter interaction: the choice of the gauge

Before any further analysis, it should be noted that the effective Hamiltonian approach is never completely rigorous for time-dependent problems. In some cases it is not even appropriate; for instance, processes which are chaotic and which spread out to involve a large part of the phase space are generally not describable by projection methods using a small active space. Nevertheless, a suitable choice of representation sometimes makes the spectra of the unperturbed system treatable by the use of projection techniques and can thus facilitate the treatment of strongly perturbed systems. This is the case for both photodissociation and photoionization processes, although they involve different non-perturbative mechanisms.

By using a quantum description of the field-matter interaction, the relaxation of a molecule submitted to a cw laser field is described by using equations (2.9) and (2.10) with

$$H = H^{\text{mol}} + H^{\text{rad}} + V. \tag{3.1}$$

The analysis of equations (2.11) and (2.12) in the framework of these dissipative processes gives the usual result that the description of the permanent regime predominantly involves poles of $(z - H)^{-1}$ which are situated near the real axis but on higher Riemann sheets and which are revealed by the addition of an optical potential. The relatively small number of these resonances induced by the field-matter interaction explains why one can describe the essential features of the dynamics using a small active space (in the permanent regime, i.e. for times beyond the short temporary regime corresponding to the turning on of the interaction).

Different approaches have thus used partitioning techniques, from the Möwer partitioning (Möwer 1966) to the artificial channel model (Shapiro 1972, Bandrauk and Turcotte 1985), which transform the half-collision problem into a true collision problem. These techniques create an energy dependence of the transition operator $T(E)$ which is neglected in the final solution and which is a symptom of the impossibility of finding an exact solution by partitioning. The Bloch wave operator theory has been used in this context more recently and for similar reasons leads to an energy dependence of the effective Hamiltonian which is also neglected. Nevertheless, it makes it possible to select the active space in a self-consistent manner and to control the degree of approximation which is introduced. We will now analyse these points more closely, first indicating how the stationary approach can be adapted to the semi-classical description of the electromagnetic field and of the matter-field interaction. A simple photodissociation process will be used as an illustration.

In the intense field regime one does not use a quantum description with a time-independent Hamiltonian (equation (3.1)) but rather uses a more appropriate semi-classical description.

Using the dipole approximation and the length (electric field) gauge interaction term $\vec{\mu} \times \vec{E}$, the Hamiltonian can be written as

$$H(\theta + \omega t) = H_o(q, r) - \vec{\mu}(q, r)\vec{E}_o \cos(\theta + \omega t). \qquad (3.2)$$

The field–matter interaction is assumed to be turned on at $t = 0$. The initial phase θ appears as a parameter. q denotes the various internal vibration-rotation degrees of freedom and r is the interfragment axis coordinate. By writing equation (3.2) we have assumed that a particular chemical bond breaks down preferentially, with an associated coordinate r which serves to describe the reactive dynamics when the two fragments separate. For the diatomic molecules H_2 and SiO used as examples in this review the definition of r is straightforward. Jolicard and Atabek (1990) discussed the case of the CH_3NO_2 molecule, for which the dissociation occurs preferentially along the CN axis, and used the distance between the centre-of-mass of the CH_3 and NO_2 fragments as the interfragment coordinate R. More complicated situations involving several interacting continua or dissociations which produce a larger number of fragments can also be investigated by introducing an optical potential on each interfragment axis.

The choice of the gauge is a central point for the problem of multiphoton inelastic transitions and ionization/dissociation processes. A general discussion concerning this choice can be found in Reiss (1979, 1980). The electric field gauge which is used here exhibits some defects in the strong field regime: crossed vector-potential terms occur in this gauge and prevent separation of the Schrödinger equation into centre-of-mass and relative-coordinate equations. Another defect relates to the asymptotic behaviour of H. In the generalized Floquet treatment of photoreactive processes (**Peskin** *et al* 1994a), the asymptotic Floquet channel functions, which play a central role, are proportional to complex scaled outgoing waves when the Hamiltonian satisfies the asymptotic condition, i.e. when both the time-dependent and the time-independent potential terms vanish asymptotically. Unfortunately the asymptotic behavior of the Hamiltonian is gauge dependent. The length gauge and the momentum gauge Hamiltonians, for example, do not satisfy the asymptotic conditions, whereas the acceleration gauge Hamiltonian does. This question has been analysed in detail by Peskin *et al* (1994a) in the framework of the (t, t') theory. It has been proved that one can use the Hamiltonians which do not satisfy the asymptotic conditions and nevertheless obtain the Floquet channel functions after carrying out complex-scaled transformation such as the Kramers–Henneberger transformation (**Henneberger** 1984). These transformations then make the use of these different gauges partly equivalent, since the defects introduced by incorrect asymptotic behaviour can be corrected *a posteriori*. Other defects exist (e.g., a relatively slow rate of convergence with respect to the Floquet basis size) when the length gauge is used, but they do not have any crucial importance in our case. Our aim here is to analyse the improvement introduced by an effective Hamiltonian theory in the treatment of photoreactive processes induced by time-periodic Hamiltonians. From this point of view, equation (3.2) is representative of this situation and the conclusions concerning the advantages of the Bloch formulation are undoubtedly robust and independent of the choice of the gauge.

3.2. Quantum formulation, Floquet formalism and semi-classical point of view

The Hamiltonian (equation (3.2)) is time dependent, in contrast to the purely quantum version (with a quantized field) of equation (3.1); thus the stationary wave operator cannot *a priori* be used to partition the Hilbert space. Nevertheless, one can take advantage of the periodicity of the Hamiltonian to transform this time-dependent approach into an equivalent

time-independent infinite dimensional Floquet eigenvalue problem (Shirley 1965) and to generalize it to the complex quasi-vibrational energy (QVE) formalism by including finite L^2 representations of the molecular continua (Chu 1981). These representations can use absorbing boundary conditions produced by the optical potential $-iV_{\text{opt}}$.

Guérin and Jauslin (2003) have analysed the connections between the Floquet formalism and the quantum and semi-classical points of view for non-dissipative systems. Their approach to the problem will be used here as a starting point to introduce our developments.

The Floquet Hamiltonian is defined in an enlarged Hilbert space

$$\mathbf{K} = \mathbf{H} \otimes \mathbf{L}_2(\mathrm{d}\theta/2\pi) \tag{3.3}$$

where $\mathbf{L}_2$ denotes the space of square integrable functions on the circle of length 2π and $\mathbf{H}$ the molecular Hilbert space, which is assumed to be finite, since the optical potential is introduced to discretize the continuum associated with the radial variable r. The eigenstates $\{|\alpha\rangle\}$ of $H_o - iV_{\text{opt}}$, plus a complete time Fourier basis $\{n\}$, with $\langle\theta|n\rangle = \exp(in\theta)$, form a product basis which spans this extended (spacetime) Hilbert space $\mathbf{K}$. The period $\theta = 2\pi$ corresponds to an optical period $T = 2\pi/\omega$ for a continuous laser field in the usual Floquet theory. It will be equated in the generalized Floquet approach (see section 7 of this review) to the full duration of the laser pulse. On the enlarged Hilbert space the Floquet Hamiltonian is defined as

$$H_F = H(\theta) - iV_{\text{opt}} - i\hbar\omega\frac{\partial}{\partial\theta} \tag{3.4}$$

where H_F is 2π periodic as a consequence of changing the variable from t to θ.

The introduction of the optical potential allows dissipative systems to be treated using finite representations while retaining the validity of the Floquet theorem. Similarly, Moiseyev (Moiseyev and Korsch 1990, Moiseyev *et al* 1990) introduced the complex-scaled Floquet Hamiltonian and described the ionization/dissociation of a molecular system by using a single quasi-energy resonance.

The advantage of the Floquet Hamiltonian (equation (3.4)) arises from the fact that it is time independent and that the dynamics on $\mathbf{K}$ and $\mathbf{H}$ are essentially identical. More precisely, the propagator in the $\mathbf{K}$ space has the simple expression

$$U_{H_F}(t, t_o) = \mathrm{e}^{-iH_F(t-t_o)/\hbar} \tag{3.5}$$

and a direct relation exists between U_{H_F} and the propagator $U(t, t_o; \theta)$ associated with $H(\theta + \omega t)$ (equation (3.2)) which is a solution of $i\hbar\partial/\partial t U(t, t_o; \theta) = H(\theta + \omega t)U(t, t_o; \theta)$ in the standard $\mathbf{H}$ Hilbert space;

$$\tau_{-\omega t}U(t, t_o; \theta)\tau_{\omega t_o} = U_{H_F}(t - t_o, \theta). \tag{3.6}$$

Here $\tau_{\omega t} = \mathrm{e}^{\omega t \partial/\partial\theta}$ is a phase translation operator which acts on the functions ξ of $\mathbf{L}_2$ to give $\tau_{\omega t}\xi(\theta) = \xi(\theta + \omega t)$ (Guérin and Jauslin 2003). Finally, the description of the similarity between the two evolutions is completed by noting the relation between the wavefunctions (Peskin and Moiseyev 1993),

$$\phi(t) = \tau_{\omega t}\Psi(t, \theta) = \Psi(t, \theta + \omega t) \tag{3.7}$$

where ϕ is the standard solution in the $\mathbf{H}$ Hilbert space and Ψ is the extended wavefunction driven by U_{H_F} in the $\mathbf{K}$ space.

Although the Floquet approach appears essentially as a mathematical device to simplify the treatment of the dynamics, it can also be used to prove the equivalence of the semi-classical approach (associated with equation (3.2)) and the purely quantum approach (associated with equation (3.1)) under some precise conditions in the strong field regime. These ideas, present

in the pioneering work of Shirley (1965), have been developed more explicitly by Bialynicki–Birula and Bialynicka-Birula (1976), Bialynicki–Birula and Van (1980) and by Guérin *et al* (1997). The proof of the equivalence starts by studying a quantized photon field in a cavity of finite volume in interaction with the molecule and considers in a second step the molecule and the radiation in free space by taking the limit: $V \to \infty$ (infinite cavity volume), $\overline{n} \to \infty$ (large average photon number), $\rho = \overline{n}/V = C^{te}$ (constant photon density). On assuming that the number of photons exchanged during the field-molecule interaction is very small compared to the average photon number $\overline{n}$, the quantum Hamiltonian (equation (3.1)) is shown to be identical, up to an additive constant, to the Floquet Hamiltonian H_F (Guérin *et al* 1997)

$$(H^{\text{mol}} + H^{\text{rad}} + V) - \hbar\omega\overline{n} \to H_F \tag{3.8}$$

and the dressed state dynamics in the tensorial product $\mathbf{H} \otimes \mathbf{F}$ of the Hilbert space of the molecule and the Hilbert space of the photons is shown to be identical to the Floquet dynamics in the $\mathbf{K}$ space.

This double correspondence, first between the semi-classical treatment and the Floquet treatment, and second between the Floquet treatment and the quantum treatment, establishes a formal equivalence between the semi-classical dynamics and the quantum dynamics at the strong field limit. A last question remains nevertheless, since the two dynamical processes do not occur in the same space. In the enlarged Hilbert space $\mathbf{K}$, the phase θ does not have a definite value. To recover the semi-classical equation, it is necessary to fix a particular value of θ, which can be done by choosing the initial condition of the photon field as a coherent state (see Klauder (1963) and Klauder *et al* (2001) for more details concerning these coherent states). At the limit $\overline{n} \to \infty$, these coherent states correspond, in the phase representation, to the square root of a δ-function (Guérin and Jauslin 2003)

$$(\phi_{\theta_0}(\theta))^2 = 2\pi\delta(\theta - \theta_0) \tag{3.9}$$

and can be represented on the Fourier basis $e^{in\theta}$ by a uniform distribution.

Having sketched the formal developments which have demonstrated the (intuitively reasonable) equivalence between different theoretical formalisms, we should emphasize that in fact it is often not necessary to recover the exact semi-classical result. In experiments the phase between the molecule and the field is averaged uniformly on $[0, 2\pi]$, since many molecules contribute to the experimental result. It thus seems more judicious to take an initial photon state which corresponds to this arbitrary phase. This state which implicitly introduces the phase average has also the advantage of having an elementary representation in the Floquet basis set, namely: $(e^{in\theta})_{n=0}$. The matrix representation of the Floquet Hamiltonian in the extended basis set has the elements

$$\langle n, \alpha | H_F | m, \beta \rangle = [(H_o - iV_{\text{opt}}) + n\hbar\omega]\delta_{n,m}\delta_{\alpha,\beta}$$
$$- \vec{\mu}_{\alpha,\beta} \times \frac{1}{2\pi} \int_0^{2\pi} \vec{E}(\theta) \exp(i(n-m)\theta) \, d\theta. \tag{3.10}$$

One can express the probability of transition from the initial molecular state $|\alpha\rangle$ to the final molecular state $|\beta\rangle$ after a lapse of time Δt (Chu 1989). This probability is averaged over the relative phase between the field and the molecular state, a condition which is simply obtained by taking the Fourier state $|n = 0\rangle$ as the initial state. The probability is given by

$$P_{\alpha \to \beta}(\Delta t) = \sum_n |\langle n, \beta | \exp(-iH_F\Delta t/\hbar)|0, \alpha\rangle|^2 \tag{3.11}$$

or equivalently, by using the complete basis set of quasi-energy eigenvectors (i.e. the eigenvectors $|\lambda\rangle$ of H_F), by

$$P_{\alpha \to \beta}(\Delta t) = \sum_n \left| \sum_\eta \langle n, \beta | \lambda_\eta \rangle \langle \lambda_\eta | 0, \alpha \rangle \exp(-\mathrm{i} E_\eta \Delta t / \hbar) \right|^2. \qquad (3.12)$$

In equation (3.12) the use of the optical potential produces a non-Hermitian Hamiltonian and an associated bi-orthogonal set with the property

$$\langle \lambda_\alpha^\dagger | \lambda_\beta \rangle = \delta_{\alpha, \beta} \qquad (3.13)$$

where the adjoint vectors (solutions of $H_F^\dagger | \lambda_\alpha^\dagger \rangle = E_{\lambda_\alpha}^\dagger | \lambda_\alpha^\dagger \rangle$) are the complex conjugates of the direct eigenvectors: $\left| \lambda_\alpha^\dagger \right\rangle = |\lambda_\alpha\rangle^*$.

The large dimension of the H_F matrix prevents the use of standard algorithms of diagonalization. A truncation of H_F is possible but it produces an 'edge effect' which makes it hard to isolate the quasi-energies E_η which are associated with a single Brillouin zone. Time-dependent methods such as the time-dependent-complex-coordinate-Floquet method (Ben-Tal *et al* 1991) or the complex-scaled-adiabatic-switch method (Ben-Tal *et al* 1993) have been proposed to reduce the computational effort to that needed for the propagation of the Schrödinger equation over one optical cycle. We will now investigate an effective Hamiltonian procedure to handle the H_F eigenproblem.

3.3. The use of projected dynamics in an active space

The exponential form of the evolution operator (equation (3.11)) is appropriate for the dynamical evolution of a quantum system driven by a localized, time-independent Hamiltonian. The semi-classical picture of the interaction of a continuous electric field with a molecule is not normally presented in this context. However, the introduction of a generalized Hilbert space **K**, described using a finite L^2 representation, with $|\alpha, n = 0\rangle$ in place of $\Psi(t = 0)$ and with H_F in place of H, makes possible the treatment of this time-periodic example. In this section we will simply use the generic term H to designate the time-independent matrix which drives the dynamics in this finite representation. This notation covers both the case of equation (2.9) with H and the case of equation (3.11) with H_F.

A technique for evaluating the terms appearing in (3.11) involves partitioning the dynamical space within which the evolution operator acts and then simplifying the relaxation scheme which is deduced from the Schrödinger equation. The choice of the relevant subspace and the construction of the effective Hamiltonian which governs the projected dynamics are both carried out using stationary Bloch wave operator techniques. Intrinsically, we assume the existence of a reduced model space S_o spanned by eigenvectors of $H^o = H_o(q, r) - \mathrm{i} V_{\mathrm{opt}}$ and of a direct correspondence, via the wave operator, between this space and the active space S in which the dynamics is concentrated. These spaces are the analogues for the dynamical problem of the model space A and its associated target space as introduced in section 2 of part I of this review. The formal definition of the model space and its selection are two central points which will be treated in detail in this section. Denoting the projection operator of the model space (which necessarily includes the initial state) by P_o, the operator governing the relaxation issuing from S_o takes the following form for a time increment Δt.

$$U_P(\Delta t) = \exp(-\mathrm{i} H \Delta t / \hbar) P_o. \qquad (3.14)$$

If P_o and Q_o are the projection operators associated with the model space S_o and its complement S_o^+ and P and Q those associated with the target spaces S (also called the active space) and its complement S^+, then the Hamiltonian H and the subsequent relaxation can be decoupled within

the subspaces S_o and S_o^+ by constructing the non-unitary transformation (Jolicard and Grosjean 1991, Jolicard *et al* 1994)

$$T = 1 + X_P + X_Q \tag{3.15}$$

where X_P and X_Q are reduced wave operators of the type introduced in part I, except that two are used, associated with the two subspaces S_o and S_o^+. We set

$$\Omega_P = P(P_o P P_o)^{-1} = P_o + X_P$$
$$\Omega_Q = Q(Q_o Q Q_o)^{-1} = Q_o + X_Q. \tag{3.16}$$

Introducing the inverse of the transformation T, namely

$$T^{-1} = P_o P + Q_o Q \tag{3.17}$$

leads to the rigorous equation

$$U_P(\Delta t) = \Omega_P \exp[-\mathrm{i}(P_o H^{\mathrm{eff}} P_o)\Delta t/\hbar] P_o P P_o$$
$$+ \Omega_Q \exp[\mathrm{i}(Q_o H^{\mathrm{eff}} Q_o)\Delta t/\hbar] Q_o Q P_o \tag{3.18}$$

with

$$H^{\mathrm{eff}} = T^{-1} H T. \tag{3.19}$$

The calculation of Ω_Q in the large space S_o^+ represents a difficult task and equation (3.18) is tractable only if one neglects the relaxation path through the space S_o^+, i.e. if one suppresses the second term on the rhs of equation (3.18). Inspection of equation (3.18) reveals the conditions which can justify this approximation. One can distinguish: (i) the case where the factor $Q_o Q P_o$ is very small (This stationary condition supposes a perturbative regime and leaves out the states which are weakly coupled to the initial state $|\alpha, n = 0\rangle$.), (ii) the case where the dynamical term $\exp[-\mathrm{i}(Q_o H^{\mathrm{eff}} Q_o)\Delta t/\hbar$ produces a negligible contribution. States which, for example, introduce a rapid decay rate, as indicated by negative imaginary components of the diagonal part of $Q_o H^{\mathrm{eff}} Q_o$, belong to this case.

This simplified scheme is completed by introducing the matrix Λ, with columns which are the eigenvectors $|\lambda\rangle$ of H in the active space S. According to the Bloch formulation, the projection $P_o \Lambda P_o$ of Λ into S_o is the matrix which diagonalizes $P_o H^{\mathrm{eff}} P_o$ and Ω_P is the operator which transforms these projected vectors back to the exact eigenvectors:

$$\Lambda P_o = \Omega_P (P_o \Lambda P_o). \tag{3.20}$$

Finally, the introduction of equation (3.20) into equation (3.18) and the expansion of $P_o P P_o$ as $P_o P P_o = (P_o \Lambda P_o) \times (P_o \Lambda P_o)^\dagger$ leads to the result

$$U_P(\Delta t) = \Lambda P_o \exp[-\mathrm{i}(P_o E^{\mathrm{eff}} P_o)\Delta t/\hbar](P_o \Lambda P_o)^\dagger \tag{3.21}$$

where $P_o E^{\mathrm{eff}} P_o$ gives the eigenvalue spectrum of H in the space S_o.

Equation (3.11) must now be reconsidered. The introduction of the eigenvectors of H_F into (3.21) and its use in (3.11) gives the final expression

$$P_{\alpha \to \beta}(\Delta t) = \sum_n \left| \sum_{\eta \in S_o} \langle n, \beta | \lambda_\eta \rangle \langle \lambda_\eta | 0, \alpha \rangle \exp(-\mathrm{i} E_\eta \Delta t/\hbar) \right|^2 \tag{3.22}$$

which reveals that the approximations introduced in this treatment simply involve limiting the exact expansion (3.12) to the eigenvectors $|\lambda_\eta\rangle$ of the active space S.

