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Wave-packet dynamics: new physics and chemistry in femto-time

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Abstract

We present a review of wave-packet dynamics, with a focus on 'femto-chemistry'. We review basic theory and simple properties of wave-packets, the application of two-state models to wave-packet dynamics, and wave-packet processes in the presence of light. We also discuss the treatment of wave-packets in dissipative problems.

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Contents

1. Introduction ........................................... 367
2. Theory of wave-packet dynamics ......................... 369
   2.1. Basic theory of coupled energy levels ............... 369
   2.2. Simple properties of wave-packets ................ 374
   2.3. Numerical methods for quantum propagation ......... 377
   2.4. Time-dependent two-state models ................ 381
3. Wave-packet processes ................................ 387
   3.1. Wave-packet generation .......................... 387
   3.2. Processes induced by chirped pulses ............... 390
   3.3. Pump-probe schemes ................................ 393
   3.4. Wave-packet splitting at crossings ................. 397
   3.5. Wave-packet interference ......................... 401
4. Spontaneous emission ................................ 404
   4.1. Importance of spontaneous emission ............... 404
   4.2. Numerical solution by density matrix methods ... 405
   4.3. Numerical solution by simulation methods .......... 408
   4.4. Dynamical effects of spontaneous emission on wave-packets 410
5. Conclusions ........................................... 412
   Acknowledgments ..................................... 413
A. Summary of exactly solvable two-state models ........ 413
   References ........................................... 415
1. Introduction

In this review we present an overview of wave-packet dynamics in physics and chemistry. Our point of view is based on a theoretical framework, and on the different applications of that framework in molecular physics and the interactions of matter and light. The experimental work on femtosecond excitation and the observation of the subsequent wave-packet dynamics is quite extensive and has been reviewed recently (Zewail 1993, Beddard 1993). Therefore, we have, for the most part, only given illustrative examples of the experimental work that has been performed. For simplicity we concentrate on two-state systems and one spatial dimension, which still encompasses a wide range of phenomena. The theoretical approaches we describe will also consider the dynamics and response of single molecules; the propagation effects of femtosecond pulses, and problems of inhomogeneous broadening are not considered here. Since, apart from trivial cases, the dynamics of wave-packets can only be solved numerically, we describe the appropriate computational approaches in some detail. However, the semiclassical nature of the wave-packet allows some simple models which can reveal the physics behind the numbers. We will review some of these semiclassical approaches, though, unfortunately, space does not permit us to cover this area comprehensively.

Sadly, wave-packets have been a side issue in quantum mechanics for a long time. Their use in theory has been limited to simple textbook examples, which help the undergraduate students to understand how Fourier transforms connect the position and momentum representations and yield the Heisenberg uncertainty principle (see, for example, Schiff 1968, Merzbacher 1970). Most of the scattering theory, however, has been based on the time-independent view of interfering plane and spherical waves, and in atomic and molecular physics, interactions of matter with light have been treated by finding the wavefunctions for all the quantum states of the system and calculating their static overlap integrals (Franck–Condon factors). In these systems the time evolution for each state has been assumed to be independent of the other states and unitary, thus only contributing to the phase of the wavefunction of the corresponding quantum state.

Erwin Schrödinger introduced the concept of wave-packets which follow a classical trajectory in order to bridge the disturbing gap between the classical and quantum descriptions of nature (Schrödinger 1926). This approach culminated in Ehrenfest’s theorem which states that in the classical limit the quantum mechanical expectation values behave classically (Ehrenfest 1927). For a long time the wave-packets had no real practical use because their preparation seemed impossible. However, recent advances in the physics and chemistry of laser interactions with atoms and molecules have brought the wave-packets and their dynamics into the limelight. For example, it became possible to prepare wave-packets by exciting atoms to Rydberg states with short pulses (see the review by Alber and Zoller 1991, and Nauenberg et al 1994 and, for example, ten Wolde et al 1988, 1989, Noordam et al 1989). A whole new realm of phenomena opened when femtosecond pulse technology emerged. With ultrashort pulses one can now prepare a molecular wave-packet and probe its evolution—and observe molecular reactions in the time domain (see the reviews by Gruebele and Zewail 1990, Zewail 1990, 1993, Beddard 1993, Garraway et al 1993). This is because the time-scale for many molecular vibrations is of the order of femtoseconds, or tens of femtoseconds. It makes it possible to chart the path a chemical process takes in
terms of intermediate states—the final goal is the manipulation of the reaction in order to achieve precise control over the output products (see, for example, Herek et al 1994).

Wave-packets are being utilized in other areas of physics too. For example, the low temperatures achieved in laser cooling lead to cold collisions of atoms, which require a wave-packet treatment because of the strong possibility of laser-induced excitation and subsequent spontaneous decay during such a collision makes it difficult to use any time-independent methods (Julienne et al 1993). Wave-packets are also proving useful in the field of atom optics, where the packet represents an atomic matter wave (see, for example, Ruprecht et al 1994), and in semiconductor physics (see, for example, Leo et al 1991).

One of the major reasons for studying wave-packet dynamics in the context of molecules is the possibility for enhancing, or controlling chemical reactions (see Tannor and Rice 1985, Rice 1992, Brumer and Shapiro 1995) by the careful application of pulses of light with optimal frequency, intensity, duration, and timing. A simple example, which can be called 'controlled', is the photodissociation of a molecule. Here new products are formed by using a light pulse to transfer a stable ground-state wave-packet to an unstable dissociating potential (such as in Dantus et al (1987) where the diatomic molecule I–CN is broken). In a recent experiment, Herek et al (1994) have demonstrated control over the dissociation of NaI. A ‘clocking’ pulse is used to interrupt the dissociation process, which is itself started by femtosecond excitation. Another approach is the Tannor–Rice scheme (Tannor and Rice 1983, Tannor et al 1986, Kosloff et al 1989, Tersigni et al 1990, Amstrup et al 1991) which uses two pulses of light. A typical problem is to overcome a barrier on the ground-state potential (see figure 1) and this is achieved in two steps. First the ground-state wave-packet is promoted to a suitable excited state with a pulse of light. The wave-packet evolves on the excited state. The state is chosen (if possible) so that when the second pulse arrives the packet is transferred downwards onto the other side of the barrier on the ground state. The method can be generalized to overcome barriers on excited states and the concepts of control theory can be used to design optimally shaped light pulses to produce the desired products (Shi et al 1988, Shi and Rabitz 1989, 1990).

However, in practice it seems difficult to produce femtosecond pulses with such very specific shapes (see Amstrup et al 1991, Amstrup et al 1993). It may be more appropriate to use standard pulse shapes and from this point of view the use of semiclassical models for wave-packets can lead to a good understanding of how the control of wave-packets can work. Recent experiments now show many features of wave-packet control (see Scherer et al 1991 and especially Potter et al 1992, Herek et al 1994). This review includes situations of wave-packet excitation, wave-packet motion on coupled levels, and wave-packet interference effects, which can give an insight into the problems of wave-packet control.

**Figure 1.** An illustration of how wave-packet dynamics can be used to overcome a chemical barrier. The barrier is on the lower (usually ground-state) potential surface and prevents the wave-packet from moving to the right. However, by coupling the wave-packet to the upper level with ultra-short pulses the packet can be transferred across the barrier. The curves indicate potential energy as a function of a nuclear coordinate.
The femtosecond time-scale often allows one to exclude the spontaneous decay of the excited-state population from calculations. However, in the processes following the excitation it can play a role and it may interfere with the excitation process itself. There is a related problem in the treatment of molecular excitation subjected to $T_2$ dephasing, which cannot be easily neglected in solution (see Fleming and Wolynes 1990). In general, adding dissipation into wave-packet dynamics is a great challenge to theoreticians. Since there have been recent advances in the numerical approach to wave-packet dynamics with spontaneous decay, we have chosen to present the currently used methods in detail. For the problem of cold atomic collisions in the presence of laser fields, spontaneous decay is essential, and approaches based on dissipative wave-packet dynamics have been successful in the theoretical description of cold collisions (Holland et al 1994a, b, Suominen et al 1994).

In principle, once we are restricted to one spatial dimension and a two-state system, the wave-packet dynamics can be posed as a straightforward problem; all that needs to be done is to solve the time-dependent Schrödinger equation with the proper Hamiltonian for the system. In section 2 we introduce the theory of the wave-packets and their dynamics. We start by showing how to obtain the proper Hamiltonian in molecular physics in section 2.1, and then describe some general properties of wave-packets in section 2.2. Then in section 2.3 we present the numerical tools used for solving the wave-packet dynamics from a coupled Schrödinger equation. In section 2.4 we give simple semiclassical pictures of wave-packet dynamics in some simple, but generic, cases. The approach is based on purely time-dependent quantum models, and provides useful insights into the dynamics without extensive numerical work. It is by no means the only semiclassical approach available (see, for example, Heller (1975) for alternative methods), but its apparent simplicity allows one to use it for qualitative and occasionally even for quantitative interpretation of the physics of the problem at hand.

