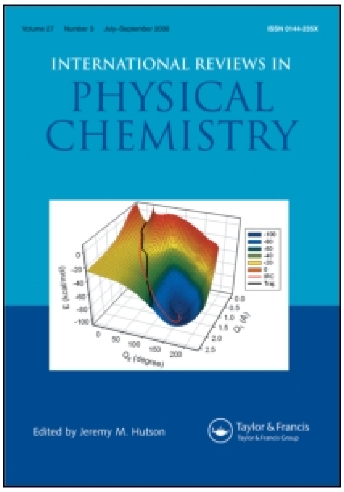
This article was downloaded by:
On: *21 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Reviews in Physical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

Molecular multiphoton transitions. Computational spectroscopy for perturbative and non-perturbative regimens

André D. Bandrauk[ab]

[a] Theoretical Department, Institute of Molecular Science, Myodaiji, Okazaki, Japan [b] Laboratoire de Chimie Théorique, Faculté des Sciences, Université de Sherbrooke, Sherbrooke, Qué, Canada

To cite this Article Bandrauk, André D.(1994) 'Molecular multiphoton transitions. Computational spectroscopy for perturbative and non-perturbative regimens', International Reviews in Physical Chemistry, 13: 1, 123 — 161

To link to this Article: DOI: 10.1080/01442359409353292

URL: http://dx.doi.org/10.1080/01442359409353292

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

INTERNATIONAL REVIEWS IN PHYSICAL CHEMISTRY, 1994, VOL. 13, NO. 1, 123–161

Molecular multiphoton transitions. Computational spectroscopy for perturbative and non-perturbative regimens

by ANDRÉ D. BANDRAUK†
Theoretical Department, Institute of Molecular Science, Myodaiji, Okazaki, 444, Japan

The total Schrödinger equation for an electromagnetic field interacting with a molecule is shown to lead to time independent or time dependent coupled differential equations. The time independent equations result from using a quantized representation, i.e., photon number states, of the electromagnetic field. The stationary states of such a quantized field–molecule system are called *dressed* states. Appropriate numerical methods are presented in order to treat radiative and non-radiative interactions simultaneously for any coupling strength, i.e. from the perturbative, Fermi-Golden rule limit, to the non-perturbative regime for both types of interactions. Both bound–bound, bound–continuum and continuum–continuum radiative and non-radiative transitions can be treated exactly in the present scheme. The relationship between the quantized time independent approach and the time dependent semiclassical field method is achieved through consideration of the *coherent* states of the quantized radiation field. In this limit, multiphoton transitions are more conveniently treated by coupled partial differential equations both in time and space. The time dependent approach is therefore more appropriate for very short laser pulses, especially for pulse time durations less than the molecular natural time-scales, in which case stationary states are ill-defined. Examples of both time-independent and time dependent calculations are presented. In the first case, *coherent laser control* of multiphoton transitions is illustrated by a time independent, all state, coupled equations method. Finally, high intensity direct photodissociation by subpicosecond pulses is presented as an example of laser pulse effects from a time dependent calculation in the non-perturbative regime, where *laser-induced avoided crossings* can be created by the pulse itself. The coupled equations methods are in principle exact and can be readily implemented for diatomics and triatomics with current computer technology.

1. Introduction

Recent advances in laser technology are providing chemists with the possibility of increasing resolution in spectroscopic measurements, thus giving more accurate information on energy levels and spectroscopic constants of molecules; see for instance (Herzberg 1966, Huber and Herzberg 1979, Lefebvre-Brion and Field 1986). The traditional approach in spectroscopy has been to use resonant single photon excitation or even two photon spectroscopies such as the Raman effect, to map out the energy levels of a particular molecule. Such methods have been perturbative, in so far as the effect of the radiation field on the molecule is negligible, and a Franck-Condon factor approach in interpreting radiative transition probabilities is found to be usually quite adequate. More recently attempts are being made to correlate spectroscopic information with potential energy surfaces (Murrell *et al.* 1984, Yamashita and Morokuma 1991).

---

† Permanent address: Laboratoire de Chimie Théorique, Faculté des Sciences, Université de Sherbrooke, Sherbrooke, Qué., J1K 2R1, Canada.

Molecular dynamics is being explored currently by new time-resolved multiphoton experimental techniques (Crim *et al.* 1990, Zewail 1991). In fact the interaction between the disciplines of molecular dynamics and multiphoton molecular spectroscopy is fast evolving into a new area of modern research, *laser control* of chemical dynamics and reactions (Bandrauk and Wallace 1992, Moffatt 1992, Bandrauk 1993). The complexity of multiphoton processes involved in such new studies requires theoretical interpretation in parallel with the experimental progress. Empirical (Murrell *et al.* 1984) and *ab initio* surfaces (Yamashita and Morokuma 1991), are an essential starting point. However, the description of radiative transitions requires theoretical methods and techniques much akin to those used in molecular dynamics (Takada *et al.* 1992).

The radiative transitions induced by lasers can be described in a systematic theoretical approach by the use of the field–molecule or *dressed* state representation (George *et al.* 1977, 1982, Bandrauk *et al.* 1978, 1987, 1988). The approach results in a very practical numerical method, a *coupled equations* method to calculate multiphoton transition probabilities in molecules as a function of the potential surfaces, the relevant radiative transition moments, and the non-radiative dynamics such as non-adiabatic effects (Bandrauk and Child 1970), and others (Herzberg 1966, Lefebvre-Brion and Field 1986). Such theoretical or numerical methods, can span perturbative (weak field) to non-perturbative, nonlinear (strong field) radiative interaction regimes and can therefore provide an appropriate theoretical framework for elucidating the role of resonant and non-resonant transitions, interfering radiative or photon pathways, etc. to various multiphoton transition amplitudes or probabilities. Dynamics can be inferred from the dependence of these transition amplitudes on the potential surfaces and the non-radiative (radiationless), such as non-adiabatic, spin–orbit, etc., processes operating between these surfaces. Such calculations based on the dressed state method are *time independent* and have been fully developed to treat bound–bound, bound–continuum, continuum–continuum, transitions in a unified way by using techniques of collision or S-matrix theory (Bandrauk *et al.* 1985, 1987, 1988, Miret-Artes *et al.* 1992).

Current laser technology has made considerable progress in the production of short light pulses on time scales ranging from picoseconds (10^{-12} s), typical of nuclear vibrational motions, to femtosecond (10^{-15} s), a time scale usually associated with electronic motion. Simultaneous with these short pulse developments has been the concentration of ever increasing intensities on these short time-scales. Thus intensities from terawatts (10^{12} W cm^{-2}) to petawatts (10^{15} W cm^{-2}) are currently being produced (Corkum 1985, Watanabe *et al.* 1991). These developments presage the new emerging discipline of *nonlinear photochemistry* where non-perturbative multiphoton transitions are expected to occur (Bandrauk and Wallace 1992, Bandrauk 1993). Concurrent with the development of such intense pulses is the shaping of these short pulses to control short time excitations of nuclear and electronic motion (Scherer *et al.* 1991, Zewail 1991). These new experimental developments require therefore perturbative and non-perturbative *time-dependent* theoretical descriptions, reflecting the importance of the pulse's properties as well as the *coherence* induced by such sources.

In this review we shall report on the theoretical and numerical methods that have been developed to treat spectroscopic phenomena in a unified way. In particular the present author's contributions with his collaborators will be emphasized. In parallel with the computational progress of quantum chemists (Yamashita and Morokuma 1991) and dynamical theorists (Clary 1986, Takada *et al.* 1992), we will report on methods and approaches used in what one might appropriately call the area of *computational spectroscopy*. These theoretical and numerical methods encompass the perturbative limits of both radiative and non-radiative (dynamical) interactions in a systematic way for both time-independent (or long pulses) and time-dependent (short pulses) radiative interactions. In the final analysis, it is clear that by increasing laser intensities, one can achieve radiative transition rates superior to non-radiative relaxation rates. Thus non-perturbative treatments of radiative and non-radiative processes simultaneously is a primary objective of the present theoretical and computational approach.

2. Field–molecule Hamiltonian and coupled equations

We have emphasized in the introduction that it is possible to treat electromagnetic field–molecule interactions as time independent systems for long pulses whereas for short pulses a time dependent approach is more practical. The connection between the two limits can be made by starting from a full quantum approach to the field–molecule problem (Bandrauk 1993). In the time-independent approach, one calculates the stationary eigenstates of the field–molecule system. These are called *dressed* states (George *et al.* 1977, 1982, Bandrauk *et al.* 1978, 1987, 1988, 1989, Cohen-Tannoudji *et al.* 1983). In the limit of large photon numbers, which are eigenvalues of the quantum states of the radiation field, one can recover the semiclassical time-dependent electromagnetic field through the concept of the *coherent* state (Glauber 1963, Loudon 1973, Mittleman 1982, Bandrauk 1993).

We first introduce the full quantum description. The total Hamiltonian for a molecular system interaction with a quantized radiation field is

$$\hat{H}(r,R)=\hat{T}_{\mathrm{N}}+\hat{H}_{\mathrm{el}}(r,R)+\hat{H}_{\mathrm{f}}+\hat{V}_{\mathrm{int}}(r,R), \tag{1}$$

where $\hat{T}_{\mathrm{N}}$ is the nuclear kinetic-energy operator and $\hat{H}_{\mathrm{f}}$ is the Hamiltonian of the free quantized radiation field. The electronic Hamiltonian $H_{\mathrm{el}}(r,R)$ and the interaction potential $\hat{V}_{\mathrm{int}}(r,R)$, which includes both radiative and radiationless interactions, depend parametrically on the internuclear distance R and implicitly on the electronic coordinates r. In the present case we limit ourselves to a single nuclear coordinate (e.g., a diatomic molecule), and a single radiation mode, i.e., a monochromatic mode of frequency ω. Equation (1) can be easily generalized to many modes, both nuclear, R_{α}, $\alpha=1,N$ and radiation, ω_i, $i=1,m$. The quantum field hamiltonian $\hat{H}_{\mathrm{f}}$, in view of the harmonic solutions of the free classical Maxwell equations (Loudon 1977, Bandrauk 1993), is conventionally written as a harmonic oscillator system,

$$\hat{H}_{\mathrm{f}}=\hbar\omega(\hat{a}^{+}\hat{a}+1/2), \tag{2}$$

where $\hat{a}^{+}$ and $\hat{a}$ are the creation and annihilation operators of the quantum field oscillator. These satisfy the following relations,,

$$\hat{a}^{+}\hat{a}|n\rangle=n|n\rangle; \qquad [\hat{a},a^{+}]=1, \tag{3}$$

$$\hat{a}^{+}|n\rangle=(n+1)^{1/2}|n+1\rangle; \qquad \hat{a}|n\rangle=n^{1/2}|n-1\rangle. \tag{4}$$

$|n\rangle$ are the quantum radiation field eigenstates of the photon number n. To these eigenstates, there correspond photon wavefunctions $\psi_{\mathrm{n}}(E)$ where E, the electric field amplitude, appears as a coordinate (Bloch and Nordsieck 1937, Nguyen-Dang and Bandrauk 1983, 1984). Thus a state of well defined photon number n has an infinite distribution of electric field amplitude values, i.e. $-\infty\leqslant E\leqslant\infty$. This is an *incoherent* electric field state.

The radiative and non-radiative couplings contained in $\hat{V}_{\mathrm{int}}(R)$ depend on the representations used to define the system. Thus for the radiation field one encounters the problem of *gauge* representations (Loudon 1977, Mittleman 1982), whereas for the nuclear dynamics one has a choice of either *adiabatic* or *diabatic* electronic Hamiltonians (Bandrauk and Child 1970, Lefebvre-Brion and Field 1986).

We first address briefly the gauge freedom inherent in any radiation-matter interaction description. For a single charged particle interacting with a quantized radiation field and some static potential $V(r)$, the total time-independent quantum Hamiltonian is defined in the minimum or Coulomb gauge as, (Loudon 1977, Cohen-Tannoudji *et al.* 1989),

$$\hat{H}^{c}=\frac{1}{2m}\left(\mathbf{p}+\frac{e\hat{\mathbf{A}}}{c}\right)^{2}+V(r)+\hat{H}_{f}, \tag{5}$$

where the momentum

$$\hat{\mathbf{p}}=\frac{\hbar}{i}\nabla_{r}$$

and $\hat{\mathbf{A}}$ is the transverse quantum vector potential of the electromagnetic field. The latter can be expressed in terms of the field operators, equations (3, 4) as,

$$\hat{\mathbf{A}}=\frac{c}{\omega}\left(\frac{\omega}{2V}\right)^{1/2}\hat{\varepsilon}(\hat{a}+\hat{a}^{+})\,. \tag{6}$$

In equation (6), $\hat{\varepsilon}$ is the polarization (unit vector perpendicular to the propagation direction); V is the field volume (e.g. laser cavity); c and ω are the velocity of light and corresponding frequency. We have assumed here the dipole approximation $r/\lambda \ll 1$, where r is the atomic dimension ($\sim 10^{-8}$ cm) and λ is the radiation wavelength ($\lambda_{\text{vis}} \sim 10^{-5}$ cm) so that the amplitude A is a spatial constant instead of a plane wave: $\exp[i(\mathbf{k}\cdot\mathbf{r})]=\exp[2\pi i(r/\lambda)]\simeq 1$, where $\mathbf{k}$ is the wave-vector $|\mathbf{k}|=\omega/c$.

The Hamiltonian $\hat{H}^{c}$ defined in equation (5) is called the Coulomb or velocity gauge Hamiltonian as it can be derived from a rigorous Lagrangian formulation of field–molecule interaction, subject to a constraint. This is the classical condition that $\nabla\cdot\mathbf{A}=0$, consistent with the classical Maxwell equation $\nabla\cdot\mathbf{B}=0$ (no magnetic poles) and the potential definition $\mathbf{B}=\nabla\times\mathbf{A}$. The Coulomb gauge condition $\nabla\cdot\mathbf{A}=0$, implies $\mathbf{A}$ is transversal, $\mathbf{k}\cdot\varepsilon=0$. It can be seen that the Hamiltonian (5) is invariant under the following unitary transformation to the wavefunction,

$$\Psi(r)=\exp[-ie\hat{F}(r)/\hbar]\,\Psi(r), \tag{7}$$

where $\hat{F}(r)$ is a time-independent scalar operator function, provided $\hat{\mathbf{A}}$ is changed in the following manner,

$$\hat{\mathbf{A}}'=\hat{\mathbf{A}}+\nabla\hat{F}. \tag{8}$$

Thus a phase change in the Schrödinger wave Ψ produces a change in the vector potential A, since the new Hamiltonian is

$$\hat{H}'=\exp(+ie\hat{F}/\hbar)\,\hat{H}\exp(-ie\hat{F}/\hbar), \tag{9}$$

and remains invariant if $\hat{\mathbf{A}}'$ is transformed according to equation (8). Clearly the unitary transformation (9) generates a new Hamiltonian. There is obviously an infinite number of such transformations and some have been considered for molecular problems by Bandrauk *et al.* (1986).

We examine here the electric field gauge transformation which gives a Hamiltonian expressible in terms of the physical (dynamical) variables of the total system, i.e., fields, polarizations, velocities and positions (Power and Thirunamachandran 1983). Let Ψ^c be the wave function that satisfies the Coulomb gauge Schrödinger equation $\hat{H}^c\Psi^c = E\Psi^c$. The electric field transformation is obtained from the following equations,

$$\Psi^E = \exp(-ie\mathbf{r}\cdot\mathbf{A}\hbar)\,\Psi^c, \tag{10}$$

$$\hat{H}^E = \exp(ie\mathbf{r}\cdot\mathbf{A}/\hbar)\hat{H}^c\exp(-ie\mathbf{r}\cdot\mathbf{A}/\hbar), \tag{11}$$

$$= \frac{\hat{\mathbf{p}}^2}{2m} + V(r) + \hat{H}_f - e\mathbf{r}\cdot\hat{\mathbf{E}}, \tag{12}$$

where we have defined the electric operator $\hat{\mathbf{E}}$ as,

$$\hat{\mathbf{E}} = \frac{i}{\hbar}\left[\hat{H}_f, \frac{\hat{\mathbf{A}}}{c}\right] = i\left(\frac{\hbar\omega}{2V}\right)^{1/2}\hat{\varepsilon}\,(\hat{a}^+ - \hat{a}). \tag{13}$$

Equation (13) is the quantum Heisenberg equation of motion for the electric field operator $\hat{\mathbf{E}}$, whose classical value $\mathbf{E}$ is related to the classical vector potential $\mathbf{A}$ by the relation $\mathbf{E} = -1/c\,\delta\mathbf{A}/\delta t$, i.e. $\mathbf{E}$ and $\mathbf{A}/c$ are canonically conjugate dynamical field variables in the classical and quantum theory respectively (Loudon 1977 Cohen-Tannoudji *et al.* 1977, Bandrauk 1993).

Equation (12) shows that in the new Hamiltonian, the radiative interaction is dipolar, $e\mathbf{r}\cdot\mathbf{E}$, involving the particle dipole moment and the electric field. In the Coulomb gauge, this interaction would involve two terms $e\hat{\mathbf{A}}\cdot\hat{\mathbf{p}}/mc$ and $e^2\hat{\mathbf{A}}^2/2mc^2$. In the dipole approximate, $r/\lambda \ll 1$, the last term is independent of particle coordinates and introduces a constant energy shift, called the *ponderomotive* energy (Mittleman 1982, Bandrauk, 1993). At high intensities, this laser induced energy shift can dominate the photoionization dynamics of atoms and molecules (Bandrauk and Wallace 1992).

Thus in both gauges, the radiative interactions are different, as is the momentum operator, $\hat{\mathbf{p}} = (\hbar/i)\nabla_r$. By explicit calculation one obtains that it is the velocity operator which is *invariant* to the transformation (7) and (9),

$$\dot{\hat{\mathbf{r}}} = (i\hbar)^{-1}\,[\hat{\mathbf{r}}, \hat{H}^c] = \frac{1}{m}\left(\hat{\mathbf{p}} - \frac{e\hat{\mathbf{A}}}{c}\right), \tag{14}$$

$$= \exp(ie\mathbf{r}\cdot\hat{\mathbf{A}}/\hbar)\,\dot{\hat{\mathbf{r}}}\exp(-ie\mathbf{r}\cdot\hat{\mathbf{A}}/\hbar), \tag{15}$$

$$= (i\hbar)^{-1}[\hat{\mathbf{r}}, \hat{H}^E] = \hat{\mathbf{p}}/m. \tag{16}$$

The electric field gauge Hamiltonian $\hat{H}^E$ defined in equation (12) has the advantage of being expressed in terms of quantum operators which have physical observables as their classical analogs. Of course both Hamiltonians, $\hat{H}^c$ and $\hat{H}^E$ are *isospectral*, i.e., they have the same energy spectrum since they are related by the unitary transformation (11). However since the wavefunctions differ, albeit by phase factors only, the equivalence between the two representations can only be ensured when complete basis sets are used in any calculation, i.e. complete molecular and photon states. Calculations with the Coulomb gauge Hamiltonian $\hat{H}^c$, equation (5), are often referred to as velocity gauge calculations, whereas the electric field Hamiltonian, $\hat{H}^E$, equation (12), gives rise to the length gauge representation.