The preceding developments, from equations (3.11) to (3.22) adopted a purely time-dependent point of view and gave a central role to the evolution operator (equation (3.11)). However, another point of view can be adopted by performing calculations in the complex

energy plane and this is the approach principally developed by P Durand in Toulouse. A Laplace–Fourier transform of equation (2.13) leads to the Green function

$$\phi(z) = \frac{1}{z - H}\phi \tag{3.23}$$

where $\phi(z)$ is the Laplace–Fourier transform of $\Psi(t)$ associated with the initial condition $\Psi(t = 0) = \phi$. By assuming, as previously, the existence of a finite model space S_o corresponding to an active space S, one includes the relevant information in the resolvent projected into this model space (Durand and Paidarovà 1998)

$$\frac{1}{z - H}P_o = \Omega(z)\frac{P_o}{z - H^{\text{eff}}(z)} \tag{3.24}$$

where the wave operator and the effective Hamiltonian have the following definitions in this energy space:

$$\begin{cases} \Omega(z) = P_o + \frac{Q_o}{z - H}HP_o \\ H^{\text{eff}}(z) = P_o H \Omega(z) \end{cases}. \tag{3.25}$$

Various observables can be calculated using this decomposition. For example, the state-to-state probability amplitudes inside the active space are (Durand and Paidarovà 1998)

$$U_{fi}(t) = \frac{1}{2i\pi}\int_C dz \langle \phi_f | \frac{P_o}{z - H^{\text{eff}}(z)} | \phi_i \rangle \exp(-izt/\hbar) \tag{3.26}$$

for a closed integration path C in the complex plane.

This last equation is computationally tractable when the effective Hamiltonian is energy independent. The aim of the theory is thus to select model spaces which include all the relevant states within the energy range of interest in order to reduce the energy dependence of H^{eff}. In the limiting case of a energy-independent effective Hamiltonian, ($H^{\text{eff}}(z) \equiv H^{\text{eff}}$) the transition amplitudes given by (3.26) are identical to those deduced from equation (3.21) and the time and energy formulations become equivalent. The regions of applicability of the two formulations are nevertheless different. The time formulation, which has the advantage of indicating the circumstances which produce a time-independent Hamiltonian (see equation (3.18)) is better adapted to describe systems exhibiting a large energy dispersion. The manipulation of energy-dependent quantities is, on the other hand, of great interest in spectroscopic applications which determine observables such as lineshapes. In a recent publication Durand *et al* (2001) show that the theory of the Fano profiles (Fano 1935, 1961), arising from the interaction between an autoionized state and a continuum can be investigated by a Bloch effective Hamiltonian approach using a two-dimensional model space (two resonances or a resonance and a quasi-bound state) interacting with a non-structured quasi-continuum. This approach seems to offer a promising avenue of research for the study of asymmetric Fano profiles.

3.4. The selection of the active space

The preceding discussion has emphasized the central importance of the selection of the model space S_o. A wrong choice induces a strong energy dependence in equation (3.26) and creates, via the complementary space S_o^+, a second transition path which is too important to be neglected (see equation (3.18)). The selection of S_o constitutes a central problem in degenerate perturbation theory in general and the question is even more intricate when the model space is not just the space into which the reduced quantum information is projected (as in the eigenvalue problem) but is rather a space representing the active space within which the dynamics is confined. For the small test matrices treated in part I it was seen that a poor

(non-perturbative) choice of the model (A) space could be remedied by using sufficiently robust numerical methods when finding eigenvalues. For the dynamical problem the matrices involved are very large complex ones and so the initial choice of a 'good' model space becomes crucial.

Various approaches for a proper definition of S_o have been proposed in the literature. They include the rotating frame approximation (Whaley and Light 1984), the multitier approach (Sibert *et al* 1984), the adiabatic reduced coupled equations method (Voth and Marcus 1986), the low frequency expansion method (Nadler and Marcus 1987) and various artificial intelligence techniques (Tietz and Chu 1983, Chang and Wyatt 1986, Iung and Leforestier 1992) One of the main drawbacks of the majority of these algorithms arises from the energy cutoff criterion which is used to reduce the dimension of the active space. The arbitrary energy cutoff can lead to erroneous results (Iung and Leforestier 1991). From this point of view the algorithm based on the wave operator formalism is more flexible (Jolicard *et al* 1994, Wyatt and Iung 1996). To describe this selection algorithm we will assume that the full Hamiltonian (or the full Floquet Hamiltonian, if one considers the example presented in section 3) is subdivided into two operators H_o and V, with the zero-order Hamiltonian H_o being chosen to describe the system in an approximate but reasonable manner.

According to equation (3.22), the active space is composed of eigenvectors $|\lambda_j\rangle$ of H (or H_F) which have a large projection on the initial state, which is denoted by $|i\rangle$ in the present example (our notations introduce a direct state-to-state correspondence between the H_o eigenvectors $|j\rangle$ and the H eigenvectors $|\lambda_j\rangle$). Because of the symmetry of the Hamiltonian, we can assume a rough proportionality between the amplitude $|\langle i|\lambda_j\rangle|$ and the amplitude $|\langle j|\lambda_i\rangle|$ for each j. In the framework of this approximation the selection procedure is then reduced to the selection of the largest components of $|\lambda_i\rangle$ or of the proportional entity $\Omega|i\rangle$. These components can be obtained by using the RDWA recursive treatment, which is based on the repeated use of the first-order formula for the reduced wave operator, as explained in sections 4.3 and 5.1 of part I. Such an approach leads to the equations:

$$\Omega = P_o + X \quad \text{with} \quad X = \lim_{N \to \infty} X^N$$

$$X^N = X^{N-1} + \sum_{\beta \in S_o^+} |\beta\rangle\langle i| \left(\frac{\langle \beta|H^N|i\rangle}{\langle i|H^N|i\rangle - \langle \beta|H^N|\beta\rangle} \right) \tag{3.27}$$

with

$$H^0 = H \qquad H^N = (1 - X^{N-1})H(1 + X^{N-1}) \quad N > 0. \tag{3.28}$$

Because of near degeneracies, some of the X elements diverge. To overcome this problem, all the partial contributions $X_{\beta,i}^N$ possessing a modulus larger than some upper limit are changed into new values with modulus smaller than this limit by means of a suitable reduction factor, as discussed in section 3.1 of part I, which also explained how for poorly converging iterations the SCM approach can replace the RDWA approach. After a small number N_{it} of iterations, a large number of states $|\beta\rangle$ are connected by the RDWA iteration (more precisely, a state $|\beta\rangle$ participates if at least one path $|i\rangle \to |\beta\rangle$ formed by a sequence of n couplings with $n \leqslant N_{it}$ exists). The states $|\beta\rangle$ are then reordered such that those having the largest magnitudes of X are up near the top of the list and finally the model space S_o, the dimension N_o of which is imposed, is constructed by taking the N_o first vectors.

This procedure, called the wave operator sorting algorithm by Wyatt and Iung, has been tested with success in the study of overtone spectroscopy and of the dynamics of energy flow in benzene (Wyatt *et al* 1992a, 1992b, Wyatt and Iung 1993a, 1993b, Iung and Wyatt 1993). In this application, a very large primitive space ($N \sim 10^{11}$) is reduced to an active space
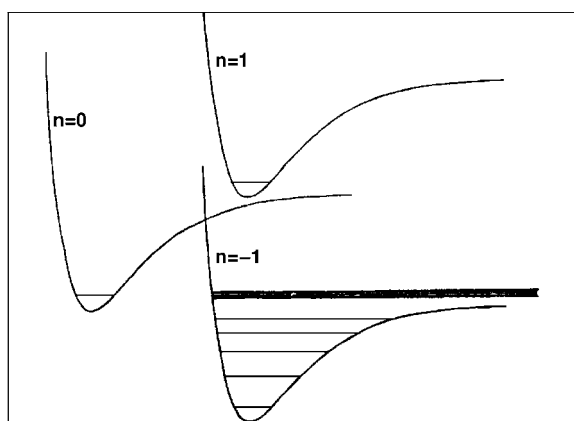
Figure 1. A schematic representation in the dressed picture of the potential surfaces involved in the photodissociation of HF and of the states selected to constitute the model space. The field intensity is $I = 1\,\mathrm{TW\,cm}^{-2}$ and the laser frequency is ω ($\hbar\omega = 0.060\,\mathrm{a.u.} = 13168.5\,\mathrm{cm}^{-1}$).
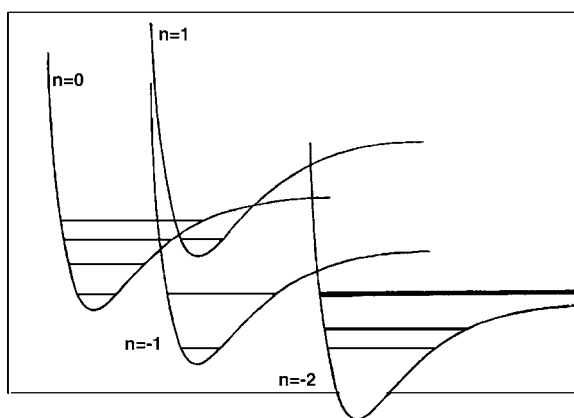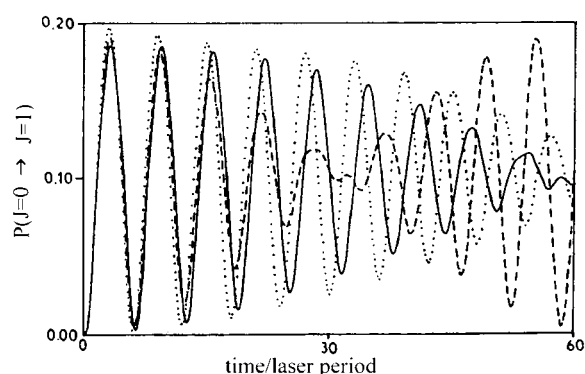

Figure 2. The same as figure 1 but for a laser frequency equal to ω' ($\hbar\omega' = 0.02914\,\mathrm{a.u.} = 6395.5\,\mathrm{cm}^{-1}$). The surface number $n = -2$ is the dressed surface associated with the absorption of two photons.

of about 10^6 elements in which algorithms such as the recursive residue generation method (RRGM) can be used to describe the dynamics.

The two examples which are presented here concern much smaller systems, but nevertheless reveal the essential features of the method. Figures 1 and 2 relate to a model used to test the wave operator sorting algorithm for a photodissociation processes. The wave operator theory and the iterative integration algorithms which are used can use large vector spaces and non-Hermitian Hamiltonians, and their performance is not affected too adversely by the increase of the basis size when more realistic systems are treated. The test model here is a diatomic molecule subjected to a continuous wave laser field. The parameters selected for the ground potential surface and for the transition dipole moment (equation (3.2)) are those of a modified Stine and Noid hydrogen fluoride Morse function (**Stine and Noid** 1979, **Leforestier and Wyatt** 1983). The two figures show schematic representations in the dressed picture of the potential surfaces, for the dressed states which actually participate in the photodissociation. In each case the initial state is $|v = 0, n = 0\rangle$, the laser intensity
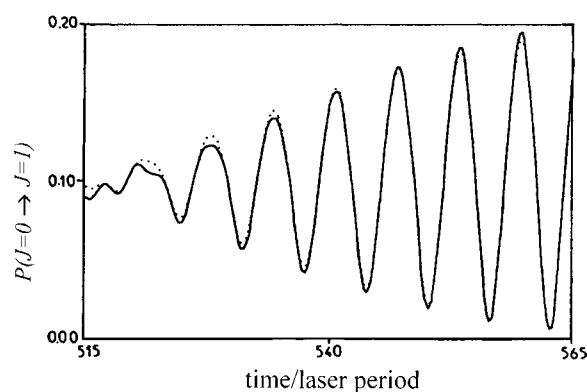
Figure 3. The transition probability $P_{J=0\to J=1}$ as a function of time in laser field periods units. The continuous line corresponds to an exact integration of the Schrödinger equation. Dotted and dashed lines correspond to model spaces of sizes ($N_o = 11$) and ($N_o = 17$) selected with the wave operator theory.

Figure 4. The same as figure 3 but with model spaces of sizes ($N_o = 11$) and ($N_o = 39$) based simply on energy windows.

is $1\,TW\,cm^{-2}$ and the active space dimension is arbitrarily taken equal to 12. In figure 1, the laser frequency ($\omega = 0.060\,a.u.$) produces a direct transition from the ground state to the continuum. In figure 2, the laser frequency ($\omega = 0.02914$) is tuned to the frequency of the bound–bound transition ($v = 0 \to v = 2$). The results show that the selection algorithm is not limited by any criterion based solely on energy. It selects not only states of the continuum which are in near resonance with the initial state but also (sometimes with a greater priority) bound states of the adjacent blocks ($n = -1, n = -2$). This choice of off-resonance bound states is physically understandable, since the photodissociation process principally takes place in the potential well, where the bound states mainly suffice to give a complete basis set.

The pertinence of the selection process is clearly shown in the second example, which involves the inelastic transitions of a rigid rotator subjected to a strong laser field. Figures 3 and 4 correspond to a pure quantum description (see equation (3.1)) of a rigid rotator corresponding to the HF molecule ($\hbar B = 21\,cm^{-1}$, $\mu = 1.91$ Debyes) subjected to an intense electromagnetic field with an intensity of $1\,TW\,cm^{-2}$ and frequency ω ($\hbar\omega = 1500\,cm^{-1}$). The interaction between the field and the rotator is represented by using a product basis $|J, m; n\rangle$ of 220 states, 20 rotational states $0 \leqslant J \leqslant 19$ and 11 field states: $-5 \leqslant n \leqslant 5$. Figures 3 and 4 compare the probability of transition $P_{J=0\to J=1}$ obtained by integration of the

Schrödinger equation in the full space with results obtained using an effective Hamiltonian in reduced model spaces. When a selection process is used within the wave operator theory (figure 3), the results are of high quality after a large number of optical cycles, even when using small model spaces ($N_o = 11$, $N_o = 17$).

By contrast, the use of a basis set corresponding to an energy window centred on the initial state introduces phase errors after a few optical cycles, even when using larger model spaces ($N_o = 11$, $N_o = 39$) (figure 4). This serves to illustrate the point made previously that the wave operator selection process is more flexible and general than one which is crudely based on energy criteria.

4. Temporal analysis of the time-dependent wave operator

The two equations (2.25) and (2.26) are the basic equations needed for the development of the time-dependent wave operator theory. Interesting and sometimes original information concerning adiabatic and non-adiabatic transport mechanisms in time-dependent perturbation theories is implicit in these equations and will be exploited in a discussion of inelastic and photoreactive interactions in section 7. As a first step it is useful to study some properties of the wave operator $\Omega(t, 0)$ and in particular its relationship in the adiabatic limit with the stationary Bloch wave operator.

4.1. From the time-dependent wave operator to the stationary one

A preliminary inspection of (2.25) reveals that the term $U(t, 0; H^{\text{eff}})$ describes a first evolution step within the active space S_o, while the off-diagonal part of the second acting term (involving X) describes a transition from S_o to the complementary space without any reverse path (a reverse path would involve $P_o U Q_o$). One can then expect, by a good choice of S_o, to concentrate into the first term $U(t, 0; H^{\text{eff}})$ the fast evolution which the time-dependent Hamiltonian produces between states which are in near resonance or are strongly coupled, separating out in this way the fast and the adiabatic evolutions. In other words, we approach the problem of the relationships between the time-dependent wave operator and the Bloch wave operator at the adiabatic limit. This problem has been analysed (Jolicard 1989, Jolicard and Austin 1991a) by adapting the RDWA method for this time-dependent problem. At the Nth order of this time-dependent RDWA one has

$$
\begin{cases}
U(t, 0; H) P_o = (P_o + X^N(t, 0)) U(t, 0; H^N) P_o \\
H^N = (1 - X^N) H (1 + X^N) - i\hbar \frac{\partial X^N}{\partial t} \\
X^N = \mathbf{R}^{-1} \left(\frac{1}{i\hbar} \int_0^t \mathbf{R} \left(\sum_{n=0}^{N-1} Q_o H^n P_o \right) dt' \right)
\end{cases}
\tag{4.1}
$$

where $H^{N=0}$ is the initial H matrix and $\mathbf{R}$ is a phase adding operator defined by

$$
\mathbf{R}(A) = \exp\left(\frac{i}{\hbar} \int_0^t H_{\text{diag}} \, dt' \right) A \exp\left(-\frac{i}{\hbar} \int_0^t H_{\text{diag}} \, dt' \right).
\tag{4.2}
$$

In equation (4.1) the term $-i\hbar \partial X^N / \partial t$ is obtained by using

$$
-i\hbar \frac{\partial X^N}{\partial t} = [X^N, H_{\text{diag}}] + \sum_{n=0}^{N-1} Q_o H^n P_o.
\tag{4.3}
$$

The adiabatic limit is reached by introducing the perturbation $V \equiv H - H_o$ adiabatically between the times $t = -\infty$ and $t = 0$ according to the equation

$$
H(t) = \lim_{\gamma \to 0^+} (H_o + V \exp(\gamma t)).
\tag{4.4}
$$

In this limit the frequencies which characterize the inelastic transitions $S_o \rightarrow S_o^+$ are large compared to the frequencies ω_p appearing in the spectrum of the time-dependent perturbation $V(t)$:

$$\frac{|H_{jj} - H_{\alpha\alpha}|}{\hbar} \gg \omega_p \tag{4.5}$$

where j labels states of the model space and α states of the complementary space. Fortuitous exact resonances $H_{jj} = H_{\alpha\alpha}$ can destroy this inequality, but this difficulty is easily overcome by incorporating the offending resonant state α in the model space.

The time integrals which are present in the expression for X^N in equation (4.1) are calculated using the identity

$$I(t, \omega) = \int_{-\infty}^{t} F(t') \exp(i\omega t') \, dt'$$

$$= \exp(i\omega t) \left[\frac{-i}{2\pi} \mathbf{P} \int_{-\infty}^{+\infty} \frac{f(\omega') \exp(-i\omega' t)}{\omega - \omega'} \, d\omega' \right] + \frac{1}{2} f(\omega) \tag{4.6}$$

where f designates the Fourier transform of F and $\mathbf{P}$ the Cauchy principal part. In the adiabatic limit ($\omega \rightarrow \infty$) equation (4.6) leads to the result

$$\lim_{\omega \rightarrow \infty} I(t, \omega) = \exp[i(\omega t - \pi/2)] \frac{F(t)}{\omega}. \tag{4.7}$$

Introducing this result into the expression for X^1 in equation (4.1) and subsequently into those for X^N, $(N > 1)$, leads to the approximation

$$X \simeq \sum_{\alpha \in S_o^+} \sum_{j \in S_o} |\alpha\rangle \langle j| \left(\frac{\sum_n \langle \alpha | H^n | j \rangle}{H_{jj} - H_{\alpha\alpha}} \right). \tag{4.8}$$

This result is nearly identical to that for the RDWA series which gives the reduced Bloch wave operator at time t (i.e. with $H = H(t)$). One then observes that, at the adiabatic limit, the time-dependent wave operator is transformed into a temporal succession of instantaneous Bloch wave operators. The only time dependence surviving in equation (4.8) is the adiabatic one included in $H^n(t)$. The introduction of (4.8) into (4.3) then gives the consistent result $\partial X^N / \partial t = 0$ associated with the static case.

Finally, by assuming that the RDWA series converges in the limit $N \rightarrow \infty$, our development makes the lhs of equation (2.26) vanish and transforms this equation into the equation defining the reduced Bloch wave operator. By introducing the adiabatic evolution parameter $s = \lim_{\gamma \rightarrow 0^+} \exp(\gamma t)$, $-\infty \leqslant t \leqslant 0$ (see equation (4.4)), and the time duration T of the perturbation, one can then summarize this result by the formal equation:

$$\lim_{T \rightarrow \infty} U_T(s) (P_o U_T(s) P_o)^{-1} = P(s)(P(0) P(s) P(0))^{-1}. \tag{4.9}$$

This last equation is a generalized form of the adiabatic theorem (Messiah 1964). It involves the wave operator $\Omega(s)$ whereas the usual adiabatic theorem treats a single eigenstate $|\lambda_i(s)\rangle$ which is assumed to be well isolated during the evolution. In the present formulation it is not supposed that the states of the model space are individually isolated during the evolution but more simply that the eigenvalues of the model space do not cross the eigenvalues of the complementary space during the evolution (Nenciu 1980, Nenciu and Rasche 1992). Thus a constraint on individual states is replaced by a less onerous constraint on two groups of states.