In section 3 we relate the rather general theory of wave-packet dynamics given in section 2 to molecular, femto-time, physics and chemistry. We start with the wave-packet generation by short pulses in section 3.1, and describe the effect of pulse chirping in such processes in section 3.2. In section 3.3 we discuss how wave-packets have been created and probed in some of the experiments, and in section 3.4 we concentrate on the specific issue of wave-packet dynamics at curve crossings. The quantum mechanical properties of the wave-packet can lead to interference effects, which are discussed in section 3.5.

In section 4 we introduce the effects of spontaneous decay, and discuss its role in theoretical and experimental wave-packet dynamics in section 4.1. In sections 4.2 and 4.3 we show how the numerical approaches presented in section 2 need to be modified. The dynamical effects that spontaneous decay can have on wave-packets are discussed in section 4.4. In section 5 we summarize our presentation and present some views on the future prospects of wave-packet dynamics in femto-time. We have also included an appendix where we give further details of the purely time-dependent quantum models used in the semiclassical description of wave-packet dynamics.

2. Theory of wave-packet dynamics

2.1. Basic theory of coupled energy levels

The standard way to obtain the dynamics of molecular wave-packets is by the use of the Born–Oppenheimer potential surfaces. These surfaces correspond to the different electronic configurations of the molecule. Since the electrons are at least three orders of magnitude
lighter than the nuclei, one can make the adiabatic assumption that any change in the electronic configuration is instantaneous compared with the time-scales of the nuclear motion. Hence we can average out the electronic coordinates and obtain potential surfaces which only depend on the nuclear coordinates. The wave-packet contains information about the relative position and momentum of the atoms. Furthermore, its components on different potential surfaces correspond to the probability of the molecule being in a particular electronic state. In this framework the vibrational effects manifest themselves as oscillations of the wave-packet, in the case when it is trapped in a well in the potential surface. Next we shall briefly present the basics of the potential surface construction (Born–Oppenheimer approximation) and the laser–molecule interactions, and connect the resulting curve crossing picture to the Condon approach, which is often used in the time-dependent description based on actual vibrational state populations rather than on their superposition, the wave-packet.

2.1.1. Potential surfaces. A molecule consists of nuclei and electrons. We denote the full set of three-dimensional nuclear coordinates by \( \vec{R} \), and the electronic ones by \( \vec{r} \). The Hamiltonian for a molecule in an external laser field is

\[
H = T_e(\vec{r}) + T_N(\vec{R}) + V_{ee}(\vec{r}) + V_{NN}(\vec{R}) + V_{en}(\vec{r}, \vec{R}) - \vec{D} \cdot \vec{E} \tag{2.1}
\]

where the subscripts e and N denote the electronic and nuclear variables, \( T \) is the kinetic energy operator and \( V \) is the Coulombic interaction. The laser field \( \vec{E} = E(\vec{R}, t)\vec{e} \), couples to the system by the dipole operator \( \vec{D} \) (dipole approximation). We ignore for the moment the relativistic spin–orbit coupling, but return to it later.

In the spirit of the adiabatic assumption we write the set of electronic states \( \{ |\phi_n\rangle \} \) for fixed nuclear configuration \( \vec{R} \) as solutions of the eigenvalue problem

\[
H_{el}|\phi_n\rangle = U_n(\vec{R})|\phi_n\rangle \tag{2.2}
\]

where

\[
H_{el} = T_e(\vec{r}) + V_{ee}(\vec{r}) + V_{NN}(\vec{R}) + V_{en}(\vec{r}, \vec{R}) . \tag{2.3}
\]

Next we expand the time-dependent molecular wavefunction in these states:

\[
|\Phi(t)\rangle = \sum_n \phi_n(\vec{R}, t)|\phi_n\rangle . \tag{2.4}
\]

This is still exact. In the Born–Oppenheimer approximation we set

\[
T_N(\phi_n(\vec{R}, t)|\phi_n) \simeq [T_N\phi_n(\vec{R}, t)]|\phi_n\rangle \tag{2.5}
\]

i.e. \( (\partial/\partial \vec{R})|\phi_n\rangle \simeq 0 \). By applying \( (\phi_m|H \) to (2.4) with the orthonormality condition \( (\phi_m|\phi_n) = \delta_{n,m} \) we get the Schrödinger equation

\[
\hbar \frac{\partial}{\partial t} \phi_m(\vec{R}, t) = [T_N + U_m(\vec{R})]\phi_m(\vec{R}, t) - \sum_n (\phi_m|\vec{D} \cdot \vec{e} |\phi_n) E(\vec{R}, t)\phi_n(\vec{R}, t) . \tag{2.6}
\]

In the absence of the external field equation (2.6) describes the time evolution of the component of the wave-packet residing on the potential surface \( U_m(\vec{R}) \), which corresponds to the electronic state \( |\phi_m\rangle \). In the Born–Oppenheimer approximation this evolution is completely independent of the other states and their possible occupation; this is the bare-states representation of the potentials.

The above equations assume that \( (\phi_m|\partial/\partial \vec{R} |\phi_n) = 0 \) and ignore relativistic effects such as the spin–orbit interaction \( H_{SO} \) and the spin–spin interaction \( H_{SS} \). These terms provide energy shifts (diagonal elements) and couplings between various bare states (off-diagonal elements). By modifying the bare electronic basis in different ways one can decide how
Wave-packet dynamics in femto-time

Figure 2. A two-surface system. The full curves show the diabatic basis formulation, and the broken curves show the corresponding adiabatic formulation. These formulations differ only near the point where the Born-Oppenheimer approximation fails and the surfaces cross in the diabatic formulation.

these terms appear in (2.6); these modifications are discussed in detail, e.g. in the book by Lefebvre-Brion and Field (1986).

Often the neglected terms are not important, but when two or more potential surfaces become degenerate for some particular nuclear configuration \( \tilde{R}_d \) (surface or level crossing) they can have a significant effect by coupling the involved potential surfaces. One can add these terms into the off-diagonal part of (2.6) in the same manner as the laser-induced coupling has been added. However, it is equally possible to define a new electronic basis by diagonalizing the Hamiltonian in respect of these coupling terms. This new basis is often called adiabatic (see figure 2), and then the surface crossings may appear as avoided crossings (unless the coupling at the crossing is truly zero, e.g. because of symmetry reasons). Similarly the original basis is sometimes called diabatic. However, the terms 'diabatic' and 'adiabatic' are, used rather freely in the literature and the definitions presented here are by no means unique. It should be noted that even in the adiabatic formulation one has off-diagonal terms which arise from the \( \tilde{R} \) dependence of the new basis. We shall return to the question of choosing the basis when we discuss the purely time-dependent models in section 2.4. In case of laser-induced transitions one has the same choice to make, i.e. whether to use the bare states with laser-induced coupling terms (diabatic), or field-dressed potentials obtained by diagonalizing the molecule-laser Hamiltonian (adiabatic). It should be noted that in this review the presence of any naturally arising surface couplings is mostly ignored, and we concentrate on the ones induced by the external field. Therefore the electronic basis that we call diabatic in respect of the laser coupling can be either the bare states basis or the adiabatic states basis. One should keep this carefully in mind.

2.1.2. The diatomic case. We shall now discuss the diatomic case in a frame fixed to the internuclear axis. The discussion is kept on a very simple level, and we do not discuss the various Hund cases or other such details. We shall derive the time-dependent wave-packet equations for a single position coordinate, namely the interatomic distance of a diatomic molecule. This is often the necessary requirement for obtaining a numerical solution within a reasonable time span and under the restrictions set by available computer memory (see section 2.3). In the chosen frame the nuclear kinetic operator of relative motion becomes

\[
T_{\text{rel}} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial R^2} + \frac{2}{R} \frac{\partial}{\partial R} \right) + \frac{\hbar^2 l(l + 1)}{2m R^2}
\]

(2.7)

where \( m \) is the reduced mass of the two-nuclei system and \( l \) is the angular momentum quantum number. The centrifugal term arises from molecular rotations, which we ignore by setting \( l = 0 \); it could, of course, be included in the potential surfaces. Rotations do not
always decouple from the other degrees of freedom, but for simplicity we assume here that they do. By redefining the wavefunction as

$$\Phi_n(R, t) = \frac{\Psi_n(R, t)}{R}$$  \hspace{1cm} (2.8)

we get the radial Schrödinger equation for the components of the wavefunction $\Psi(R, t)$:

$$\frac{\hbar}{\delta t} \Psi_n(R, t) = \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial R^2} + U_n(R) \right] \Psi_n(R, t) + \sum_m \tilde{\mu}_{nm} E(R, t) \Psi_m(R, t)$$  \hspace{1cm} (2.9)

where $\tilde{\mu}_{nm} = -\langle \varphi_n | \vec{D} \cdot \vec{E} | \varphi_m \rangle$ couples the potential surfaces labelled $n$ and $m$.