For either gauge, Coulomb (velocity) or electric field (length), the appropriate zeroth-order wavefunctions for describing the nuclear dynamics on electronic surfaces in the presence of a quantized radiation field are the electron–field states $|a,n\rangle=|a\rangle|n\rangle$, defined as eigenstates of the unperturbed Hamiltonian $\hat{H}_0$,

$$\hat{H}_0=\hat{H}_{\mathrm{el}}(r,R)+\hat{H}_{\mathrm{f}}, \tag{17}$$

$$\hat{H}_{\mathrm{f}}|n\rangle=n\hbar\omega|n\rangle, \tag{18}$$

$$\hat{H}_{\mathrm{el}}(r,R)|a\rangle=V_{\mathrm{a}}(R)|a\rangle, \tag{19}$$

$$\hat{H}_0|a,n\rangle=[V_{\mathrm{a}}(R)+n\hbar\omega]|a,n\rangle. \tag{20}$$

In equation (18) we have neglected the field zero-point energy for large photon number n, and finally (a) is designated as a collective quantum number for the molecular electronic states $|a\rangle$.

We now look for solutions of the total Schrödinger equation $H|\Psi(E)\rangle=E|\Psi(E)\rangle$ at the total energy E. We expand the wavefunction in terms of the basic field–molecule states, taking into account equations (17–20),

$$|\Psi(E)\rangle=\frac{1}{R}\sum_{an}F_{an}(R)|an\rangle. \tag{21}$$

The F's are appropriate nuclear radial functions for propagation on the potentials of the electronic–photon states $|an\rangle$. By substituting the expansion (21) into the total Schrödinger equation for any gauge, and premultiplying by a particular state $|an\rangle$, one obtains the set of one dimensional second-order differential equations for $F_{an}(R)$ for a diatomic molecule, or a single nuclear coordinate,

$$\left\{\frac{\mathrm{d}^2}{\mathrm{d}R^2}+\frac{2M}{\hbar^2}[E-V_a(R)-n\hbar\omega]\right\}F_{an}(R)=\frac{2M}{\hbar^2}\sum_{a'n'}V_{an,a'n'}(R)F_{a'n'}(R), \tag{22}$$

where M is reduced mass of the nuclei. Here we treat rotationless molecules, although later on, we will explicitly illustrate calculations for different rotational quantum numbers, J, M. Equation (22) can be generalized to many nuclear coordinates by increasing the dimensionality of the differential equation (Kodama and Bandrauk 1981) and to many laser modes by increasing the number of distinct frequencies ω and corresponding photon numbers n (Nomura and Fujimura 1990).

Equation (22) for the field–molecule representation constitutes a system of *coupled equations* which can be systematically expressed in matrix form as,

$$\mathbf{F}''(R)+\mathbf{W}(R)\mathbf{F}(R)=0, \tag{23}$$

where the diagonal energy matrix elements are,

$$W_{an,an}(R)=\frac{2M}{\hbar^2}[E-V_a(R)-n\hbar\omega]. \tag{24}$$

The non-diagonal elements describe the interstate couplings,

$$W_{an,a'n'}(R)=\frac{2M}{\hbar^2}[V^m_{an,a'n}(R)+V^r_{an,a'n'}(R)]. \tag{25}$$

There are two types of matrix elements: non-radiative (V^m) with $n=n'$, and radiative (V^r) with $n\neq n'$. Thus as a result of equations (4), (6) or (13), the radiative couplings $\hat{\mathbf{A}}\cdot\hat{\mathbf{p}}$ or $\hat{\mathbf{E}}\cdot\hat{\mathbf{r}}$ change the photon number by one only, $n'-n=\Delta n=\pm 1$. Non-radiative couplings, such as non-adiabatic couplings remain diagonal in n, since these are present in the free molecule. These last couplings, as mentioned previously, can be non-adiabatic or non-diabatic depending on whether the electronic representation is adiabatic or diabatic (Lefebvre-Brion and Field 1986, Nakamura 1992). Numerical solutions of the coupled equations (23) in any gauge or electronic representation sums automatically over all bound and continuum nuclear states of the electronic potentials $V_a(R)$. Thus only the electronic $|a\rangle$ and photon $|n\rangle$ states need be specified in any explicit calculation. Examples of this will be illustrated in later sections.

Each field operator, the vector potential $\hat{\mathbf{A}}$, equation (6) or the electric field $\hat{\mathbf{E}}$, equation (13), are sums of annihilation $\hat{a}(\Delta n = -1)$ or creation $\hat{a}^+(\Delta n = +1)$ harmonic oscillator operators. The first corresponds to absorption, the second to emission of photons. These two operators occur simultaneously in the radiative matrix elements $V^r_{an,a'n'}$, equation (25), since in equation (5) we have $\hat{\mathbf{A}} \cdot \hat{\mathbf{p}}/mc$ or $e\mathbf{r} \cdot \hat{\mathbf{E}}$ in equation (12). Thus in the field-molecule or dressed state representation every electronic-field state $|a, n\rangle$ is coupled to two other states, $|b, n+1\rangle$ and $|b, n-1\rangle$. This is illustrated in figure 1 where we show *resonant absorptions* (solid lines), $|a, n\rangle \rightarrow |b, n-1\rangle$ such that $\hbar\omega = E_b - E_a$ at a fixed internuclear distance R. This is accompanied simultaneously by a *non-resonant*, also called virtual, transition to the $|b, n+1\rangle$ field–molecule states (dotted lines). Resonant emission $|b, n-1\rangle \rightarrow |a, n\rangle$ also undergo virtual absorptions $|b, n-1\rangle \rightarrow |a, n-2\rangle$. Neglect of the virtual transitions, i.e., keeping only the resonant transitions corresponds to invoking the *rotating wave approximation* (RWA). This considerably simplifies the numerical problem, i.e. reducing an infinite number of coupled equations to two dressed states only (box in figure 1). The exact treatment should also include *spontaneous* emission, the dashed line in figure 1, between dressed

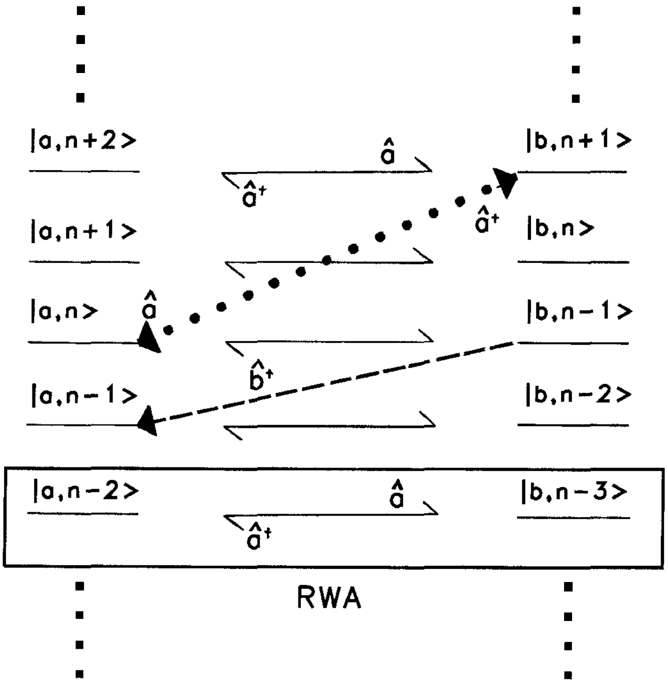


Figure 1. Dressed (field–molecule) states for a two level system $|a\rangle$ and $|b\rangle$ interacting with a coherent quantum electromagnetic field composed of photon number states $|n\rangle$. $\hat{a}(\hat{a}^+)$ are stimulated absorption and emission operators, whereas b^+ is the spontaneous emission operator. $\rightleftharpoons$: resonant stimulated transition; $\cdots\rightarrow$: virtual stimulated transition; $--\rightarrow$: spontaneous emission. Box corresponds to rotating wave approximation, RWA.

states of the same photon quantum number. Thus dressed states include all laser induced or laser stimulated processes through the operators $\hat{a}(\hat{a}^+)$, whereas spontaneous emission produces photons independent of the incident laser through the operator b^+ which creates photons into empty modes.

We now estimate the accuracy of RWA, i.e. a two dressed state approach for each resonant absorption–emission process. The energy separation between a resonant and a virtual transition is $2\hbar\omega$, i.e. the energy between the states $|b, n+1\rangle$ and $|b, -1\rangle$. The radiative coupling between the resonant states can be expressed in terms of the *Rabi* frequency, ω_R. Thus in the length gauge this is defined in the classical limit for a classical field $E(t) = E_0 \cos \omega t$, as

$$\hbar\omega_R = e\mathbf{r}_{ab}E_0, \tag{26}$$

where E_0 is a constant amplitude. As we will show below, this can also be expressed equivalently in the quantum theory as,

$$\hbar\omega_R = 2\langle a, n|e\mathbf{r}\cdot\hat{\mathbf{E}}|b, n-1\rangle = 2er_{ab}\left(\frac{n\hbar\omega}{2V}\right)^{1/2}, \tag{27}$$

where we have used the quantum expression (13) for $\hat{\mathbf{E}}$. Using now the standard definition of the field intensity (Loudon 1977),

$$I = cn\hbar\omega/V, \tag{28}$$

where c is the velocity of light, then the radiative coupling (26) is expressed as

$$\hbar\omega_R(\text{cm}^{-1}) = 1{\cdot}17\times10^{-3}[I(\text{W cm}^{-2})]^{1/2}er_{ab}(\text{a.u.}). \tag{29}$$

ω_R is the Rabi frequency in cm^{-1}, so that $\omega_R c$ is the rate of radiative transitions (s^{-1}) (Allen and Eberly 1975, Chelkowski and Bandrauk 1988, 1990). The intensity is expressed in watts cm^{-2} and the transition moment r_{ab} in atomic units (1 a.u. $= 0{\cdot}519\times10^{-8}$ cm). Thus for an intensity of $10^8\ \text{W cm}^{-2}$ and a 1 a.u. transition moment, $\hbar\omega_R = 12\ \text{cm}^{-1}$ or about 4×10^{11} radiative transitions per s.

The RWA, will be valid provided the radiative perturbation, as measured by $\hbar\omega_R$, is much less than the energy separation between resonant and virtual transitions, or equivalently the photon energy,

$$\hbar\omega_R \ll 2\hbar\omega. \tag{30}$$

Furthermore, since RWA implies a two electronic state description, states $|a\rangle$ and $|b\rangle$, then such a two state model will be adequate for each resonant absorption or emission if the radiative interaction $\hbar\omega_R$ is much less than any neighbouring excitation energy. As an example, at current accessible intensities of $10^{15}\ \text{W cm}^{-2}$, then $\hbar\omega_R \simeq 37\,000\ \text{cm}^{-1}/\text{a.u.} = 4{\cdot}6\ \text{ev/a.u.}$ Thus with visible or ultraviolet light frequencies at these intensities both corrections to RWA and multistate excitations, including ionization, (Keldysh 1965, Dietrich and Corkum 1992) will become indispensable. It is clear from equation (29) that even at intermediate intensities such as $10^{10}\ \text{W cm}^{-2}$, the radiative couplings approach vibrational energies ($\omega_v \sim 100$–$1000\ \text{cm}^{-1}$) even though RWA is valid. This means that even in a two electronic state description, considerable modification of the electronic surfaces, and consequently of the nuclear vibrational spectrum and dynamics can occur at moderate intensities. Such radiative perturbations can be shown to be more properly described by *laser-induced avoided crossings* (George *et al.* 1977, 1982, Bandrauk *et al.* 1978, 1981, 1988, 1989, 1993).

In summary of this section, we emphasize that using a full quantum description of the field–molecule system, the total Schrodinger equation for the system reduces to the coupled differential equations (22–25), where both radiative (field-induced) and non-radiative (radiationless) perturbations can be treated simultaneously for any coupling strength, i.e. from perturbative (weak) to non-perturbative (strong) interactions. The criterion for a radiative perturbative or non-perturbative regime is the Rabi frequency ω_R, defined in equation (29). For ω_R less than all natural frequencies of a molecule (rotation, vibration, electronic), then a perturbative treatment can be applied. Otherwise convergent numerical solutions of equation (22) must be called upon. This will involve using many electron–field states for high intensities. Proper boundary conditions, such as initial bound states, and (or) final continuum states very often need to be introduced to describe multiphoton molecular transitions. This problem will be addressed further on but we first examine the time dependent description of multiphoton processes and its correspondence to the time independent coupled equations (22–25) based on dressed states.

3. Time dependent theory of transition amplitudes

The passage from the time independent quantum photon theory to the time dependent large photon number limit, sometimes called the *semiclassical* theory (Loudon 1977, Mittleman 1982, Bandrauk 1993) is conveniently obtained from the special properties of the quantum harmonic oscillator, which very often reproduce exactly the classical observables (DeLange and Raab 1991). In the classical electromagnetic theory, one can write the Hamiltonian for the free field as normal modes, $H=\hbar\omega a^* a$, where the normal modes a are linear combinations of the field dynamical variables A and E due to the Maxwell relation: $E=-1/c\,\partial A/\partial t$, i.e. E is to be considered as the momentum canonical to the coordinate A. Thus one has,

$$a=\frac{\omega A}{c}-\mathrm{i}E, \qquad a^*=\frac{\omega A}{c}+\mathrm{i}E. \tag{31}$$

The quantization condition emanating from the commutation rule, $[\hat{a},\hat{a}^+]=1$, equation (3) is equivalent to the commutation relation for the field operators

$$\left[\frac{\hat{\mathbf{A}}}{c},\hat{\mathbf{E}}\right]=\mathrm{i}\hbar, \tag{32}$$

and the concomitant Heisenberg equation of motion, equation (13). The time dependence of the quantum field operators $\hat{a}$, $\hat{a}^+$, is obtained by performing a unitary transformation which removes the unperturbed field Hamiltonian $\hat{H}_f$ from the total Hamiltonian (1), (this is often called the interaction representation (Loudon 1977, Mittleman 1982)). Thus from the commutation relations, equation (3), one readily obtains,

$$\hat{a}(t)=\exp(\mathrm{i}\hat{H}_f t/\hbar)\,\hat{a}\exp(-\mathrm{i}\hat{H}_f t/\hbar)=\hat{a}\exp(-\mathrm{i}\omega t), \tag{33}$$

$$\hat{a}^+(t)=\hat{a}^+\exp(+\mathrm{i}\omega t), \tag{34}$$

in agreement with the definition of $\hat{a}$ as an annihilation operator, ($\Delta n=-1$, $\Delta E=-\hbar\omega$), and $\hat{a}^+$ as a creation operator ($\Delta n=+1, \Delta E=+\hbar\omega$). One can therefore reexpress the electric field operator $\hat{\mathbf{E}}$, equation (13) as a time dependent operator,

$$\hat{\mathbf{E}}(t)=\hat{\mathbf{E}}^+(t)=\mathrm{i}\left(\frac{\hbar\omega}{2V}\right)^{1/2}\hat{\varepsilon}\,[\hat{a}^+\exp(+\mathrm{i}\omega t)-\hat{a}\exp(-\mathrm{i}\omega t)]. \tag{35}$$

In the quantum theory it is customary to look for representations which have as basis sets eigenstates of the relevant physical operators. We will now show that there exist eigenstates of the positive, $\hat{\mathbf{E}}^+$ and negative $\hat{\mathbf{E}}^-$, frequency components of the electric field operator, which is equivalent to finding the eigenstates of $\hat{a}^+$ and $\hat{a}$. These eigenstates are called *coherent states* (Glauber 1963, DeLange and Raab 1991). Thus we assume there exists states $|z\rangle$ such that

$$\hat{a}|z\rangle = z|z\rangle, \qquad \langle z|\hat{a}^+ = \langle z|z^*, \tag{36}$$

so that

$$\langle z|\hat{a}^+(t) - \hat{a}(t)z\rangle = [z^* \exp(\mathrm{i}\omega t) - z\exp(-\mathrm{i}\omega t)]. \tag{37}$$

Setting $z = |z|\exp(\mathrm{i}\phi)$, where ϕ is the phase of the variable z, one obtains a wave amplitude like function,

$$\langle z|\hat{\mathbf{E}}|z\rangle = E_0 \cos(\omega t - \phi), \tag{38}$$

$$E_0 = 2\left(\frac{\hbar\omega}{2V}\right)^{1/2}|z|. \tag{39}$$

This simple exercise shows that the expectation value of the electric field operator $\hat{\mathbf{E}}$ in the coherent state representation is a classical oscillatory wave with a time independent amplitude E_0, as well defined frequency ω and phase ϕ, typical of classical coherent waves (Goldin 1982). In addition each frequency component $\hat{E}^{\pm}(t)$ has as eigenvalue the amplitudes

$$\frac{E_0}{2}\exp[\pm\,\mathrm{i}(\omega t - \phi)].$$

Expanding the coherent states in terms of the photon number eigenstates, one can show that the coherent states have the following properties, (Loudon 1977, Goldin 1982, DeLange and Raab 1991).

$$|z\rangle = \exp(-|z|^2/2)\sum_n |z|^n (n!)^{-1/2}|n\rangle, \tag{40}$$

$$\langle z|\hat{H}_{\mathrm{f}}|z\rangle = (|z|^2 + 1/2)\hbar\omega = E_{\mathrm{f}}. \tag{41}$$

The probability P_n of finding the nth photon quantum state in the quantum coherent state obeys a *Poisson* distribution law,

$$P_n = |z|^{2n}(n!)^{-1}\exp(-|z|^2). \tag{42}$$

This has a maximum at the value $|z| = n^{1/2}$. The mean square fluctuation of the field energy E_{f} can be calculated as $[\langle H_{\mathrm{f}}^2\rangle - \langle H_{\mathrm{f}}\rangle^2]^{1/2}/\langle H_{\mathrm{f}}\rangle = 1/|z| = n^{-1/2}$. Thus for large photon numbers the average field energy $E_{\mathrm{f}} = (n + 1/2)\hbar\omega$ has vanishing fluctuation for large n. We conclude therefore that one can express the time-dependent electric operator $\hat{\mathbf{E}}(t)$, equation (39) for a quantum coherent state $|z\rangle$ as,

$$\langle z|\hat{\mathbf{E}}|z\rangle = 2\left(\frac{n\hbar\omega}{2V}\right)^{1/2}\cos(\omega t - \phi). \tag{43}$$

This corresponds to a coherent classical wave with the amplitude E_0 expressible in terms of photon number as,

$$E_0 = 2\left(\frac{n\hbar\omega}{2V}\right)^{1/2}. \tag{44}$$

This is in agreement with the quantum Rabi frequency expression, equation (27). We have thus shown the full equivalence between the time independent, quantum theory and the time dependent semiclassical approach. As an example of this equivalence, let us consider a 1 ev ($8000\,\mathrm{cm}^{-1}$) photon with intensity $I=10^{-3}\,\mathrm{W\,cm}^{-2}$. Then from equation (28) one obtains a photon density $n/V=2\times10^{5}\,\mathrm{cm}^{-3}$. This is already a high quantum number at this relatively low intensity. Clearly, the semiclassical expressions (43) and (44) for the quantum electric field is more than adequate.