The wave operator formalism should nevertheless be used with caution because of the intermediate normalization condition satisfied by Ω. Consider, for example, the adiabatic evolution of a state which begins as an eigenvector $|i\rangle$ of H_o at $t = -\infty$. If the eigenvalue is

isolated during the evolution, then the adiabatic evolution produces a series of instantaneous eigenvectors.

$$U(t, -\infty; H)|i\rangle = |\lambda_i(t)\rangle \exp(\mathrm{i}\phi(t)) \tag{4.10}$$

where the phase $\phi(t)$ is the sum of the dynamical phase and the Berry geometrical phase (Berry 1984, 1990)

The same evolution, when described by the full wave operator formalism, leads to the result

$$U(t, -\infty; H)|i\rangle = \Omega(t)|i\rangle \exp\left[\frac{1}{\mathrm{i}\hbar} \int_{-\infty}^{t} H^{\mathrm{eff}}(t')\,\mathrm{d}t'\right]. \tag{4.11}$$

As the definition of Ω imposes the constraint $\langle i|\Omega(t)|i\rangle = 1$ at any time, it might seem that the unitarity of the evolution operator is not preserved. In fact, Ω is a non-unitary transformation which generates complex effective Hamiltonians. At the adiabatic limit, the complex contribution $(\mathrm{Im}(H^{\mathrm{eff}}))$ tends to zero but still gives a finite integral over the interval $]-\infty, t]$ (Jolicard and Grosjean 1985); this produces the term $\exp(1/\hbar \int \mathrm{Im}(H^{\mathrm{eff}})\,\mathrm{d}t')$ which imposes the unitarity. The demonstration of the conservation of the norm in equation (4.11) is not straightforward in the general case. Nevertheless, for a one-dimensional model space, one has a simple relationship between the wavefunction and the wave operator

$$\Omega(t) = \frac{|\Psi(t)\rangle\langle i|}{\langle i|\Psi(t)\rangle}. \tag{4.12}$$

In this case, the use of equations (2.25) and (4.12) gives for the phase term the result

$$\exp\left\{\frac{1}{\mathrm{i}\hbar} \int^{t} H^{\mathrm{eff}}\,\mathrm{d}t'\right\} = \exp\left\{\int^{t} \frac{\mathrm{d}}{\mathrm{d}t'} \ln(\langle i|\Psi(t')\rangle)\,\mathrm{d}t'\right\}. \tag{4.13}$$

This shows that the phase term exactly compensates the intermediate normalization factor $1/\langle i|\Psi(t)\rangle$ present in the expression for $\Omega(t)$ (equations (4.11) and (4.12)).

$$|U(t, -\infty; H)|i\rangle|^2 = \frac{\||\Psi(t)\rangle\|^2}{|\langle i|\Psi(t)\rangle|^2} \left|\exp\left(\frac{1}{\mathrm{i}\hbar} \int_{-\infty}^{t} H^{\mathrm{eff}}(t')\,\mathrm{d}t'\right)\right|^2 = \||\Psi(t)\rangle\|^2 \tag{4.14}$$

and that finally the wave operator formulation does not modify the norm of the wavefunction.

The separation between the fast dynamical processes described by the term $U(t, 0, H^{\mathrm{eff}})$ (cf equation (2.25)) and the more adiabatic contributions described by $\Omega(t, 0)$ is a fundamental feature of the wave operator theory, with major consequences both for the understanding of quantum dynamics and for the numerical integration procedures. In the case of a one-dimensional model space, this feature reveals itself via the presence of a term $\Omega(t)|i\rangle$, whose time variation essentially depends on the perturbation $V(t)$, and also a rapid phase factor $\exp\left(\int E^{\mathrm{eff}}/(\mathrm{i}\hbar)\,\mathrm{d}t\right)$ which principally depends on the unperturbed spectrum. This can be easily understood by considering equation (4.12). The division by $\langle i|\Psi(t)\rangle$ on the rhs of this equation cancels the common phase term present in $\Psi(t)$ and so concentrates into $\Omega(t)|i\rangle$ the smoother relative evolutions of the different components.

The wave operator theory generalizes this case to degenerate model spaces by offering the possibility of collecting into $\exp\left(\int H^{\mathrm{eff}}/(\mathrm{i}\hbar)\,\mathrm{d}t\right)$ the rapid phase terms (including eventually exponentially decreasing terms) which are produced by strong and near-resonant couplings inside S_o. With a good choice of S_o all the time dependence is extracted from Ω, except for an adiabatic one which is generated by the perturbation itself.

An important feature is that this partition between fast and adiabatic terms, which is obviously relevant at the adiabatic limit, is maintained even outside the purely adiabatic regime. Various applications confirm this point by revealing that the Fourier transform of

$\Omega(t)$ essentially overlaps the spectrum of the perturbation $V(t)$ and does not include the high frequencies $\omega_{j\alpha}$ which characterize the spectrum of the non-perturbed system. These high frequencies and also the fast evolution which appears inside the quasi-degenerate model space are introduced by the separated phase term $\left(\exp\left(\int H^{\text{eff}}/(i\hbar)\,dt\right)\right)$. The linearly perturbed harmonic oscillator is a good illustration of this feature. The Hamiltonian of this analytically solvable system is

$$H(t) = H_o + F(t)V = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + \frac{1}{2}kr^2\right) + F(t)\sqrt{\frac{\hbar}{m\omega}}r. \qquad (4.15)$$

$F(t)$ is an integrable function which is non-zero only for a finite interval of time $[0, T]$ and the oscillator of frequency ω is initially in its ground state $|i = 0\rangle$. The analytical integration of the TDSE and the expansion of the solution in the harmonic oscillator basis set gives

$$\Psi(t) = \sum_{n=0}^{\infty} c_n(t)|n\rangle \qquad (4.16)$$

with

$$\begin{cases} c_n(t) = \exp\mathcal{G}(t)\exp\left(-i\left(n+\frac{1}{2}\right)\omega t\right)\frac{(\mathcal{F}(t))^n}{\sqrt{n!}} \\ \mathcal{F}(t) = \frac{1}{i\hbar}\int_0^t F(t')\exp(i\omega t')\,dt' \\ \mathcal{G}(t) = \left(\frac{1}{i\hbar}\right)^2 \int_0^t F(t')\exp(-i\omega t')\,dt'\int_0^{t'} F(t'')\exp(i\omega t'')\,dt''. \end{cases} \qquad (4.17)$$

For the same problem, the integration of the wave operator equation (2.26) leads to

$$\begin{cases} \Omega(t) = \sum_{n=0}^{\infty} d_n(t)|n\rangle\langle i=0| \\ d_n(t) = \exp(-in\omega t)\left(\frac{(\mathcal{F}(t))^n}{\sqrt{n!}}\right) \end{cases} \qquad (4.18)$$

the effective energy being given by

$$\begin{aligned} E^{\text{eff}}(t) &= \langle i|H^{\text{eff}}(t)|i\rangle \\ &= \frac{\hbar\omega}{2} + \frac{1}{i\hbar}F(t)\exp(-i\omega t)\int_0^t F(t')\exp(i\omega t')\,dt'. \end{aligned} \qquad (4.19)$$

The approximation (4.7) is valid not only at the pure adiabatic limit but also as soon as ω is large compared to the frequencies which are present in the spectrum $f(\omega')$ associated with $F(t)$. Using this approximation in (4.18) and (4.19) leads to the results

$$\begin{aligned} d_n(t) &\simeq \frac{(-1)^n}{\sqrt{n!}}\left(\frac{F(t)}{\hbar\omega}\right)^n \\ E^{\text{eff}}(t) &\simeq \frac{\hbar\omega}{2} - \frac{(F(t))^2}{\hbar\omega}. \end{aligned} \qquad (4.20)$$

The expansion coefficients do not include any high frequency phase terms; their time dependence is simply governed by the coupling term $F(t)$. The high transition frequency ω is introduced separately via $E^{\text{eff}}(t)$. By contrast, the wavefunction mixes these different contributions and the expansion coefficients $c_n(t)$ of the wavefunction in equation (4.17) introduce a phase term $\exp i(-\omega t/2 + \int^t (F(t')/\hbar)^2/\omega\,dt')$ with a major contribution which depends linearly on the transition frequency ω.

4.2. The evolutive active space

Equations (4.1) form a self-consistent group of equations which can be used to propagate the solution of the TDSE. The originality of this approach is that it permits iterative treatments of

the integration process. When the system manifests a strongly adiabatic character, i.e. when the time-dependent perturbation evolves slowly within the time scale of the unperturbed system, the evolving state vector remains trapped in a small active space. This is a favourable situation for the use of the wave operator approach, which is well able to describe purely adiabatic time evolutions or even intermediate situations in which the evolution combines rapid changes inside a small quasi-degenerate active space with an adiabatic evolution between this space and its complementary space. Similar features are shown by the adiabatic formulation of Nguyen-Dang (Nguyen-Dang 1989, Nguyen-Dang *et al* 1991), even though the two theories are different.

In other cases, the definition of an appropriate active space can be more complicated. Difficulties can result from the chaotic nature of the system and/or from an inappropriate choice of the basis set. If, for example, one uses a DVR spatial grid basis $\{|i\rangle, i = 1$ to $N\}$ to span the whole vector space S, then the initial function commonly has a large set of non-zero coefficients, the dispersion of which increases during the propagation of the wave packets under the influence of the kinetic couplings. This is not consistent with the wave operator formalism, which, to be tractable, should assume that the initial wavefunction $|\Psi(t = 0)\rangle$ belongs to a small subspace. Nevertheless, this serious difficulty can be partially overcome by some simple adaptations.

A first obvious adaptation is to integrate the basic equation (2.26) with the iterative procedure (4.1) over a small time interval Δt, repeating this elementary procedure step by step on the whole time interval $[0, T]$.

A second less simple adaptation is to define at each time step a new non-orthogonal basis $\{|i'\rangle, i' = 1$ to $N\}$:

$$\begin{cases} |i'\rangle = |i\rangle & i \neq l \\ |l'\rangle = |\Psi(t)\rangle \end{cases} \tag{4.21}$$

where the index l denotes the vector which has the largest modulus $|\langle l|\Psi(t)\rangle|$ in the orthogonal basis. In this new representation the initial wavefunction for the next step is identical to the lth basis vector. The model space is thus permanently a one dimensional space. The non-linear equation which drives the wave operator in this representation is identical to (2.26), but with a new Hamiltonian

$$H = B^{-1}HB \tag{4.22}$$

in place of H. The transformation matrix B and its inverse are, in fact, given by simple expressions which facilitate a fast recalculation of H at each step:

$$\begin{cases} B_{jk} = \delta_{jk} \leftrightarrow B_{jk}^{-1} = \delta_{jk} & \text{for } k \neq l \\ B_{jl} = \langle j|\Psi(t)\rangle \leftrightarrow B_{jl}^{-1} = -B_{jl}/B_{ll} & \text{for } j \neq l \\ B_{ll} = \langle l|\Psi(t)\rangle \leftrightarrow B_{ll}^{-1} = 1/B_{ll}. \end{cases} \tag{4.23}$$

This variable representation approach has been tested with success on the 1D propagation of Gaussian wave packets and on the two-colour IR multiphoton dissociation of diatomic molecules (Jolicard and Austin 1991b). It generates couplings which involve complex variables but reduces the amplitudes of the non-diagonal elements and systematically increases the separation between the diagonal elements.

A third form of adaptation exploits the properties of equations (4.1). It is not necessary to start the iteration with $H^{N=0} = H$, i.e. with $X^{N=0} = 0$; the recursion permits the introduction of an arbitrary initial trial wave operator. This feature is particularly interesting when H exhibits rapid time modulations of small amplitude as a kind of background noise around smoothly varying couplings. In such a case one can select relatively large time steps and

calculate a coarse grained solution with the usual algorithms such as the Chebyshev method (Kosloff 1988, Leforestier *et al* 1991) or the Lanczos method (Park and Light 1986), later using this preliminary result as a trial solution in the Bloch recurrence procedure to improve the solution.

5. Analyses in an extended Hilbert space and the generalized Green function approach

In this section we will investigate the integration of the basic equation (2.26) when $H(t)$ is either periodic or possesses a finite duration T. The interaction of molecules with cw laser fields or with short laser pulses as well as inelastic molecular collisions (without orbiting effects) are typical phenomena requiring such a theoretical approach for their description. The basic equation of motion (2.26) for the time-dependent wave operator is a time evolution equation within the usual Hilbert space. After the introduction of the Floquet operator $H_F = H - i\hbar\partial/\partial t$ and of a generalized Hilbert space, formed by the product of the usual Hilbert space with the vector space arising from the time variable t (see section 3), (2.26) can be re-written as

$$H_F(t)\Omega(t) = \Omega(t)H_F^{\text{eff}}(t) = \Omega(t)H_F(t)\Omega(t). \tag{5.1}$$

The equivalence between (2.26) and (5.1) is easily verified by working out the two sides of (5.1), using identities such as $P_o\frac{\partial}{\partial t}(P_o + Q_0 X(t)P_o) = 0$ and finally by multiplying the two members on the left by Q_o.

As previously noted, a discretization of the molecular continua can be introduced by using optical potential techniques. For the new variable t, $(0 \leqslant t \leqslant T)$, a box normalization can be used, since the Hamiltonian is purely T-periodic or is dressed on a finite time interval. Such procedures transform the rigorous equation (5.1) into an approximate finite matrix equation in which the time t is a new variable of the extended Hilbert space and is treated on the same footing as the molecular variables. However, in spite of its form, equation (5.1) cannot be regarded as an eigenvalue equation, except for the very special situation in which H_F^{eff} is time independent. As the operator H_F is a non-local operator with respect to the time, it is also impossible to regard this equation as a simple juxtaposition of instantaneous eigenvalue equations at successive instants. Despite these complications, the theory is sufficiently flexible to have led to significant progress in the understanding of quantum adiabatic transport processes.

The feature which is most useful from a calculational point of view is that the fundamental equation (5.1) of the time-dependent wave operator theory is identical to the fundamental equation of the Bloch wave operator theory if the Floquet Hamiltonian H_F (working in the generalized Hilbert space) is taken in place of the usual Hamiltonian H.

5.1. The time and the energy points of view

The correspondence between the dynamics described in the usual Hilbert space by H and that described in the extended Hilbert space by H_F has been exploited by different authors. The (t, t') theory of Peskin and Moiseyev (1993), which is closely related to the Fock–Schwinger proper-time method (Itzykson and Zuber 1980), exploits this similarity and constructs solutions of the time-dependent Schrödinger equation by using techniques previously developed for the time-independent one, with applications to multiphoton ionization processes (Peskin *et al* 1994a) and to reactive diffusion processes (Peskin and Miller 1995).

This theory uses the following equation to connect the Schrödinger wavefunction $\Psi(t)$ to the (t, t') wavefunction $\Psi(t, t')$ in the extended Hilbert space:

$$\Psi(t) = \Psi(t', t)|_{t'=t} = [\exp\{-iH_F(t')t/\hbar\}\Psi(t=0)]_{t'=t}. \tag{5.2}$$

This similarity has also been exploited by Durand (e.g., Durand and Paidarovà 1998) in an original treatment using an energy space representation. By introducing the unit step function $\Theta(t)$ and the initial wavefunction ϕ, Durand starts from the evolution equation:

$$\left(H(t) - i\hbar\frac{\partial}{\partial t}\right)\Theta(t)\Psi(t) = -i\hbar\delta(t, 0)\phi \tag{5.3}$$

which generalizes the Green's function equations (2.11) and (2.12) to the case of a time-dependent Hamiltonian. The definition of the square-integrable wavefunction: $\phi(t) = \lim_{\epsilon\to 0}\exp(-\epsilon t/\hbar)\Theta(t)\Psi(t)$ and of a partial energy-dependent solution $\phi(E, t)$, corresponding to the use of a delocalized initial function $\exp(-iEt/\hbar)\phi$ instead of $\delta(t)\phi$, leads to the formal solution in energy space:

$$\phi(z, t) = \frac{1}{z - H_F}\phi \tag{5.4}$$

with $z = E + i\epsilon$. The time-dependent wavefunction $\phi(t)$ is then recovered by means of an inverse Laplace–Fourier transformation.

The analyses made by Durand prove that the function $\phi(z, t)$ directly corresponds to the wavefunction $\Psi(t', t)$ (equation (5.2)) of the Peskin–Moiseyev (t, t') theory via an inverse Laplace–Fourier transform. Modifying the dynamical theory to introduce a set of n states ϕ_i, forming a model space S_o, allows the transformation of the rhs of equation (5.4) to give the more tractable expression:

$$\frac{1}{z - H_F}P_o = \Omega(z)\frac{P_o}{z - H_F^{\text{eff}}(z)} \quad \text{with} \quad H_F^{\text{eff}}(z) = P_oH_F\Omega(z). \tag{5.5}$$

In this energy version of the theory one can note, just as in the time version, the similarity between the Bloch and the time-dependent wave operator equations through the simple substitution $H \to H_F$ (compare equations (3.24) and (5.5)). In fact, equation (5.1) is perfectly equivalent to the group of equations (5.4) and (5.5). Nevertheless, the choice of which point of view to adopt is not entirely arbitrary. The present formalism is aimed at the study of processes involving time-dependent Hamiltonians for which the total energy is usually not conserved. In the case of large dispersions, it is better to adopt the time-dependent point of view and to integrate equation (5.1), despite the attractive simplicity of equation (5.5). The integration of (5.4) and (5.5) is, in fact, a considerable task when the energy dispersion generated during the evolution process is large.

There are, however, some specific problems for which a time-independent approach is appropriate. Scattering processes occurring over a finite time interval $[0, T]$, with a time-dependent Hamiltonian for which $V(t = 0)$ and $V(t = T) = 0$, can be formally described using stationary formalisms if one assumes that the molecular system is initially in a stationary state of H_o, i.e.

$$e^{iEt/\hbar}\Psi(t)|_{t\to 0} \to \phi_{E_i}^i \tag{5.6}$$

where

$$H_o(q)\phi_{E_i}^i(q) = E_i\phi_{E_i}^i(q). \tag{5.7}$$

A total energy E in the extended Hilbert space can be defined in this case and the S matrix elements can be expressed by using the full Green operator

$$G(E) = (E - H_F + i\epsilon)^{-1}. \tag{5.8}$$

The S matrix elements are (Peskin and Miller 1995)

$$S_{f,i} = \delta_{f,i} - 2i\pi \langle\!\langle \phi_{E_f}^f, E - E_f | (H_F - E) + (H_F - E)G(E)(H_F - E) | \phi_{E_i}^i, E - E_i \rangle\!\rangle. \quad (5.9)$$

The main problem associated with this L^2 formulation of quantum scattering is that a finite basis set of functions which are computationally convenient for matrix calculations might be poor at representing the required asymptotic behaviour of the scattering stationary states. More precisely, the basis functions decay asymptotically to zero when a (DVR) is used, or are periodic in time when a Fourier basis set is used (Kosloff and Kosloff 1983, Bačić and Light 1989). This is contrary to the required behaviour of the scattering states, which as $t' \to \infty$ should only contain the incoming wave $\exp\{i(E - E_i)t'/\hbar\}$ along the time coordinate. These fundamental difficulties were analysed by Peskin and were overcome by the introduction of smooth time-dependent imaginary valued boundary operators (Peskin and Miller 1995)

$$\epsilon(t) = \epsilon_i(t) + \epsilon_f(t). \quad (5.10)$$

In this framework the operator identities established by Seideman and Miller (1992) and Thompson and Miller (1993) can be used to give a simplified expression for the S matrix:

$$S_{f,i} = S_{f,i}^o + 2i\pi \langle\!\langle \phi_{E_f}^f | i\epsilon + i\epsilon G(E)\epsilon | \phi_{E_i}^i \rangle\!\rangle. \quad (5.11)$$

An alternative approach is to solve the inhomogeneous Schrödinger equation which includes the correct asymptotic conditions (Peskin *et al* 1995).

$$[E - H_F + i\epsilon(t)]e^{iEt/\hbar}\Psi(t) = i\epsilon_i(t)\phi_{E_i}^i + i\epsilon_f(t)\phi_{E_f}^f. \quad (5.12)$$

In this context the wave operator theory represents a new technique of integration of the TDSE, and is currently in development; the factorization result described by equation (5.5) illustrates its potentiality and the simplifications which it can introduce. By directly using the time-dependent equation (5.1) and exploiting the similarity between this equation and the Bloch equation for the stationary case one can investigate efficiently the adiabatic transport mechanisms associated with photoreactive control processes and describe, in a single treatment, rapid evolutions inside the model space plus transition processes between this space and the complementary space. Two techniques of integration are investigated in the following sections. Sections 5.2 and 5.3 introduce an expansion on the complete basis set of Floquet eigenstates in the generalized Hilbert space and explore the relationship between the number of eigenstates actually taking part in the dynamics and the time dependence of the effective Hamiltonian. Section 5.4 generalizes the Green function approach to a situation involving an explicitly time-dependent effective Hamiltonian.