2.1.3. The laser–molecule interaction. We can often assume that the laser field couples only two selected potential surfaces (even for quite short pulses), so that we can ignore the rest of the set $\{\Psi_m\}$. We label these surfaces as 1 and 2 (occasionally the labels g (ground) and e (excited) are used, if one of the surfaces corresponds to the ground state of the molecule), and usually 1 is the surface which lies lower in the energy scale. Futhermore, quantization of the electric field is seldom needed, so we can describe the field classically; $E \propto \cos(\omega t)$, where $\omega$ is the laser frequency. The case where $\omega$ may change during the system time evolution is discussed separately in section 3.2. Any spatial dependence of the field can be ignored, as the field wavelength usually greatly exceeds the molecular dimensions. Hence $E(R, t) \approx E(t) \cos(\omega t)$. Besides, a proper description of this dependence is not trivial in the relative coordinate system if there is centre-of-mass motion involved as well.

The potential surfaces depend usually quite strongly on $R$, so the laser field brings the two surfaces into a resonance, or at least into a near resonance only at certain values of $R$. In practice the resonance means that we have in the field an oscillating component which counteracts the quantum mechanical oscillations:

$$\tilde{\mu}_{12} E(t) \sim \frac{1}{2} \mu_{12} E(t) \exp[-i(U_2(R) - U_1(R) - \hbar \omega t)/\hbar]$$  \hspace{1cm} (2.10)

$$\equiv \frac{1}{2} \mu_{12} E(t) \exp[-i\Delta(R)t/\hbar]$$  \hspace{1cm} (2.11)

where $\Delta(R)$ is the local detuning and $\mu_{12}$ is the time-independent dipole moment, which may depend on $R$. We have dropped the other, rapidly oscillating interaction term, as it usually averages to zero and does not contribute to the real interaction process; this is called the rotating-wave approximation RWA (see, for example, Stenholm 1984).

The rotating-wave approximation is important, because now we do not have to use excessively small time steps in order to follow the rapid oscillations with frequencies $[U_2(R) - U_1(R) + \hbar \omega]/\hbar$ in the numerical approach. Moreover, if we rewrite the state vector as

$$\Psi(R, t) = \begin{pmatrix} \Psi_1(R, t) \\ e^{-i\omega t} \Psi_2(R, t) \end{pmatrix}$$  \hspace{1cm} (2.12)

we obtain the two-state equation

$$\frac{i\hbar}{\delta t} \begin{pmatrix} \Psi_1(R, t) \\ \Psi_2(R, t) \end{pmatrix} = \begin{pmatrix} T(R) + U_1(R) \\ V \\ T(R) + U_2(R) - \hbar \omega \end{pmatrix} \begin{pmatrix} \Psi_1(R, t) \\ \Psi_2(R, t) \end{pmatrix}$$  \hspace{1cm} (2.13)

where $T(R)$ is the kinetic energy operator from (2.9). The surface coupling $V = \hbar \Omega_{12}/2$ is defined to be real; $\Omega_{nm} = \mu_{nm}(R) E(t)/\hbar$ is the local Rabi frequency for the surfaces $n$ and $m$. It contains the field envelope (pulse shape) $E(t)$.

We can see that in the energy scale the upper surface is simply shifted down by one photon energy, $\hbar \omega$. Hence the laser-induced resonances appear as surface crossings. In
Wave-packet dynamics in femto-time

numercials the required size for the time steps is now determined by $\Delta(R)$ as all high-frequency terms have disappeared. One should note that this approach is only possible if we apply the rotating-wave approximation. However, when the RWA is not valid the two-state approximation usually breaks down too. Since the zero-point of the energy can be freely chosen, formulations different from the above are possible: one could, for example, shift the lower surface up, rather than the upper one down.

Thus we have reduced resonant laser-induced transitions to surface crossings which look very much like those arising from the failures of the Born–Oppenheimer approximation. We shall later see (section 2.4) that these cases share many common characteristics, such as the diabatic and adiabatic formulation. For simplicity we shall in the future use the notation

$$\Psi(R, t) = \begin{pmatrix} \Psi_1(R, t) \\ \Psi_2(R, t) \end{pmatrix}$$

(2.14)

for the state vector.

2.1.4. The Condon approach. The electronic state potential surface structure derived above is the basis for wave-packet dynamics. However, we can proceed one step further and write the state vector component $\Psi_n(R, t)$ as a superposition of the vibrational states $\chi_v$ associated with it:

$$\Psi_n(R, t) = \sum_v C^{(m)}_v(t)\chi^{(m)}_v(R).$$

(2.15)

Here

$$[T_R + U_m(R)]\chi^{(m)}_v(R) = \varepsilon_v^{(m)}\chi^{(m)}_v(R)$$

(2.16)

where $\varepsilon_v^{(m)}$ is the quantized energy of the $v$th vibrational state. Together with (2.9) this leads to

$$i\hbar\frac{\partial}{\partial t}C^{(m)}_v(t) = \varepsilon_v^{(m)}C^{(m)}_v(t) + \sum_{n,m} \hbar\Omega_{nm}(t)\langle \chi^{(m)}_v | \chi^{(n)}_v \rangle C^{(n)}_v(t).$$

(2.17)

To solve (2.17) is almost equivalent to solving the wave-packet equation. We need to calculate a set of matrix elements, namely the Franck–Condon factors:

$$M(n, v; m, \eta) = \langle \chi^{(m)}_\eta | \chi^{(n)}_v \rangle.$$ 

(2.18)

These are overlap integrals and we must know the vibrational eigenfunctions $\chi^{(m)}_v(R)$ in order to calculate them. One also must assume that $\mu_{nm}(R)$ can be taken outside the integral (the Condon approximation); this is not always true. The basis for this approach is the Franck–Condon principle, which states that the time taken for a transition to occur between the vibrational states is very short compared to the period of vibration of a molecule, so the nuclear configuration remains unchanged while the transition occurs (see, for example, Richards and Scott 1985).

The Condon approach is very attractive from the spectroscopic point of view: the terms $\mu_{nm}M(n, v; m, \eta)$ give directly the relative intensities of the lines in the molecular spectrum. For very short pulses with large bandwidth the number of factors needed, and hence the number of coupled equations, is large. This is especially so if one of the involved electronic states is a dissociating one and has at least a partly continuous energy level structure. If the vibrational levels are strongly coupled one cannot use perturbation theory to solve (2.17). Then the wave-packet approach becomes an attractive alternative.
2.2. Simple properties of wave-packets

A wave-packet represents a quantum system that is localized in its position coordinate. In the context of diatomic molecules, the wave-packet represents the fact that there is some uncertainty in the separation of the two atoms. A typical wave-packet is the Gaussian wavefunction

\[ \Psi(R) = \frac{1}{\mathcal{N}} \exp \left[ i k R - \frac{(R - R_0)^2}{4\sigma^2} \right] \]  \hspace{1cm} (2.19)

which represents a wave-packet with a width \( \Delta R = \sigma \), a position \( R_0 \) and a momentum \( \hbar k \). The normalization factor is

\[ \mathcal{N} = \left( 4\pi \sigma^2 \right)^{1/4} . \]  \hspace{1cm} (2.20)

For now we will consider only a single electronic level described by a potential \( U(R) \) within the Born-Oppenheimer approximation as discussed in section 2. Then the wave-packet obeys the Schrödinger equation

\[ i\hbar \frac{\partial}{\partial t} \Psi(R, t) = \left[ \frac{\sigma^2}{2m} + U(R) \right] \Psi(R, t) . \]  \hspace{1cm} (2.21)

From the Schrödinger equation we can obtain differential equations for expectation values of position and momentum:

\[ \frac{\partial}{\partial t} \langle R \rangle = \frac{\langle p \rangle}{m} \]  \hspace{1cm} (2.22)

\[ \frac{\partial}{\partial t} \langle p \rangle = - \left\{ \frac{\partial U(R)}{\partial R} \right\} . \]  \hspace{1cm} (2.23)

These equations indicate the trajectory of the wave-packet. The first equation is quite natural and the second is a quantum mechanical equation of motion. Note that in general

\[ \left\{ \frac{\partial U(R)}{\partial R} \right\} \neq \frac{\partial \langle U(R) \rangle}{\partial \langle R \rangle} . \]  \hspace{1cm} (2.24)

which means that the quantum mechanical trajectory may differ from the classical one for which equality holds in (2.24). Nevertheless, for many purposes the classical trajectory equations describe the mean motion of the wave-packet very well as we shall see. There are also some important exceptions to (2.24): all quadratic potentials (including the harmonic oscillator), the linear slope, and the flat potential. In these special cases the quantum and classical trajectories agree.