We turn next to the problem of establishing the correspondence between the time independent coupled equations developed in the previous section and the above time dependent theory. The connection between the two descriptions is obtained by the definition of the scattering (S-matrix) or transition (T-matrix) amplitudes for the formal time dependent S-matrix theory (Goldberg and Watson 1964, Watson and Nuttall 1967, Levine 1969). The definition of the transition amplitude from an initial field–molecule state $|\phi_i\rangle=|\phi_i,n_i\rangle$ to some final state $|\phi_f\rangle=|\phi_f,n_f\rangle$ is given by

$$S_{fi}=\lim_{t\to\infty}\langle\phi_f|\Psi_i^{+}\rangle, \tag{45}$$

where Ψ_i^{+} is the exact scattering wavefunction (state) which evolves from the initial field-molecule state $|\phi_i\rangle$ at $t=-\infty$. The transition amplitude is obtained by integrating over all coordinates: electron, photon and nuclear.

An equivalent, time-reversed formulation yields the definition

$$S_{fi}=\lim_{t\to-\infty}\langle\Psi_f^{-}|\phi_i\rangle, \tag{46}$$

where now ϕ_i is the initial field–molecule state and Ψ_f^{-} is the exact scattering state that evolves backward in time from the final state $\Psi_f^{-}=\phi_f$ at $t=+\infty$. Both exact wavefunctions $\Psi_{i(f)}^{+(-)}$ satisfy the same time dependence equation:

$$\left(i\hbar\frac{\partial}{\partial t}-\hat{H}\right)|\Psi\rangle=0, \tag{47}$$

where $\hat{H}$ is the full quantum time independent Hamiltonian, equation (1). In the two equations (45, 46), the initial (final) field–molecule state is defined as the state which evolves from the initial (final) molecular state as the radiation field (laser) is adiabatically switched on, i.e. the initial (final) field and molecular states must be free, i.e. non-interacting at $t=\pm\infty$. This is usually accomplished by defining the time independent interaction V_{int}, equation (1) as

$$V_{\mathrm{int}}(t)=\lim_{\varepsilon\to0^{+}}V_{\mathrm{int}}\exp(-\varepsilon|t|), \tag{48}$$

so that the effective time dependent interaction (48) is switched on and off at an infinitely slow rate (*adiabatic* switching; see Bandrauk (1993) for the gauge problem).

Clearly equation (45) is most useful when the initial state is a continuum state, whereas equation (46), serves as the appropriate equation for *half-collision* problems where the initial state is a bound state and the final state is a continuum (dissociation, ionization, etc.) state. For molecular photodissociation, the time-dependent half-collision amplitude has been studied in detail by Shapiro and Bony (1985). The half-collision description has also been discussed by Krstic and Mittleman (1990) for the ionization of atoms.

The exact, time independent scattering functions $\Psi^{+(-)}$ are obtained from the exact time independent integral form of the Schrödinger equation, called the *Lippman–Schwinger*. Thus writing the total Schrödinger equation as $(E-\hat{H})|\Psi\rangle=(E-\hat{H}_0-V)|\Psi\rangle=(E-H_0)|\phi_0\rangle=0$ and rearranging, one obtains

$$|\Psi\rangle=|\phi_0\rangle+G_oV|\Psi\rangle=(1+GV)|\phi_0\rangle, \tag{49}$$

where we have defined the resolvents or Green functions (operators),

$$G_0=(E-\hat{H}_0)^{-1}, \qquad G=(E-\hat{H})^{-1}, \tag{50}$$

$$G=G_0+G_0VG=G_0+GVG_0. \tag{51}$$

Projecting onto some free (asymptotic) field–molecule state $\phi_j\neq\phi_0$, equation (49) becomes

$$\langle\phi_j|\Psi\rangle=G_{0j}\langle\phi_j|V|\Psi\rangle, \tag{52}$$

where

$$G_{0j}=\langle\phi_j|G_0|\phi_j\rangle=(E-E_j)^{-1}. \tag{53}$$

We now apply the scattering boundary conditions via the standard limiting procedure (Goldberger and Watson 1964, Levine 1969)

$$G_0^{\pm}=\lim_{\varepsilon\to 0} G_0(E\pm \mathrm{i}\varepsilon), \tag{54}$$

$$\langle R|G_{0j}^{\pm}|R'\rangle=\exp\left[\pm\mathrm{i}\mathbf{k}_j\cdot(\mathbf{R}-\mathbf{R}')\right]/4\pi|\mathbf{R}-\mathbf{R}'|, \tag{55}$$

$$k_j=\left[\frac{2M}{\hbar^2}(E-n_j\hbar\omega)\right]^{1/2} \tag{56}$$

$G_0^{\pm}$ is an outgoing $(+)$ ingoing (-1), spherical wave in coordinate space which thus defines the appropriate scattering function $\Psi^{+(-)}$ from the boundary conditions. The matrix element $\langle\phi_j|V|\Psi^{\pm}\rangle$ in equation (52) is therefore the transition amplitude which can be reexpressed in terms of the asymptotic free state ϕ_0 from which $\Psi^{\pm}$ evolved at times $t=\mp\infty$. We define formally the *transition* operator T,

$$\langle\phi_j|T|\phi_0\rangle=\langle\phi_j|V|\Psi^{\pm}\rangle, \tag{57}$$

or equivalently

$$|\Psi^{\pm}\rangle=|\phi_0\rangle+G_0^{\pm}T|\phi_0\rangle. \tag{58}$$

Comparing this new expression to the last equation (49), one obtains the general relation between Green functions, transition operators and interactions,

$$G_0T=GV, \tag{59}$$

for which follows, using the equations (51),

$$T=(1+VG)V=(1+GV)V, \tag{60}$$

or equivalently

$$T=V+VG_0T=V+TG_0V. \tag{61}$$

Equations (59–61) are exact relations for the transition operator which allows one to calculate transition amplitudes in terms of the perturbation $V$and the non-interacting field–molecule eigenstates of $\hat{H}_0$, equation (17). As an example, iteration of equation (61) generates the multiphoton perturbation expansion (Born expansion),

$$T=V+VG_0V+VG_0VG_0V+\dots, \tag{62}$$

corresponding to one, two, three, etc., photon processes if V is the radiative interaction. The rate of transition between zeroth order initial ϕ_i and final ϕ_f, field–molecule states is defined as,

$$W_{f,i}=\frac{2\pi}{\hbar}|\langle\phi_f|T|\phi_i\rangle^2\delta(E_f-E_i), \tag{63}$$

where $E_f=E_b+n_b\hbar\omega=E_a+n_a\hbar\omega=E_i$.

In conclusion, we emphasize that in the adiabatic limit, i.e. slow turn on and off of the radiative interaction, transition amplitudes can be obtained from the time independent coupled equations (22) using as radiative matrix elements the large photon semiclassical expressions (27) and (44). An equivalent description in the adiabatic limit is to use the time dependent quantum description. Thus by using the unitary transformation (interaction representation), equation (33), one can remove the free field Hamiltonian $\hat{H}_f$ from equation (1) with the result that $\hat{H}$, via V_{int}, becomes time dependent. Thus in the time dependent case, one would obtain from equations (12), (33), and (35),

$$\hat{H}=\hat{H}^{\text{m}}+V_{\text{in}}(t), \tag{64}$$

$$V_{\text{in}}(t)=-\sum_i e\mathbf{r}_i\cdot\hat{\mathbf{E}}(t), \tag{65}$$

where $\hat{H}^{\text{m}}$ is the molecular Hamiltonian $\hat{T}_{\text{N}}+\hat{H}_{\text{el}}(R)$. The appropriate expansion for the time dependent wavefunction would now be in the interaction representation,

$$|\Psi_{\text{int}}(t)\rangle=\exp(-\mathrm{i}\hat{H}_{\text{f}}t/\hbar)|\Psi(t)\rangle, \tag{66}$$

$$=\sum_n\exp(-\mathrm{i}n\omega t)\,P_n^{1/2}|a,n\rangle F_n(R,t), \tag{67}$$

where P_n is the Poisson photon distribution, equation (42). Thus the nuclear radial functions F_n will act as time dependent coefficients modifying this distribution. Inserting the expansion (67) into the time dependent Schrödinger equation (47) with the time dependent Hamiltonian (64, 65) and function (66, 67), one gets the following time dependent matrix equation for the time dependent nuclear states $F_n(R,t)$,

$$i\hbar\frac{\partial F}{\partial t}(R,t)=-\frac{\hbar^2}{2M}[F''(R,t)+W(R,t)F(R,t)]. \tag{68}$$

The equation (68) has the same form as the time independent coupled equations (23–25) except now the diagonal energy matrix is

$$W_{an,an}(R)=-\frac{2M}{\hbar^2}[V_a(R)+n\hbar\omega], \tag{69}$$

and the radiative matrix element becomes

$$W_{an,a',n\pm1}=\frac{2M}{\hbar^2}e\mathbf{r}_{ab}E_0/2, \tag{70}$$

where E_0 is the semiclassical electric field amplitude defined previously in equations (39) and (44). In obtaining equations (68) and 70) we are assuming that the incident field is sufficiently intense so that the initial mean photon number n_i and the mean final photon number n_f as defined by the coherent state parameters $|z_i|$ and $|z_f|$, equations (40–42) remain so large that the photon number fluctuations are always negligible. This allows the approximation $P_{n_i}^{1/2} \simeq P_{nf}^{1/2} = P_n^{1/2}$ in obtaining equation (68). Thus the time dependent equations (68) become equivalent to the time dependent equations (23) in the adiabatic limit, i.e. for the case of slowly varying field amplitudes. This is achieved in the limit of large photon numbers so that photon number fluctuations and photon number changes $\Delta n = n_i - n_f$ are always much less than the mean photon occupation number n_i of the initial coherent state.

In the case of ultrashort, intense laser pulses, the switch on time can be faster than molecular time scales, thus inducing impulsive transitions. In such a case the adiabatic theorem is no longer satisfied. This is concurrent with a difficulty in expressing the laser pulse adequately in terms of coherent quantum states, since such a pulse can only be defined in terms of a large number of radiation modes of frequency ω_k, $k = 1, m$ with as many independent phases ϕ_k. For such problems, direct solution of time dependent equation (47) with $V_{\text{int}}(t)$ as the radiative perturbation with a arbitrary time dependent field $E(t)$ is a more convenient, if not, more efficient method.

We will illustrate below examples of these two approaches, the time independent dressed state approach which is most useful for long pulses, and finally the time dependent approach, which is most convenient for short intense pulses. The time dependent method, by the adiabatic S-matrix theorem, equations (45, 46) would give the same result as the time independent dressed state approach for long pulses, where coherent electric fields can be well defined, i.e. according to equation (43), a well defined frequency and phase exist. However the time dependent approach would require much more computational time, as one would have to integrate the time dependent equations (68) beyond the natural time-scales of the molecule (electronic and nuclear), which time-scales define the natural frequencies of the stationary states of the free, unperturbed system. In the opposite limit of intense ultrashort pulses, stationary states are not possible to define. Energy levels become time dependent thus making it difficult to define proper time independent transitions amplitudes and rates, (Lami and Rahman 1982, Aubanel *et al.* 1992, Bandrauk 1993 chap. 1.) In such a case, total transition probabilities for a given pulse length, and not rates, can only be defined. This will be illustrated in the last part of this article.

4. Artificial channel method

In the previous section we have established the equivalance of a time independent, dressed state approach to a time dependent method based on semiclassical (large photon number) expressions for field amplitudes and the adiabatic theorem in order to calculate multiphoton transitions rates, equation (63). The coupled equations (22–25) define the differential equations to be solved for a single nuclear coordinate and single laser mode (monochromatic), thus providing us with nuclear amplitudes $F_{an}(R)$ for a particular electron–field state $|an\rangle$ propagating on a field–molecular surface (potential), $V_a(R) + n\hbar\omega$.

In traditional spectroscopy, one starts usually in a well defined initial molecular bound state. Thus the appropriate initial boundary condition for the coupled equations is a bound state wavefunction. As final states, one must take into account the possibility of dissociation, either direct or via predissociation, so that the nuclear states F_{an} must include continuum states in their spectrum. Since there is an infinite number of such states, a basis set expansion for F_{an} with subsequent diagonalization of the ensuing matrix equations would not be practical. A more convenient method is the numerical solution of the coupled equations based on a scattering matrix (S-matrix) formalism, which thus rigorously takes into account all bound and continuum states. However, since S-matrix elements or equivalently transition amplitudes implies the presence of initial and final continuum channels, i.e. continuum entrance and exit channels, then to each initial and final bound state must be coupled an additional entrance and exit scattering channel, so that the coupled equations are augmented by these extraneous channels. This is the basis of the *artificial* channel method which transforms bound–bound, bound–continuum transition into an S-matrix problem (Bandrauk and Atabek 1988, Bandrauk and Gélinas 1987, Miret-Artes *et al.* 1992). The procedure was first introduced (Shapiro 1972) to calculate Franck–Condon factors in direct photodissociation and was subsequently generalized to Raman scattering, a two photon process by (Atabek *et al.* 1980, Kodama and Bandrauk 1981), and to multiphoton transitions including non-adiabatic interactions in electronic states (Bandrauk *et al.* 1982, Bandrauk and Turcotte 1982, Bandrauk and Gélinas 1986, 1987, Bandrauk *et al.* 1991). It has now also been applied to predissociation problems (Du and Dalgarno 1991).

We present the artificial channel method here as first applied to the effect of non-adiabatic interactions on multiphoton transitions (Bandrauk *et al.* 1982, Bandrauk and Gélinas 1987) and recently to multiphoton dissociation ionization (Bandrauk *et al.* 1991). The method is succinctly summarized in figure 2 which illustrates a two photon transition with different energy photons, $\hbar\omega_1$ and $\hbar\omega_2$ from some initial state $|a\rangle$ to some final state $|b\rangle$ via intermediate states $|I\rangle$ which are themselves coupled radiatively or non-radiatively, or both to a continuum $|c\rangle$. As a result of coupling between the bound states $|I\rangle$ and the continuum states $|c\rangle$, the true intermediate states are called *resonances*, as they will acquire a finite lifetime (Levine 1969, Bandrauk and Atabek 1988).

Introducing the extraneous (artificial) channels $|C1\rangle$ and $|C2\rangle$ allows one to extract all physically relevant transition amplitudes from the transition amplitude T_{C1C2} between these two entrance and exit channels. Thus using the integral equation theory of the T-matrix operator, equations (60), one can express T_{C1C2} as,

$$T_{C1C2} = \exp(\mathrm{i}\eta_1)\, V_{1a} G_{ab} V_{b2} \exp(\mathrm{i}\eta_2). \tag{71}$$

In this last expression, η_1 and η_2 are the zeroth-order elastic phase shifts for the scattering by the uncoupled channels $|C1\rangle$ and $|C2\rangle$. V_{1a} and V_{1b} are the extraneous *weak* couplings between the entrance (initial) channels $|C1\rangle$ and $|a\rangle$ and the exit (final) channels $|b\rangle$ and $|C2\rangle$. G_{ab} is the total resolvent operator between the initial bound state $|a\rangle$ and the final bound state $|b\rangle$. Using the integral equation relations between the exact, G, and unperturbed, G_0, resolvent operators, equation (51) and the exact relation (59) between T and G, one obtains the useful relation

$$G = G_0 + G_0 T G_0. \tag{72}$$

Equation (72) allows one to calculate the matrix element G_{ab} in terms of the physical two photon amplitude T_{ab},

$$G_{ab} = (E - E_a + \mathrm{i}\Gamma_a)^{-1} T_{ab} (E - E_b + \mathrm{i}\Gamma_b)^{-1}. \tag{73}$$

In deriving equation (73), one assumes that the only perturbation of states $|a\rangle$ and $|b\rangle$ are due to the continua $|C1\rangle$ and $|C2\rangle$ and not due to the radiative transitions involving the intermediate state $|I\rangle$. In the coupled equation this is achieved by using *asymmetric*