5.2. Wavefunction expansion using a basis of Floquet eigenstates

The presence of the Floquet Hamiltonian $H_F(t) = H(t) - i\hbar \partial/\partial t$ in equation (5.1) suggests the introduction of a complete basis set for the generalized Hilbert space $\mathbf{K}$ (equation (3.3)), a suitable basis being formed by the Floquet eigenstates $\{\lambda\}$ which belong to this space. The existence of these eigenstates is proved by the Floquet theorem, which assumes that the perturbation terms are periodic in time. This requirement of time periodicity is not still rigorously fulfilled in the examples analysed in section 7, i.e. the semi-classical description of inelastic molecular collisions and of the photodissociation produced by short laser pulses. In these cases, the perturbation $V(t)$ has the general form:

$$V(t) = \sum_i A^i \left(q, \frac{\partial}{\partial q} \right) F^i(t) \quad (5.13)$$

where the terms A^i represent quantum mechanical operators depending both on the quantum variables q and on the associated momenta $-i\hbar\partial/\partial q$ and $F^i(t)$ is a pure time function introduced by the semi-classical treatment of the collision or by the use of intermediate representations. $V(t)$ in (5.13) is not periodic. Nevertheless, if one supposes that the perturbation vanishes at the two boundaries of the time interval $[0, T]$, i.e. $V(0)$ and $V(T) = 0$, one can regard $V(t)$ as the first cycle of a periodic function with period T. This is, of course, just a mathematical artefact, with all physical interpretations taking place within the first period $(t \leqslant T)$. The principal consequence of this procedure is the existence of a complete set of eigenvectors λ_η of H_F in $\mathbf{K} = \mathbf{H} \otimes \mathbf{L}_2(\theta/2\pi)$ where the period $\theta = 2\pi$ corresponds to the full duration of the interaction. The eigenvectors obey the equation

$$H_F\left(q, \frac{\partial}{\partial q}, t\right)\lambda_\eta(q, t) = E_\eta\lambda_\eta(q, t) \tag{5.14}$$

and satisfy the orthonormality condition (Chu 1989)

$$\langle\langle\lambda_\eta|\lambda_{\eta'}\rangle\rangle = \frac{1}{T}\int_0^T dt \, \langle\lambda_\eta(q, t)|\lambda_{\eta'}(q, t)\rangle = \delta_{\eta\eta'}. \tag{5.15}$$

In this section we denote by $\{j, n\}$ the unperturbed basis consisting of the product of a complete set of H_o molecular eigenstates $\{j\}$ and of the Fourier functions $\{n\}$ with $\langle t|n\rangle = \exp(in\theta(t))$. We also assume an arbitrary phase between the initial molecular state and the perturbation by selecting the state $|i, n = 0\rangle$ as initial state. The expansion of the wavefunction $|\Psi(t)\rangle$, which obeys $H_F|\Psi(t)\rangle = 0$, leads to the equation

$$|\Psi(t)\rangle = \sum_\lambda e^{-iE_\lambda t/\hbar}|\lambda(t)\rangle\langle\langle\lambda|i, n = 0\rangle\rangle. \tag{5.16}$$

This result from dynamical theory shows the same apparent simplicity for the expansion of $|\Psi(t)\rangle$ on H_F eigenvectors as exists for the case of time independent Hamiltonians. This is nevertheless only a formal appearance. The time dependence is not only concentrated in the complex phase terms $\exp(-iE_\lambda t/\hbar)$ but also in the eigenvectors, which are functions of time, even if $|\lambda(t = 0)\rangle = |\lambda(t = T)\rangle$. Another difficulty comes from the large dimension of the $\mathbf{K}$ space. Equation (5.16) is tractable only if the number of H_F eigenstates which effectively participate in the time development is very small and this is, unfortunately, not *a priori* the case. In this equation, a convenient labelling of the Floquet eigenstates $|\lambda_{j,n}\rangle$ can be produced by using the two indices j and n referring to the non-perturbed system. This choice assumes a state-to-state correspondence between the non-perturbed states (eigenvectors of $H_o - i\hbar\partial/\partial t$) and the Floquet eigenstates:

$$(j, n) \Longleftrightarrow \lambda_{j,n}. \tag{5.17}$$

This correspondence is established in the context of a perturbation approach by adiabatically transforming $H_F^o = -i\hbar\partial/\partial t + H_o$ into $H_F = -i\hbar\partial/\partial t + H$. The introduction of the new indices into (5.16) leads to

$$|\Psi(t) = \sum_j \sum_{m=0}^{N-1} e^{-iE_{\lambda_{j,m}}t/\hbar}|\lambda_{j,m}(t)\rangle\langle\langle\lambda_{j,m}|i, n = 0\rangle\rangle. \tag{5.18}$$

The number of states resulting from the double sum over j and m is thus very large, being equal to the product of the number of states in the molecular basis and the number of Brillouin zones selected to represent the time variation. The calculation of so many eigenvectors is too large a task. One can nevertheless drastically reduce the number of Floquet states by taking into account the periodicity of the Hamiltonian, which implies the relationships:

$$\begin{cases} \langle\langle\lambda_{j,m}|i, n\rangle\rangle = \langle\langle\lambda_{j,0}|i, n - m\rangle\rangle \\ E_{\lambda_{j,n}} = E_{\lambda_{j,0}} + n\hbar 2\pi/T. \end{cases} \tag{5.19}$$

By substituting equation (5.19) into (5.18) one can remain in the first Brillouin zone, though from a purely formal point of view the higher Brillouin zones are included in the summation over m in the following expression:

$$|\Psi(t)\rangle = \sum_j e^{-iE_{\lambda_{j,0}}t/\hbar} \sum_{m=0}^{N-1} \langle\langle\lambda_{j,0}|i,-m\rangle\rangle \sum_{k=-m}^{N-1-m} e^{i2\pi kt/T} \langle k|\lambda_{j,0}\rangle. \tag{5.20}$$

Finally, by taking into account the periodic property, $\langle n|\lambda\rangle = \langle n \pm N|\lambda\rangle$, in $\mathbf{L}_2(d\theta/2\pi)$ and by assuming that the number N of Brillouin zones is large enough to suppress any edge effects, one can write (5.20) more simply as

$$|\Psi(t)\rangle = \sum_j e^{-iE_{\lambda_{j,0}}t/\hbar}|\lambda_{j,0}(t)\rangle\langle\lambda_{j,0}(t=0)|i\rangle \tag{5.21}$$

where all the Floquet eigenvectors which contribute belong to the first Brillouin zone. At this point, the main problem is to discover how many vectors $\{j\}$ of this zone really contribute appreciably to $|\Psi(t)\rangle$. This question has a double interest because it also concerns the degree of adiabaticity of the process, e.g., the answer to questions such as: at the final time $t = T$ does the system remain in the initial state $|i\rangle$ or has it spread out over many states $|k\rangle$? By introducing the identity

$$|\lambda_{j,0}(t=0)\rangle = |\lambda_{j,0}(t=T)\rangle \tag{5.22}$$

in (5.21) one obtains the result

$$\Psi(t) = \sum_k c_k(t)|k\rangle$$

$$\text{with} \quad c_k(t=0) = \sum_j \langle k|\lambda_{j,0}(t=0)\rangle\langle\lambda_{j,0}(t=0)|i\rangle$$

$$\text{and} \quad c_k(t=T) = \sum_j e^{-iE_{\lambda_{j,0}}T/\hbar}\langle k|\lambda_{j,0}(t=0)\rangle\langle\lambda_{j,0}(t=0)|i\rangle. \tag{5.23}$$

It is evident by considering (5.23) that the adiabatic situation (i.e. $c_k(t=0) = c_k(t=T) = \delta_{k,i}$) corresponds to a situation for which a unique state $|\lambda_{i,0}\rangle$ is present, characterized by the asymptotic conditions: $\langle k|\lambda_{i,0}(t=0)\rangle = \langle k|\lambda_{i,0}(t=T)\rangle = \delta_{i,k}$. In contrast, a development to which several states $|\lambda_{j,0}\rangle$ contribute cannot simultaneously satisfy the requirement $c_k(t=0) = \delta_{i,k}$ imposed by the initial conditions and the condition $c_k(t=T) = \delta_{i,k}$, because of the presence of the complex phase factors $\exp(-iE_{\lambda_{j,0}}T/\hbar)$. The degree of degeneracy of the active space spanned by the states $|\lambda_{j,0}\rangle$ is thus correlated with the degree of non-adiabaticity of the process.

The choice of the model space states is obviously of prime importance. For purely inelastic molecular collisions the molecular states $|k\rangle$ which are eigenstates of H_o are bound states of the two isolated molecules. In the case of reactive processes scattering states and shape and Feshbach resonances also participate, but the discretization of the continua requires the introduction of complex transformations in order to reproduce the non-Hermitian character of the Hamiltonian when resonance states are considered. In the context of complex scaling methods, the complex coordinate method (CCM) (Baslev and Combes 1971, Aguilar and Combes 1971, Simon 1972), together with improved versions such as the exterior complex scaling method (Simon 1979), the smooth exterior scaling approach (Rom *et al* 1990) and the complex stabilization method (Junker 1980, Moiseyev 1982) are certainly the most suitable. Within the framework of these theories, resonance state calculations can be performed (Moiseyev 1998) by using bound state techniques (Rescigno and Mc Curdy 1978,
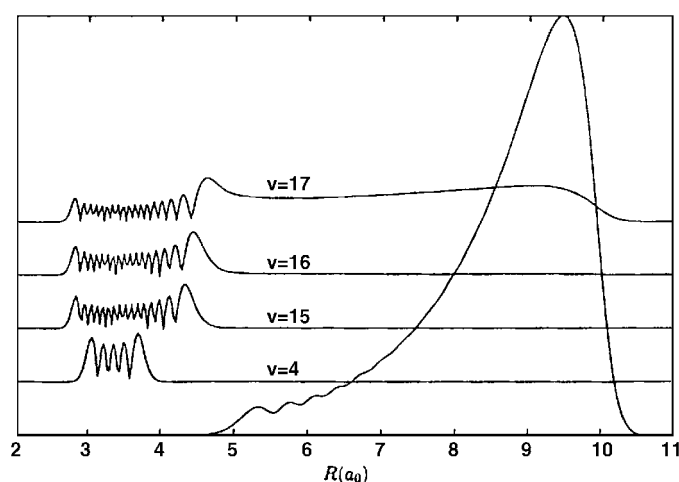
Figure 5. The moduli of a few eigenvectors of the $E^1\Sigma^+$ potential surface of SiO, i.e. the bound
state ($v = 4$) and the three shape resonance ($v = 15, 16, 17$), are compared to the moduli of a
scattering state situated near the resonance ($v = 16$). The delocalization of this scattering state far
away from the potential well is evident. Note the asymptotic absorption by the optical potential.

Moiseyev and Corcoram 1979), the coupled channel approach (Atabek and Lefebvre 1980)
or even the finite difference boundary value method (Atabek and Lefebvre 1981). The
optical potential technique is another, more coarse grained procedure, which results from
the introduction of an imaginary absorbing potential $-iV_{opt}$ in the asymptotic spatial region.
Its use is not always legitimized (as the CCM is) by rigorous mathematical theorems, but its
implementation is simple and it is able to reproduce the complex nature of the resonance states
on the second Riemann sheet.

The molecular states $|k\rangle$ which constitute the model space are in this case the eigenvectors
of $H_o - iV_{opt}$ but the corresponding Floquet eigenstates $|\lambda_{k,0}\rangle$ do not contribute equally to the
sum in equation (5.21). One should distinguish between the Floquet eigenstates issuing from
the bound and the resonance eigenstates of $H_o - iV_{opt}$ and those issuing from the states which
discretize the molecular continua. The latter, which in the L^2 representation play the role of
the scattering states in an exact description of the continuum, do not contribute significantly
to the model space, except perhaps for very sudden variations of the field envelope. The
reason for this is that equation (5.21) requires that the Floquet eigenstates should have a
non-negligible overlap with the initial state $|i\rangle$ at $t = 0$ in order to participate effectively.
This is well illustrated by figure 5 which refers to the case of the SiO molecule (Jolicard *et al*
1997).

It is clear from the figure that the scattering states concerned are strongly modified by
the presence of the optical potential and possess a negligible overlap with the bound states.
The optical potential has another effect; it produces large imaginary parts in the eigenvalues
of these modified scattering states. In this way the few scattering states with an overlap with
$|i\rangle$ which is not strictly equal to zero have a very small lifetime and cannot contribute to the
permanent regime of the relaxation process.

Figure 6 presents a simplified view of the active spaces in different circumstances. For
a direct transition from a ground surface to an upper structureless surface, an active space
of ultimate simplicity, that of one dimension, is sufficient (case *a* of figure 6). This is the
adiabatic case as defined previously in the analysis of equation (5.23). No other bound state is
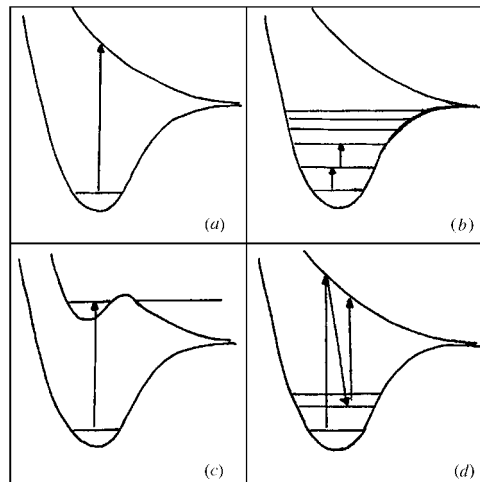
Figure 6. Schematic representation of the composition of the active space. The four schemes correspond to different types of transitions: (*a*) A direct one photon transition to the dissociative surface, (*b*) A multiphoton process produced by an IR laser, (*c*) An indirect photodissociation involving a shape resonance, (*d*) The multiphoton non-adiabatic response to the switching on of an intense and very short laser pulse

populated at the end of the interaction in this case, but the term 'adiabatic' here does not mean that nothing happens. Although the active space is non-degenerate, a dissipative process is still involved. It is the imaginary part of $E_{\lambda_{i,0}}$ in the phase term of (5.21) which produces the decreasing of the norm.

When the laser is tuned to a bound state-bound state transition as in IR photodissociation experiments (see figure 6(*b*)), the active space includes the Floquet states issuing from the bound states connected by the laser field. Similarly we may include in the active space the Floquet states issuing from shape or Feshbach resonances connected by the laser in indirect photodissociation processes (figure 6(*c*)) or those issuing from bound states of the ground surface in the study of a non-adiabatic response to the sudden switching on of intense laser pulses (figure 6(*d*)).

5.3. The effective Hamiltonian as an indicator of the active space size

We now address the problem of the relationship between the number of Floquet eigenvectors of the first Brillouin zone taking part in the dynamics and the time dependence of the effective Hamiltonian (Jolicard *et al* 2003a). In the limiting case where H_F^{eff} is strictly time independent and the initial active space S_o is one dimensional, equation (5.1), which governs the dynamics, turns out to be a single stationary eigenvalue equation. However, such an elementary case is not attainable, because the definition of $\Omega(t)$ (cf equation (2.18)) would require constant components $\langle i|\Omega(t)|i\rangle$ during the whole evolution in time and such a constraint is inconsistent with the possibility of identifying $\Omega(t)$, which describes the whole dynamical process, with a generalized eigenstate. Nevertheless, for some specific time-dependent behaviours of $H_F^{\text{eff}}(t)$, it is possible to approach an adiabatic situation in which only one Floquet eigenvector appears in the wave operator $\Omega(t)$. We will now briefly indicate how $H_F^{\text{eff}}(t)$ serves as an indicator of the more or less adiabatic character of the evolution in terms of the Floquet eigenstates.

We assume an initial active space S_o of dimension one with the projector $P_o = |i\rangle\langle i|$ and introduce the effective energy
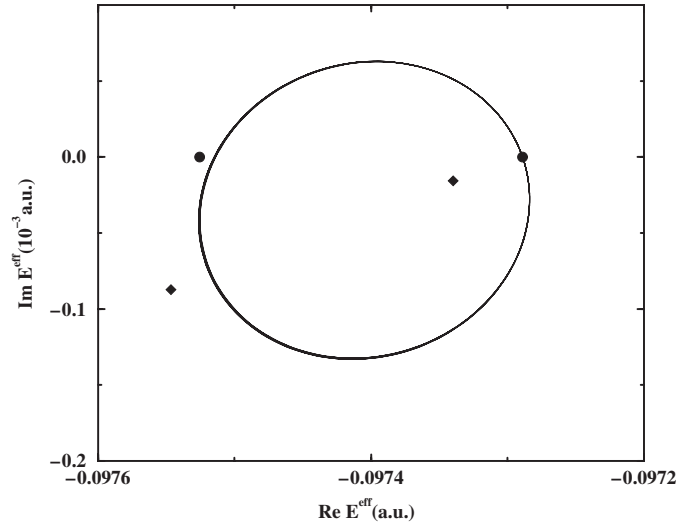
Figure 7. Time-dependent trajectory of the complex effective energy $E^{\text{eff}}(t)$ (equation (5.24)) between times $t = 35.07$ fs and $t = 37.49$ fs. The resonance energy $E_{\lambda_{v=0,n=0}}$ which contributes principally to the dynamics and the corresponding non-perturbed energy $E^o_{v=0,n=0}$ inside the loop are indicated by the filled diamond and circle, respectively. The energies plotted outside the loop are $E_{\lambda_{v=1,n=-5}}$ (filled diamond) and the corresponding non-perturbed energy (filled circle). The trajectory is a superposition of a few almost identical loops, consistently with the adiabatic equation (5.27). The more distant Floquet eigenvectors, which make a negligible contribution, are not shown.

$$E^{\text{eff}}(t) = \langle i|H^{\text{eff}}(t)|i\rangle = \langle i|H_F(t)\Omega(t)|i\rangle. \tag{5.24}$$

The use of the identities: $\Omega(t) = |\Psi(t)\rangle\langle i|/\langle i|\Psi(t)\rangle$ and $H_F\Psi(t) = 0$ leads to

$$E^{\text{eff}}(t) = \frac{i\hbar\langle i|\partial\Psi(t)/\partial t\rangle}{\langle i|\Psi(t)\rangle} = \frac{\langle i|H(t)\Psi(t)\rangle}{\langle i|\Psi(t)\rangle}. \tag{5.25}$$

Introducing equation (5.21) into equation (5.25) gives the following expression:

$$E^{\text{eff}}(t) = \frac{i\hbar\sum_j \frac{\partial}{\partial t}[e^{-iE_{\lambda_{j,0}}t/\hbar}\langle i|\lambda_{j,0}(t)\rangle]\langle\lambda_{j,0}(t=0)|i\rangle}{\sum_j e^{-iE_{\lambda_{j,0}}t/\hbar}\langle i|\lambda_{j,0}(t)\rangle\langle\lambda_{j,0}(t=0)|i\rangle}. \tag{5.26}$$

The adiabatic regime is reached when just a single term, namely $\lambda_{i,n=0}$, contributes to equation (5.21) and the indicator of this situation in terms of the effective energy is (see equation (5.26)) an E^{eff} of the form

$$E^{\text{eff}}(t) = E_{\lambda_{i,n=0}} + i\hbar\frac{\langle i|\frac{\partial}{\partial t}\lambda_{i,n=0}(t)\rangle}{\langle i|\lambda_{i,n=0}(t)\rangle}. \tag{5.27}$$

This indicator of the adiabaticity of the process in terms of E^{eff} is easily visible when the Hamiltonian is constant over a large time interval. On this interval the eigenstate $\lambda_{i,n=0}$ is time independent and the effective Hamiltonian becomes constant and equal to $E_{\lambda_{i,n=0}}$. The indicator is accurate, since such a behaviour is rapidly washed out even when only a few eigenvectors λ (with non-degenerate eigenvalues) contribute to $E^{\text{eff}}(t)$.

A second favourable situation, illustrated by figure 7, corresponds to the case of a periodic Hamiltonian. This figure relates to the photodissociation of H_2^+, via an excitation step and a

dissociation step.

$$H_2^+\left(^2\Sigma_g^+, v = 0, J = 0\right) + n\hbar\omega_o \rightarrow H_2^+\left(^2\Sigma_u^+\right) \rightarrow H^+ + H(1s). \tag{5.28}$$
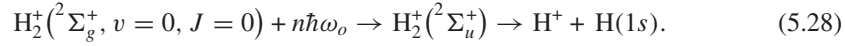
This same example will be analysed in more detail later in section 7. The field-matter coupling between the two surfaces $^2\Sigma_g^+$ and $^2\Sigma_u^+$, namely $V(t) = -\mu(R)E(t)\cos(\omega_o t)$, is characterized by the carrier wave angular frequency ω_o and by a Gaussian envelope function of the form

$$E(t) = \begin{cases} \epsilon_o \exp\left[-\left(\frac{t-t_1}{\tau}\right)^2\right] & \text{for} \quad t \leqslant t_1 \\ \epsilon_o & \text{for} \quad t_1 \leqslant t \leqslant t_2 \\ \epsilon_o \exp\left[-\left(\frac{t-t_2}{\tau}\right)^2\right] & \text{for} \quad t \geqslant t_2 \end{cases} \tag{5.29}$$

with $\hbar\omega_o = 0.295868$ a.u. $= 64935.5\,\text{cm}^{-1}$ (corresponding to a wavelength $\lambda_o = 154\,\text{nm}$), with a maximum amplitude ϵ_o (leading to an intensity of $I = 10^{12}\,\text{W cm}^{-2}$) and with $t_1 = (T - T_o)/2$ and $t_2 = (T + T_o)/2$. In the case of figure 7 the switch on and switch off times τ are equal to 5 fs and the plateau duration is $T_o = (t_2 - t_1) = 25\,\text{fs}$. The representation interval is $T = 3000$ a.u. $= 72.56\,\text{fs}$.