In free space, \( U = 0 \), the wave-packet (2.19) not only moves with speed \( \hbar k/m \), but also spreads as shown in figure 3. This spreading, or dispersion, is at a rate that is independent of its velocity and can be calculated from the equations of motion for \( \langle R(t) \rangle \) and \( \langle R^2(t) \rangle \):

\[ \Delta R(t) = \sqrt{\langle R^2(t) \rangle - \langle R(t) \rangle^2} = \sigma \sqrt{1 + t^2 \left( \frac{\hbar}{2m\sigma^2} \right)^2} . \]  \hspace{1cm} (2.25)

The spreading is quadratic in time, for small \( t \), becoming linear in time for large \( t \). It is clear from (2.25) that there is a characteristic time-scale over which the spreading takes place. This dispersion time-scale may be written as

\[ \tau_d = \frac{2m\Delta R^2(0)}{\hbar} \]  \hspace{1cm} (2.26)

for the Gaussian wave-packet (2.19). For wave-packets of other shapes the same time-dependent behaviour (2.25) is seen with a dispersion time-scale that differs by a numerical
Wave-packet dynamics in femto-time

Figure 3. Wave-packet dispersion, or spreading. A Gaussian wave-packet moving from left to right increases in width as time increases (in the absence of a potential surface with spatial dependence).

factor from \( (2.26) \). The momentum of the packet also has a width associated with it. However, in the absence of a potential this remains constant. For the packet given by \( (2.19) \), the momentum width is \( \Delta p = \hbar/(2\sigma) \) so that the packet starts as a minimum uncertainty state with \( \Delta R(0) \Delta p = \hbar/2 \).

The dispersion time-scale is important for setting the regime in which time-dependent wave-packet dynamics can be observed. If the wave-packet is observed over a time-scale which is much longer than \( \tau_d \), it will, in general, be more difficult because of the spreading effects. Of course, the time-scale has been found from wave-packet spreading in the absence of a potential and in the case of a harmonic oscillator, as we see below, there is no spreading of this kind. However, the dispersive time-scale is still seen to play a role in determining spreading in realistic potentials and is especially important during dissociation. We can make an estimate of its size for a special case. If we take the mass \( m \) to be that of the iodine molecule \( \text{I}_2 \), and if we suppose \( \Delta R(0) = 0.1 \ \text{Å} \) (a reasonable value for the width of the ground state wavefunction) then we find \( \tau_d \sim 805 \ \text{fs} \). This will set the scene for time-dependent wave-packet dynamics in \( \text{I}_2 \).

The reason for experimental interest in Gaussian wave-packets such as \( (2.19) \) is that they are naturally found as the ground-state wavefunction of a harmonic potential. This can approximate the ground state of many molecular potentials. For example, when the Hamiltonian of the Schrödinger equation \( (2.21) \) is the harmonic oscillator

\[
H = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 (R - R_0)^2
\]  

the lowest vibrational state is the ground state, which is of the form of \( (2.19) \),

\[
\Psi(R) = \frac{1}{\mathcal{N}} \exp \left[ -\frac{(R - R_0)^2}{4\sigma^2} \right]
\]  

where the width of the Gaussian packet is related to the oscillator frequency in the Hamiltonian \( (2.27) \) by

\[
\sigma = \sqrt{\frac{\hbar}{2m\omega}}.
\]  

Note that if we invert this expression to obtain

\[
\frac{1}{\omega} = \frac{2m\sigma^2}{\hbar}
\]  

we have an equation which bears a close resemblance to the free wave-packet dispersion time-scale \( (2.26) \). The wave-packet \( (2.28) \) is stationary. However, to obtain wave packet dynamics it is only necessary to transfer this ground-state packet to some other potential where it is not in equilibrium. This process is discussed in detail in section 3.1 and here we will only discuss the result of perfect transfer of the packet to another harmonic potential.
For example, if the packet finds itself in another potential of exactly the same shape, but displaced from the centre, it will simply oscillate. It will not change shape and its centre will exactly follow the classical trajectory. However, if the potential is harmonic with a different period, the packet will breathe while moving along the classical trajectory. The breathing means that the packet changes its width as it moves about the well, but, unlike the case of dispersion, its original shape will return. If the packet is wider at the turning point than the natural ground-state wavefunction of the new harmonic well, it will become narrower than the local ground state when it is at the centre of the well (Takahasi 1965, Nieto 1985, Stenholm 1986). In the example shown in figure 4 we see the reverse case. The wave-packet starts in the bottom left of the figure in a harmonic well centred on $R = 0$. As the packet approaches the centre of the well it becomes broader while preserving its Gaussian shape. This happens because the initial wave-packet is narrower than the ground-state wave-packet of the harmonic well. The wave-packet dynamics seen in figure 4 is entirely harmonic.

Real potentials may not be harmonic and if the distortion is only slight we may have an anharmonic potential, which, for example, may be of the form $U(R) = \frac{1}{2}m\omega^2 (R - R_0)^2 + \chi (R - R_0)^3$. If a Gaussian wave-packet is placed in such a potential well (with weak anharmonicity $\chi$) it will initially oscillate in the well as it would in a harmonic potential (see figure 5(a)). However, after a time it breaks up into pieces so that it is spread about the potential surface (figure 5(b)). A remarkable feature of the anharmonic well is that it can show revivals where the wave-packet reforms (Parker and Stroud 1986, Averbukh and Perelman 1989a, 1989b, and see Alber and Zoller 1991). Furthermore, fractional revivals take place where the wave-packet reforms as two (or even more) separate pieces (Averbukh and Perelman 1989b) as seen in figure 5(c). This feature has also been studied in radial (electronic) Rydberg wave-packets (ten Wolde et al 1989, Yeazell et al 1990, Meacher et al 1991).

Figure 4. Wave-packet breathing. A wave-packet in a perfectly harmonic potential shows a periodic change in its width if its initial width does not match that of the ground-state wave-packet, which is given by (2.29). The figure shows two complete oscillations of the wave-packet motion. The initial wave-packet has a width 61% narrower than a ground-state packet of the potential, and it is displaced from the centre of the potential well by two ground-state wave-packet widths. The potential is given by $M\omega^2 R^2/2$ as found in (2.27) with $R_0 = 0$. The vibrational frequency of the oscillator is $\omega$. 

Wave-packet dynamics in femto-time

Figure 5. Wave-packet revivals. A wave-packet in an anharmonic potential will break up into pieces. But as time progresses it may revive again. The figure shows wave-packet motion in an excited state of Na₂. The initial evolution is shown in (a) for times up to 1 ps. By 12 ps (b) the wave-packet has broken up, but in the region of 22 ps (c) there is a fractional revival with the emergence of two wave-packets. A complete revival takes place at 44 ps (not shown). (Taken from Meier and Engel 1993.)

1991) and is reminiscent of the collapse and revival phenomenon found in quantum optics (Narozhny et al 1981, Averbukh 1992, Shore and Knight 1994). The phenomenon has also been predicted and observed for molecular wave-packets in Na₂ (Baumert et al 1992b, Engel et al 1993, Meier and Engel 1993, Baumert et al 1993c).

2.3. Numerical methods for quantum propagation

In this section we give an outline of some numerical methods that are used in the solution of fully quantized wave-packet problems. A common feature of the methods we have focused on is that they treat the quantum mechanical motion by discretizing the wave-packet and propagating it on a lattice of points. This differs from the approach in which one finds the eigenstates of the potential (which may also be found on a lattice) and expands the wave-packet in that basis, using time-dependent coefficients. Such an expansion in (often vibronic) eigenstates is appropriate for systems comprising of oscillators with low vibrational excitation. This approach has been taken where pump–probe experiments are modelled by two coupled harmonic oscillators with just a few vibrational eigenstates (see, for example, Walmsley et al 1988, Pollard et al 1990a, Pollard et al 1992, Pollard and Mathies 1992).