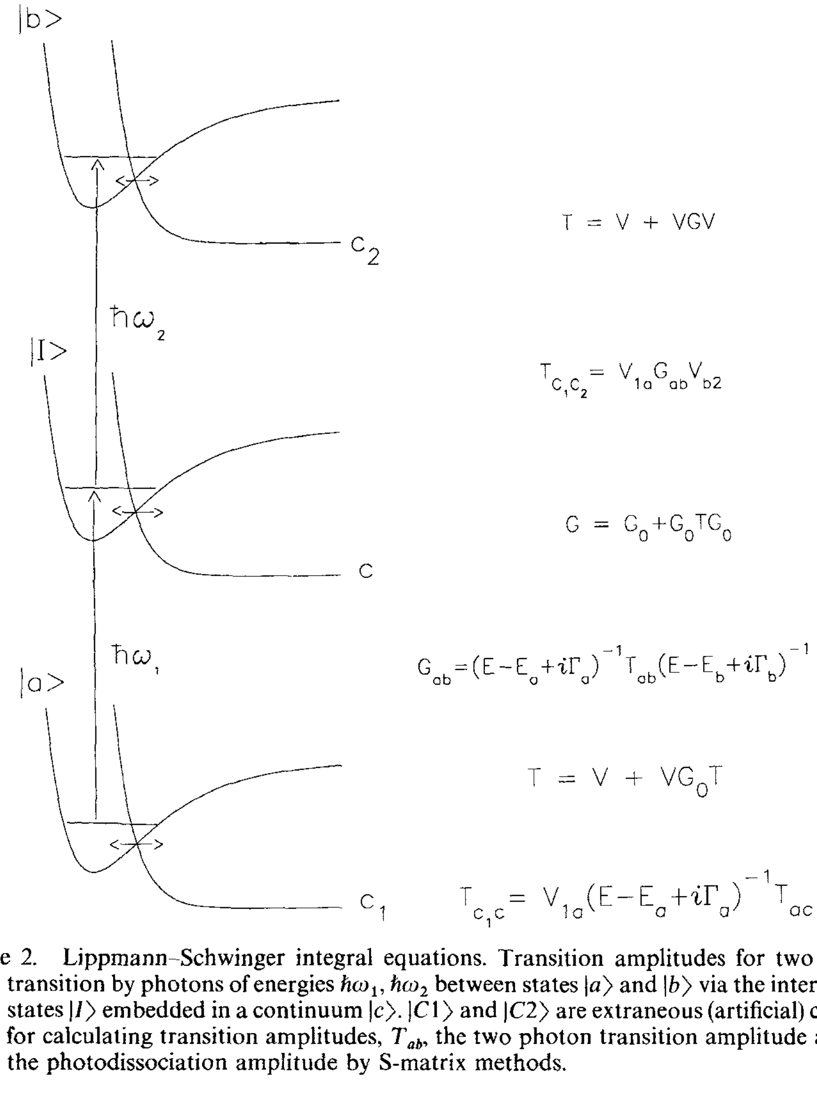


Figure 2. Lippmann–Schwinger integral equations. Transition amplitudes for two photon transition by photons of energies $\hbar\omega_1$, $\hbar\omega_2$ between states $|a\rangle$ and $|b\rangle$ via the intermediate states $|I\rangle$ embedded in a continuum $|c\rangle$. $|C1\rangle$ and $|C2\rangle$ are extraneous (artificial) channels for calculating transition amplitudes, T_{ab}, the two photon transition amplitude and T_{ac}, the photodissociation amplitude by S-matrix methods.

couplings, V_{aI}, $V_{Ib} \neq 0$ but the reverse transition is not allowed, $V_{Ia} = V_{bI} = 0$. This procedure eliminates radiative perturbation of states $|a\rangle$ and $|b\rangle$ (see Kodama and Bandrauk 1981, Bandrauk *et al.* (1982)). The appropriate expressions for the energies of the states $|a\rangle$ and $|b\rangle$ perturbed only by the extraneous continua $|C1\rangle$ and $|C2\rangle$ are

$$E_a = E_a^0 + \Delta E_a, \qquad E_b = E_b^0 + \Delta E_b, \tag{74}$$

$$\Delta E_a - i\Gamma_a = \mathrm{Re}\, I_a + \mathrm{Im}\, I_a, \qquad \Delta E_b - i\Gamma_b = \mathrm{Re}\, I_b + \mathrm{Im}\, I_b, \tag{75}$$

$$I_a = \lim_{\varepsilon \to 0} \int \frac{|V_{1a}|^2 \, dE_{C1}}{(E - E_{C1} + i\varepsilon)}, \qquad I_b = \lim_{\varepsilon \to 0} \int \frac{|V_{b2}|^2 \, dE_{C2}}{(E - E_{C2} + i\varepsilon)}, \tag{76}$$

$$G_C^0 = \lim_{\varepsilon \to 0} (E - E_c + i\varepsilon)^{-1} = \mathrm{PP}(E - E_c)^{-1} - i\pi\delta(E - E_C). \tag{77}$$

In equation (77), the Green function G_C^0 for the continuum states $|c\rangle$ has a real, principal part, PP, implying non-resonant transitions, $E \neq E_C$, whereas the imaginary part treats the resonant transition $E = E_c$ due to the delta function δ. The net result is that state $|a\rangle$ undergoes an energy shift, reminiscent of second-order perturbation theory, the real part of the integral I_a, whereas the imaginary part is the corresponding width Γ_a, consistent with a Fermi-Golden rule, Franck–Condon expression,

$$\Delta E_a = \mathrm{PP}\int \frac{|V_{1a}|^2\,\mathrm{d}E_{C1}}{E - E_{C1}}, \qquad \Gamma_a = \pi|V_{1a}|^2. \tag{78}$$

Similar expressions for ΔE_b and Γ_b are obtained, reflecting the weak perturbations of initial and final states $|a\rangle$ and $|b\rangle$ by the artificial continuum channels $|C1\rangle$ and $|C2\rangle$. It is to be noted that one can write the Franck–Condon factor: $V_{1a} = (\Gamma_a/\pi)^{1/2}$ so that a two channel calculation of the T-matrix involving channels $|a\rangle$ and $|c\rangle$ only, i.e. T_{aa} gives the value of Γ_a and consequently V_{1a} from a standard resonance pole analysis of T_{aa} (Levine 1969, Bandrauk and Atabek 1988).

The equations presented above give access to the physical transition amplitude between the two bound states $|a\rangle$ and $|b\rangle$, i.e. at resonance $E = E_a = E_b$,

$$T_{ab} = -\exp(-\mathrm{i}\eta_1)(\pi\Gamma_a)^{1/2} T_{C1C2}(\pi\Gamma_b)^{1/2}\exp(-\mathrm{i}\eta_2)\,. \tag{79}$$

All quantities on the right-hand side of equation (79) are calculated from numerical solutions of the coupled differential equations, as described below. Thus as illustrated in figure 2, T_{ab} is a two photon amplitude. The equation (79) was previously used to obtain Raman-scattering amplitudes from an intermediate continuum $|c\rangle$, for the one dimensional (Atabek *et al.* 1980), and for multimode systems (Kodama and Bandrauk 1981). In both cases exact analytic expressions were also obtained for T_{ab} (Raman) enabling one to check rigorously the numerical methods. The Raman scattering calculations were later extended to include predissociation, i.e. non-adiabatic coupling between the states $|I\rangle$ and $|c\rangle$ in figure 2 (Bandrauk *et al.* 1982). This was the first *exact* calculation for Raman scattering amplitudes in diatomic molecules.

Other interesting physical transition amplitudes which can be obtained by the artificial channel procedure are the two bound–continuum transition amplitudes T_{ac} and T_{cb}. The first is obtained from T_{C1C}, i.e. from equation (61), one can write,

$$T_{C1C} = \exp(\mathrm{i}\eta_1)\, V_{1a}(E - E_a + \mathrm{i}\Gamma_a)^{-1} T_{ac}, \tag{80}$$

so that on resonance, $E = E_a = E_c$,

$$T_{ac} = -\mathrm{i}\exp(-\mathrm{i}\eta_1)(\pi\Gamma_a)^{1/2} T_{C1C}. \tag{81}$$

Again all expressions on the right-hand side can be numerically calculated, giving the transition amplitude from the initial bound state $|a\rangle$ to the continuum $|c\rangle$ via the intermediate bound states $|I\rangle$. In the absence of these intermediate bound states, then $T_{ac} = V_{ac}$, i.e., the Franck–Condon factor between $|a\rangle$ and $|c\rangle$. This was the original procedure used by Shapiro (1972) to calculate Franck–Condon factors. It is to be emphasized that equation (81) gives a transition amplitude T_{ac} and not a transition probability such as $\Gamma_a = \pi|T_{ac}|^2$, equations (75–77), which is the standard resonance pole method to calculate transition probabilities by coupled equations in dynamics. Thus by the present artificial channel method, all phase information is retained in the amplitude, whereas such information is lost in the resonance pole method.

Thus calculation of T_{C1C} gives access to the numerical evaluation of amplitudes T_{ac} for direct photodissociation processes or for photodissociation mediated by intermediate *resonances* $|I\rangle$, such as in predissociation (Bandrauk and Child 1970, Bandrauk *et al.* 1981, 1982). In like fashion, one could obtain the continuum–bound transition amplitudes T_{cb} from equation (61),

$$T_{CC2}=T_{cb}(E-E_b+\mathrm{i}\Gamma_b)^{-1}V_{b2}\exp(\mathrm{i}\eta_2), \tag{82}$$

which at resonance, $E=E_b=E_C$ gives

$$T_{cb}=-\mathrm{i}T_{CC2}(\pi\Gamma_b)^{-1/2}\exp(-\mathrm{i}\eta_2). \tag{83}$$

The amplitude T_{cb} would therefore correspond to predissociative or radiative *recombination* into the resonances $|I\rangle$ followed by radiative absorption (emission into the final bound state $|b\rangle$.

In summary, equation (81), (82) and (83) represent multiphoton transition amplitudes for bound–bound transitions, bound–continuum or continuum–bound transitions which can be obtained exactly from numerical calculations of **S** or **T** matrix elements between the various continua $|c\rangle$, $|C1\rangle$ and $|C2\rangle$. Figure 2 can be generalized to multiphoton transitions by introducing more intermediate bound state potentials $V_{Ij}(R)$, more continuum potentials $V_C^{\kappa}(R)$ and radiative or non-radiative couplings between these. We stress the fact that in the dressed state representation, the crossing of $V_I(R)$ and $V_C(R)$ could represent also a radiative transition. In view of the formal analogy between radiative and non-radiative matrix elements, equation (25), then both types of couplings enter into the numerical method simultaneously.

The input into the coupled equations (22–24) now augmented by two artificial channels $|C1\rangle$ and $|C2\rangle$ are the diagonal matrix elements, equation (24) which can be generalized to include angular momentum,

$$W_{ii}(R)=\frac{2M}{\hbar^2}[E-V_i(R)-n_i\hbar\omega_i]-\frac{J(J+1)}{R^2}. \tag{84}$$

The non-radiative non-diagonal matrix elements can be written in a *diabatic* representation, as potential matrix elements,

$$W_{ij}(R)=\frac{2M}{\hbar^2}V_{ij}(R), \tag{85}$$

where $V_{ij}(R)=\langle\phi_i(r,R)|\hat{H}_{el}(r,R)|\phi_j(r,R)\rangle$ is the matrix element for the electronic Hamiltonian in a diabatic basis. Thus in this basis, the diabatic electronic states are not eigenstates of $\hat{H}_{el}$ but correspond very often to intuitive chemical states such as the covalent, ionic valence bond states of alkali halides (see for example Bandrauk and Gauthier 1990). In practice, any two non-crossing adiabatic surfaces obtained from the usual *ab initio* adiabatic calculations (Yamashita and Morokuma 1991), with residual *non-adiabatic* couplings depending on derivatives $\partial/\partial R$, can be transformed into crossing diabatic surfaces with a residual *non-diabatic* interaction $V_{ij}(R)$ operative between them (Bandrauk and Child 1970, Lefebvre-Brion and Field 1986, Bandrauk and Gélinas 1987). The radiative coupling for a diatomatic molecule can be written as,

$$V^{r}_{ij}(R)=\gamma\left[\frac{(2J+1)}{(2J'+1)}\right]^{1/2}\langle J1M\lambda|J'M'\rangle\sum_m\langle J1\Omega m|J'\Omega'\rangle\rangle d_m(R)\delta_{n',n\pm1}. \tag{86}$$

Ω is the electronic angular momentum projection on the internuclear axis, λ is the field polarization with respect to laboratory axes, d_m is the $m=0$, ± 1 component of the electronic transition moment r_{ab} along the molecular axis, and finally γ is the field dependent unit conversion factor in equation (29), i.e. $\gamma = 0{\cdot}585 \times 10^{-3}$ $[I(\mathrm{W\,cm^{-2}})]^{1/2}$ $(\mathrm{a.u.})^{-1}$. (Note this is $\omega_\mathrm{R}/2$ as given by equation (27)). The Clebsch–Gordan coefficients in equation (86) fix the selection rules $\Delta J = 0$, ± 1; $\Delta m = 0$, ± 1 (Herzberg 1966, Lefebvre-Brion and Field 1986).

Thus using appropriate transition moments, either from spectroscopic data or *ab initio* electronic calculations, one uses as input for the coupled equations (22–25) augmented by the artificial channels, the diagonal electronic potentials $W_{ii}(R)$, equation (84), the diabatic non-diagonal non-radiative potentials $W_{ij}(R)$, equation (85) and the non-diagonal radiative potentials $(2M/\hbar^2)V^{\mathrm{r}}_{ij}(R)$, equation (86). Equations (22) are completely diabatic, with both radiative and non-radiative perturbations appearing as non-diagonal potentials, functions of R, the internuclear coordinate. Thus both radiative and non-radiative couplings appear on an equal footing, and for any coupling strength. In the limit of large radiative and (or) non-radiative couplings, a more efficient representation is the adiabatic representation, with avoided crossings now appearing instead of the diabatic crossing exhibited in figure 2 between states $|l\rangle$ and $|c\rangle$. In an adiabatic representation, both electronic state avoided crossings (non-crossing rule of states of same symmetry, (Lefebvre-Brion and Field 1986)) and laser-induced avoided crossings (see §8) (George *et al.* 1977, 1978, Bandrauk and Sink 1978, 1981, Bandrauk and Atabek 1988, Bandrauk and McCann 1989), remain coupled by non-adiabatic interactions dependent on nuclear momenta, i.e. $\langle \phi_i^{\mathrm{ad}}/\partial/\partial R/\phi_j^{\mathrm{ab}}\rangle \partial/\partial R$ where ϕ^{ad} are the corresponding adiabatic electronic states. It is possible to express the coupled equations (22) in a complete adiabatic representation (Nguyen-Dang *et al.* 1989, 1991). Such a time independent adiabatic representation is very useful when electronic transition moments diverge as in the case of the $1\mathrm{s}\sigma_\mathrm{g}$ to $2\mathrm{p}\sigma_\mathrm{u}$ transitions in H_2 and H_2^+ (Bandrauk *et al.* 1991). In this case the dipole transition moment $er_{\mathrm{ab}} = eR/2$ in the electric field gauge, whereas in the Coulomb gauge, the momentum transition moment $ep_{ab} = [(V_u(R) - V_g(R))/\hbar\omega]er_{ab}$ (equation 16), is convergent asymptotically due to the degeneracy of the σ_g and σ_u states. However since a two-electronic state model may not be sufficient to ensure gauge equivalence, then the adiabatic electric field representation of Nguyen-Dang should be superior as all couplings, radiative and non-radiative are localized around the diabiatic crossing points, which is a special feature of adiabatic representations (Bandrauk and Child 1970, Lifebvre-Brion and Field 1986).

The disadvantage of the adiabatic representation is that derivatives of the nuclear functions, $\partial F_{\mathrm{an}}/\partial R$ must be evaluated. In our work we have therefore adhered to the diabatic representation where all couplings, radiative and non-diabatic are of pure potential type (polynomials of R). Thus at the formal level, radiative and non-radiative couplings are analogous, so that radiative bound–continuum transitions, i.e. photodissociation processes can be treated as *diabatic predissociation* problems (Bandrauk and Sink 1978, 1981, Bandrauk and McCann 1989). All one needs to do is to specify the functional forms of the diabatic electronic potentials $V_i(R)$, the transition moments er_{ij} and the non-diabatic couplings (85). The coupled equations (22) including the artificial channels coupled to the initial (final) potentials $V_{a(b)}(R)$, are integrated numerically by a Fox–Goodwin algorithm (Fox 1957, Norcross and Seaton 1973). The numerical continuum functions are then compared with the analytic asymptotic functions,

$$k_j^{1/2}F_j^{(i)}(R) = \sin(k_jR - J\pi/2)\,\delta_{ij} + R_{ij}\cos(k_jR - J\pi/2), \tag{87}$$

$$k_j = \lim_{R\to\infty} [W_{jj}(R)]^{1/2}. \tag{88}$$

The coefficients R_{ij} define a scattering matrix $S = (1 + iR)(1 - iR)$ from which the transition amplitudes follow: $S_{ij} = \delta_{ij} - 2\pi_i T_{ij}$ (Levine 1969, Norcross and Seaton 1973).

Thus in conclusion, adding to the physical channels the two extraneous continuum channels $|C1\rangle$ and $|C2\rangle$ as entrance and exit channels for the initial $|a\rangle$, and (or) final $|b\rangle$ states, we can obtain numerically the transition amplitudes T_{C1C2}, T_{C1C}, T_{CC2} from which one extracts the physical multiphoton transition amplitudes T_{ab}, T_{ac}, T_{cb}. These amplitudes contain all the phase information due to the various radiative and non-radiative processes. The present method therefore allows one to calculate individually separate amplitudes, and to analyse their physical content individually. Total probabilities are then obtained by summing first all amplitudes from given initial to final states and then squaring the total amplitude according to equation (63).

The method is most useful when the initial state $|a\rangle$ is unperturbed in the multiphoton process. We remind the reader that time independent transition rates, equation (63) can only be obtained in the adiabatic limit (see § 3), so that the initial and final states are stationary. For the physical continuum $|c\rangle$ this creates no problem, since the non-diabatic interaction is localized around the crossing point (figure 2). However for radiative transitions, at high intensities (large Rabi frequencies, ω_R, equation 27), dynamic Stark shifts can become important. The artificial channel method has been generalized for this non-perturbative initial state. By choosing the artificial and true initial state to be identical, it is possible to search for the initial state in all the stationary dressed states, such as in figure 1 (Bandrauk and Turcotte 1985, Bandrauk and Atabek 1988, Miret-Artes *et al.* 1992). This general artificial channel method, involving both extraneous continuum and bound channels added to the the physical channels allows one to treat the strong-field, overlapping resonance, non-perturbative, time independent regime. Of course as we have pointed out in the previous section, non-perturbative radiative transitions often involve short pulses, for which time dependent calculations are then more appropriate.

In many cases it is however often possible to identify weak (perturbative) and strong non-perturbative radiative transitions. This was the case in the 10 photon photoionization of H_2 where the first transition was a weak non-resonant five photon transition followed by strong resonant single photon transitions between Rydberg and doubly excited electronic states (Bandrauk *et al.* 1991). Equation (81) was used in a many dressed state calculation (up to 100 coupled equations on a CRAY-XMP supercomputer) to obtain all the photodissociation and photodissociation–ionization amplitudes in the process $H_2 + 10\hbar\omega = H_2^+ + e^-$. It was proven in this artificial channel coupled equation calculation that laser-induced avoided crossings (see § 6) play a predominant role in creating anomalous kinetic energy distributions of protons at high laser intensities, $I \sim 10^{13}\,\mathrm{W\,cm^{-2}}$. This anomalous effect had been experimentally discovered previously (Bucksbaum *et al.* 1990).