The figure shows the time-dependent trajectory of the complex effective energy $E^{\text{eff}}(t)$ on the plateau between the times $t = 1450$ a.u. $= 35.07\,\text{fs}$ and $t = 1550$ a.u. $= 37.49\,\text{fs}$. On this plateau the Hamiltonian $H(t) = H_o + \epsilon_o\cos(\omega_o t)$ is purely periodic. One observes an overall ellipse-like form, obtained as a superposition of a few almost identical closed loops, with the generalized Floquet eigenenergy $E_{\lambda_{i=0,n=0}}$ being located inside the ellipse. This is consistent with the adiabatic formula for the effective energy (equation (5.27)). The single eigenvector $\lambda_{i=0,n=0}$ induces a periodic behaviour in $E^{\text{eff}}(t)$, with a period equal to $2\pi/\omega_o$ which is related to the periodicity of the terms $\langle i|\frac{\partial}{\partial t}\lambda_{i,n=0}(t)\rangle$ and $\langle i|\lambda_{i,n=0}(t)\rangle$ which contribute to the time dependence of $E^{\text{eff}}(t)$ in equation (5.27).

5.4. A generalized Green function integration

Both the preceding account of the (t, t') theory and the comparison of the stationary and the time-dependent formulations of the wave operator theory have shown how the treatment of the TDSE can be drastically simplified by a simple substitution ($H \rightarrow H_F$) and by the enlargement of the Hilbert space to include the time variable. When the perturbation has a finite time duration and vanishes at the ends of the time interval, our analysis indicates that the basis set provided by the generalized Floquet eigenstates is a good adiabatic basis, i.e. a basis which requires only a small number of states for the description of the dynamical process. In this context, only generalized Floquet states possessing the same energy contribute if the initial state is an eigenvector of $H_o = H(t = 0)$ and if one assumes rigorous completeness of the basis and consequently a rigorous description of the continuum. For an initial state $|i\rangle \times |n = 0\rangle$, this common total energy is simply equal to E_i. Nevertheless, this principle of degeneracy is rendered inexact by using a finite representation of the time interval $[0, T]$; further, an expansion such as (5.18) includes states $|\lambda_{j,m}\rangle$ which are not in exact resonance with the initial state but are simply in near resonance. Another surprising consequence of this $L_2(T)$ representation relates to the generalized Floquet eigenstates which are resonance states (e.g., the eigenstates generated from the bound states by the field-matter coupling in the theoretical description of a photodissociation experiment). The width $\Gamma_{j,m}$ of these resonances is not only, as expected, a specific property of the molecular system and of its coupling with the field, but also depends on the representation used. More precisely, the product $\Gamma_{j,m} \times T$ of the width and the time interval is a constant. Nevertheless, one recovers the degeneracy principle in the limit of a rigorous representation of the continuum, since $\Gamma_{j,m} \rightarrow 0$ when $T \rightarrow \infty$. On the other hand, the apparently surprising dependence of $\Gamma_{j,m}$ on T is understandable,

since $\exp(-\Gamma \times T/\hbar)$ is related to the survival probability for the complete interaction (see section 7.2).

One can partly remove these difficulties by performing a direct iterative integration of equation (5.1) without the use of an explicit finite representation. For this, we simply assume that the initial state is $\Psi(t = 0) = |i, n = 0\rangle$ and we introduce a corresponding one-dimensional Hilbert space with projection operator $P_o = |i\rangle\langle i|$. This operator is defined in the initial Hilbert space but it can be generalized to the extended Hilbert space by using the definition $P_o = \sum_{n=0}^{N_t-1} |i, n\rangle\langle i, n|$. Similarly the projection operator of the complementary space, which is written as $Q_o = \sum_{j \neq i} |j\rangle\langle j|$ in the usual Hilbert space **H**, has the generalized form $Q_o = \sum_{j \neq i} \sum_{n=0}^{N_t-1} |j, n\rangle\langle j, n|$ in the extended Hilbert space. By multiplying (5.1) on the left by Q_o and by applying the resulting operators to the initial state $|i, n = 0\rangle$, one obtains the result

$$Q_o H_F |i, n = 0\rangle = [X P_o H_F + Q_o X P_o H_F Q_o X - Q_o H_F Q_o X]|i, n = 0\rangle. \tag{5.30}$$

To separate the diagonal element of H_F associated with the initial state one can partition the first term on the right of equation (5.30) to obtain

$$X P_o H_F |i, n = 0\rangle = X|i, n = 0\rangle\langle i, n = 0|H_F|i, n = 0\rangle + X P_o' H_F |i, n = 0\rangle$$

with

$$P_o' = \sum_{n \neq 0} |i, n\rangle\langle i, n|. \tag{5.31}$$

After a few algebraic manipulations this gives (Zucconi *et al* in preparation)

$$X|i, n = 0\rangle = \frac{[Q_o H_F - X P_o' H_F]|i, n = 0\rangle}{\langle i, n = 0|H_F|i, n = 0\rangle Q_o + Q_o(X P_o H_F - H_F)Q_o} \tag{5.32}$$

where $\langle i, n = 0|H_F|i, n = 0\rangle$ is a simple scalar and where the term on the right of equation (5.32) should be understood as a product ordered in the following order $[\langle i, n = 0|H_F|i, n = 0\rangle Q_o + Q_o(X P_o H_F - H_F)Q_o]^{-1} \times [Q_o H_F - X P_o' H_F]|i, n = 0\rangle$.

Equation (5.32) is not simply a standard Green equation and its integration is not performable by a simple matrix inversion, since X is also present in the denominator on the right. A short analysis reveals three main difficulties.

(i) The first comes from the dimension of the unknown reduced wave operator. $X = Q_o X P_o$ is not a single column but is, in the $\{|j, m\rangle\}$ representation, a rectangular matrix with N_t columns and $(N_o-1) \times N_t$ rows, where N_t is the number of Fourier functions introduced to span the time interval and N_o is the dimension of the molecular basis. Fortunately, the time-dependent terms in $H_F(t)$ have a simple structure. The time derivative $i\hbar \partial/\partial t$ is diagonal in the Fourier basis ($\langle j, m|i\hbar \frac{\partial}{\partial t}|i, n\rangle = n\hbar\omega\delta_{j,i}\delta_{m,n}$) and the couplings $V(t)$ are such that all the elements are identical on the same diagonal ($\langle j, m|V(t)|i, n\rangle = f(j, i, |m - n|)$). This particular structure of H_F in equation (5.1) generates general periodicity properties in $\Omega(t)$ and thus in $X(t)$, namely:

$$\langle j, m|X|i, n\rangle = \langle j, m + 1|X|i, n - 1\rangle. \tag{5.33}$$

It is thus sufficient to calculate only one column of the matrix X, for example, that corresponding to the initial state $|i, n = 0\rangle$, all the others being deduced from this first one by using equation (5.33). Nevertheless, one has to assume that the non-negligible components of this reference column are far from the borders of the matrix, in order to avoid edge effects when using the periodicity rule (5.33).

(ii) A second difficulty is the presence of the unknown X on the right of (5.32), and more precisely in the denominator. This feature implies that an iterative method of solution will be required. Equation (5.32) can thus be solved by forming a sequence: $X^{N+1}|i, n = 0\rangle = f(X^N)$ where the iterative rule $X^N \rightarrow f(X^N)$ is deduced from (5.32). The initial value in the iteration is arbitrary, the simplest choice being $X^{N=0} = 0$. This series has a finite radius of convergence, which depends both on the iterative rule used and on the structure of the matrix H_F.

(iii) The iterative procedure is obviously made more difficult by the large dimension of the matrix $Q_o H_F Q_o$ present in the denominator on the right of (5.32).

To handle this last difficulty, one can use a mathematical artefact by introducing a new matrix $H' = Q_o H' Q_o$. H' is, *a priori*, a general matrix belonging to the complementary space, but practical reasons usually require it to be diagonal. Equation (5.32) can then be rewritten in the form:

$$X|i, n = 0\rangle = \left(1 - \frac{Q_o H_F Q_o - Q_o X P_o H_F Q_o - Q_o H' Q_o}{\langle i, n = 0|H_F|i, n = 0\rangle Q_o - Q_o H' Q_o} \right)^{-1}$$
$$\times \frac{Q_o H_F|i, n = 0\rangle - X P_o' H_F|i, n = 0\rangle}{\langle i, n = 0|H_F|i, n = 0\rangle - Q_o H' Q_o}. \tag{5.34}$$

By using a perturbative development of the first matrix on the right of equation (5.34), $(1 - Y)^{-1} = 1 + Y + Y^2 + \cdots$, one obtains the following equation:

$$X|i, n = 0\rangle = Z + Y \times X|i, n = 0\rangle$$

$$\text{with} \quad Z = \frac{[Q_o H_F - X P_o' H_F]|i, n = 0\rangle}{\langle i, n = 0|H_F|i, n = 0\rangle Q_o - Q_o H' Q_o}$$

$$\text{and} \quad Y = \frac{Q_o[H_F - X P_o H_F - H']Q_o}{\langle i, n = 0|H_F|i, n = 0\rangle Q_o - Q_o H' Q_o}. \tag{5.35}$$

Using this equation requires only the inversion of diagonal matrices if $Q_o H' Q_o$ is chosen as a diagonal matrix. Its integration nevertheless remains complicated because of the dependence of Z and Y on X. At this point, different procedures of integration can be used. One possibility is the use of a double loop procedure. An exterior loop (index k) increments the X-dependence of the terms Y and Z and an interior loop (index n) increments the term $X|i, n = 0\rangle$. By this means, equation (5.35) is transformed into the double series:

$$X_k^{n+1}|i, n = 0\rangle = Z_{k-1} + Y_{k-1} X_k^n|i, n = 0\rangle$$

with

$$Z_{k-1} = \lim_{n \to \infty} Z(X_{k-1}^n) \text{ and } Y_{k-1} = \lim_{n \to \infty} Y(X_{k-1}^n). \tag{5.36}$$

One can also use a more simple single loop iteration:

$$X^{n+1}|i, n = 0\rangle = Z(X^n) + Y(X^n)X^n|i, n = 0\rangle. \tag{5.37}$$

In this case the incrementation step replaces all the terms X present on the right with the values deduced from the term $X|i, n = 0\rangle$ on the left at the preceeding step.

The procedures represented by equations (5.35) and (5.36) or (5.35) and (5.37) thus permit an original iterative solution in an L_2 vector space of a purely time-dependent quantum dynamical problem. No restriction on the number of time-dependent coupling terms $F^i(t)$ present in equation (5.13) is imposed, although the functions should have non-vanishing values on a common finite time interval. The integration process gives the wave operator at any time

by using the Fourier transforms of its components expressed in the Fourier basis. It thus gives direct access to the wavefunction by using the equation:

$$|\Psi(t)\rangle = \Omega(t)\exp\left[\frac{1}{i\hbar}\int^t P_o H(t')\Omega(t')P_o\,dt'\right]|\Psi(t=0)\rangle. \qquad (5.38)$$

Integration calculations based on this formalism are currently in progress and promising results have been already obtained by the Besançon group. The main problem is to ensure the convergence of the iterative process described by equations (5.36) or (5.37). This convergence depends on the choice of the diagonal matrix H' and can be improved by the use of mathematical devices such as Padé approximants, just as was found for the test calculations in part I. These different technical aspects are further analysed in section 6.

6. The integration of the time-dependent wave operator equation

The effectiveness of the wave operator formulation directly hinges on the capacity to integrate the non-linear differential equations which this theory introduces. Two types of approach can be considered: (i) The integration of the basic differential equation (2.26) in the ordinary Hilbert space, (ii) the integration of the equivalent equation (5.1) in the extended Hilbert space. In the second case, the solution proposed in section 5 involved discretizing the time variable on a finite Fourier basis set. Iterative solution methods then led to equation (5.37), which will be further analysed in this section. We will first return to equation (2.26).

6.1. The integration of $i\hbar\,\partial X/\partial t = Q_o(1-X)H(1+X)P_o$

The equation for the reduced wave operator $X(t)$ is a non-linear equation. This means that it is not possible to use efficient propagation algorithms such as the Chebyshev scheme (Tal-Ezer and Kosloff 1984) or the short iterative Lanczos propagation (Park and Light 1986), which are effective for the linear Schrödinger equation. Nevertheless, the use of a finite-order differencing scheme leads to expressions which, although more complicated than the equivalent expressions for the Schrödinger equation, do not require greater CPU integration time (and can sometimes require less). The reason is that the reduced wave operator X has a smoother time variation than does the corresponding wavefunction $|\Psi(t)\rangle$.

The wave operator approach thus seems particularly well suited for the time integration of systems controlled by slowly varying Hamiltonians over large time intervals. It can, for example, be used to solve eigenvalue problems by indirect methods. The indirect methods involve wave packet propagation and extract the required results from some asymptotic features of the time-dependent behaviour, e.g., from a relaxation of the eigenstates induced by imaginary time (Kosloff and Tal-Ezer 1986), from Fourier transform of the wavefunction time correlation function (Feit *et al* 1982) or from filter-diagonalization methods (Neuhauser 1990, 1991). In the wave operator approach to the eigenvalue problem, the operator H is generated from the unperturbed operator H_o by adiabatically switching on the perturbations over a large time interval. The integration of the subsequent wave operator equation then gives a coarse grained trial operator for the eigenvalue problem.

The second-order and fourth-order differencing schemes are derived from the symmetrized expansions (Jolicard and Killingbeck 1995b):

$$X(t+\Delta t) = X(t-\Delta t) + 2\Delta t\,X'(t) + O(\Delta t^3)$$

$$X(t+\Delta t) = X(t-\Delta t) + 2\Delta t\,X'(t) + \frac{\Delta t^3}{3}X'''(t) + O(\Delta t^5). \qquad (6.1)$$

By neglecting the time derivatives of the H matrix and by applying these differencing schemes to (2.26), one obtains the following expressions for the first and third derivatives:

$$X'(t) = [1 - \Omega(t)]C^{(1)}(t)$$

$$X'''(t) = [1 - \Omega(t)]\{6[C^{(1)}(t)]^3 - 3C^{(1)}(t)C^{(2)}(t) - 3C^{(2)}(t)C^{(1)}(t) + C^{(3)}(t)\}$$

(6.2)

where the $C^{(n)}$ are non-commuting matrices involving n applications of $H(t)$ to $\Omega(t)$:

$$C^{(n)}(t) = H^n(t)\Omega(t). \tag{6.3}$$

The propagation schemes arising from equations (6.1) and (6.2) are unitary, conserve norm and energy and, by preserving time reversal symmetry, are conditionally stable. Nevertheless, the application of these schemes involves some difficulties when they are used to investigate adiabatic processes.

We will consider here for simplicity the second-order differencing scheme. Two conflicting features characterize this scheme. First, it has a stability limit $\Delta t_o = \hbar/E_{\max}$, where $E_{\max}$ is the eigenvalue with the largest absolute value of the Hamiltonian $\tilde{H}(t) = (1 - X(t))H(t)(1 + X(t))$. If the time step Δt exceeds Δt_o, then exponentially diverging solutions take over. Second, the adiabatic limit requires us to take a large switching time T_s. The consequence is that the integration requires many time steps to ensure that $\Delta t < \Delta t_o$. Thus there can be an appreciable final error in the phase of the wave operator since for $\Delta t < \Delta t_o$ the error which accumulates in the phase is proportional to $(\Delta t)^3$ per time step and thus to $(\Delta t)^2$ over a fixed time interval t.

For the propagation of non-adiabatic processes the switching time and the number of time steps can be reduced drastically, but similar difficulties exist when the Hamiltonian introduces large eigenvalues $E_{\max}$. Nevertheless, one can improve the scheme by introducing in (6.1) the modified reduced wave operator (Jolicard *et al* 1999).

$$\tilde{X}(t) = \exp\left(\frac{i}{\hbar}D(t)\right) X(t) \exp\left(-\frac{i}{\hbar}D(t)\right) \tag{6.4}$$

where $\left(D(t) = \int_0^t \tilde{H}_d \, dt'\right)$ is the time integral of the diagonal part of $\tilde{H}(t)$. This leads, in place of (2.26), to the new equation:

$$i\hbar\frac{\partial \tilde{X}(t)}{\partial t} = [\tilde{X}(t), H_d(t)] + \exp\left(\frac{iD(t)}{\hbar}\right) Q_o \tilde{H}(t) P_o \exp\left(\frac{-iD(t)}{\hbar}\right)$$

with

$$\tilde{H}(t) = (1 - X(t))H(t)(1 + X(t)). \tag{6.5}$$

This differential equation is integrated between $(t - \Delta t)$ and $(t + \Delta t)$ by assuming that the components of the matrix $H(t)$ and of the reduced wave operator $X(t)$ both have a smooth time evolution as compared with that of the phase terms $\exp(\pm iD(t)/\hbar)$, and so both can be treated as constant on the time interval $[t - \Delta t, t + \Delta t]$. An analytical expression for the integral is obtained, leading to the new differencing scheme:

$$X(t + \Delta t) = X(t - \Delta t)\exp(-2i\omega\Delta t) + [Q_o\tilde{H}(t)P_o - \hbar\omega X(t)]\left(\frac{\exp(-2i\omega\Delta t) - 1}{\hbar\omega}\right)$$

(6.6)

or, equivalently,

$$X(t + \Delta t) = X(t) + \left[X(t - \Delta t) - X(t) + \frac{Q_o\tilde{H}(t)P_o}{\hbar\omega}\right]\exp(-2i\omega\Delta t) - \frac{Q_o\tilde{H}(t)P_o}{\hbar\omega} \tag{6.7}$$

where we have introduced the compact notations: $\omega_{j\alpha} = (\tilde{H}_{jj} - \tilde{H}_{\alpha\alpha})/\hbar$ and $\left[\frac{\tilde{H}(t)}{\hbar\omega}\exp(-2i\omega\Delta t)\right]_{j\alpha} = \frac{\tilde{H}_{j\alpha}(t)}{\hbar\omega_{j\alpha}}\exp(-2i\omega_{j\alpha}\Delta t)$.

The two equivalent equations (6.6) and (6.7) have been derived by using a smoothness assumption for $H(t)$ and $X(t)$; this is clearly better justified for the high part of the spectrum (large ω values) than for the low part (small ω values). Nevertheless this approximation, which has the advantage of partly solving the stability problem associated with the upper part of the spectrum, also operates in the adiabatic regime, since the introduction of the limit ($\omega \to 0$) in (6.6) leads to the standard second-order scheme: $X(t + \Delta t) = X(t - \Delta t) + \frac{2\Delta t}{i\hbar} Q_o \tilde{H}(t) P_o$. One then obtains an unexpectedly good result even at this unfavourable limit.

In equation (6.7) the rapidly oscillating terms $\exp(-2i\omega\Delta t)$ on their own would require small time steps; however, these terms are multiplied by a smoothly varying term $[X(t - \Delta t) - X(t) + Q_o \tilde{H}(t) P_o / \hbar \omega]$. The time average of these couplings over an interval $\Delta t \gg 1/\omega$ is consequently negligibly small. To summarize, one can partly solve the stability problem by using the following final scheme:

 (i) A positive boundary frequency ω_b is defined, separating the high and low parts of the spectrum. It is related to the time step Δt by requiring that $\omega_b \Delta t \ll 2\pi$.
(ii) For matrix elements $X_{j\alpha}$ for which $|\omega_{j\alpha}| \leqslant \omega_b$, equation (6.6) is used to propagate the wave operator matrix elements from t to $t + \Delta t$.
(iii) For matrix elements $X_{j\alpha}$ for which $|\omega_{j\alpha}| > \omega_b$, the oscillating terms are neglected in (6.7), giving a result similar to that for the stationary RDWA iterative scheme:

$$X(t + \Delta t) = X(t) - \frac{Q_o \tilde{H}(t) P_o}{\hbar \omega}. \qquad (6.8)$$

This procedure has been tested in a calculation of the generalized Floquet eigenstates of the H_2^+ molecule subjected to a Gaussian laser pulse by adiabatically switching on the perturbation over a large time interval (Jolicard et al 1999). The width of the pulse τ was chosen to be equal to 140 a.u. (3.386 fs) and the pulse was described in the symmetric interval $[-T/2, T/2]$, where T was chosen to be 1000 a.u. (24.189 fs). Two field intensities were investigated, corresponding to 10^{12} W cm^{-2} and 2.5×10^{13} W cm^{-2}, respectively.