The lattice approach, with discretization in space, has wide applicability, and is more appropriate if the system is highly excited and would contain many eigenstates of the potential. It very naturally encompasses both the bound and free states so that dissociating potentials are easily treated. The methods are outlined below in one spatial dimension, to simplify the notation, however, they may be used in more than one dimension.

The problem is to solve the Schrödinger equation (2.13)

$$i \hbar \frac{\partial}{\partial t} \Psi(R, t) = (T_N + U(R)) \Psi(R, t)$$  \hspace{1cm} (2.31)
where

\[ T_N = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial R^2} \]  

(2.32)

is the kinetic operator and \( U(R) \) is the potential. If only one electronic level is considered, \( U(R) \) is a scalar potential function, but if there are two levels coupled by, e.g. a laser (see section 2.1), \( U(R) \) takes the matrix form

\[ U(R, t) = \begin{bmatrix} U_1(R) & V(t) \\ V(t) & U_2(R) - \hbar \omega \end{bmatrix}. \]

(2.33)

In this case the matrix \( U(R, t) \) may be time-dependent because of explicit time dependence in the coupling of the molecular levels by the laser.

The most straightforward approach to (2.31) would be to utilize a formal solution over a short time step so that

\[ \Psi(R, t + \Delta t) = \exp\left[-i\Delta t(T_N + U(R, t))/\hbar\right] \Psi(R, t) \]

\[ \sim \left[1 - i\Delta t(T_N + U(R, t))/\hbar\right] \Psi(R, t). \]

(2.34)

(2.35)

The operation of \( T_N \) would be effected by means of second-order finite differences of the discretized wavefunction \( \Psi(R) \). However, as is well known, this method is numerically unstable (see, for example, Press et al 1986 for a discussion) and this has resulted in the development of other methods such as those we describe below.

Early approaches to a numerical solution of wave-packet motion were those of Goldberg et al (1967) and McCullough and Wyatt (1969) who applied the Crank–Nicholson method. This method is still widely used and we summarize it in section 2.3.2. The action of the kinetic operator can be determined by a Fourier method (Fleck et al 1976, Feit et al 1982) rather than by second-order differencing. This is straightforward to implement in the split-operator Fourier transform method which we summarize in section 2.3.1 below. The Fourier transform method can also be implemented in a second-order differencing method in which (2.35) is replaced by (Kosloff and Kosloff 1983a, b, Kosloff 1988)

\[ \Psi(R, t + \Delta t) \sim \frac{2i\Delta t}{\hbar} (T_N + U(R, t))\Psi(R, t) + \Psi(R, t - \Delta t) \]

(2.36)

which is stable when \( \Delta t \) is small enough. (This method was previously implemented without Fourier transforms by Askar and Cakmak 1978.) We focus on the Crank–Nicholson scheme and the split-operator Fourier transform method because of their simplicity and straightforward implementation (absorbing boundary conditions can be incorporated to deal with unwanted reflections and time-dependent Hamiltonians can be treated). However, there are other methods. Some of these involve different ways of approximating the exponential operator (2.34) in the spirit of the Crank–Nicholson approach. The Chebyshev polynomials may be used (Tal-Ezer and Kosloff 1984, Leforestier et al 1991, Iitaka 1994). For problems in two or three dimensions it may be appropriate to use the Hankel transform rather than Fourier transforms (Bisseling and Kosloff 1985). Several of these methods are compared by Leforestier et al (1991) together with the short iterative Lanczos algorithm (Quéré and Leforestier 1990, Leforestier et al 1991, Tal-Ezer et al 1992).

2.3.1. Split-operator Fourier transform method. The essence of this method is to split apart the two operator components of (2.34) and treat each operator separately. In general, we note that for two operators \( A \) and \( B \) which do not commute we can write

\[ \exp(A + B) \sim \exp(A) \exp(B) \]

(2.37)
to first-order accuracy only (when the exponentials are expanded). However, it is easily verified that to second-order accuracy we have

$$\exp(A + B) \sim \exp(A/2) \exp(B) \exp(A/2)$$

(2.38)

where the position of $A$ and $B$ may be exchanged on the RHS. Equation (2.38) forms the heart of the split-operator methods. In the case (2.34) we obtain the second-order splitting in the form

$$\Psi(R, t_0 + \Delta t) \simeq U_V^{1/2}(R, t_0) U_T U_V^{1/2}(R, t_0) \Psi(R, t_0)$$

(2.39)

which is accurate to second order in $\Delta t$. The two new evolution operators are

$$U_T = \exp \left[-\frac{i\Delta t}{\hbar} T_N \right]$$

(2.40)

$$U_V = \exp \left[-\frac{i\Delta t}{\hbar} U(R, t_0) \right]$$

(2.41)

which represent the kinetic and potential evolution, respectively. In the form (2.39) above there are two $U_V$ operations for each $U_T$ operation. However, when many steps are taken, the last $U_V$ operation of a given step can be merged with the first $U_V$ operation of the next step. This means approximating (2.39) repeated over $n$ steps,

$$\Psi(R, t_0 + n\Delta t) \simeq \left[ \prod_{k=0}^{n-1} U_V^{1/2}(R, t_0 + k\Delta t) U_T U_V^{1/2}(R, t_0 + k\Delta t) \right] \Psi(R, t_0)$$

(2.42)

by the sequence

$$\Psi(R, t_0 + n\Delta t) \simeq \left[ \prod_{k=0}^{n-1} U_V(R, t_0 + k\Delta t) U_T \right] \Psi(R, t_0).$$

(2.43)

In order to calculate the action of the operator $U_T$ we note that if we perform a Fourier transform, the action of this operator is simply expressed as multiplication by an exponential. Thus

$$U_T = \mathcal{F}^{-1} \exp \left[-i\Delta t \frac{\hbar k^2}{2m} \right] \mathcal{F}$$

(2.44)

where $\mathcal{F}$ indicates the action of a Fourier transform:

$$\mathcal{F}[f] = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dR' e^{iR'R} f(R').$$

(2.45)

In a numerical procedure we use a fast Fourier transform as an efficient means to transfer to and from Fourier space for the multiplication by the exponential operator in (2.44).

The evaluation of the exponential operator $U_V$, (2.41), is straightforward if there is only one potential surface. However, if there are two coupled surfaces, such as in (2.33), we must form the exponential of a $2 \times 2$ matrix. For small $\Delta t$ it can be done by expansion, but as this would compromise the accuracy it is better to follow the formal way and diagonalize $U(R)$ to form the exponential. Here we present the results as the derivation is straightforward. If the matrix $U(R)$ is written in the shorthand form

$$U = \begin{bmatrix} U_1 & V \\ V & U_2 - \hbar \omega \end{bmatrix}$$

(2.46)

the operator $U_V$ is obtained as

$$U_V = \exp(-i\Delta t U/\hbar)$$

$$= \exp \left[-i\frac{\Delta t}{\hbar} \left( U_1 + U_2 - \hbar \omega \right) \right] \begin{bmatrix} A & B \\ B & A^* \end{bmatrix}$$

(2.47)
where the numbers \( A \) and \( B \) are found as
\[
A = \cos\phi - i\frac{\Delta t \Delta U \sin\phi}{\hbar} \quad B = -i\frac{\Delta t V \sin\phi}{\hbar}
\] (2.48)
with the phase
\[
\phi = \Delta t \sqrt{V^2 + \Delta U^2}/\hbar
\] (2.49)
and the energy difference
\[
\Delta U = \frac{U_1 - U_2 + \hbar \omega}{2}.
\] (2.50)

For a time-independent problem it may be convenient to prepare the matrix \( U_N \) in advance of the wave-packet propagation as \( U_N \) depends only on the potentials and coupling at the discretized time and space points. The method may also be used for time dependent potentials and couplings, but then no advance preparation is possible which adds to the numerical overheads. This approach, using exact diagonalization has been used by us (e.g. in Garraway and Stenholm 1991, Suominen et al 1992) and by Broeckhove et al (1990). For systems with many coupled levels one of the hybrid schemes described below may be more appropriate.