Introducing the detailed quantum rotational couplings, equation (86) allows one to calculate the transition amplitudes for specific rotational quantum numbers J and M. Such detailed amplitudes enter into calculations of multiphoton photodissociation angular distributions. Thus two-colour (two photon frequencies ω_1 and ω_2), numerical experiments were carried out to examine the effect of high laser intensities on angular distributions of the photodissociation of Li_2 (McCann and Bandrauk 1990, 1992). Previous one-photon angular photodissociation angular distributions for Ar_2^+ (Bandrauk and Turcotte 1983) showed for the first time the effect of *laser-induced* *resonances* as a cause of anomalous angular distributions. In the two colour numerical experiments, the first laser (ω_1) was considered to be weak in order to select well defined rovibration (v, J) excited levels, followed by an intense low frequency (ω_2) second laser coupling two nearby electronic states via a large transition moment. Thus equation (81) was used for this two photon transition in order to calculate the photodissociation amplitudes as a function of rotational quantum numbers and laser intensity. The differential two-photon dissociation cross-section was obtained and was shown to produce at high intensities new, non-classical angular distributions, (McCann and Bandrauk 1990, 1991) quite different from the usual classical distributions (Zare 1988). Simultaneously, an intensity dependence of the isotope yield in photodissociation was found to be quite nonlinear with respect to the second laser (ω_2) intensity (McCann and Bandrauk 1990).

In conclusion, we emphasize that the coupled equations (22–25) using the artificial channel technique can furnish exact multiphoton transition amplitudes. The necessary initial data are the relevent electronic potentials, the radiative transition moments and the non-diabatic non-radiative couplings. The numerical integration of the coupled equations gives as output transition amplitudes and also dressed state spectra, since these will appear as resonances when the transition amplitudes are calculated as a function of energy (or laser frequency). It is to be emphasized that the input data are not spectra but potentials only. The eigenstates, or equivalently the dressed states, and their eigenenergies, i.e. the spectra are obtained from the numerical solution of the coupled equations. In this sense, we can characterize this method as *computational spectroscopy*. In the next section we present a detailed example of a multiphoton calculation, where one uses the principle of interference of multiphoton amplitudes in order to control a photophysical process.

5. Laser control of predissociation

One of the fundamental predictions of quantum mechanics is the interference between transition amplitudes (Feynman 1960). An interesting result of this interference is the enhancement or suppression of transitions through the variations in the relative phases of the transition amplitudes. The exploration of such effects in order to influence photochemical reaction paths, has been recently suggested (Brumer and Shapiro 1989). A scheme relying on the coherence between one and three (1 + 3) photon transitions ($\omega_3 = 3\omega_1$), was proposed to control photodissociation products (Shapiro *et al.* 1988). A similar scheme has appeared in the atomic physics literature where experimental laser phase control of atomic ionization was first demonstrated (Chen and Elliott 1990, Chen *et al.* 1990). Finally this same (1 + 3) interference scheme has been carried out recently to provide the first example of *coherent phase-control* of molecular multiphoton ionization (Lu *et al.* 1992). In the (1 + 3) scheme, even (g) states are coupled radiatively to odd (u) states. We have recently proposed a 2 + 4 scheme coupling states of same symmetry (Bandrauk *et al.* 1992), based on numerical calculations by the artificial channel coupled equations method described in the previous section.

The multiphoton process proposed is illustrated in figure 3 in the field–molecule or dressed state representation for the Cl_2 molecule. The dressed molecular energy potentials are therefore drawn on a total energy scale (field + molecule), appropriate to the coupled equations (22–25). Two processes are distinguished in figure 3. Firstly, a *resonant* two-photon excitation of frequency ω_2 occurs from the ground state of Cl_2,

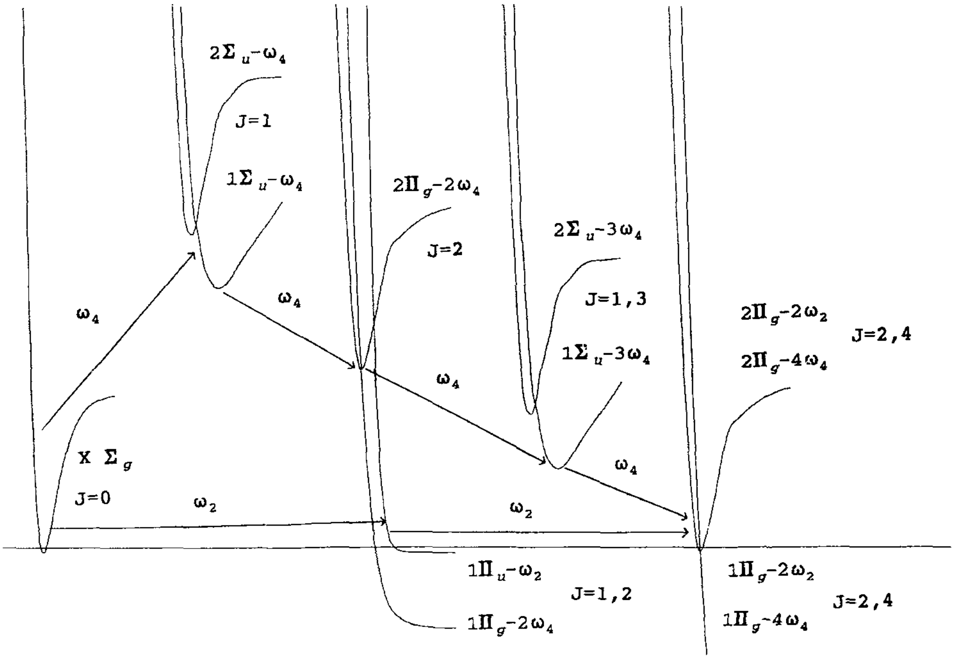


Figure 3. Dressed state representation of 2+4 photon interference of the excitation of $|{}^1\Sigma_g^+, v=0, J=0\rangle$ to $|\Pi_g, C, J=2\rangle$. $\omega_2=2\omega_4$. $\Sigma_g\to\Pi_u\to\Pi_g$ transition is resonant and is represented by horizontal arrow. $\Sigma_g\to\Sigma_u\to\Pi_g\to\Sigma_u\to\Pi_g$ is non-resonant and is represented by oblique arrows. $1\Sigma_u$, $2\Sigma_g$ and $1\Pi_g$, $2\Pi_g$ electronic states interact non-diabatically.

the $X\Sigma_g^+$ electronic state, via the repulsive $1\Pi_u$ state to some final vibrational level, v, of the $2\Pi_g$ state which then predissociates by non-radiative interaction with the repulsive $1\Pi_g$ state. Secondly, a *non-resonant* four-photon transition of frequency ω_4 proceeds first from the $X\Sigma_g^+$ ground state to the $2\Sigma_u^+$ highly excited valence state. This state interacts non-adiabatically with the $1\Sigma_u^+$, Rydberg electronic state (Peyerimhoff and Buenker 1981). These two states are radiatively non-resonantly coupled to the Π_g states, which again recouple radiatively (again non-resonantly) to the Σ_u states, and finally one last radiative transition leads to the same predissociated level, v, of the Π_g states as in the two photon process. Given that all these transitions are non-resonant it is important to note that the $X\Sigma_g^+\to 2X\Sigma_u^+$ transition moment is large. This non-resonant transition is strong and is responsible for the anomalous Raman line intensities in Cl_2 (Ghandour *et al.* 1983).

In the (2+4) scheme, we rely on this intense ($\Sigma_g^+\to\Sigma_u^+$) non-resonant transition to drive the four-photon transition efficiently. Thus one requires only moderate intensities to obtain a four-photon transition amplitude T_4 comparable, in magnitude to T_2, the resonant two-photon transition amplitude. T_2 is initiated by a first weak transition moment, $\langle X\Sigma_g^+|er|1\Pi_u\rangle \simeq 0{\cdot}1$ a.u., followed by a large moment $\langle 1\Pi_u|er|1\Pi_g\rangle \simeq eR/2$, similar to the $X\Sigma_g^+\to 2\Sigma_u^+$ transition moment (Bandrauk and Gélinas 1987). Previous experimental work on the spectroscopy of the predissociated $2\Pi_g$ state (Li *et al.* 1988) allows for an adequate estimate of the nonradiative coupling between the Π_g states.

The photopredissociation transition amplitudes from the initial bound state $|0\rangle$ to the final continuum state $|c\rangle$ can be expressed as a Born series, (see equation 62) in terms of the radiative V_n and non-radiative V_{vc} interactions,

$$\langle 0|T_2|c\rangle = \langle 0|V_2 G_c^2(\Pi_u - \hbar\omega_2)V_2[G_v^2\Pi_g - 2\hbar\omega_2)V_{vc} + 1]|c\rangle, \tag{89}$$

$$\begin{aligned}\langle 0|T_4|c\rangle = {} & \langle 0|V_4 G^4(\Sigma_u - \hbar\omega_4)V_4 G^4(\Pi_g - 2\hbar\omega_4) \\ & \times V_4 G^4(\Sigma_u - 3\hbar\omega_4)V_4[G_v^4(\Pi_g - 2\hbar\omega_4)V_{vc} + 1]|c\rangle.\end{aligned} \tag{90}$$

The continuum Green function G_C^2 appears only in the two photon amplitude T_2 and has been previously defined in equation (77). The bound states Green functions appearing above are defined as,

$$G^4 = (E - H_0)^{-1},\ \langle \Pi_g|G_v^n|\Pi_g\rangle = (E - n\hbar\omega - E_v + \mathrm{i}\Gamma_v)^{-1}, \tag{91}$$

and the resonance condition is

$$E = E_0 + 2\hbar\omega_2 = E_0 + 4\hbar\omega_4\ .$$

Γ_v is the predissociation line width of the final level v in the Π_g electronic states. The last two terms in equation (89) and (90) reflect the two possible pathways to the dissociative nuclear level $|c\rangle$ in the Π_g states, i.e. directly $(+1)$ or via the predissociating bound state, v, though the term $G_v V_{vc}$.

The half-collision equations (22–25) for the processes illustrated in figure 3 are converted into a scattering problem by introducting an artificial channel $|C_0\rangle$, which is weakly coupled to the initial state $|X\Sigma_g^+, v=0, J=0\rangle$. The amplitude T_2 is modulated by the phase factor $\exp(\mathrm{i}\phi)$ representing the phase difference between the two coherent laser beams,

$$E_2 = E_0(\omega_2)\exp[\mathrm{i}(\omega_2 t - \phi)], \qquad E_4 = E_0(\omega_4)\exp(\mathrm{i}\omega_4 t). \tag{92}$$

We emphasize that the amplitudes T_2 and T_4 contain all the appropriate information about molecular potentials, radiative and non-radiative couplings.

The total transition amplitude under the influence of the two laser fields, equation (92) can be written as:

$$T = T_2\exp(\mathrm{i}\phi) + T_4. \tag{93}$$

Cancellation will occur whenever $|T_2| = |T_4|$ and

$$\arg(T_2) + \phi - \arg(T_4) = \pi(\text{modulo } 2\pi), \tag{94}$$

and *enhancement* when the two components of (93) are in phase.

All relevant potentials and transition moments were obtained from the previously published *ab initio* calculations (Peyerimhoff and Buenker 1981). The non-radiative coupling matrix elements between the Σ_u^+ and Π_g states, see figure 3, were obtained by deperturbing the 2 × 2 adiabatic *ab initio* potentials (Bandrauk and Gélinas 1987), into diabatic electronic potentials with corresponding non-diabatic couplings $V_{ij}(R)$ between them. As a consequence, both radiative and non-radiative couplings become equivalent non-diabatic couplings, the first non-diagonal in photon number, whereas the second leaves the photon number unchanged. From the Π_g state spectra, a non-diabatic coupling of $V_{12} = 350\,\mathrm{cm}^{-1}$ gave energy level and corresponding widths, obtained by a resonance analysis of a two channel S-matrix calculation, in good agreement with the experimental spectra (Li *et al.* 1988)

The artificial channel method described in the previous Section was used to calculate the photon, T_2 and four photon, T_4, amplitudes as a function of intensity of the two laser beams, $I_2(\omega_2)$ and $I_4(\omega_4)$. Then using equation (93) with a variable phase ϕ led to beats in the total transition probability $|T|^2$. In figure 4 we present results for a fixed value of $I_4=5\times10^8\,\mathrm{W\,cm}^{-2}$. Such an intensity gives a resonant electronic Rabi frequency, equation (27) of about $2\,\mathrm{cm}^{-1}$ per atomic unit of transition moment. This radiative coupling produces negligible energy shifts of perturbations to the initial state since the transition is non-resonant. This makes use of equation (81) an exact method to calculate the photopredissociation amplitude from the $X\Sigma_g^+$ levels to the Π_g continuum states.

Thus fixing I_4, one has two independent parameters: I_2, the intensity of the second two photon beam (ω_2) and ϕ, its phase relative to the I_4 beam. We report in figure 4 results for the $J=0$ to $J=2$ transition. The four photon transition gives products in $J=2$ and $J=4$, whereas the two photon transition produces only a $J=2$ final state. Thus only the $J=2$ angular momentum state can show any interference effect. In fact, the invariance of the $J=0$ to 4 transition amplitude with respect to the phase ϕ was used as a check of the consistency of the numerical results since this transition is only produced by the four-proton beam of frequency ω_4 and intensity I_4. In figure 4 we show the result obtained by the coupled equations for the photopredissociation probability from the initial $|X\Sigma_g^+, v=0, J=0\rangle$ bound state to the final $|1\Pi_g, E_C, J=2\rangle$ continuum state, where $E= =E_0+2\hbar\omega_2=E_0+4\hbar\omega_4$. The non-adiabatic coupling $V_{12}=350\,\mathrm{cm}^{-1}$ is considered to be of intermediate coupling strength (Bandrauk and Child 1970). Figure 4 shows the photodissociation probability through the $v=0$ level of the $2\Pi_g$ electronic state as a function of I_2 and ϕ. An absolute minimum, corresponding to a decrease by at least four orders of magnitude is found at $I_2=7500\,\mathrm{W\,cm}^{-2}$ and $\phi=0{\cdot}38\pi$. Figure 5 summarizes the overall photopredissociation probabilites

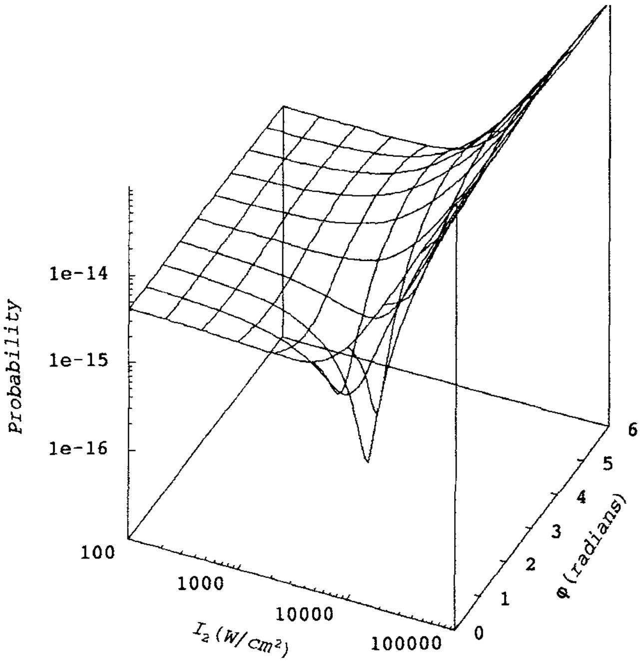


Figure 4. Photopredissociation probability of $v=0$ level of $2\Pi_g$ electronic state for non-diabatic coupling $V_{12}=350\,\mathrm{cm}^{-1}$, $I_4=5\times10^8\,\mathrm{W\,cm}^{-2}$. Minimum occurs at $I_2=7500\,\mathrm{cm}^{-1}$, $\phi=0{\cdot}38\pi$, $\omega=2\omega_2=4\omega_4=66421\,\mathrm{cm}^{-1}$.

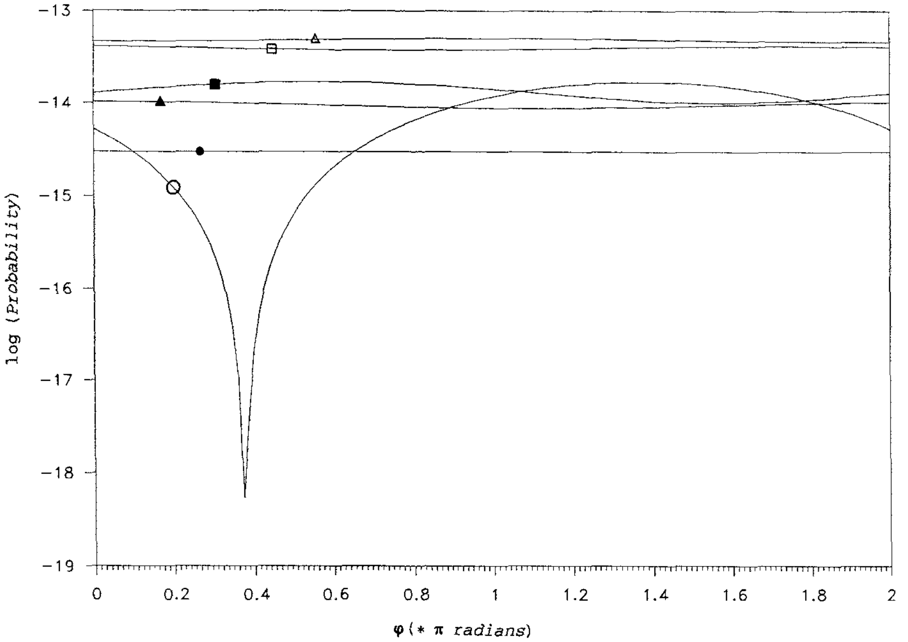


Figure 5. Photopredissociation probability of $v=0$–5 levels $2\Pi_g$ electronic state for non-diabatic coupling $V_{12}=350\,\text{cm}^{-1}$ at intensities $I_2=7500\,\text{W cm}^{-2}$, $I_4=5\times10^8\,\text{W cm}^{-2}$. $V=$ ○, 0; △, 1; ■, 2; ▲, 3; □, 4; and ●, 5.

through the various $2\Pi_g$ vibrational levels as a function of ϕ for fixed intensities $I_4=5\times10^8\,\text{W cm}^{-2}$, $I_2=7500\,\text{W cm}^{-2}$. Thus the deep minimum for $v=0$, in figure 4 is the predominant feature. In fact figure 5 shows clearly a sharp minimum (suppression) at $\phi=0{\cdot}38\pi$ and also a slight maximum (enhancement) at $\phi=1{\cdot}38\pi$ in the predissociation of $v=0$. Thus as a general rule, as seen from figure 5, for fixed intensities I_2 and I_4, only one level of the $2\Pi_g$ state undergoes complete suppression of predissociation and also the most enhancement. This same behaviour is found for other non-diabatic coupling parameters V_{12} between the Π_g electronic states (Bandrauk *et al.* 1992).