The procedure transforms the initial stationary problem into an adiabatic time-dependent one by introducing:

$$H \to (H - Q_o \tilde{H}^{(n=0)} P_o) + Q_o \tilde{H}^{(n=0)} P_o \times \left(\frac{t}{T_s} - \frac{1}{2\pi} \sin(2\pi t/T_s) \right). \qquad (6.9)$$

The switching function $F(t) = \frac{t}{T_s} - \frac{1}{2\pi} \sin(2\pi t/T_s)$ varies from 0 at $t = 0$ up to 1 at $t = T_s$. At $t = 0$ the zeroth-order wave operator $\Omega^{(n=0)} = P_o$ is an eigenvector of the first submatrix $(H - Q_o \tilde{H}^{(n=0)} P_o)$ on the right of equation (6.9). The reduced wave operator equation of motion is then integrated on the interval $[0, T_s]$ by using N_{time} identical time steps. The result of this integration is a first-order expression

$$X^{(n=1)} = X(t = T_s). \qquad (6.10)$$

The procedure of integration can then be repeated since $X^{(n=1)}$ is an eigenvector of $(H - Q_o \tilde{H}^{(n=1)} P_o)$ with $\tilde{H}^{(n=1)} = (1 - X^{(n=1)}) H (1 + X^{(n=1)})$. Figures 8 and 9 represent, on a logarithmic scale, a measure of the defect of the calculated wave operator with respect to the exact eigenvector, namely the quantity:

$$\| H\Omega^{(n)} - \Omega^{(n)} (P_o H \Omega^{(n)}) \|. \qquad (6.11)$$

The switching time used was $T_s = 5000$ a.u. and only 20 time steps of integration were used in order to reduce the CPU time.

The two figures correspond, respectively, to the weak coupling regime and the strong coupling regime. Each show five curves which correspond to five values of the factor $\delta = \omega_b \Delta t / \hbar$, with the symbols ∇: $\delta = 0.0$, +: $\delta = 0.1$, $\square$: $\delta = 0.5$, $\times$: $\delta = 1.0$, $\triangle$: $\delta = \infty$.
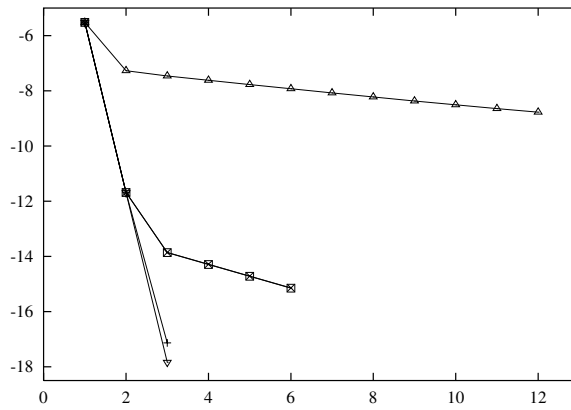
Figure 8. A measure of the defect of the wave operator with respect to the exact eigenvector $\|H\Omega^{(n)} - \Omega^{(n)}(P_o H\Omega^{(n)})\|$ is shown on a logarithmic scale as a function of the iteration order n. The field intensity is equal to 10^{12} W cm^{-2}. The five curves correspond to five values of the factor δ (see the text), namely ∇: $\delta = 0.0$, $+$: $\delta = 0.1$, $\square$: $\delta = 0.5$, $\times$: $\delta = 1.0$, $\triangle$: $\delta = \infty$.
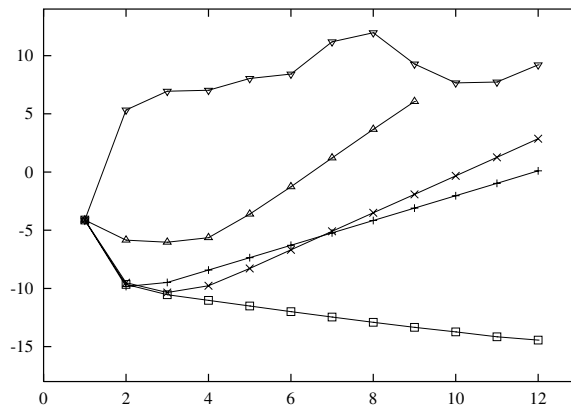
Figure 9. The same as for figure 8 but with a field intensity $I = 2.5 \times 10^{13}$ W cm^{-2}.

In the low coupling regime, a fast convergence is observed for $\delta = 0.0$, which corresponds to the use of (6.8) alone. In this low coupling regime, the energy of the initial state $E_{j=1,n=0}$ is never in close resonance with that of other states, so that it is possible to use a stationary approximation such as (6.8) in which the time step has the simple role of gradually introducing the whole coupling. The poorest results correspond to $\delta = \infty$, i.e. to the use of (6.6) alone. The reason for this is the use of the very large time step value $\Delta t = 250$ a.u. and the presence of states which are strongly coupled to the initial state and which are situated at a distance of $\omega \sim 0.2$. For these states the product $\omega\Delta t$ is about 50 and the corresponding phase terms $\exp(-2i\omega\Delta t)$ evidently cannot be described correctly by the integration process.

The most interesting test for this mixed integration scheme arises in the strong coupling regime, where many intruder states are in pure resonance with the initial state. The exclusive use of (6.8), i.e. $\delta = 0.0$, or of (6.6), i.e. $\delta = \infty$, produces rapid divergence which are due, respectively, to resonances ($\omega = 0$) which are inconsistent with equation (6.8) and to large values of the product ($\omega\Delta t$) in equation (6.6). By contrast, the choice $\delta = 0.5$ imposes a coherent mixing of these two solutions and produces a slow convergence.

6.2. The integration of $H_F \Omega = \Omega H_F \Omega$

The integration of equation (5.1) was considered in section 5, where an iterative method of solution was proposed (see equations (5.35) and (5.37)). We will now analyse more closely the convergence behaviour of the iterative approach and improve some aspects of the integration procedure.

One can first note that equation (5.35) is the TDSE solution which propagates in time the wave operator issuing from $\Omega(t = 0) = |i, n = 0\rangle\langle i, n = 0|$ with a one-dimensional model space. The wavefunction $\Psi(t)$ is then simply obtained by using expression (5.38) with $\Omega(t) = \sum_n \exp(in\omega t)\langle n|\Omega$. However, one can work directly with the full operator X by integrating equation (5.1) in a degenerate model space if the size of the model space is not too large. In this case the integration calculates the periodic Floquet eigenstates which participate in the wavefunction expansion. The assumption of a small model space is evidently more easily justified for H than for H_F in the extended Hilbert space but even in this last case one can artificially reduce the dimension of the model space by using a constrained adiabatic trajectory method. This method, currently being tested on semi-classical collisions and photodissociation processes, forces the adiabaticity of the processes on a lengthened time interval by involving asymptotic time-dependent optical potentials and permits a description of the dynamical processes which is so economical that the use of a single generalized Floquet eigenvector will suffice. It will be published in a special '*Gert Billing Festschrift*' issue to appear in 2004 in *J. Phys. Chem.* (Jolicard *et al* in preparation).

The problem is then identical to the problem of the stationary Bloch wave operator equation ($H\Omega = \Omega H\Omega$), except that a Floquet Hamiltonian H_F which includes time-dependent absorbing potentials is taken in place of H and the extended Hilbert space is considered in place of the usual one. In this paragraph we will use the generic term H to designate equally H or H_F.

Starting from (5.1), one obtains after a few algebraic manipulations.

$$X H^{\text{eff}} - H' X = Q_o(H - H')X + Q_o H P_o \quad \text{with} \quad H^{\text{eff}} = P_o H(P_o + X) \tag{6.12}$$

where H' is an arbitrary diagonal matrix in the complementary space $S_o^\dagger$.

By projecting equation (6.12) to the left on an arbitrary state $|f\rangle$ of the complementary space, and by setting $E'_f = \langle f|H'|f\rangle$, one can derive an iterative integration procedure described by the equations

$$\langle f|X^{(n+1)} = \langle f|[Z + Y X^{(n)}][P_o H P_o + P_o H X^{(n)} - E'_f P_o]^{-1}$$
$$\text{with} \quad Z = Q_o H P_o$$
$$\text{and} \quad Y = Q_o(H - H')Q_o. \tag{6.13}$$

The iterates arising from the use of equations (5.35) and (6.13) are different, as expected, since the first corresponds to the TDSE with imposed initial conditions and the second to a generalized eigenvalue problem (even if the time-dependent potentials impose adiabaticity and finally give a Floquet eigenstate proportional to the wavefunction). The matrices Y and Z do not have the same form in (5.35) and (6.13). Nevertheless, the structure of the two equations is similar and the improvements which are proposed here can be applied to both, i.e. to the calculation of the Bloch wave operator in a degenerate space or to the construction of an L_2 iterative solution of the TDSE.

The first difficulty appearing in the iterative use of (6.13) is the inversion of the matrix $P_o(H + H X^{(n)})P_o - E'_f P_o$ at each step of the iteration. For this, one can introduce the matrix $T^{(n)}$ which diagonalizes the effective Hamiltonian at the Nth step, namely

$$(T^{(n)})^{-1}(P_o H(P_o + X^{(n)}))T^{(n)} = E_{\text{eff}}^{(n)} \tag{6.14}$$

and then transform equation (6.13) into the new iterative formula

$$\langle f|X^{(n+1)} = \langle f|[Q_o(H - H')X^{(n)} + Q_oHP_o]T^{(n)}\left[E_{\mathrm{eff}}^{(n)} - E_f'P_o\right]^{-1}(T^{(n)})^{-1}. \tag{6.15}$$

As the model space S_o usually has a small dimension this inversion is without problems whenever the matrix H' is diagonal (the condition is identical for the procedure associated with equation (5.35)).

A second, more drastic difficulty, relates to the convergence of the sequence of iterates arising from the use of (6.15). To increase the radius and also the speed of convergence two modifications of the procedure have been tested (Jolicard *et al* 2003).

(i) The first concerns the choice of the arbitrary diagonal matrix H'. The simplest choice is to identify H' with the diagonal part of H. This option makes the diagonal elements (which are often the largest elements) zero in Y (equation (6.13)). Another choice, $E_f' = (E_f')^{(n)} = \langle f|(1 - X^{(n)})H(1 + X^{(n)})|f\rangle$ leads to the RDWA approach which has been explained in section 3.4.

Nevertheless, the divergence of this series is more commonly due to accidental near resonances in the denominator between the eigenvalues of the effective Hamiltonian $H^{\mathrm{eff}} = P_o(H + HX)P_o$ and the diagonal elements of $Q_oH'Q_o$. To suppress these effects a second option is to identify $Q_oH'Q_o$ with the diagonal part of Q_oHQ_o, except for a reduced group of N_p states, which are selected as the states of S_o^+ whose eigenvalues are the nearest in the complex plane to the eigenvalues of the states included in the space S_o. For these states usually responsible for accidental resonances the corresponding diagonal elements H_{jj}' are chosen to be $H_{jj} + \delta_{jj}$, where the complex shift δ_{jj} is chosen to produce a minimum distance δE between H_{jj}^{eff} and the nearest eigenvalue of the complementary space S_o^+. In the simplest case of a one-dimensional model space, this option involves moving all the N_p nearest eigenvalues outside a circle which is centred on the effective eigenvalue and has the radius δE.

(ii) The second modification is the introduction of non-linear transformations such as Padé approximants (Killingbeck 1991), Aitken's Δ^2 method (Bender and Wu 1969) or the Borel transformation to improve the convergence. In our example, it is the diagonal $[N, N]$ Padé approximant which has been tested. The convergence criteria for Stieltjes series cannot be applied in the present case (Baker 1965), but non-Stieltjes series have often been found to be summable using Padé methods (Austin and Killingbeck 1982). The procedure which has been tested involves a two-step calculation. It is presented here in a simple form by assuming a one-dimensional model space.

During the first step the series (6.15) is calculated up to a finite order N_{iter}, (typically $N_{\mathrm{iter}} \sim 20$). Simultaneously the N_p states (j) which generate accidental resonances, and thus fast divergences of the series (6.13), are selected and the corresponding N_p series of N_{iter} elements stored:

$$X_{j,i}^{n=0}, X_{j,i}^{n=1}, \ldots, X_{j,i}^{n=N_{\mathrm{iter}}} \qquad j = 1 \text{ to } N_p$$

The Padé procedure is applied to these N_p series by considering successively the real parts and the imaginary parts using the scalar Wynn epsilon algorithm, as explained in part I. These calculations lead to N_p complex values $\left(X_{j,i}^{\mathrm{Pad}}\right)$, $j = 1$ to N_p. In a second step, the series (6.13) is calculated again by keeping these N_p components constant and equal to their Padé values. A test of convergence is made at the end of this second step. If the test is not satisfied, the two steps are repeated by starting with the non-converged X operator.

The effects of the two modifications (the use of the δ shifts and of the Padé procedure) are shown in figure 10. This figure shows, on a logarithmic scale, the quantity
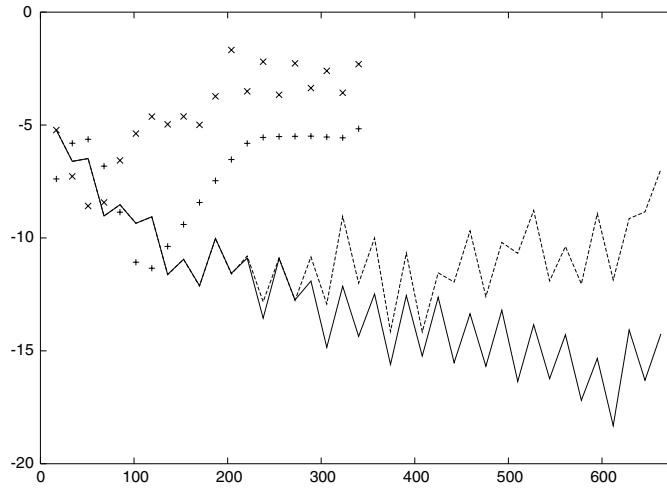
Figure 10. Illustration of the effect of the choice of the matrix H' and of the use of Padé procedure in the integration of equation (6.12). The figure presents the defect $\|H\Omega - \Omega(P_oH\Omega)\|^2$ on a logarithmic scale as a function of the number of product $H \times \Omega$ formed during the computation. The four curves correspond to the four options: $\times$: $\delta E = 0.$ and no Padé, $+$: $\delta E = 10^{-3}$ and no Padé, dashed line: $\delta E = 0.$ with Padé, continuous line: $\delta E = 10^{-4}$ with Padé.

$\|H\Omega - \Omega(P_oH\Omega)\|^2$ as a function of the number of product $H \times X$ formed during the computation.

The eigenvector investigated is the generalized Floquet state $\lambda_{v=0,n=0}$ of the H_2^+ molecule subjected to a Gaussian laser pulse (equation (5.29)) with an intensity of 4×10^{12} W cm^{-2}. The complete basis introduces 102 400 states, from which $N_b = 300$ are selected to participate in the Padé procedure. Four curves are presented which correspond to four different options: $\times$: $\delta E = 0.$ and no Padé procedure, $+$: $\delta E = 10^{-3}$ and no Padé procedure, dashed line: $\delta E = 0$ with the Padé procédure, continuous line: $\delta E = 10^{-4}$ with Padé procédure. These figures show that the Padé procédure is highly effective, particularly when it is combined with a convenient choice of the H' matrix.

6.3. The time-dependent optical potential

Our discussion of the time-dependent wave operator equation has touched on the use of a TDOP. This concept has been discussed earlier in the literature in a different context. The TDOP allows for some spurious effects produced by the projection of the wavefunction into a finite subspace. These effects are reduced by the inclusion of pseudostates which represent the infinite complement of the original representation space in a global way, as in the absorber state approach (Riera 1984, Errea *et al* 1985, 1987), or by using a formulation of TDOP to eliminate the couplings between the two segments of Hilbert space (Austern 1967, Schultheis *et al* 1984, Lüdde *et al* 1993).

The splitting of the wavefunction into two complementary space components

$$|\Psi\rangle = \left|\Psi_{P_o}\right\rangle + \left|\Psi_{Q_0}\right\rangle \tag{6.16}$$

and the projection of the TDSE into the model space leads to

$$\begin{cases} P_oH_FP_o\left|\Psi_{P_o}\right\rangle = -P_oH_FQ_o\left|\Psi_{Q_o}\right\rangle \\ Q_oH_FQ_o\left|\Psi_{Q_o}\right\rangle = -Q_oH_FP_o\left|\Psi_{P_o}\right\rangle \end{cases} \tag{6.17}$$

where the source terms on the right-hand sides of equations (6.17) are neglected in methods which solve truncated close-coupling equations.

The optical potential model remedies in a global way the undesirable effects of truncating to a limited subspace by introducing in (6.17), in place of the exact term $-P_o H_F Q_o |\Psi(t)\rangle$, the term $-i V_{\mathrm{opt}}(t) |\Psi_{P_o}(t)\rangle$ which defines the TDOP $V_{\mathrm{opt}}(t)$.

In the perturbative approach of Austern (1967), the calculation of the component $|\Psi_{Q_o}\rangle$ is carried out by using a Fourier transform of $|\Psi_{P_o}(t)\rangle$ in the second equation of (6.17) together with an explicit expansion in terms of the stationary eigenfunctions of $Q_o H Q_o$ which obey the equation

$$H_{Q_o Q_o} \phi_{E_{Q_o}} = E_{Q_o} \phi_{E_{Q_o}}. \tag{6.18}$$

A simplified description of the continuous spectrum of the projected Hamiltonian leads finally to the approximation

$$V_{\mathrm{opt}}(t) \propto \sum_{E_{Q_o}} H_{P_o Q_o} |\phi_{E_{Q_o}}\rangle \langle \phi_{E_{Q_o}}| H_{Q_o P_o}. \tag{6.19}$$

In the treatment of Schultheis *et al* (1984), a stationary state expansion of $P_o H P_o$ is used and the optical potential is arbitrarily chosen to be both diagonal in the energy representation and linear in the time (leading to satisfactory results).

In the treatment of Lüdde *et al* (1993) a different point of view is adopted by introducing a dynamical basis in the P_o space (assumed to be a stationary space, i.e. $\mathrm{d}/\mathrm{d}t\, P_o = 0$), by solving the truncated close-coupling equations for an orthonormal set of N initial conditions.

$$P_o H_F P_o |\Psi_{P_o}^j(t)\rangle = 0 \qquad j = 1 \text{ to } N. \tag{6.20}$$

The definition of the P_o space amplitudes: $c_{P_o}^j(t) = \langle \Psi_{P_o}^j(t) | \Psi_{P_o}(t) \rangle$ leads to the exact P_o space coupled channel equations

$$\frac{\mathrm{d}}{\mathrm{d}t} c_{P_o}^k(t) = -\sum_{j=1}^{N} \int_{-\infty}^{t} K_{kj}(t, t') c_{P_o}^j(t')\, \mathrm{d}t' \tag{6.21}$$

where the non-local optical potential $K(t, t')$ is given by the expression

$$K_{kj}(t, t') = \langle \Psi_{P_o}^k(t) | H_F(t) U_{Q_o}(t, t') H_F(t') | \Psi_{P_o}^j(t') \rangle \tag{6.22}$$

where $U_{Q_o}(t, t')$ is the propagator within the complementary Q_o space.

This last expression for the optical potential has an advantage over the earlier ones cited above in that it leads to a formally exact description of the dynamics in the P_o segment of the Hilbert space. However, the description of the Q_o space dynamics still requires an approximate treatment. For this Lüdde *et al* (1993) proposed various schemes, including an instantaneous approximation of $K(t, t')$ as well as what they term a non-Markovian approximation of $K(t, t')$. Probably the most successful scheme is their 'doorway approximation', which involves a dynamical extension of the P_o space by the part of the Q_o space to which it is directly coupled. This scheme was applied to some electron-ion scattering problems by Henne *et al* (1993).

The TDOP approach outlined above appears at first sight to be quite different from the TDWOT, but a detailed analysis reveals some conceptual similarities between the two methods. Both methods have the same aim, namely the suppression of any reflecting quantum flux from the Q_o space back to the P_o space. From this point of view equations (2.26) and (5.1) are equivalent to equation (6.21), except that (2.26) has the formal advantage of being an equation of motion for the reduced time-dependent wave operator in a form which does not involve any particular basis set expansion.

It should be noted, however, that the TDOP method which is associated with the TDWOT framework (Jolicard *et al* 2004) involves a point of view which is quite distinct from that of the TDOP methods outlined above. In TDWOT the optical potential is not used to isolate the two subspaces (since this isolation is achieved by the wave operator) but is used to impose obedience to consistent boundary conditions over a lengthened time interval in order to transform the problem of solving the dynamical equation (5.1) for the time-dependent wave operator into the problem of solving an equivalent eigenvalue problem.