2.3.2. Crank–Nicholson method. The Crank–Nicholson method preceded the Fourier methods of the previous section. The basic Crank–Nicholson time-step takes the form
\[
\Psi(R, t_0 + \Delta t) = [1 + i\Delta t H_{\text{eff}}(R, t_0)/2\hbar]^{-1} \left[ 1 - i\Delta t H_{\text{eff}}(R, t_0)/2\hbar \right] \Psi(R, t_0)
\] (2.51)
which may be regarded as a form of second-order expansion of the exponential operator in (2.34). As in the Fourier method the time step is manifestly unitary and it is performed by solving the equation
\[
[1 + i\Delta t H_{\text{eff}}(R, t_0)/2\hbar] \Psi(R, t_0 + \Delta t) = [1 - i\Delta t H_{\text{eff}}(R, t_0)/2\hbar] \Psi(R, t_0).
\] (2.52)
The action of the kinetic operator is replaced by finite differences and so (2.52) is determined (in the case of a single energy level) by the inversion of a tri-diagonal matrix. The method easily generalizes to two coupled levels, but in that case the process of solving for \( \Psi(R, t_0 + \Delta t) \) becomes more complicated.

2.3.3. Hybrid schemes. There are various ways of redesigning the above basic methods. For example, for a system of two coupled levels, the Hamiltonian in (2.31) can be split in a different way (Holland et al 1994a, b):
\[
H = T_N + U(R) \rightarrow H_{\text{wp}} + H_{\text{int}}
\] (2.53)
where \( H_{\text{wp}} \) contains the diagonal part of the Hamiltonian and is propagated separately using, for example, the Crank–Nicholson algorithm
\[
H_{\text{wp}} = T_N + \begin{bmatrix} U_1 & 0 \\ 0 & U_2 - \hbar \omega \end{bmatrix}.
\] (2.54)
The coupling is contained within \( H_{\text{int}} \) and is propagated separately over short steps:
\[
H_{\text{int}} = \begin{bmatrix} 0 & V(t) \\ V(t) & 0 \end{bmatrix}.
\] (2.55)
Holland et al (1994a, b) carry out this second propagation using a Runge–Kutta method. Under certain conditions (slow wave-packet motion) it is possible to make fewer \( H_{\text{wp}} \) steps than \( H_{\text{int}} \) steps and speed up the calculation.
2.4. Time-dependent two-state models

So far we have described the basics of wave-packet dynamics with an emphasis on the numerical solution methods. Analytical solutions for wave-packet evolution on potential surfaces are known only for very simple one-level problems, such as the Gaussian wave-packet on a flat surface, which we discussed in section 2.4. However, wave-packet problems usually involve many parameters, and hence any attempt to span the whole parameter space can become tedious and time consuming. Moreover, when one tries to establish an optimal control over the system, i.e. when the task is to find the initial conditions which lead to certain end-products, simpler descriptions of the problem are needed. Even if they can provide only approximate results, or remain purely qualitative, they are quite valuable when mere numbers are not enough, and one seeks physical insight into the problem at hand. Here we discuss how the purely time-dependent two-state models with semiclassical approximations can provide such an approach to the wave-packet dynamics.

The approach mentioned above applies to cases where the wave-packet is reasonably well defined in position and momentum, and behaves very much like a classical object when it evolves along the potential surfaces. We ignore the internal coherences of the wave-packet and regard it simply as a distribution of probability. In section 3.5 we describe some cases where the phase effects and a semiclassical description of wave-packet motion can be added to the model, but in the current semiclassical description the only quantum part is the interaction which causes transfer of wave-packet components between the potential surfaces, dominantly in the immediate vicinity of the surface crossings.

There are two basic cases, which correspond to very different processes. The first one, the local excitation approach, treats the laser-induced excitation of an initially stationary wave-packet. The second one, the classical trajectory approach, describes the transfer which occurs when a moving wave-packet traverses a surface crossing. In the latter case the crossing is not necessarily laser-induced, but can arise from the breakdown of the Born–Oppenheimer approximation as discussed in section 2.1. Both approaches involve purely time-dependent two-state models: pulse models and chirped pulse models for the local excitation approach, and level crossing models for the classical trajectory approach.

We shall next present the general theory and classification of these models, and then discuss the details of their actual use in wave-packet dynamics.

2.4.1. General theory. The basic way to describe systems with two possible energy levels and explicit time dependence is the Hamiltonian

$$H(t) = \begin{pmatrix} \beta_1(t) & V(t) \\ V(t) & \beta_2(t) \end{pmatrix}$$ (2.56)

where $\beta_1$ and $\beta_2$ are the level energies, and $V$ is the interaction term that couples the two levels. By writing the two-component state vector $C(t)$ as

$$C(t) = \exp \left[-\frac{i}{2\hbar} \int^t dt' (\beta_1 + \beta_2) \right] \begin{pmatrix} C_1(t) \\ C_2(t) \end{pmatrix}$$ (2.57)

we obtain from the Schrödinger equation

$$i\hbar \frac{\partial C(t)}{\partial t} = H(t) C(t)$$ (2.58)

the basic equation

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} C_1(t) \\ C_2(t) \end{pmatrix} = \begin{pmatrix} \alpha(t) & V(t) \\ V(t) & -\alpha(t) \end{pmatrix} \begin{pmatrix} C_1(t) \\ C_2(t) \end{pmatrix}$$ (2.59)
where the new level energy factor is $\alpha \equiv (\beta_1 - \beta_2)/2$. The state vector $C(t)$ is given in the time-independent (diabatic) basis $\{\tilde{D}_1, \tilde{D}_2\}$, where

$$
\tilde{D}_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \tilde{D}_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.
$$

The second way to formulate the problem is to use the instantaneous eigenstates of the diabatic Hamiltonian $H$. They are obtained by diagonalizing $H$, but since the Hamiltonian has an explicit time dependence, the coupling between the eigenstates does not vanish. After the appropriate transformation (see, for example, Davis and Pechukas 1976 or Suominen et al 1991) we obtain the adiabatic basis, for which the basis vectors are time-dependent and can be expressed in the diabatic basis as follows:

$$
\chi_1(t) = \pm \begin{pmatrix} \cos(\theta/2) \\ -\sin(\theta/2) \end{pmatrix} \quad \text{and} \quad \chi_2(t) = \pm \begin{pmatrix} \sin(\theta/2) \\ \cos(\theta/2) \end{pmatrix} \quad \tan(\theta) = -\frac{V}{\alpha}.
$$

The adiabatic Hamiltonian is

$$
H_a = \begin{bmatrix} -E(t) & -i\hbar \eta(t) \\ i\hbar \eta(t) & E(t) \end{bmatrix}
$$

where

$$
E(t) = \sqrt{a^2 + V^2} \quad \eta(t) = \chi_1^T \chi_2' = \pm \frac{1}{2} \theta' = \pm \frac{V \alpha' - \alpha V'}{2(a^2 + V^2)}.
$$

These determine the adiabatic energy levels $E_i = (-1)^i E$, $i = 1, 2$, and the adiabatic coupling $\eta$. The sign of the coupling depends on the relative sign of $\chi_1$ and $\chi_2$ (as in equation (2.61)); this has some consequences that are discussed later. In order to avoid confusion all multicomponent objects given in the diabatic basis appear in parentheses ($\tilde{\cdot}$), and the square brackets $[\cdot]$ correspond to the adiabatic basis. For the time derivative we sometimes use the prime for brevity, as in (2.63).

In the adiabatic basis, with the Hamiltonian $H_a$ and the state vector $a(t)$, the corresponding Schrödinger equation can be written as follows:

$$
a(t) = \begin{bmatrix} a_1(t) e^{i\Delta(t)/2} \\ a_2(t) e^{-i\Delta(t)/2} \end{bmatrix} \quad \frac{\partial}{\partial t} \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = \begin{bmatrix} 0 & -\eta e^{-i\Delta} \\ \eta e^{i\Delta} & 0 \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \end{bmatrix}
$$

where

$$
\Delta(t) = \int_0^t dt' [E_2(t') - E_1(t')]/\hbar = 2 \int_0^t dt' E(t')/\hbar.
$$

The model is analytically solvable if we can solve the time evolution of the state vector from known initial conditions. We define the state populations in the two basis systems as

$$
P_i^{\text{dis}}(t) = |C_i(t)|^2 \quad \quad P_i^{\text{adis}}(t) = |a_i(t)|^2 \quad \quad i = 1, 2.
$$

In many cases it is necessary to know only the final populations $P_i^{\text{dis}}(\infty)$ or $P_i^{\text{adis}}(\infty)$ of the states when the initial ones, i.e. $P_i^{\text{dis}}(-\infty)$ or $P_i^{\text{adis}}(-\infty)$ are known. If

$$
\lim_{t \to \pm \infty} |a(t)| = \infty \quad \text{and/or} \quad \lim_{t \to \pm \infty} V(t) = 0
$$

then, apart from a possible exchange of state labels, the initial and final populations are the same in both bases. If there are an odd number of level crossings then, for example, $P_i^{\text{dis}}(-\infty) = P_i^{\text{adis}}(-\infty)$, but $P_i^{\text{dis}}(\infty) = P_2^{\text{adis}}(\infty)$ because in the diabatic picture the levels cross and in the adiabatic picture the crossing is avoided.
2.4.2. Basis choices and approximate methods. The two bases described above correspond in many ways to those used in the potential surface construction. If we look at the derivation above, especially at the coupling terms, we see that for sufficiently weak interactions the diabatic basis is practical: one can use perturbation theory if no analytic solutions can be found. For strong couplings the adiabatic coupling $\eta(t)$ tends to be small and one is tempted to use perturbation theory in that basis. However, here the perturbation theory fails; the essential parameter is a small exponential which appears in all orders of the perturbative Born series for the final populations (Davis and Pechukas 1976). Despite this, the perturbation approach has been widely used since the first term in the series has a prefactor $(\pi/3)^2 \approx 1.1$ for the exponential term; by calculating the total sum of the Born series one obtains a prefactor 1 and the same exponential term.