We conclude by emphasizing that in spite of the complex dependence of the transition amplitudes, T_2 and T_4, on the relative laser beam phase ϕ, due to the non-diabatic dynamics of the Π_g states of Cl_2, phase interference of radiative transition amplitudes remains operative. Thus in equations (89) and (90), both the continuum $G_C(\Pi_u)$ and the bound $G_v(\Pi_g)$ Green operators (functions) have real and imaginary parts. The imaginary part of G_C, equation (77) comes from the resonant continuum states of the Π_u repulsive state (figure 3) whereas the imaginary part of G_v, equation (91), come from the finite width and therefore lifetimes of the predissociating vibrational levels v of the Π_g states. These imaginary parts of the Green functions are in large part responsible for the complex behaviour of the phases (arguments) of T_2 and T_4, equation (94). Nevertheless, figure 4 and 5 show it is possible to efficiently suppress the predissociation of a particular vibrational Π_g level at a definite angle ϕ. Clearly, suppression of the photopredissociation channel should show up as the elimination of the high energy kinetic component in the photodissociating Π_g and Π_u states, figure 3. Furthermore suppression of particular rovibrational levels might be used to decongest predissociation spectra.

6. Photodissociation as predissociation

As suggested by the coupled equations (22–25) in the dressed state formalism, multiphoton processes correspond to redistribution of energy between the field and molecular states. Thus as illustrated in figure 6 for the photodissociation of H_2^+, the ground electronic–vibrational photon bound state $|^2\Sigma_g^+, v, n\rangle$ of total energy $E = E_v + n\hbar\omega$ is *degenerate* with some $(n-1)$ photon–nuclear continuum state $|^2\Sigma_u^+, c, n-1\rangle$ of total energy $E = E_c + (n-1)$. On a total energy scale, the field electronic potentials $[V(^2\Sigma_g^+) + n\hbar\omega]$ and $[V(^2\Sigma_g^+) + (n-1)\hbar\omega]$ cross at some distance R_c, the radiative crossing point and are coupled via the radiative interaction $dE_0/2$ where d is the electronic transition moment, $\langle ^2\Sigma_g^+|er|^2\Sigma_u^+\rangle$ and E_0 is the maximum electric field amplitude expressed in photon numbers by equation (44). We thus arrive at the conclusion that photodissociation is the analog of predissociation (Bandrauk and Sink 1978, 1981, Bandrauk and Atabek 1988, Bandrauk and McCann 1989). Such a situation, figure 6, corresponds to the classical case of a discrete state embedded in a continuum, the time evolution of which can be studied by the method of Green functions (Goldberger and Watson 1964, Mower 1966).

If originally the initial bound state was in the eigenstate $|a\rangle$ of some Hamiltonian $\hat{H}_0$, e.g. equation (17) then though some time independent perturbation V(radiative and (or) non–radiative), equation (25)), at time t it will have evolved according to the expression,

$$|\Psi(t)\rangle = \exp(-i\hat{H}t/\hbar)|a\rangle, \tag{95}$$

where $\hat{H} = \hat{H}_0 + V$, and $\hat{H}_0|a\rangle = E_a^0|a\rangle$. The decay amplitude $I_a(t)$, i.e. the probability amplitude that the system starting at $t = 0$ in $|a\rangle$ remains in this state after t is defined by

$$I_a(t) = \langle a|\Psi(t)\rangle = \langle a|\exp(-i\hat{H}t/\hbar)|a\rangle. \tag{96}$$

This may be expressed in terms of the time independent (energy dependent) Green functions introduced in equations (50–51),

$$I_a(t) = \frac{1}{2\pi i}\int_{-\infty}^{\infty} \exp(-iEt/\hbar) G_{aa}(E)\, dE. \tag{97}$$

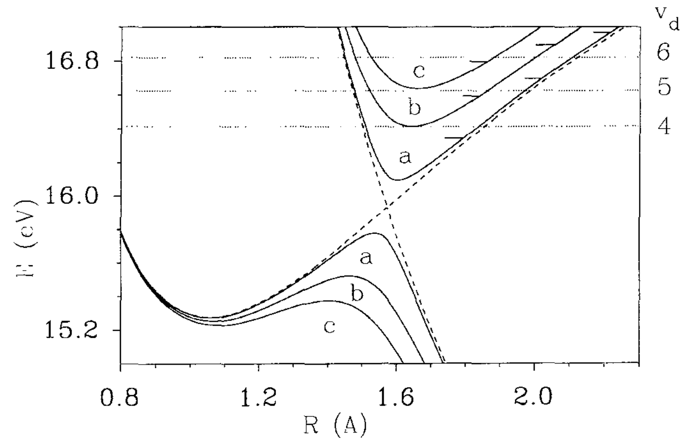


Figure 6. Laser-induced avoided crossing between $|^2\Sigma_g^+, n\rangle$ and $|^2\Sigma_u^+, n-1\rangle$ dressed electronic potentials in the direct photodissociation of H_2^+ at wavelength $\lambda = 213$ nm, for intensities I (W cm^{-2}): (*a*) $3{\cdot}2 \times 10^{12}$, (*b*) $2{\cdot}6 \times 10^{13}$, (*c*) 6×10^{13}. Also shown are adiabatic (—) and diabatic vibrational levels (····), v_d.

The transition amplitude between the state $|a\rangle$ and the continuum $|c\rangle$ is given by

$$I_{ca}(t)=\frac{1}{2\pi \mathrm{i}}\int_{-\infty}^{\infty}\exp(-\mathrm{i}Et/\hbar)G_{ca}(E)\,\mathrm{d}E. \tag{98}$$

Iterating equation (51) which defines the exact G with respect to the unperturbed G_0, we get

$$G(E)=G^0(E)+G^0(E)VG^0(E)+G^0(E)VG^0(\mathrm{E})VG(E), \tag{99}$$

from which it follows exactly by evaluating matrix elements (see Bandrauk and Turcotte 1982),

$$G_{aa}(E)=(E-E_a-\mathrm{i}\Gamma_a)^{-1}, \tag{100}$$

where E_a and Γ_a, are the energy shifts and widths defined previously in equations (74–77). Examples of models for which these expressions can be evaluated analytically have been reported previously (Sink and Bandrauk 1978, Kodama and Bandrauk 1981). The direct photodissociation Green function, G_{ca}, can be obtained from equation (51),

$$G_{ca}(E)=G_c^0\,V_{ca}G_{aa}=\lim_{\varepsilon\to 0^+}\frac{V_{ca}/(E-E_c+\mathrm{i}\varepsilon)}{(E-E_a+\mathrm{i}\Gamma_a)}. \tag{101}$$

The transition amplitudes (97) and (98) are found next by performing contour integrations in the lower half energy plane, i.e., $\operatorname{Im} E<0$ in order to encircle the resonance pole at $E=E_a-\mathrm{i}\Gamma_a$. One thus obtains readily from the residue theorem (Levine 1969),

$$I_a(t)=\exp(-\mathrm{i}E_a t/\hbar)\exp(-\Gamma_a t/\hbar), \tag{102}$$

from it follows that the population of state $|a\rangle$ evolves as,

$$P_a(t)=|I_a(t)|^2=\exp(-2\Gamma_a t/\hbar). \tag{103}$$

The photodissociation amplitude is obtained in like fashion by considering the two poles in the lower half-energy plane in equation (101), i.e. at $E_c-\mathrm{i}\varepsilon$ and $E_a-\mathrm{i}\Gamma_a$. The resulting integration gives:

$$I_{ca}(t)=\frac{V_{ca}}{(E_c-E_a+\mathrm{i}\Gamma_a)}\{\exp(-\mathrm{i}E_c t/\hbar)-\exp[(-\mathrm{i}E_a-\Gamma_a)t/\hbar]\}. \tag{104}$$

Integrating the square of this expression over the continuum energy E_c to get the total photodissociation probability P_c from state $|a\rangle$ (we assume that V_{ca} and therefore ΔE_a and Γ_a are independent of energy (see equations 74–77), thus avoiding extra poles from new bound states created by energy dispersion of these parameters (Laplante and Bandrauk 1976)), we obtain

$$P_c(t)=\int|I_{ca}(t)|^2\,\mathrm{d}E_c=\frac{\pi|V_{ca}|^2}{\Gamma_a}[1-\exp(-\Gamma t/\hbar)], \tag{105}$$

Since $\Gamma_a=\pi|V_{ca}|^2$, equation (78), we obtain finally the kinetic equation,

$$P_c(t)=[1-\exp(-2\Gamma_a t/\hbar)], \qquad P_a+P_c=1. \tag{106}$$

We further note, that for constant width Γ_a, the *dissociation rate* $\mathrm{d}P_c/\mathrm{d}t=(2\Gamma_a/\hbar)$, is also constant.

The above results are exact only for a model of *one* energy bound state $|a\rangle$ coupled to one continuum mainfold $|c\rangle$ (which itself contains an infinite number of states of energy E_c). Molecular systems are multilevel systems, so these expressions must be generalized. More general expressions for the Green functions have been obtained for multilevel systems, relating thus the artificial channel coupled equations method (section 4) to time dependent theory (Bandrauk and Turcotte 1985, Bandrauk and Atabek 1988). In general, more than one bound state must be considered, and for strong perturbations the phenomenon of overlapping resonances, $(E_a - E_b) \simeq \Gamma_a, \Gamma_b$ can occur (Fano 1961, Levine 1969, Miret-Artes *et al.* 1992). For strong fields, one must therefore always consider renormalization of the spectrum since the laser field can even create new bound states by the mechanism of laser-induced avoided crossings (section 8). Furthermore, more and more experiments are being carried out with short laser pulses (Scherer 1991, Zewail 1991), so that a complete time dependent theory is more convenient as one can now describe multiphoton spectroscopy in terms of the pulse parameters, shape, duration and phase (Warren 1993).

7. Solutions of time-dependent Schrödinger equations

As pointed out in the previous sections, recent developments in laser physics and chemistry have pointed out the need for efficient algorithms to solve the time dependent Schrödinger equation (47) with a time dependent perturbation, equations (64–65). In general in describing molecular multiphoton transitions, one has to have recourse to a linear parabolic partial differential equation, which can be written from equation (68) as,

$$i\hbar\frac{\partial F_m}{\partial t} = -\frac{\hbar^2}{2M}\frac{\partial^2 F_m(R,t)}{\partial R^2} + V_{mm}(R)F_m(R,t) + \sum_{M'} V_{mm'}(R,t)F_{m'}(R,t). \tag{107}$$

In the above, $V_{mm}(R)$ is the time-independent field-free molecular (electronic) potential and $V_{mm'}(R,t)$ is the time-dependent semiclassical electromagnetic field-molecule interaction,

$$V_{mm'}(R,t) = d_{mm'}(R)E(z,t). \tag{108}$$

R is the ensemble of molecular nuclear coordinates whereas z is the electromagnetic field coordinate (beyond the dipole approximation), and $d_{mm'}(R)$ is a multidimensional transition moment representing transitions between different electronic states of quantum number m. Expression $E(z,t)$ in terms of a single mode, coherent quantum field state would give the time dependent dressed state equations, (68).

For short pulses, by the Fourier transform theorem, the field envelope $f(t)$, where we now write

$$E(r,t) = f(t)E_0 \cos(\mathbf{k}\cdot\mathbf{z} - \omega t) \tag{109}$$

would contain many frequency components distributed around the central frequency with a frequency spread $\Delta\omega \simeq 2\pi/\tau$, where τ is the time duration of the pulse. This implies therefore a multimode description (Goldin 1982), complicating the coupled time dependent dressed state equations (68). A more straightforward method is therefore to solve equation (107) directly.

Of course the laser pulse itself satisfies an equation, Maxwell's wave equation which for polarizable media is written as (Allen and Eberly 1975, Lamb 1980).

$$c^2\frac{\partial^2 \mathbf{E}}{\partial z^2} - \frac{\partial^2 \mathbf{E}}{\partial t^2} = 4\pi\frac{\partial^2 \mathbf{P}}{\partial t^2}, \tag{110}$$

where $\mathbf{E}=\mathbf{E}(z,t)$ is the field, and $\mathbf{P}=\mathbf{P}[\mathbf{E}(z,t)]$ is the field induced polarization for pulse propagation along the z-axis. The polarization is in general a nonlinear functional of the pulse shape and is determined by its microscopic definition

$$\mathbf{P}=n_0\langle\Psi(t,r,R,\mathbf{E})|d\Psi(t,r,R,\mathbf{E})\rangle. \tag{111}$$

Ψ is the total time dependent wavefunction which itself becomes a functional of the field $\mathbf{E}$, d is the total dipole moment operator and n_0 is the molecular density. The set of coupled equations (107–111) describing the complete interaction of the field–molecule system is called the *Maxwell–Schrödinger* equations. In equation (109), the field envelope $f(t)$ is assumed to be a function of t only. In the slowly varying envelope approximation, $f=f(z,t)$ satisfies itself a parabolic partial differential equation of the same form as the time dependent Schrödinger equation (Chelkowski and Bandrauk 1988, 1990). This allows one to study the effect of the multiphoton molecular transitions on the propagation of the pulse itself by the same numerical technique, the *split operator* method of solving general time-dependent Schrödinger equations or other parabolic partial differential equations such as equation (107).

The most general time dependent solution to the time dependent Schrödinger equation can be written for a time increment Δt, as

$$\Psi(x,t+\Delta t)=\hat{U}(t+\Delta t,t)(x,t), \tag{112}$$

where $\hat{U}$ is the evolution operator (Pechukas and Light 1966),

$$\hat{U}(t+\Delta t,t)=\hat{T}\exp\left[-\frac{\mathrm{i}}{\hbar}\int_t^{t+\Delta t}\hat{H}\,\mathrm{d}t\right], \tag{113}$$

and $\hat{T}$ is the time ordering operator. Since $\hat{H}$ can be written as $\hat{K}+V(R,t)$, where $\hat{K}$ is the kinetic energy operator, $-\hbar^2/2M\partial^2/\partial R^2$, we can split the total Hamiltonian $\hat{H}$ in terms of differential operators A and polynomial functions, B,

$$\hat{H}=A+B, \qquad A=K, \qquad B=V(R)+V(R,t). \tag{114}$$

The most general method of splitting the exponential evolution operator $\hat{U}$ is based on the Trotter formula, (Trotter 1950, Willcox 1967, Suzki 1985),

$$\exp[\lambda(A+B)]=\lim_{m\to\infty}[\exp(\lambda A/m)\exp(\lambda B/m)]^m. \tag{115}$$

From this exact formula follows the most currently used standard second-order accurate expression, S_2, (Feit and Fleck 1984, Kono and Lin 1986),

$$\exp[\lambda(A+B)]=S_2(\lambda)+O(\lambda^3), \tag{116}$$

$$S_2(\lambda)=\exp(\lambda A/2)\exp(\lambda B)\exp(\lambda A/2). \tag{117}$$

We have shown recently (Bandrauk and Shen 1991, 1992), that equation (116) can be expressed as

$$\exp[\lambda(A+B)]=\exp[\lambda s(A+B)]\exp[\lambda(1-2s)(A+B)]\exp[\lambda s(A+B)], \tag{118}$$

so that higher-order accuracy is obtained by substituting equation (116) into equation (118). This operation gives after manipulation,

$$\exp[\lambda(A+B)]\doteq S_2(s\lambda)S_2[(1-2s)\lambda]S_2(s\lambda)+C_3\lambda^3[2s^3+(1-2s^3]+O(\lambda^4). \tag{119}$$

To get third-order accuracy, the leading error term with coefficient $C_3[O(\lambda^3)]$, must vanish, i.e.

$$2s^3+(1-2s)^3=0. \tag{120}$$

Thus if s is a real root of equation (120), we can obtain finally

$$S_3(\lambda)=S_2(s\lambda)S_2[(1-2s)\lambda]S_2(s\lambda)+O(\lambda^4), \tag{121}$$

By iterating (121) further, we can obtain the general iterative method,

$$\exp[\lambda(A+B)]=S_n(s\lambda)+O(\lambda^{n+2}), \tag{122}$$

where

$$S_n(\lambda)=S_{n-1}(s\lambda)S_{n-1}[(1-2s)\lambda]S_{n-1}(s\lambda), \tag{123}$$

and s is root of the more general equation

$$2s^n+(1-2s)^n=0. \tag{124}$$

Since $\lambda=\mathrm{i}\Delta t$, only real roots of s can be admitted, as otherwise imaginary roots will create divergent exponentials, with concomitant loss of accuracy upon iterating the evolution equation (112) for a large number of time steps $t=m\Delta t$. In fact equation (124) always has real roots when n is *odd*. Furthermore, due to the symmetric decomposition inherent in the generative equation (123), then *unitarity* and *reversibility* simultaneously are conserved at each iteration step,

$$S(\lambda)S(-\lambda)=S(\lambda)S^+(\lambda)=1. \tag{125}$$

This conservation of unitarity and reversibility of the integration–iteration scheme also implies that the accuracy is of order $\lambda^{n+2}=(\Delta t)^{n+2}$ (Bandrauk and Shen 1992).

The iterative schemes developed above have been tested against the exactly solvable model: the forced harmonic oscillator with $V(x,t)=x^2+x\sin(t)$, for which the exact solutions are, (Husimi 1953), $(m=\hbar=1)$,

$$\Psi(x,t)=\left(\frac{\sqrt{2}}{\pi}\right)^{1/4}\exp\left\{-\frac{[x-\xi(t)]^2}{\sqrt{2}}\right\}\exp\left[\frac{\mathrm{i}t}{\sqrt{2}}+\xi(x-\xi)+\int_0^t L\,\mathrm{d}t\right],$$

$$\xi(t)=[\sin(\sqrt{2}t)-\sqrt{2}\sin(t)]/\sqrt{2},$$

$$L=\tfrac{1}{2}\dot{\xi}^2-\xi^2+\xi\sin(t). \tag{126}$$

L is the Lagrangian of the classical forced harmonic oscillator.