7. The wave operator in the treatment of inelastic and photoreactive processes

The laser control of molecular dynamical processes is today one of the major goals of photochemistry. The possibility of reaching large radiation field intensities using short-pulsed lasers has motivated an increasing amount of experimental and theoretical work (Corkum 1985, Cornaggia *et al* 1986, Bandrauk and Wallace 1992) By varying the intensity, the frequency and the pulse shape of the field (Chelkowski *et al* 1990), it is possible to control scalar observables such as total or partial dissociation rates and vector observables such as alignment and orientation. Isotope selectivity (Atabek *et al* 1994, Charron *et al* 1996) and electron transfer dynamics (Coalson *et al* 1996) are also areas of applicability for control processes.

From a purely theoretical point of view the interest in laser control has led to several interesting problems. We present here a few of those which seem to us to be the most pertinent and analyse the points of view and the methods which arise from wave operator theory.

Gas-phase short pulse laser experiments are generally carried out using non-perturbative intensities at which different processes are in competition. Non-linear optical effects in the absorption spectrum and various phenomena related to the deformation of the molecule by its multiphoton coupling with the laser field often appear simultaneously in experiments. Examples of such phenomena include the bond-softening effect underlying the above-threshold dissociation (ATD) process (Zavriyev *et al* 1990, Giusti-Suzor *et al* 1990) and the vibrational trapping phenomenon (Yao and Chu 1992, Giusti-Suzor and Mies 1992, Atabek *et al* 1994). In the ultraviolet (UV) spectral region, such non-linear processes are well described using the Floquet representation, in which they refer to effects induced at avoided crossings of low order between dressed potentials. In the strong field regime, ionization effects modify the dissociation processes (Chelkowski *et al* 1992); for example, the stabilization of the laser-induced vibrationally trapped states, which is observed for H_2^+ at intensities of about 10^{13} W cm^{-2} and for times shorter than 50 fs, is destroyed at higher intensities by the presence of competing ionization and Coulomb explosion effects (Chelkowski *et al* 1995). In the infrared (IR) spectral region, a quasi-static adiabatic picture is more appropriate and new vibrational trapping effects which have a dynamical origin can occur. These new types of phenomena, named dynamical dissociation quenching (DDQ), depend crucially on a proper synchronization between the field oscillations and the wave packet dynamics (Châteauneuf *et al* 1998, Abou-Rachid *et al* 1999). Alignment of molecules along the electric field axis can also be produced, via their anisotropic polarizability, by using non-resonant linearly polarized laser fields. A variety of photodissociation effects can be produced. Ultrashort pulses which create a superposition of rotational states can be used (Seideman 1999) as well as nanosecond pulses which produce an adiabatic alignment resulting from the creation of an effective double-well potential whose minima are in the directions of the field polarization (Ortigoso *et al* 1999). Molecular orientation effects are produced by strong electrostatic fields via the permanent dipole moments of the molecule (Hain *et al* 1999). Such orientation effects are enhanced in the presence of a coherent laser field (Friedrich and Herschbach 1999) as a consequence of the breaking by the electrostatic field of the double-well symmetry induced

by the laser field. The importance of the simultaneous presence of permanent and field-induced dipole moments has been investigated by Dion *et al* (1999a) and new methods of orientation of polar molecules using two-frequency IR laser have been proposed by Dion *et al* (1999b).

A further interesting theoretical feature of laser control effects arises from the possibility of analysing them using extended Hilbert spaces and the Floquet Hamiltonians which operate in these spaces. From this point of view laser control theory provides a good illustration of the Floquet formalism, involving an adiabatic separation between the fast field-oscillation dynamics and the slow time-modulation introduced by time variations of the field envelope which are caused by adiabatic modulations of the field frequency or by internal molecular motions. Appropriate intermediate representations can then be invoked by considering instantaneous Floquet eigenvector basis sets and taking into account the quasi-periodicity of the radiative coupling in each optical period (Shirley 1965). Many studies have revealed that the description of the dissociation processes needs only a few eigenstates of these representations, provided that the perturbation duration spans only a few optical cycles, and also that adiabatic transport techniques can be used when describing these non-adiabatic behaviours, by taking into account different degrees of approximation, e.g., by neglecting some non-adiabatic couplings (Nguyen-Dang *et al* 1995) or by introducing high-frequency approximations in the Floquet analysis (Keller *et al* 2000). These dressed state models emphasize the importance of the laser-induced avoided crossings by clearly showing that dissociation processes or inelastic transitions are characterized by the presence or absence of nonadiabatic jumps at the avoided crossings of instantaneous Floquet states (Guérin and Jauslin 1997, Guérin *et al* 1997). In the case of dissociation, the dissipative character of the process complicates the scheme and its analysis requires some care: the Floquet eigenenergies of the metastable resonances are complex and the concept of avoided crossings has to be extended to the complex energy plane, as illustrated by figure 11. This generalization introduces a competition between two mechanisms which generate non-adiabaticity, yielding a final wavefunction which is not identical to the initial wavefunction multiplied by a phase factor. The first mechanism is produced by one or many non-adiabatic transitions occurring at the avoided crossings, and the second is associated more simply with the dissipative character of the process, i.e. the complex nature of the Floquet eigenvalues. The photodissociation of H_2^+ by UV lasers is, for example, often described using a single generalized Floquet eigenstate. In such a case the photoreaction process is correlated with an exponential decrease of the norm of this single eigenstate.

The crucial consequence of the near-adiabatic character of these processes in the framework of the Floquet theory (Chu 1985, 1989) is the small dimension of the active space into which the dynamics controlled by the effective Hamiltonian is projected. This has led to the rapid development of new attempts to extend the standard Floquet theory, for example, the exact adiabatic representation of Nguyen-Dang (1989), which has been applied to the general laser-driven two- and three-level system (Nguyen-Dang *et al* 1991) and the time-dependent density functional theory (TDDFT)-Floquet formalism (Telnov and Chu 1998), which provides a general time-independent approach for the treatment of multiphoton processes of many-electron quantum systems in the presence of quasi-periodic laser fields. The Berry phase concept (Berry 1984), which is closely related to the Floquet formalism and was first introduced for time-periodic quantum systems in an adiabatic context, was later extended to non-adiabatic and non-periodic systems (Aharonov and Anandan 1987, Anandan 1988). Moore and Stedman (1990) showed that Berry's formalism can be extended to a non-adiabatic time evolution by a proper choice of the initial states. Their approach, based on the knowledge of the exact evolution operator, has recently been simplified by Monteoliva *et al* (1994), who proposed a method for calculating Berry phases for non-adiabatic time-periodic
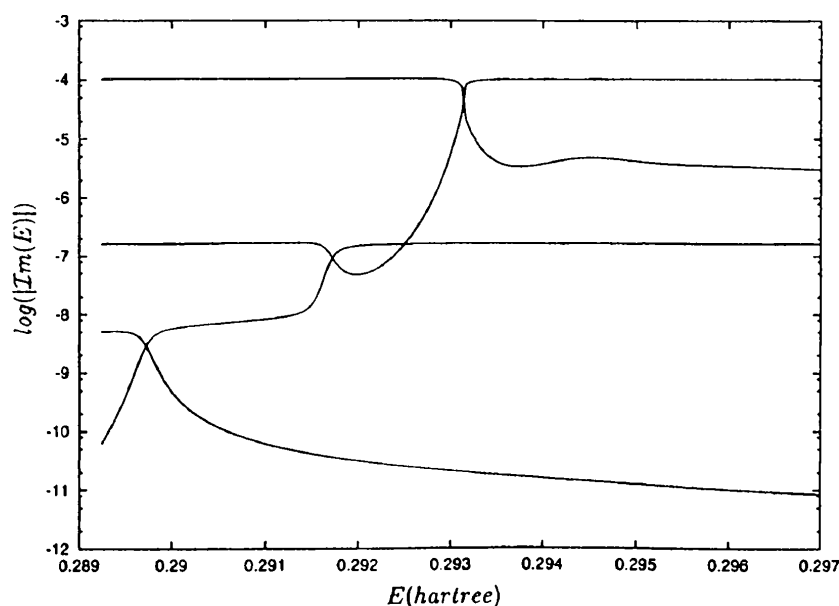
Figure 11. Photodissociation of SiO: The imaginary part on a logarithmic scale of the four eigenvalues of the Floquet eigenstates corresponding to the initial vibrational state $v = 0$ of the $X^1\Sigma^+$ potential surface and to the three shape resonances of the $E^1\Sigma^+$ potential surface as a function of the photon energy. The figure illustrates the rapid mixing of the widths which appears when the laser is tuned to the transition between the bound state and one of the three resonances.

quantum systems in cases when a dynamical invariant is known. Berry's super-adiabatic basis concept (Berry 1990) has also been used by Dresse and Holthaus (1999) in a Floquet treatment of quasi-periodic Hamiltonians, by introducing unitary transformations to construct basis sets which are well adapted to the fast part of the dynamics.

The last and certainly most interesting feature of laser control theory is its status as an inverse problem (Warren *et al* 1993, Gross *et al* 1993, Holthaus and Just 1994, Brown and Rabitz 2002). In a control experiment, the final required result is known in principle. One wishes, for example, to produce a maximum value of the photodissociation probability or a well-defined orientation of the molecule, but does not know the time-perturbations which produce such results. The conventional propagation methods are consequently relatively inadapted, because their use requires the repetition of many propagations to adjust the few coupling parameters which determine the success of the control process.

The TDWOT is an efficient tool to overcome several difficulties. In particular, it offers the possibility of generalizing the adiabatic theorem and of solving in the complex plane the degenerate eigenvalue problems associated with avoided crossings. Equation (5.1), which illustrates the close relation of the TDWOT with both the eigenvalue equation theory and the Floquet theory, suggests its potential in handling problems for which we require a full dynamical description of only part of a system. TDWOT is not, of course, the only theory able to describe the dynamics of a subsystem of interest and various effective Hamiltonian theories have been developed for the calculation of effective interactions. In the time-dependent self-consistent field (TDSCF) approach, for example, the solution is sought by expressing the wavefunction in a Hartree product form (Gerber *et al* 1982, 1988, Billing and Mikkelsen 1997) and the problem is reduced to an approximate one involving separable modes. When this

method allows for some coupling between the modes, this coupling is of an average type and the correlation between the modes is not described correctly. Thus, the TDSCF intrinsically incorporates approximations of which it is difficult to estimate the consequences. One can simply expect that this treatment is valid if the coupling is weak or extremely localized in time but must also anticipate that it involves large errors when the wave packet breaks down into many parts. The TDWOT, in contrast, aims at a rigorous treatment. When approximations are made, they result from the use of a finite expansion on the Floquet eigenstates (equation (5.16)), but the subsequent errors can be quantified and controlled.

We can investigate the pertinence of the TDWOT in the treatment of molecular interactions by considering successively two differents types of dynamical process. The first type, illustrated by dissociations induced by short and intense laser pulses and by inelastic collisions (see section 7.1), corresponds to the case of interactions of short duration ($T < 10^{-13}$ s). The second type, illustrated by the case of long duration laser pulses, involves quasi-periodic interactions for which the TDWOT leads to a degenerate active space solution (see section 7.2).

7.1. Short duration interactions

We will first consider the photodissociation of the H_2^+ ion subjected to a very short and intense laser pulse. This system, described in section 5.3, is characterized by a pulse (described by equation (5.29)) whose total duration is equal to about 35 fs (with switch-on and switch-off times of 5 fs), included in a larger interval of 72.56 fs which is used for the mathematical representation. For such a short time the TDWOT proposes two different integration techniques. The first, called *'generalized Green function integration'* has been described in section 5.4. It is an iterative integration process for the wave operator equation; its implementation is made easier by the small Fourier basis needed to span the short time interval. The use of this iterative procedure (based on equation (5.35)) is currently being developed. The main advantage of this option lies in the possibility of repeated rapid calculations of the wavefunction for a series of slightly different Hamiltonians, each one using the solution from the preceeding step as a starting solution.

The second technique uses the expansion of the wavefunction in the complete basis provided by the generalized Floquet eigenstates (equation (5.21)), i.e. the eigenvectors of the whole Floquet Hamiltonian in the extended Hilbert space; it is the use of this basis that gives the method its originality. The nature of these eigenstates is not trivial. At the adiabatic limit they are certainly the simple juxtaposition at successive instants of the instantaneous Floquet eigenstates. This relationship, which makes the generalized Floquet eigenstates appear as a generalization of the instantaneous Floquet eigenstates, links together the quasi-stationary and the dynamic processes, which are often treated as irreconcilable in the literature. This is, for example, the case for the two different forms of stabilization, the quasi-stationary stabilization, which refers to the limiting case of plane-wave monochromatic radiation, and the dynamic stabilization, which refers to laser pulse radiation (Gavrila 2002). Outside the adiabatic limit the relationship between instantaneous and generalized Floquet eigenstates is certainly more intricate. In contrast to the instantaneous Floquet eigenvectors, which simply include in their components the static informations about the geometry of the avoided crossings and about the magnitude of the non-adiabatic couplings, the generalized eigenvectors also include dynamical information about the influence of the cross-velocities. The total history of the dissociation process is thus implicit in the initial expansion of the wavefunction described by equation (5.21) and a purely dynamical problem is transformed into a static eigenvalue one. In this context it is easy to understand both the reliability of the generalized Floquet approach
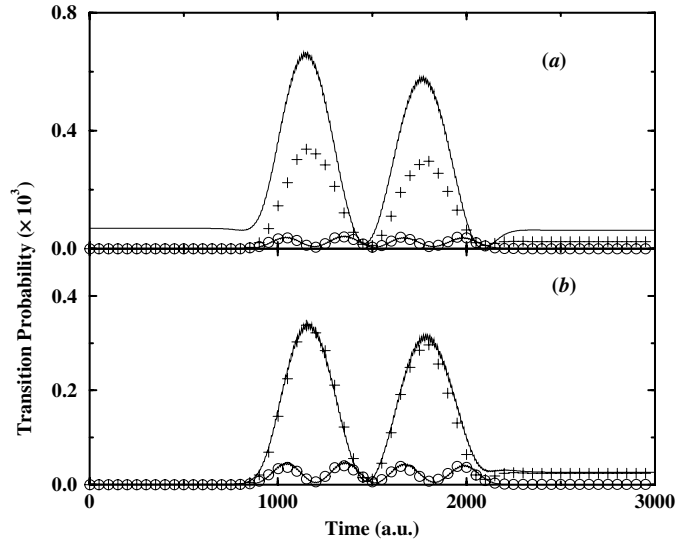
Figure 12. Inelastic transition probabilities during the photodissociation of H_2^+ as a function of the time. $P_{0 \to 1}$ (diamonds) and $P_{0 \to 2}$ (circles) are exact solutions obtained by integration of the Schrödinger equation. Solid lines indicate the results corresponding to the Floquet eigenstates expansion (equation (5.21)) with a single (a) or two (b) eigenstates.

and the validity of a single state generalized Floquet approximation, at least for calculating a global observable such as the photodissociation probability. By introducing expansion (5.21) into the expression for the total dissociation rate (Jolicard *et al* 2002):

$$P_{\text{diss}}(t) = 1 - \sum_{\text{bound states } v} |\langle v | \Psi(t) \rangle|^2 \qquad (7.1)$$

and by limiting the expansion to the initial bound state $v = 0$, one obtains the approximation:

$$P_{\text{diss}}(T) \simeq 1 - \exp(-\Gamma_{\lambda_{v=0,n=0}} \times T/\hbar). \qquad (7.2)$$

By introducing into this last equation the generalized Floquet eigenvalue: $E_{\lambda_{v=0,n=0}} = -0.9733\,9795(-1) - \mathrm{i}\,0.1563\,5260(-4)$, (see figure 7), and the representation interval $T = 72.56\,\text{fs}$, one gets $P_{\text{diss}}(T) = 0.089\,55$, in good agreement with the exact results $P_{\text{diss}} = 0.088\,06$. This result also illustrates that it is not the width Γ of the generalized Floquet eigenstate which possesses a physical meaning, but rather the product $\Gamma \times T$.

The process is thus globally adiabatic (one generalized Floquet eigenstate is sufficient to correctly describe the dissociation process) but not rigorously adiabatic. The non-adiabaticity, which is related to the degeneracy of the active space (see the comments after equation (5.23)), is revealed by an analysis of the inelastic transition probabilities.

In figure 12 the probability $P_{0,2}(t)$ is seen to decay to zero in accordance with the predictions of an adiabatic transport model. An approximate calculation with a single generalized Floquet state $|\lambda_{v=0,n=0}\rangle$ is thus appropriate (figure 12(a)). $P_{0,1}(t)$ ends up with a finite value at the end of the interaction, as is typical of a non-adiabatic transport process. The approximate calculation working with only $|\lambda_{v=0,n=0}\rangle$ fails to produce the correct probability and even gives non-zero values at the time origin (figure 12(a)). Accurate results are obtained by introducing the second generalized Floquet eigenstate $|\lambda_{v=1,n=0}\rangle$ into the calculation (figure 12(b)).

These results lead to some questions which are currently been investigated. What is the exact relation between the generalized Floquet eigenstates and the instantaneous Floquet eigenstates? Can the first type really just be regarded, in the adiabatic perturbation regime, as a simple juxtaposition of the second type at successive times? Can this generalized Floquet state approach be improved by defining super-adiabatic basis sets and asymptotic transformations in order to reduce the active space size for non-adiabatic processes?

The application of this technique is not limited to the description of photoreactive processes but can also be applied to the semi-classical treatment of inelastic molecular collisions. The so-called $V_q R_c T_c$ method, in which both rotation and translation are treated classically, was introduced many years ago by Billing (1975, 1978). This approach reduces the quantum dimensionality of the problem and for heavy diatomic molecules such as CO or N_2 it gives results which are, for a wide range of energies, much better than the quantum infinite order sudden (IOS) approximation when both are compared to the coupled-states (CS) results. Billing (1986) tested this approach on the system He–N_2 by using the potential energy surface (PES) of Banks *et al* (1986). The PES is given by the following expression:

$$V(R, r, \gamma) = \sum_{i=0}^{2} V_i(R, \gamma)(r - \bar{r})^i / \bar{r}^i \tag{7.3}$$

where

$$V_i(R, \gamma) = \frac{\partial^i}{\partial r^i} \left(\sum_{j=1}^{2} C_j \exp(-\alpha_j R_j) - a_j R_j^{-6} \right) \tag{7.4}$$

for $i = 0$ and $i = 1$; for $i = 2$ only the short range term is included in equation (7.4). R is the distance from He to the centre-of-mass of N_2, r the N_2 interatomic distance and γ the angle between R and r.

The time-dependent Hamiltonian which drives the quantum oscillator is given by the Hamiltonian $H_o(r)$ of the isolated N_2 molecule plus a time-dependent perturbation relating to the matrix elements of the potential (equation (7.3)) and the Coriolis coupling. Five different functions $F_i(t)$ (cf equation (5.13)) reproducing, on a common time interval, the translational and rotational parts of these couplings are generated by integrating the classical equations of motion after a symmetrization procedure of the initial kinetic+rotational energy U, namely for the transition $v \rightarrow v'$:

$$E - E_v = \tfrac{1}{2} \Delta E + U + \Delta E^2 / 16U \tag{7.5}$$

where E is the total energy and $\Delta E = E_{v'} - E_v$.

The Floquet procedure can be implemented by integrating for each collision the classical part of the motion, by expressing the different time-functions $F_i(t)$ in a finite discrete Fourier basis $|n\rangle$, $\langle t|n\rangle = \exp(in2\pi/T)$, where T is the common time interval on which the functions $F_i(t)$ are found, and finally by expressing the wavefunction as an expansion as described by equation (5.21). For each transition $v \rightarrow v'$ the summation in (5.21) is limited to the two generalized Floquet eigenstates, $|\lambda_{v,0}\rangle$, and $|\lambda_{v',0}\rangle$ which are associated with the initial and the final vibrational states.

Figure 13, which compares the Floquet results with results obtained by a direct integration of the TDSE, reveals a good agreement between the Floquet treatment and the exact one. One can understand this by noting that the vibrational relaxation is an adiabatic process. We see in figure 13 that the probabilities $P_{1\rightarrow0}$, and $P_{1\rightarrow2}$ increase to rather large values at the turning point and that the small final values are indicators of the small asymmetries of the trajectories around the turning points. The Floquet treatment, which includes this concept
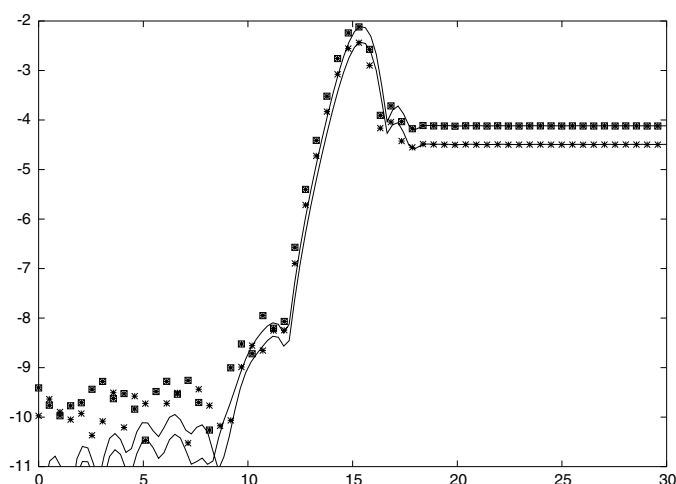
Figure 13. Rotational transition probabilities $P_{1 \to 0}$ and $P_{1 \to 2}$ for He + N_2 on a logarithmic scale, as a function of time. The solid lines are the 'exact' semi-classical results. The dots correspond to the Floquet expansion (equation (5.21)) limited to two states.

of quasi-symmetry through its use of periodic Floquet eigenfunctions, is consequently an efficient approach.