In the adiabatic limit, $(\eta \to 0)$, and the diabatic basis, the population transfer induced by the level crossing is practically complete. In the adiabatic limit with the adiabatic basis the situation is reversed and no population transfer takes place from one adiabatic state to another: the change is built into the time dependence of the basis. Davis and Pechukas (1976) have shown that, if we continue the time axis analytically into the complex plane, we can do the time evolution in the adiabatic basis along a contour which passes just below the complex zero point $t_c$ of the energy term $E(t)$. In the adiabatic limit the main contribution to the population transfer comes from the vicinity of this point; the level coupling $\eta$ then becomes universal, i.e. independent of the particular model at hand. Also the nature of the adiabatic state changes abruptly as the dominance in the superposition of the two states goes from one diabatic state to the other one; this is very much like crossing a Stokes line for asymptotic series, and resembles the turning point problem in the WKB theory.

The result of this approach can be summarized as follows. If $P_{1}^{\text{adi}}(-\infty) = 1$ (i.e. state 2 is initially empty), then we have

$$P_{2}^{\text{adi}}(\infty) = e^{-2\text{Im} \Delta_c}$$

$$\Delta_c = \int_0^{t_c} dt \frac{E(t)}{\hbar}$$

(2.68)

in the adiabatic limit. This treatment of the problem by Davis and Pechukas (1976) was based on ideas expressed by Dykhne (1960, 1962), so the model is called the Dykhne-Davis-Pechukas (DDP) model. Since $\Delta_c \to 0$ as $\hbar \to 0$, the adiabatic limit is often associated with the semiclassical limit, but this need not to be the case in general.

In the DDP model only the complex zero points $t_c$ located in the upper half of the complex time plane are considered. If there are more than one such $t_c$ the situation becomes complicated. In the adiabatic limit only the one closest to the real axis is taken into account. If one applies the DDP theory to all points, one occasionally obtains a solution which is valid even outside the adiabatic limit (Suominen 1992a). If there is more than one of these points at the same distance from the real axis, then they all need to be taken into account: in the case of two symmetric points this can lead to the expression

$$P_{2}^{\text{adi}}(\infty) = 4 \sin^2(\text{Re} \Delta_c) e^{-2\text{Im} \Delta_c}$$

(2.69)

where $\Delta_c$ can be calculated using either of the two $t_c$'s (Suominen 1992b). In pulse models the integral $\text{Re} \Delta_c$ is usually equal to the pulse area, and the oscillations in $P_2$ are a manifestation of the well known area theorem (see, for example, Allen and Eberly 1975 or Shore 1990). Equation (2.69) can lead to a situation where $P_{1}^{\text{adi}}(-\infty) = P_{1}^{\text{adi}}(\infty) = 1$ even when we are not in the adiabatic limit. The parabolic model discussed in section 3.4 and in the appendix is an example of a model in which such a situation can occur. The DDP approach is the correct ‘perturbation theory’ in the adiabatic basis. Of course, it is not perfect: poles or other strong singularities in $E(t)$ in the complex plane can cause problems.
(Suominen et al 1991, Berry and Lim 1993, Lim 1993). One can also use the DDP approach to find the time evolution of the system in the adiabatic limit by using a superadiabatic basis (Berry 1990, Lim and Berry 1991, Berry and Lim 1993, Lim 1993).

2.4.3. The local excitation approach. The local excitation approach is based on the stationary character of the initial wave-packet, which resides on the lowest vibrational state of some potential well. This well, and hence the wave-packet, is brought into resonance with some other potential surface by a laser pulse as shown schematically in figure 6(a). In a strictly monochromatic case the resonance is actually limited only to a few spatial points. The finite duration of the pulse gives it a finite bandwidth, which reduces the importance of the resonance points, especially if the pulse is very short. For each position point \( R \) we can define a local detuning \( \Delta(R) \). If the pulse is not chirped, \( \Delta(R) \) remains constant during the pulse. We can now slice the initial wave-packet into spatially narrow and well localized components, as indicated in figure 6(a). Each component is assumed to be excited independently of the others. It is easy to see that the local excitation approach is closely related to the Franck–Condon principle, which states that the excitation process takes place without any changes in the nuclear configuration \( \{ R \} \). The effect of the pulse at each \( R \) can be described using (2.59); now \( \alpha = \Delta(R)/2 \) and \( V(t) \) is the pulse envelope. For simplicity we set \( \hbar \equiv 1 \) from now on. So, if we have a purely time-dependent pulse model with solution \( P_2^{\text{dia}}(\infty) \) for the final population (initially \( P_2^{\text{dia}}(-\infty) = 0 \)), we can take an average over the parameter \( R \) using the initial wave-packet \( |\Psi_1(R, -\infty)\rangle \) as a weight:

\[
\bar{P}_2^{\text{dia}} = \int dR \ |\Psi_1(R, -\infty)\rangle |P_2^{\text{dia}}(\infty)|_{\alpha=\Delta(R)/2}^2 .
\]  

(2.70)

This approach can be taken even further: if the actual time evolution \( P_2^{\text{dia}}(t) \) for the pulse model is known, it can replace \( P_2^{\text{dia}}(\infty) \) in (2.70):

\[
\bar{P}_2^{\text{dia}}(t) = \int dR |\Psi_1(R, -\infty)\rangle |P_2^{\text{dia}}(t)|_{\alpha=\Delta(R)/2}^2 .
\]  

(2.71)

If the locally excited wave-packet components remain local during the process, the above approach holds. However, the second potential surface may force the components...

Figure 6. In (a) we see how a laser interaction brings two potential surfaces into resonance at certain spatial points. When these points overlap adequately with the initial wave-packet, and the laser bandwidth is suitably large, we can assume that the initial wave-packet completely overlaps with the effective resonance region. If this is not the case, we can under certain conditions apply the local excitation model based on the spatial slicing of the initial wave-packet. In (b) we show schematically the splitting of a moving wave-packet into two components at a curve crossing.
Wave-packet dynamics in femto-time

to move while the pulse is still on. Also, once the initial wave-packet is not bound by the well potential, it experiences its natural spreading (2.25), which can be strong enough to destroy the local excitation approach. We shall return to this breakdown in section 3.1 with some examples.

The above approach requires analytical solutions for pulse models, at least for the final populations. One should note that since the condition (2.67) is fulfilled in pulse models, we can use the adiabatic counterpart of $P_2^{\text{dia}}(\infty)$ in (2.70). Hence the DDP method may be used in the adiabatic limit. In general, the available number of analytically solvable models is quite small, at least for symmetric pulse shapes. The most important symmetric model is the Rosen–Zener pulse model (Rosen and Zener 1932), for which

$$\alpha = \Delta/2 \quad V(t) = V_0 \text{sech}(t/T) \quad P_2^{\text{dia}}(\infty) = \sin^2(\pi V_0 T) \text{sech}^2(\pi \Delta T/2).$$ (2.72)

The full solution $P_2^{\text{dia}}(t)$ for this model is given in terms of hypergeometric functions. The result (2.72) contains the area theorem; $2\pi V_0 T$ is the pulse area. Hence $\pi$-pulses with $2V_0 T = n$ with $n$ equal to an odd integer provide maximum excitation. For $2\pi$ pulses ($n$ equal to an even integer) the system is transparent; although population is transferred, the final state is the same as the initial one. This leads to the optical self-induced transparency effects (McCall and Hahn 1967, 1969). If $\Delta = 0$ the result is trivially valid for all pulse shapes; this led Rosen and Zener to present a conjecture (Rosen and Zener 1932) that for all pulses

$$P_2(\infty) = \left[ \frac{\sin A(0)}{A(0)} A(\Delta) \right]^2 \quad A(\Delta) = \int_{-\infty}^{\infty} dt V(t)e^{i\Delta t}. \quad (2.73)$$

However, this conjecture is not necessarily correct, as noted by Robiscoe (1983), who also derives some approximate solutions for Gaussian and exponential pulse shapes.