In figures 7 and 8 we illustrate for the forced oscillator a comparison of four split-operator algorithms and their efficiency in calculating the time dependent amplitude (figure 7) and the phase of the time dependent function (see equation (126)) in figure 8. Clearly the iterative algorithm based on the split operator formula S_3, equation (121) which has fourth-order accuracy (error Δt^5), out performs the standard second-order operator S_2 equation (117), giving much more accurate amplitudes and phases for less CPU times (all calculations were performed on an IBM RISC – 6000/530 workstation). The optimum algorithm seems to be one based on S_5, which offers sixth-order accuracy (error $\sim\Delta t^7$). Recent time dependent wavepacket calculations have shown that this new S_5 algorithm allows propagation of wavepackets beyond picosecond times with much less CPU time than standard S_2 calculations (Atabek and Jolicard 1992). We

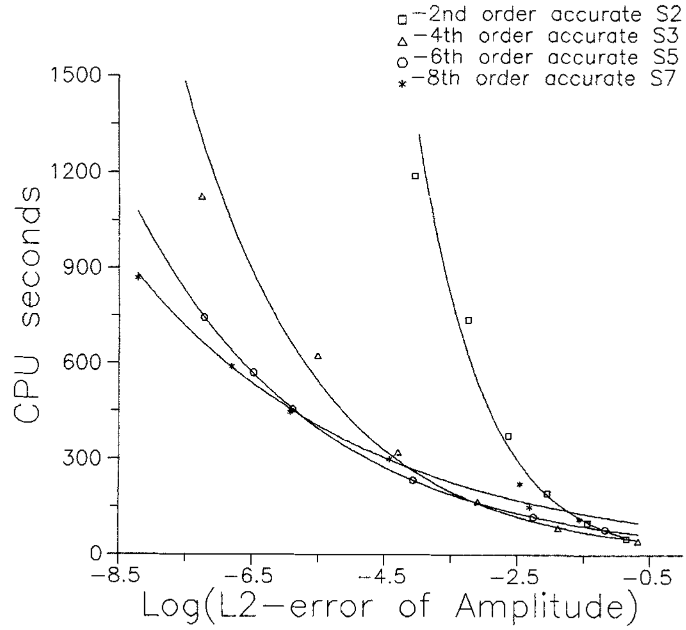


Figure 7. Amplitude errors as a function of CPU time for different split operator schemes, S_2,S_3,S_5 and S_7 for the time dependent solutions of the forced harmonic oscillator: $V(x,t)=x^2+x\sin(t)$. Exact solution is given by equation (126). All calculations were performed on a 15 megaflop IBM-RISC-6000-530 workstation.

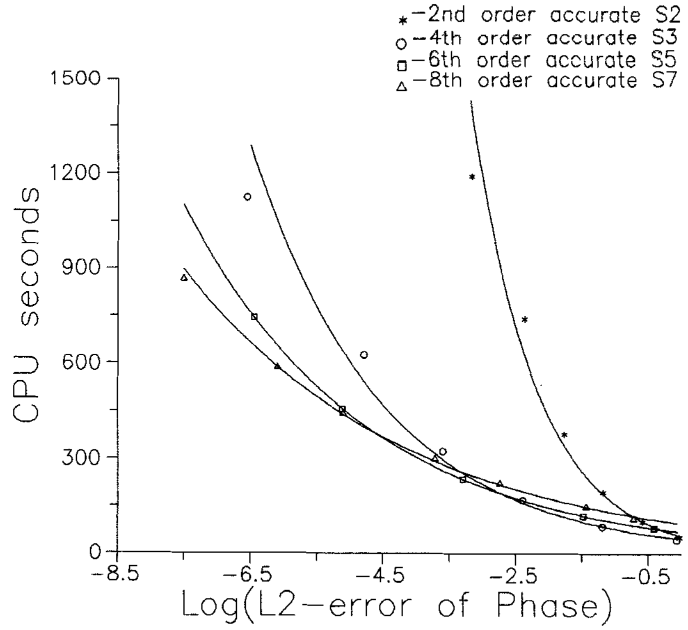


Figure 8. Phase errors as a function of CPU time for different split operator schemes, S_2, S_3, S_5 and S_7, for the time dependent solutions of the forced harmonic oscillator, $V(x,t)=x^2+x\sin(t)$. Exact solution is given by equation (126). All calculations were performed on a 15 megaflop IBM-RISC-6000-530 workstation.

conclude therefore by emphasing that these highly accurate time dependent numerical schemes owe their high accuracy to the symmetric decomposition of the evolution operator $\hat{U}$, such that unitarity and reversibility are respected at all times.

One informative application of these highly accurate time dependent calculations has been the numerical investigation of coherence effects in intense infrared multiphoton transitions. Thus more efficient multiphoton dissociation of molecular bonds using *chirped* pulses, i.e. pulses with variable frequency $\omega(t)$ and envelope $f(t)$, has been predicted (Chelkowski and Bandrauk 1990, Chelkowski *et al.* 1990). *Control* of intramolecular vibrational relaxation, IVR, (Chelkowski and Bandrauk 1991) has been another interesting finding by time dependent numerical experiments. Finally, the most obvious necessity of using time-dependent methods is for ultrashort, intense laser pulses, such that stationary states cannot be properly defined. We end this review by discussing an example of this problem in high intensity photophysics.

8. Laser induced avoided crossings

The dressed state representation of matter–radiation interaction (section 2) leads to coupled equations between time independent field–molecule states and enables one to therefore define the appropriate stationary states for any radiative and non-radiative coupling strength. One of the most useful concepts emanating from such a description is the idea of *laser-induced avoided* crossings between different resonant field–molecule potentials, figure 6, (Kroll and Watson 1976, Voronin and Samokhin 1976, Lau and Rhodes 1977, Bandrauk and Sink 1978, 1981, Yuan and George 1978, Bandrauk and McCann 1989). This is illustrated in figure 6 for H_2^+ photodissociation from an initial bound nuclear vibrational level v in the ground $^2\Sigma_g^+$ $(1\sigma_g)$ electronic potential to a continuum (dissociative) nuclear state of the repulsive $^2\Sigma_u^+$ $(2p\sigma_u)$ electronic potential.

In the time independent dressed picture, the field–molecule potential $[V_1(^2\Sigma_g^+, R) + \hbar\omega]$ crosses the $[V_2(^2\Sigma_u^+, R) + (n-1)\hbar\omega]$ potential as a consequence of conservation of total energy after absorption of one photon. The radiative interaction or electronic Rabi frequency ω_R (equation (29)),

$$V_{12}(R) = \langle ^2\Sigma_u^+, n-1|\mathbf{d}(R)\cdot\mathbf{E}_0/2|^2\Sigma_g^+, n\rangle = \hbar\omega_R/2, \tag{127}$$

is operative between the two potentials V_1 and V_2. Figure 6 shows therefore that one can describe the molecular states either in the original unperturbed (crossing) state description called *diabatic* or the new field-induced potentials obtained by diagonalizing the potential matrix $W(R)$ for energy R,

$$W(R) = \begin{bmatrix} V_1(R)+\hbar\omega & V_{12}(R) \\ V_{12}(R) & V_2(R) \end{bmatrix}, \tag{128}$$

giving rise to the laser-induced, *adiabatic* molecular potentials:

$$W_\pm(R) = \frac{V_1(R)+\hbar\omega+V_2(R)}{2} \pm \tfrac{1}{2}[(V_1(R)-V_2(R)+\hbar\omega)^2 + 4V_{12}^2(R)]^{1/2}. \tag{129}$$

The upper adiabatic surface $W_+(R)$ will support new nuclear bound states, $F_+(R)$, called adiabatic levels. These states are quasi-bound, i.e. they have a finite lifetime or energy width since in the new adiabatic representation the adiabatic nuclear functions $F_\pm(R)$ of the adiabatic potentials $W_\pm(R)$ remain coupled through the non-adiabatic interaction

$$\langle\Psi_-(R)|\frac{d}{dR}|\Psi_+(R)\rangle\frac{d}{dR}$$

where $\Psi_{\pm}(R)$ are the adiabatic electronic wavefunctions as in the theory of predissociation (Bandrauk and Child 1970, Lefebvre-Brion and Field 1986) and in non-adiabatic dynamics (Nakamura 1992). Thus for adiabatic nuclear functions $F_{+}(R)$ above the crossing point R_c (for $\lambda = 213$ nm excitation, R_c occurs at 1·6 Å, 0·59 ev with respect to the H_2^+ ground state minimum, figure 6), these nuclear states remain coupled to the continuum nuclear states $F_{-}(R)$ of the lower adiabatic potential $W_{-}(R)$ and become unstable. It is worth emphasing that without the laser field, there is no non-diabatic coupling between the Σ_g^+ and Σ_g^+ states due to their opposite symmetry (g and u). However in the presence of the field, the symmetry is broken and non-diabatic couplings arise between the states of the new laser induced adiabatic potentials $W_{\pm}(R)$, equation (129). The linewidths of such quasi-bound states can be obtained from the scattering (S matrix) coupled equations calculations described in section 4 and are related to the lifetimes through the relation

$$\tau(\mathrm{s}) = 5 \times 10^{-12}/\Gamma(\mathrm{cm}^{-1}). \tag{130}$$

Thus a linewidth of 5 cm^{-1} corresponds to a lifetime of 1 picosecond (ps). The widths Γ are related to the photodissociation rate by the equivalence $2\Gamma/\hbar = 2\pi/\hbar|T_{vc}|^2$, where T_{vc} is the exact transition amplitude from the initial unperturbed (diabatic level v to the final continuum $|c\rangle$), equations (63) and (106).

The quasi-bound states described in the dressed state representation are the time independent dressed eigenstates of the field–molecular system illustrated in figure 6 (neglecting rotations). Such a representation has been used recently to explain high intensity photodissociation of H_2^+ in order to explain the new phenomenon of *bond-softening* (Bucksbaum *et al.* 1990) and molecular *above threshold ionization*, ATI, (Allendorf and Szöke 1991). In the first experiments, long pulses (~ 100 ps) were used so that in this case a dressed state picture should be adequate (section 3). In the last experiment, subpicosecond pulses were used so that pulse shape effects might be expected to dominate. It can be therefore anticipated that for short pulses, due to the time variation of the field envelope $E_0 = f(t)$, equation (109) the laser-induced avoided crossings illustrated in figure 6 will become time dependent. Hence a complete time dependent description of direct photodissociation in the presence of intense laser pulses of duration approaching the molecular time scales (the vibrational period of H_2^+, $\tau_v \simeq 10^{-14}\,\mathrm{s} = 10$ fs), is clearly in order.

The time dependent Schrödinger equation for the time dependent nuclear functions $F_1(R,t)$ and $F_2(R,t), F = [F_1, F_2]$, is simply equation (107)),

$$\left[i\hbar\frac{\partial}{\partial t} + \frac{\hbar^2\nabla^2}{2m}\right]F(R,t) = \begin{bmatrix} V_1(R) & V_{12}(R,t) \\ V_{12}(R,t) & V_2(R) \end{bmatrix} \tag{131}$$

The potentials $V_1(R)$ and $V_2(R)$ are the well-known Σ_g^+ and Σ_u^+ potentials of H_2^+, and the radiative coupling is simply $V_{12}(R,t) = eR/2E_0(t)\cos\omega t$. $R/2$ is the electronic transition moment $\langle 1\sigma_g|r|2p\sigma_u\rangle$, called a resonance transfer moment (Mulliken 1939). $E_0(t)$ is the pulse envelope. Writing the field as $E_0/2\,[\exp(i\omega t) + \exp(-i\omega t)]$, one identifies two components: a resonant component, $\exp(i\omega t)$ and a non-resonant or virtual component, $\exp(-i\omega t)$, equation (35). Figure 6 corresponds to the resonant case, i.e., $E(t) = E_0/2 \exp i(\omega t)$ or equivalently RWA (section 2). Thus solving equation (131) with the field $E(t) = E_0(t)\cos\omega t$ corresponds to an exact calculation, whereas using only $E_0(t)/2$ with the crossing surfaces of figure 6 corresponds to an RWA calculation (e.g. Sugawara *et al.* (1991).

Both calculations were carried out in order to verify the applicability of RWA, and hence the two dressed state picture illustrated in figure 6 (Aubanel *et al.* 1992). As discussed in section 2, corrections to RWA emanate from the virtual emissions of photons from the photon state $|n\rangle$ to $|n+1\rangle$, i.e. more surfaces must be added to figure 6 (see Bandrauk *et al.* 1991 for an example of 100 dressed states). Since resonant and virtual dressed potentials are separated by twice the photon frequency (figure 1), then RWA or equivalent figure 6 are adequate provided the criterion, equation (30) is satisfied. For the present calculation at the excitation wavelength of $\lambda = 213$ nm, $\hbar\omega \sim 6$ ev. Using the transition moment $eR/2$ in the radiative matrix element, (127) and using equation (29), one obtains a radiative interaction energy $\hbar\omega_R \sim 0{\cdot}2$–$2$ ev for intensities between 10^{12} and 10^{14} W cm^{-2} at the crossing point R_c. Comprising this to the 1s–2p transition energy of 10 ev, ones sees that RWA and figure 6 should be used for intensities below 10^{14} W cm^{-2}. Higher intensities will induce virtual transitions and higher excitations than those considered in figure 6, thus limiting the two-state representation to intensities inferior to 10^{14} W cm^{-2}.

Taking as initial condition $F_v(R, t=0)$, the unperturbed nuclear wavefunction of some vibrational level v in the ground $^2\Sigma_g^+$ state of H_2^+, one propagates in time the nuclear wavefunction according to the efficient time dependent integration algorithms described in the previous section. This is achieved by first discretizing the initial function $F_v(R, t=0)$ over a grid of about 1000 space (R) points in a box sufficiently large that no reflection occurs at the large R boundary. Time integration is performed by 'marching' forward in time simultaneously all 1000 space points, thus allowing one to obtain the ground, $F_1(R, t)$, and excited, $F_2(R, t)$ nuclear functions until they propagate fully on the diabatic (unperturbed) potentials $V_1(R)$ and $V_2(R)$ after the end of the pulse. After the pulse is over one can integrate the probability density $|F(R,t)|^2$ from a point R_0 outside the right turning point of the upper, $W_+(R)$ potential ($R_0 \geqslant 3$ Å) in order to obtain the dissociation probabilities P_d, figures 9, 10. The momentum Fourier transformation gives the kinetic energy distribution of the photodissociating fragments through the relation $P(E,t) = (m/p)|F(p,t)|^2$. The momentum distributions give a measure of the influence of the pulse shape on the dissociation dynamics (Aubanel *et al.* 1992).

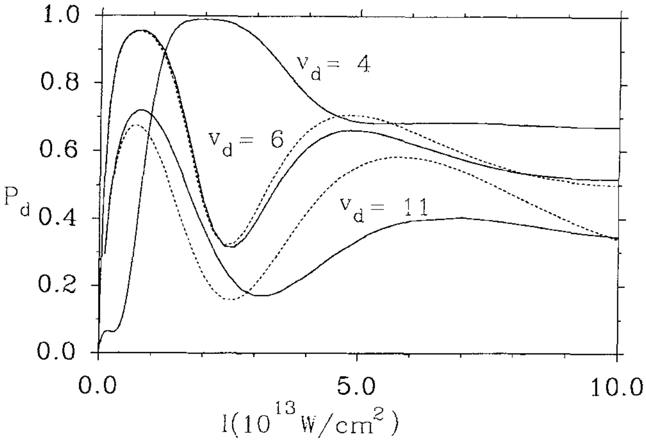


Figure 9. Photopredissociation probabilities for the $^2\Sigma_g^+ \rightarrow {}^2\Sigma_u^+$ transition of H_2^+ at $\lambda = 213$ nm, as a function of intensity I (W cm^{-2}) and initial level v_d. Minima are manifestations of molecular stabilization by laser-induced avoided crossing illustrated in figure 6. Pulse shape is defined in equation (132), i.e. 100 fs long, 1 fs rise and fall. — exact; ···· RWA.

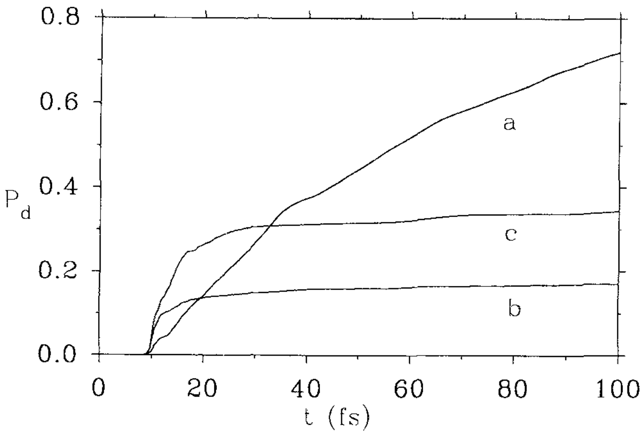


Figure 10. Photodissociation probability for $v_d = 11$ in figure 9, as a function of time, i.e., during pulse, for intensities I (W cm^{-2}): (*a*) 8×10^{12}, (*b*) $3{\cdot}2 \times 10^{13}$, (*c*) 1×10^{14}. Pulse is 100 fs long with 1 fs rise and fall.

We now discuss the numerical results. Figure 9 shows clearly an initial increase of the dissociation probability P_d for the initial unperturbed diabatic levels $v = 4, 6, 11$. The pulse evelope $E_0(t) = f(t)$, was chosen such that ($1\,\text{fs} = 10^{-15}\,\text{s}$),

$$f(t) = t, \qquad 0 \leqslant t \leqslant 1\,\text{fs}, \qquad 99 < t \leqslant 100\,\text{fs},$$

$$f(t) = 1, \qquad 1 \leqslant t \leqslant 99\,\text{fs}. \tag{132}$$

This pulse corresponds to a linear rise (fall) in 1 fs from 0 to E_0, and vise versa, the idea being to get the molecule into the constant, high intensity part of the pulse as quickly as possible, thus approaching the time-independent condition of constant field envelope E_0 related to the photon number by equation (44). The linear rise of P_d against I is consistent with the Fermi-Golden rule prediction, $P_d \propto |V_{12}|^2 \propto I$. With increasing intensity, deviation from this rule occurs as a saturation, i.e., a maximum occurs. This is then followed by a deep minimum. The minimum in P_d is a manifestation of *molecular stabilization* by suppression of the dissociation rate as shown below. Finally a constant plateau up to $I = 10^{14}$ W cm^{-2} is reached. In the $v_d = 4$ case, a plateau already occurs at the lower intensities, $I = 1\text{–}4 \times 10^{12}$ W cm^{-2}. These are also manifestations of stabilization by the laser field. In figure 9, we report both exact and RWA calculations. The first are obtained using the exact field $E(t) = E_0(t) \cos \Sigma t$ whereas RWA results from using the resonant expression $E(t) = [E_0(t)/2] \exp(i\omega t)$. One sees from figure 9 that for the lower levels, $v_d = 4$ and 6, RWA agrees fairly well with the exact calculation. Devations occur for $v_d = 11$ around $I = 10^{13}$ W cm^{-2} due to the higher density of level above $v_d = 11$. in summary, figure 9 shows clearly the existence of dissociation probability maxima approaching unity ($\sim 100\%$ yield), minima (10–20% yield) and high intensity plateaus of photodissociation yield around 50%.