In the present application the quantum basis set is very small and the Floquet approach does not have a pronounced advantage. This is undoubtedly not the case in other situations, for example for vibrational relaxation studies on polyatomic molecules, where the vibrational basis set can include more than 10^4 elements. For these large systems, the calculation using Floquet eigenstates introduces a large saving of CPU time as compared to the integration of the TDSE by using wave packet propagation techniques.

7.2. Quasi-periodic interactions

In the case of long electromagnetic pulses, with time durations of typically 10^{-12} s, the previous Floquet treatment is inapplicable. These intermediate time durations, between ultrashort pulses and cw laser fields, lead to a difficult choice of an appropriate formalism.

The standard Floquet formalism is unsuitable since the periodicity is destroyed by the adiabatic evolution of different parameters such as the field amplitude or the frequency of the laser field. Wave packet propagation can then be used (Heather 1991) but requires large CPU times for such long time intervals. To reduce the CPU time used in these propagations, the (t, t') theory (Peskin and Moiseyev 1993) avoids the introduction of the time ordering operator and allows techniques originally developed for time-independent Hamiltonians to be used. Another advantage of this Floquet formulation lies in its consistency with the use of the active space (AS) concept and the method of projection of the dynamics into this space. For cw laser fields, numerous ways of defining such active spaces have been developed in the literature. Quack's quasi-resonant approximation (Quack 1978, 1982) and Whaley and Light's rotating frame approximation are techniques producing active spaces specific to some particular Hamiltonian. More general solutions have been given by the multitier approach (Voth 1986, Voth and Marcus 1986) and by several artificial intelligence techniques (Tietz and Chu 1983, Chang and Wyatt 1986, Lederman and Marcus 1988).

The wave operator formalism can also be used to solve these problems of intermediate time durations by introducing the evolving target space concept (Jolicard and Billing 1994). This concept will be presented by assuming that the Floquet Hamiltonian which describes the interaction between the field and the molecule depends on a few parameters which evolve adiabatically over finite ranges during the interaction, namely

$$H_F = H_F(t, -i\hbar\partial/\partial t; \alpha_1(t), \ldots, \alpha_n(t))$$

with

$$\alpha_j^{\min} \leqslant \alpha_j \leqslant \alpha_j^{\max} \qquad j = 1 \text{ to } N_\alpha. \tag{7.6}$$

In this discretization model, the variation range $\left[\alpha_j^{\min}, \alpha_j^{\max}\right]$ of each parameter is divided into N_j elementary intervals of the same width, thus defining N_j discrete values α_j^l uniformly distributed between $\alpha_j^{\min}$ and $\alpha_j^{\max}$. During the time evolution the continuous functions $\alpha_j(t)$ are approximated by step functions which take the values α_j^l when $\alpha_j(t)$ satisfies the inequality: $\alpha_j^l \leqslant \alpha_j(t) < \alpha_j^{l+1}$.

The main approximation of this treatment can now be defined. It involves the instantaneous Floquet eigenstates corresponding to different sets of discrete values of the parameters α,

$$\left(H_o - i\hbar\frac{\partial}{\partial t} + V\left(t; \alpha_1^{l_1}, \ldots, \alpha_n^{l_n}\right)\right)\lambda_\beta^{(l_1,\ldots,l_n)} = E_\beta^{(l_1,\ldots,l_n)}\lambda_\beta^{(l_1,\ldots,l_n)} \tag{7.7}$$

where H_o is the Hamiltonian of the isolated molecule. The time dependence of the laser-molecule interaction V comes from the periodic term of the laser field, to which the non-periodic perturbations produced by the parameters $\alpha(t)$ are added. In the following discussion the notation is simplified by taking a unique index k in place of the set $(l_1, \ldots, l_n)$, with k evolving between 1 and $N = \prod_{j=1}^{N_\alpha} N_j$. In accordance with this choice, the Floquet eigenvectors are written as $\left|\lambda_\beta^k\right\rangle$. Moreover, we assume that during the evolution the set of parameters undergoes transitions $k \to k'$, corresponding only to the unitary variation of one of the N_α parameters: $\alpha_j^l \to \alpha_j^{l+1}$ or $\alpha_j^l \to \alpha_j^{l-1}$.

The evolutional target space approach assumes the existence of an initial active space S_o exclusively determined by the initial molecular state and by the laser-matter interaction. This initial set of adiabatic parameters, identical to the final set, corresponds to $k = 1$ in our notation. This space is spanned by a group of N_o free Floquet eigenstates. For each new value of the set of the adiabatic parameters (specified by k), a new target space $S^{(k)}$ of the same dimension is formed by solving the degenerate stationary Bloch equation ($H_F\Omega = \Omega H_F\Omega$). This corresponds to deriving the new Floquet eigenvectors $\left|\lambda_\eta^k\right\rangle$ from the relevant free vectors $\left|\lambda_\eta^{k=1}\right\rangle$ by turning on the field-matter interaction adiabatically.

The simplified relaxation scheme finally assumes that at each discontinuity of one of the parameters (represented by the transition ($k \to k'$)), the wavefunction located in the subspace $S^{(k)}$ is completely projected into the subspace $S^{(k')}$. Thus, if one assumes that at time t, the set of adiabatic parameters is specified by k and if this set is constant between the instants t and $t + \Delta t$ in the discretized picture, then the wavefunction evolution is simply given by the equation:

$$\Psi(t + \Delta t) = \sum_{\beta \in S^{(k)}} \exp\left[-\frac{iE_\beta^{(k)}\Delta t}{\hbar}\right]\langle\langle\lambda_\beta^{(k)}|\Psi(t)\rangle\rangle|\lambda_\beta^{(k)}\rangle. \tag{7.8}$$

If, in contrast, t is the instant at which the discontinuity ($k \to k'$) appears in the parameter set, one has, in conformity with the sudden approximation:

$$\lim_{\epsilon \to 0} \Psi(t + \epsilon) = \lim_{\epsilon \to 0} \Psi(t - \epsilon). \tag{7.9}$$

As the wavefunction is confined at any time in the target space corresponding to the instantaneous parameters we can set

$$\lim_{\epsilon \to 0} \Psi(t + \epsilon) = \sum_{\gamma \in S^{(k')}} \sum_{\beta \in S^{(k)}} \left[\langle\langle \lambda_\gamma^{(k')} | \lambda_\beta^{(k)} \rangle\rangle \langle\langle \lambda_\beta^{(k)} | \Psi(t) \rangle\rangle \right] | \lambda_\gamma^{(k')} \rangle \qquad (7.10)$$

so that finally the wavefunction issuing from $|i, n = 0\rangle$ at $t = 0$ can be written at any time as

$$\Psi(t) = \sum_\gamma |\lambda_\gamma^{k_n}\rangle \exp^{\phi_\gamma^{k_n}} \sum_\beta \langle\langle \lambda_\gamma^{k_n} | \lambda_\beta^{k_{n-1}} \rangle\rangle_{\gamma \neq \beta} \exp^{\phi_\beta^{k_{n-1}}} \cdots \sum_\mu \exp^{\phi_\mu^{k_1}} \langle\langle \lambda_\mu^{k_1} | i, n = 0 \rangle\rangle$$

with

$$\phi_\gamma^{k_n} = -\frac{i}{\hbar} E_\gamma^{k_n} \Delta t_{k_n} + \left(\langle\langle \lambda_\gamma^{k_n} | \lambda_\gamma^{k_{n-1}} \rangle\rangle - 1 \right). \qquad (7.11)$$

At this point we recall the adiabatic conjecture for a single Floquet state, which can be expressed in the form '*if $\Psi(t = 0)$ is identical to a Floquet state $|\lambda^{\alpha(0)}\rangle$ and if this Floquet state is isolated during the evolution, then the system remains in the instantaneous Floquet eigenstate continuously connected to $|\lambda^{\alpha(0)}\rangle$*'. The associated mathematical equations are

$$\Psi(t) = \exp(\phi_\lambda(t)) | \lambda^{\alpha(t)} \rangle$$

with

$$\phi_\lambda(t) = \frac{1}{i\hbar} \int_0^t E^{\alpha(s)} \, ds - \int_{\alpha(0)}^{\alpha(t)} \left\langle\left\langle \lambda^\alpha \left| \frac{\partial \lambda}{\partial \alpha} \right\rangle\right\rangle \right. d\alpha. \qquad (7.12)$$

It can now be seen that equation (7.11) is the mathematical expression of a further generalization of this adiabatic conjecture to deal with the case of a sequence of multi dimensional target spaces. Compared to (7.12), equation (7.11) describes situations in which the evolution consists of non-adiabatic transitions inside the successive target spaces. It also has other advantages.

- First, it reproduces correctly the sudden approximation in the case of rapid variations of the varying parameters.
- If the set of varying parameters is constant over a large time interval, the wave packet is propagated on this interval by using only one propagation step.
- The time dependence of the N_α adiabatic parameters is completely implicit in the time step values Δt_{k_n}. To a set of time steps corresponds a precise set of time functions and if the functions $\alpha_j(t)$ are changed, the only consequence is the change of the time steps. Consequently, it is possible to repeat fast calculations for different time functions $\alpha_j(t)$, without the need to repeat detailed and large CPU time consuming procedures. For this, some data should be stored during the initial construction of the target spaces, in particular, the eigenvalues $E_\gamma^{k_n}$ and the overlap matrices $\langle\langle \lambda_\gamma^{k_n} | \lambda_\beta^{k_{n-1}} \rangle\rangle$. This is possible because the strongly adiabatic character of the Floquet basis set produces small target spaces, typically of dimension less than 20, and also because each set of parameters specified by k_n is connected by the field-matter coupling to only $2 \times N_\alpha$ other different sets specified globally by k_{n-1}. This feature is particularly favourable for the study of control phenomena.

Another effective Hamiltonian approach has been proposed recently by Guérin (Guérin *et al* 2002, Guérin and Jauslin 2003) by using the quantum analogue of the Kolmogorov–Arnold–Moser (KAM) transformation developed in classical mechanics (Scherer 1994, Chandre and Jauslin 1998), also known as the Van Vleck perturbation theory (Van Vleck 1929) and by treating resonant effects by rotating wave transformations. Their studies connect the efficiency of the population transfer between the initial and target states to the topology
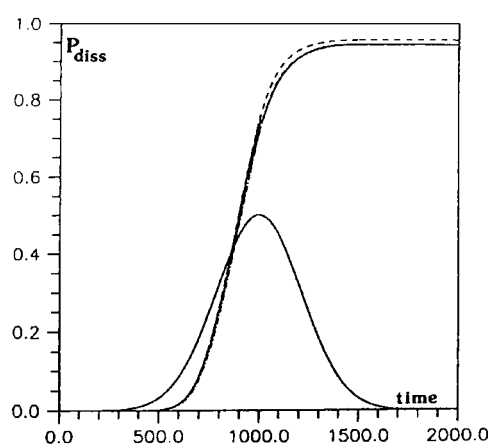
Figure 14. The probability for dissociation of H_2^+ from the ground vibrational state as a function of time. The intensity is equal to $I = 2.510^{13}\,\mathrm{W\,cm^{-2}}$. The full curve at the bottom represents the envelope of the field. The dashed, dotted and full lines refer to target spaces of increasing size ($N_o = 1$, $N_o = 6$, $N_o = 20$). These results often coincide, making it difficult to distinguish them.
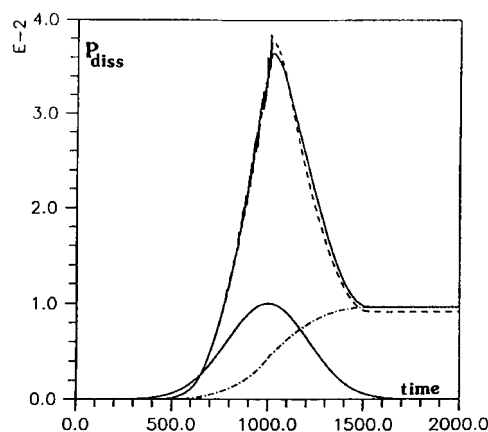
Figure 15. The same as figure 14 but with a laser frequency $\omega_o = 0.214$ a.u.. The dashed-dotted line represents the dissociation probability deduced from the norm of the wavefunction ($P_{\mathrm{diss}}(t) = 1 - \|\Psi(t)\|y^2$).

of the dressed state energy surfaces, which varies as a function of the time-dependent external field parameters (Yatsenko *et al* 2002). This topology is essentially determined by the avoided crossings of surfaces and conical intersections. More precisely the adiabatic transport appears in their studies as a global adiabatic passage along one eigenstate trajectory, combined with local diabatic evolution near conical intersections.

Our treatment does not involve the same restriction. Equation (7.11) involves different adiabatic 'trajectories' which can interfere and the corresponding diabatic transitions can in principle appear anywhere, even if they are concentrated in reality near the conical intersections. It is evident that the validity of our scheme depends primarily on the definition of the initial active space within which the dynamics is confined. For this selection, one can use the wave operator sorting algorithm, generalized to a multiple choice procedure by Jolicard and Billing (1994). Figures 14 and 15 illustrate the use of the evolutive target concept

for the study of the photodissociation of H_2^+. This system is very simple, since it involves only one adiabatic parameter, the amplitude $E(t)$ of the electric field. Figure 14 corresponds to a value of the laser frequency $\omega_o = 0.40$ a.u., which favours a direct transition from the ground state $v = 0$ of the electronic surface $(1s\sigma_g)\Sigma_g^+$ to the dissociation surface $(2p\sigma_u)\Sigma_u^+$. Figure 15 corresponds to $\omega_o = 0.214$ a.u.; this choice implies a predominance of two-photon processes. In both cases an active space of 20 states is formed by using the wave operator algorithm with a multiple-choice procedure, i.e. by varying the field intensity from $0.25\,\text{TW cm}^{-2}$ up to $25\,\text{TW cm}^{-2}$ and by varying the frequency ω of the Floquet Hamiltonian around the laser frequency ω_o. The successive calculations give similar results and produce active spaces which have in common a large majority of states (e.g., for $\omega_o = 0.40$, 18 of the 20 selected states $|n, j\rangle$ are common to all the results).

The analysis of figures 14 and 15 reveals the small size of the evolutive target space needed to give converged results (six states in the case of figure 14; this should be compared with the dimension $N = 1500$ of the full space). This justifies *a posteriori* the use of the wave operator theory. Another advantage of this formulation is its ability to reveal the detailed mechanisms which contribute to the photoreactive process. For example, one can easily explain the differences in the shapes of the dissociation probabilities in figures 14 and 15 (note that in figure 14 the probability is a purely increasing function). This strong difference results from the different behaviours of the parameter $\int_0^T \Gamma_{\lambda_{v=0,n=0}}$, where T is the duration of the laser pulse and Γ the width of the Floquet eigenstate associated with the initial state.

8. Conclusion

Within molecular physics the study of modern topics such as control methods for photoreactive processes requires the treatment of the time-dependent Schrödinger equation in spaces which have a dimension which is very large and which is often made even larger by the need to use the extended Hilbert space associated with the Floquet Hamiltonian. The need to minimize required computational CPU time and to produce simplified and effective conceptual schemes has led to renewed interest in effective Hamiltonian theories. However, the non-rigorous character of many effective Hamiltonian theories prevents them from giving an accurate description of photoreactive processes, the theory of which requires an accurate description of the various dynamical processes involved. To be useful in this context, an effective Hamiltonian theory should satisfy several criteria.

 (i) It should be possible to estimate and control the degree of approximation introduced by the theory.
 (ii) The theory should be adaptable enough to treat both the periodic and the quasi-periodic perturbations arising in the interactions between matter and cw laser fields or pulsed laser fields (i.e. should be consistent with the Floquet theory).
(iii) The theory should be applicable to the non-Hermitian Hamiltonians which are generated by analytical continuations of the resolvent in the complex plane when L^2 representations of the continua are used.
(iv) The theory should make it possible to make a rapid repetition of perturbative calculations when physical parameters are slightly modified.

The TDWOT satisfies these different requirements. We have noted in section 7 that the TDWOT is, in principle, an exact theory, unlike other procedures such as the time-dependent self consistent field (TDSCF) approach. Deficiences arising in the application of the TDWOT result from truncations of the Floquet basis sets and from the negligence of relaxation paths

in the complementary space (see section 3), but these approximations are controlled by the selection procedure for the model space.

The consistency of TDWOT with Floquet theory is intrinsically implicit in the basic equation (5.1), which reveals that the time-dependent wave operator is driven by the Floquet Hamiltonian. In this context an important feature is the representation of the dynamics using a quasi-degenerate set of instantaneous Floquet eigenstates. The control process is essentially conditioned by the dynamical effects which appear at avoided crossings of these states; the TDWOT offers a direct view and a direct control over these key processes. In this way, it introduces a generalization to the degenerate case of the adiabatic conjecture for Floquet states (see section 7.2) by driving simultaneously interfering adiabatic trajectories on the dressed state energy surfaces and by concentrating the diabatic transitions inside the evolving target space.

The various iterative methods which have been proposed for the integration of the wave operator equation, both the stationary and the time-dependent algorithms, are robust and able to work with Hamiltonians which are rotated in the complex plane or which include added complex optical potentials. The iterative nature of the methods makes possible the rapid generation of new solutions, after slight modifications of the Hamiltonian, by applying the iterative algorithms starting from the previous solution. In these calculations, the separation which $\Omega(t)$ effects between adiabatic terms outside the model space and rapidly evolving terms inside the model space is of prime importance. This separation, which is linked to the extended form of the adiabatic conjecture, improves the convergence properties of the algorithms.

Some technical aspects of the theory relating to the integration procedure, as well as some formal aspects relating to the adiabatic conjecture in the extended Hilbert space are currently still being investigated in a continuing research programme.

A permanent task is that of improving the integration procedure for the two basic equations (2.26) and (5.1). This is a technical point, but clearly decides the success or the failure of numerous studies in the strong perturbation regime. The smooth behaviour of the components of $\Omega(t)$, which results from the separation effected by this operator between the adiabatic terms and the rapidly evolving terms, reduces the number of time steps needed in an explicitly time-dependent treatment and facilitates the implementation of new algorithms, which can to some extent compensate for the difficulties due to the non-linear nature of the equations. Non-linear transformations (e.g., Padé approximants) have been tested successfully on the stationary iterative procedures and new approaches using polynomial expansions techniques are under study.

The main questions, nevertheless, concern adiabatic transport problems, for which the wave operator theory, through its close relationships with the Floquet theory, is an efficient tool. It is at present too early to evaluate prospects for the generalized Green function procedure described in section 5.4. More numerical tests should be made to validate this approach, although this iterative integration method for the TDSE with a time-dependent Hamiltonian is conceptually innovative.

On the other hand, the evolving target space concept (section 7.2) has been successfully applied in conjunction with expansion in basis sets of both generalized Floquet eigenstates (section 5.2) and of instantaneous Floquet eigenstates. These two expansions are not independent and we are currently investigating (at the adiabatic limit), the relationship between the generalized eigenvectors and the juxtaposition, at successive times, of the instantaneous ones. The use of the generalized Floquet basis set has revealed that inelastic processes can be described using very small basis sets in the intermediate perturbation regime. Further progress is certainly possible by investigating this approach. Two strategies can be adopted. For control

with quasi-periodic interactions, slightly modulated by a few adiabatic parameters, the model presented in section 7.2 could be applied with instantaneous Floquet eigenstates parametrized on multidimensional grids. For long pulses, this is certainly the best approach to obtain a detailed understanding of the relationships between the attainable experimental efficiency and the adiabatic character of the evolution in terms of Floquet states. For short pulses, the generalized Floquet formalism is certainly a good choice. By increasing the adiabaticity of such rapid processes it simplifies their study and the understanding of the different mechanisms involved. For inelastic transitions, inconsistencies arise between the non-periodic features of the relaxation process and the periodic character of the representation used; multidimensional active spaces thus become necessary. To solve this difficulty, the 'constrained adiabatic trajectory method', currently in development (Jolicard, *et al* in preparation) is a promising approach. The conjoint use of the stationary wave operator theory and of time-dependent absorbing potentials provides a compact dynamical theory in which the calculation of a single generalized Floquet eigenvector suffices to describe correctly the dynamics of the TDSE.

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