The minima in P_d correspond to molecular stabilization by suppression of the dissociation rate with increasing intensity. This is further confirmed in figure 10, where we illustrate the time dependent dissociation probability during the pulse. As explained above, since we integrate everything to the right of R_0, the outer upper state turning point, then the results illustrated in figure 10 are a measure of the nuclear wavepacket which is well past the laser-induced interaction region. Figure 10 emphasizes the different behaviour of the $v_d = 11$ initial level at its maximum dissociation intensity, $I = 8 \times 10^{12}\,\text{W cm}^{-2}$ against the minimum dissociation intensity $I \sim 3{\cdot}2$

$\times 10^{13}\,\mathrm{W\,cm^{-2}}$. Thus in the lower field case, the dissociation rises linearly with time during the pulse, suggesting a nearly constant dissociation rate or width (or $(\text{lifetime})^{-1}$; equation 130). In contrast to this rapid dissociation rate, at the two higher intensities rapid dissociation occurs only in the first 10–20 fs, then there is stabilization of the initial molecular state, i.e. dissociation ceases to occur while the molecule is in the pulse.

An interpretation of the manifestation of the minima in the photodissociation at higher laser intensities and hence of the onset of molecular stabilization can be found in our previously published theory of laser-induced resonances, (Bandrauk and Sink 1978, 1981, Bandrauk and McCann 1989, McCann and Bandrauk 1990, 1992). This is based on the formal analogy of direct intense field photodissociation in the dressed state representation, figure 6, with the theory of predissociation (Bandrauk and Child 1970). The semiclassical S matrix for the two channel problem in figure 6 can be calculated analytically as a function of the parameters of the unperturbed potentials V_1, V_2 and the time independent radiative interaction $d(R)\ E_0/2$. We emphasize that this two channel calculation is equivalent to RWA (figures 1 and 6) and can only be compared to the RWA photodissociation reported in figure 9. However, these are nearly identical to the exact results since the RWA criterion, equation (30) is well satisfied for intensities inferior to $10^{14}\,\mathrm{W\,cm^{-2}}$.

Thus in parallel with the time dependent probability calculations, P_d, figures 9 and 10, we present in table 1 the S matrix results for the linewidths Γ_r of the laser induced resonances or adiabatic levels of the upper laser-induced surface $W_+(R)$ at the maxima and minima in P_d seen in figure 9. The widths are found from the poles at energy $E=E_\mathrm{r}-\mathrm{i}\Gamma_\mathrm{r}$ of the S matrix or transition amplitudes from the 2×2 coupled equations corresponding to figure 6 (see section 4, equations (80) and (87)). It is found that in general, as predicted by the semiclassical predissociation theory (Bandrauk and Sink 1978, 1992, (Bandrauk and McCann 1989), that minimum linewidths or stable *laser induced resonances* occur whenever a quasi-degeneracy arises between some diabatic and adiabatic levels (figure 6). As an example, minima in the linewidths Γ_r of $v_\mathrm{ad}=0$, 1 as a function of intensity are found at intensities $3{\cdot}2\times10^{12}\,\mathrm{W\,cm^{-2}}$ and $2{\cdot}6\times10^{13}\,\mathrm{W\,cm^{-2}}$. v_ad is the adiabatic level of $W_+(R)$ closest to the initial unperturbed level v_d. The minima in Γ_r, the table, correspond to the RWA photodissociation probability P_d for $v_\mathrm{d}=4$ and 6, respectively. From figure 6, the simultaneous minima in Γ_r and P_d correlate with the coincidence (degeneracy) of $v_\mathrm{ad}=0$ with $v_\mathrm{d}=4$ at $I=3{\cdot}2\times10^{12}\,\mathrm{W\,cm^{-2}}$ and $v_\mathrm{ad}=1$ with $v_\mathrm{d}=6$ at $I=2{\cdot}6\times10^{13}\,\mathrm{W\,cm^{-2}}$. Similarly $v_\mathrm{d}=6$ is resonant with $v_\mathrm{ad}=0$ at $6\times10^{13}\,\mathrm{W\,cm^{-2}}$. This correlates with the onset of a minimum plateau in P_d for intensities beyond $6\times10^{13}\,\mathrm{W\,cm^{-2}}$. All adiabatic levels are above the dissociation limit at $I=4\times10^{14}\,\mathrm{W\,cm^{-2}}$, yet incomplete dissociation occurs at these very high intensities.

Table 1. Energies (eV) of diabatic (v_d) adiabatic (v_ad) levels, resonance widths $\Gamma_\mathrm{r}\,(\mathrm{cm^{-1}}$ and intensities I ($\mathrm{W/cm^2}$) for which quasidegeneracy occurs ($\lambda=213$ nm). Energies are with respect to $v=0$ of ground state of H_2.

v_d	E_d (ev)	v_ad	$I\,(\mathrm{W/cm^2})$	E_a (ev)	$\Gamma_\mathrm{r}\,(\mathrm{cm^{-1}})$
4	16·41	0	$3{\cdot}2\times10^{12}$	16·35	$2{\cdot}4\times10^{-4}$
6	16·82	1	$2{\cdot}6\times10^{13}$	16·89	$1{\cdot}3\times10^{-3}$
6	16·82	0	$5{\cdot}2\times10^{13}$	16·80	$1{\cdot}4\times10^{-2}$

We conclude therefore that at intensities below $I = 10^{14}\,\mathrm{W\,cm^{-2}}$ and for subpicosecond pulses, a two state dressed representation is capable of explaining the phenomenon of molecular stabilization of photodissociation in H_2^+, as a result of resonances created by a laser-induced avoided crossing, figure 6. The theoretical predictions obtained from the time independent dressed state calculations and the exact time dependent solutions of the field–molecule Schrödinger equation agree together and with the experimental findings (Bucksbaum *et al.* 1990, Allendorf and Szöke 1991). This is an example of the usefulness of both types of approaches, time independent and time dependent coupled equations, to elucidate nonperturbative multiphoton processes.

Acknowledgments

The author has benefited from research grants from the Natural Sciences and Engineering Research Council of Canada to carry out the research reported in this review. We also thank the Okazaki National Research Institutes, Japan, for a visiting fellowship and the hospitality of Professor Hiroki Nakamura during the preparation of this manuscript.

References

ALLEN, J., and EBERLY, J. H., 1975, *Optical Resonances and Two Level Atoms* (New York Wiley).

ALLENDORF, S., and SZOKE, A., 1991, *Phys. Rev.* A, **44**, 518.

ATABEK, O., and JOLICARD, G., 1992, *Phys. Rev.* A, **46**, 5845.

ATABEK, O., LEFEBVRE, R., and JACON, M., 1980, *J. chem. Phys.*, **72**, 2670.

AUBANEL, E., BANDRAUK, A. D., and RANCOURT, P., 1992, *Chem. Phys. Lett.*, **197**, 419.

BANDRAUK, A. D., (editor), 1993, *Molecules in Laser Fields* (New York: Marcel Dekker).

BANDRAUK, A. D., and CHILD, M. S., 1970, *Molec. Phys.*, **19**, 95.

BANDRAUK, A. D., CONSTANT, E., and GAUTHIER, J. M., 1991, *J. Phys.*, (*Paris*), **1**, 1033.

BANDRAUK, A. D., and GAUTHIER, J. M., 1990, *J. opt. Soc. Am.*, B, 7, 1420.

BANDRAUK, A. D., GAUTHIER, J. M., and MCCANN, J. F., 1992, *Chem. Phys. Lett.*, **200**, 399.

BANDRAUK, A. D., and GELINAS, N., 1987, *J. comput. Chem.*, **8**, 313; *J. chem. Phys.*, **86**, 5257.

BANDRAUK, A. D., KALMAN, O. F., and NGUYEN-DANG, T. T., 1986, *J. chem. Phys.*, **84**, 6761.

BANDRAUK, A. D., and MCCANN, J. F., 1989, *Common. At. Molec. Phys.*, **22**, 325.

BANDRAUK, A. D., and SHEN, H., 1991, *Chem. Phys. Lett*, **176**, 428; 1992, *Can. J. Chem.*, **70**, 55.

BANDRAUK, A. D., and ATABEK, O., 1988, *Adv. chem. Phys.* (New York: Wiley), **73**, chap. 19.

BANDRAUK, A. D., and SINK, M. L., 1978, *Chem. Phys. Lett.*, **57**, 569; 1981, *J. chem. Phys.*, **74**, 1110.

BANDRAUK, A. D., and TURCOTTE, G., 1982, *J. chem. Phys.*, **77**, 3867; 1983, *J. phys. Chem.*, **87**, 5098; 1985, *Ibid.*, **89**, 3039.

BANDRAUK, A. D., TURCOTTE, G., and LEFEBVRE, R., 1982, *J. chem. Phys.*, **76**, 225.

BANDRAUK, A. D., and WALLACE, S. C., (editors) 1992, *Coherence Phenomena in Atoms and Molecules in Laser Fields*, NATO ASI Series, vol. B287 (New York: Plenum).

BLOCH, F., and NORDSIECK, A., 1937, *Phys. Rev.*, **52**, 54.

BRUMER, P., and SHAPIRO, M., 1989, *Accts. Chem. Res.*, **22**, 407.

BUCKSBAUM, P. H., ZAVRIYEV, A., MULLER, H. G., and SCHUMACHER, D., 1990, *Phys. Rev. Lett.*, **64**, 1883; *Phys. Rev.* A, **42**, 5500.

CHELKOWSKI, S., and BANDRAUK, A. D., 1988, *J. Chem. Phys.*, **89**, 3618; 1990, *J. opt. Soc. Am.* B, **7**, 90; 1991, *Chem. Phys. Lett.*, **186**, 264.

CHELKOWSKI, S., BANDRAUK, A. D., and CORKUM, P. B., 1990, *Phys. Rev. Lett.*, **65**, 2355.

CHEN, C., YIN, Y., and ELLIOTT, D., 1990, *Phys. Rev. Lett.*, **64**, 507.

CHEN, C., and ELLIOTT, D. S., 1990, *Phys. Rev. Lett.*, **65**, 1727.

CLARY, D. C., 1986, *J. chem. Phys.*, **84**, 4288.

COHEN-TANNOUDJI, C., and REYNAUD, S., 1983, *Multiphoton Processes*, edited by J. H. Eberly and P. Lambropoulos (New York: Wiley), p. 103.

COHEN-TANNOUDJI, C., DUPONT-ROC, J., and GRYNBERG, J., 1989, *Photons and Atoms* (New York: Wiley).

CORKUM, P. B., 1985, *IEEE J. quant. Electron.*, **21**, 216.

CRIM, F. F., HSIA, M. C., and SINHA, A., 1990, *J. chem. Phys.*, **92,** 6333.

DELANGE, O., and RAAB, D., 1991, *Operator Methods in quantum Mechanics* (New York: Academic).

DIETRICH, P., and CORKUM, P. B., 1992, *J. chem. Phys.*, **97,** 3187.

DU, M. L., and DALGARNO, A., 1991, *Phys. Rev.* A, **43,** 3474.

FANO, U., 1961, *Phys. Rev.*, **124,** 1866.

FEIT, M. D., and FLECK, J. A., 1984, *J. chem. Phys.*, **78,** 2578.

FEYNMAN, R. P., 1960, *Quantum Electrodynamics* (New York: Benjamin).

FOX, L., 1957, *The Numerical Solution of Two-point Boundary Value Problems* (Oxford University Press).

GEORGE, T. F., 1982, *J. phys. Chem.*, **86,** 10.

GEORGE, T. F., ZIMMERMAN, I. H., YUAN, J. M., LAING, J. R., DEVRIES, P. L., 1977, *Accts. Chem. Res.*, **10,** 449.

GHANDOUR, F., JACON, M., SVENDSEN, E. N., and ODDERSHEDE, J., 1983, *J. chem. Phys.*, **79,** 2150.

GLAUBER, R. J., 1963, *Phys. Rev.*, **131,** 2766.

GOLDIN, E., 1982, *Waves and Photons* (New York: Wiley).

GOLDBERGER, M. L., and WATSON, K. M., 1964, *Collision Theory* (New York: Wiley).

HE, X., ATABEK, O., GIUSTI-SUZOR, A., and MIES, F., 1990, *Phys. Rev. Lett.*, **64,** 515.

HERZBERG, G., 1966, *Electronic Spectra of Polyatomic Molecules* (Van Nostrand: Amsterdam).

HUBER, K. P., and HERZBERG, G., 1979, *Constants of Diatomic Molecules* (Van Nostrand-Reinhold: NY).

HUSIMI, H., 1953, *Prog. Theor. Phys.*, **9,** 381.

KELDYSH, L. V., 1965, *Soviet Phys. JETP*, **20,** 1307.

KODAMA, K., and BANDRAUK, A. D., 1981, *Chem. Phys.*, **57,** 461.

KONO, H., and LIN, S. H., 1986, *J. chem. Phys.*, **84,** 1071.

KROLL, N. M., and WATSON, K. M., 1976, *Phys. Rev.* A, **13,** 1018.

KRSTIC, P., and MITTLEMAN, M., 1990, *J. opt. Soc. Am.* B, **7,** 588.

LAMB, G. L. Jr., 1980, *Elements of Soliton Theory*, (New York: Wiley).

LAMI, A., and RAHMAN, N. K., 1982, *Phys. Rev.* A, **26,** 3360.

LAPLANTE, J. P., and BANDRAUK, A. D., 1976, *J. chem. Phys.*, **65,** 2592.

LAU, A. M., and RHODES, C. K., 1977, *Phys. Rev. A*, **16,** 2392.

LEFEBVRE-BRION, H., and FIELD, R. W., 1986, *Perturbations in Spectra of Diatomic Molecules* (New York: Academic).

LEVINE, R. D., 1969, *Quantum Mechanics of Molecular Rate Processes* (Oxford University Press).

LI, L., LIPERT, R. J., PARK, H., CHUPKA, W. A., and COLSON, S. D., 1988, *J. chem. Phys*, **88,** 8.

LOUDON, R., 1973, *The Quantum Theory of Light* (Oxford University Press).

LU, S., PARK, S. M., XIE, X., and GORDON, R. J., 1992, *J. chem. Phys.*, **96,** 6613.

MCCANN, J. F., and BANDRAUK, A. D., 1990, *Phys. Rev.* A, **42,** 2806; 1992, *J. chem. Phys.*, **96,** 903.

MIRET-ARTES, S., ATABEK, O., and BANDRAUK, A. D., 1992, *Phys. Rev. A*, **45,** 8056.

MITTLEMAN, M. H., 1982, *Introduction to the Theory of Laser–Atom Interactions* (New York: Plenum).

MOFFATT, A. S., 1992, *Science*, **255,** 1643.

MOWER, L., 1966, *Phys. Rev.*, **142,** 799.

MULLIKEN, R. S., 1939, *J. chem. Phys.*, **7,** 20.

MURRELL, J. N., CARTER, S., FRANTOS, S. C., HUXLEY, P., and VARANDAS, A. J. C., 1984, *Molecular Potential Energy Functions* (New York: Wiley).

NAKAMURA, H., 1992, *Adv. chem. Phys.* (New York: Wiley), vol. 82, part 2., p. 243.

NGUYEN-DANG, T. T., and BANDRAUK, A. D., 1983, *J. chem. Phys.*, **79,** 3256; 1984, *Ibid.*, **80,** 4926.

NGUYEN-DANG, T. T., DUROCHER, S., and ATABEK, O., 1989, *Chem. Phys.*, **129,** 451.

NGUYEN-DANG, T. T., and MANOLI, S., 1991, *Phys. Rev.* A, **44,** 5841.

NOMURA, Y., and FUJIMURA, Y., 1990, *Trends in chem. Phys.*, **1,** 31.

NORCROSS, D. W., and SEATON, M. J., 1973, *J. Phys.*, **36,** 614.

PECHUKAS, P., and LIGHT, J. C., 1966, *J. chem. Phys.*, **44,** 3897.

PERELOMOV, A., 1986, *Generalized Coherent States and Their Applications* (Berlin: Springer Verlag).

PEYERIMHOFF, S. D., and BUENKER, R. J., 1981, *Chem. Phys.*, **57,** 279.

POWER, E. A., and THIRUNAMACHANDRAN, T., 1983, *Phys. Rev.* A, **28,** 2649.

SCHERER, N. F., ZIEGLER, L. D., and FLEMING, G. R., 1991, *J. chem. Phys.*, **95,** 1487.

SHAPIRO, M., 1972, *J. chem. Phys.*, **56,** 2582.

SHAPIRO, M., and BONY, H., 1985, *J. chem. Phys.*, **83**, 1588.
SHAPIRO, M., HEPBURN, J. W., and BRUMER, P., 1988, *Chem. Phys. Lett.*, **149**, 451.
SINK, M. L., and BANDRAUK, A. D., 1987, *Chem. Phys.*, **33**, 205.
SUGAWARA, M., KATO, M., and FUJIMURA, Y., 1991, *Chem. Phys. Lett.*, **184**, 203.
SUZUKI, M., 1985, *J. math. Phys.*, **26**, 601.
TAKADA, S., TSUDA, K., OHSAKI, A., and NAKAMURA, H., 1992, *Advances in Molecular Vibrations and Collision Dynamics*, edited by J. M. Bowman (Greenwich: JAI), vol. IIA.
TROTTER, H. F., 1950, *Proc. Am. Math. Soc.*, **10**, 545.
VORONIN, A. I., and SAMOKHIN, A. A., 1976, *Soviet Phys. JETP*, **43**, 40.
WARREN, W., 1993, *Molecules in Laser Fields*, edited by A. D. Bandrauk (New York: Marcel Dekker), chap. 2.
WATANABE, S., WATANABE, M., NODOMI, R., ADACHI, J., HATA, K., and SARUKURA, N., 1991, *Phys. Rev. A*, **43**, 1669.
WATSON, K. M., and NUTTALL, J., 1967, *Topics in Several Particle Dynamics* (New York: Holden-Day), chap. 1.
WILCOX, R. M., 1967, *J. math. Phys.*, **8**, 962.
YAMASHITA, K., and MOROKUMA, K., 1991, *Faraday Disc. Chem. Soc.*, **91**, 47.
YUAN, J. M., and GEORGE, T. F., 1978, *J. chem. Phys.*, **68**, 3040.
ZARE, R. N., 1988, *Angular Momentum* (New York: Wiley).
ZEWAIL, A. H., 1991, *Faraday Disc. Chem. Soc.*, **91**, 207.