There are several cases of non-symmetric pulse envelopes, whose time-dependent analytic solutions are based on hypergeometric functions, or special cases of hypergeometric functions (see, for example, Bambini and Berman 1981, Radmore 1982, Hioe and Carroll 1985, Carroll and Hioe 1990, Vitanov 1994). These pulses (and also the symmetric ones found in Bambini and Lindberg 1984) can be used to form approximations to Lorentzian and Gaussian envelopes; the usefulness of the DDP approach to these quite popular pulse shapes is limited by the fact that the integrations in $\Delta_n$ need to be performed numerically.

Another class of pulses are the chirped ones, i.e. for which $\Delta$ is not constant in time. In section 3.2 we show how the frequency variations are turned into a time-dependent variation in the relative position of the potential surfaces in the energy scale. Hence in the local excitation approach $\Delta(R)$ becomes time-dependent. One analytically solvable model for chirped pulses is the first Demkov–Kunike model (Demkov and Kunike 1969, Hioe 1984, Suominen and Garraway 1992):

$$\alpha = \tilde{E} + E_0 \tanh(t/T) \quad V(t) = V_0 \text{sech}(t/T).$$ (2.74)

Clearly the Rosen–Zener model is a special case of this model with $E_0 = 0$. The solution is in terms of hypergeometric functions, and we discuss it in the appendix. When $\tilde{E} = 0$ we have

$$P_2^{\text{dia}}(\infty) = 1 - \frac{\cos^2(\pi T \sqrt{V_0^2 - E_0^2})}{\cosh^2(\pi T E_0)}. \quad (2.75)$$

We see that because of the chirp, the area theorem cannot be applied in a straightforward way (Hioe 1984).
2.4.4. The classical trajectory approach. Now we discuss a moving wave-packet, which we slice into components in the momentum representation, in contrast to the slicing in position space for the local excitation approach. This procedure requires the momentum distribution \( W(p, t) \) of the wave-packet, which we obtain from the spatial representation of the wave-packet with a Fourier transform as described in section 2.3 (see equation (2.45)). We consider a situation where the wave-packet approaches a crossing of two surfaces, located at \( R = R_c, \) as shown in figure 6(b). If the coupling is not too strong we can replace the surfaces with their tangents evaluated at \( R_c. \) This is the spatial linearization of the problem. Next we assume that the wave-packet components have enough momentum to pass through the interaction region around \( R_c \) without being accelerated or decelerated too much. Then we can assume that the wave-packet traverses the crossing along a linear classical trajectory \( \Delta R = v_{ct} t \) near \( R_c, \) where \( v_{ct} \) is the classical speed of the wave-packet at the crossing, \( \Delta R = R - R_c, \) and the time \( t \) is measured relative to the time at which the crossing takes place. This is the temporal linearization of the problem. The situation can be turned around; in the frame moving with the wave-packet the surfaces have an energy difference which is linear in time and becomes momentarily zero when the wave-packet reaches the crossing point. If the surface coupling can be regarded constant over the region of interaction we have a purely time-dependent model with

\[
\alpha = \lambda t \quad V = V_0 \quad \lambda = \left| v_{ct} \frac{\delta (U_2(R) - U_1(R))}{\delta R} \right|_{R=R_c} \tag{2.76}
\]

This is the famous Landau-Zener model (Landau 1932, Zener 1932), which because of its simplicity has a wide range of applications. In many ways it can be regarded as a paradigm for the level crossing models, and certainly as a paradigm for wave-packet splitting in the curve crossing picture.

The solutions for this model are obtained in the form of parabolic cylinder functions (Zener 1932), and with the initial condition \( P_1^{\text{dis}}(-\infty) = 1 \) we obtain the simple and powerful expression

\[
P_2^{\text{dis}}(\infty) = \exp(-\pi \Lambda) \quad \Lambda = \frac{V_0^2}{\lambda}. \tag{2.77}
\]

It is now clear why it is useful to slice the wave-packet in the momentum representation: the probability to move from one surface to another at \( R_c \) depends on the speed \( v_{ct} \) of the components. Usually adequate results are obtained if we use the mean speed \( \langle p \rangle / m \) of the wave-packet (\( p \) is the momentum and \( m \) is the mass associated with the wave-packet) in (2.76) and (2.77) (Garraway and Stenholm 1991). However, for wave-packets with wide momentum spread the momentum average of \( P_2^{\text{dis}}(\infty) \) using the momentum distribution \( W \) as a weight must be taken (Suominen and Garraway 1993). We discuss this further in section 3.4.

The wave-packet is not merely split at the crossing, but the component entering the other, initially unpopulated surface also acquires a phase factor. Usually this phase factor can be ignored, but if the wave-packet components are recombined at a second crossing, it becomes visible. This case is discussed further in section 3.4.

If the potential surfaces merely touch each other at \( R_c, \) or have a close pass (avoided crossing even in the diabatic formulation), the linearization is not possible and the Landau-Zener model cannot be used. This situation is a rare one, though. To some extent it can be described with the parabolic model

\[
\alpha = at^2 - b \quad V = v \tag{2.78}
\]
when $b \leq 0$. Unfortunately this model has, to our knowledge, no exact analytical solution, but the DDP approach together with some additional contributions can be used in some cases. For $b \gg 0$ this model becomes a combination of two Landau-Zener cases; the aforementioned phase factor (which is found in equation (A.14)) becomes important (Suominen 1992b). Above we assumed the parabolic behaviour to arise from linearized classical motion $\Delta R = v_{\text{cr}} t$ when $|U_2(R) - U_1(R)|_{\tilde{R} = R_0} \propto (R - R_{\text{cr}})^2$. Alternatively we could use the model when the potential surfaces can be linearized, but changes in $v_{\text{cr}}$ imposed by the linear surfaces are notable in the immediate neighbourhood of $R_{\text{cr}}$, i.e. $\Delta R \propto (\Delta t)^2$.

In fact, the parabolic model is very close to models used in phase integral studies of slow atomic and molecular collisions (Crothers 1971, 1972, 1989, Delos and Thorson 1972, Child 1974, Eu 1984, Nikitin and Umanskii 1984).

3. Wave-packet processes

3.1. Wave-packet generation

3.1.1. Instantaneous excitation. One method to create a well defined quantum mechanical wave-packet is to apply a short laser pulse to a molecule in its equilibrium state. The wave-packet describing this initial state of the molecule is stationary and relatively narrow because it usually corresponds to the ground state of a potential well. A laser pulse can transfer this wave-packet onto the particular excited-state potential surface which satisfies the resonance conditions set by the centre frequency and bandwidth of the pulse. Of course, there may be several such surfaces, but for simplicity we assume only one exists. The simultaneous excitation of many vibrational states is not excluded, because these states correspond to the bound states of each electronic potential surface. Basically this situation is the one that we have already discussed to some extent in section 2.4.3 (see also figure 6(a)).

The problem we address in wave-packet creation is to use the excitation process to conserve the properties mentioned above. That is the excited-state wave-packet should also be narrow and well localized after the interaction with the pulse is over. Two major problems can arise if the pulse is not short enough. The wave-packet may evolve during the excitation process, or the pulse does not bring the two potential surfaces into a clear resonance. Hence it was the femtosecond pulse technology that finally made the wave-packet creation (and probing) possible. The use of ultrashort pulses reduced the excitation process to a simple dumping of the ground-state wave-packet on the excited-state potential surface, without any alterations in the spatial distribution. This is sometimes called Franck-Condon excitation, as it follows the principle of no changes in nuclear configuration during the excitation process (see, for example, Broeckhowe et al 1990). The short pulse hits the molecule as if it had a delta-function envelope, instantaneous in time and infinitely wide in spectrum.

The short duration of the pulse simplifies the subsequent calculations, since the excitation process and hence the ground state can be ignored. The initial state for studies is the ground-state wave-packet placed on the excited state at the position it would normally occupy if it were still on the ground-state potential surface (see figure 6(a)). The necessary conditions for the validity of this approach can be estimated using semiclassical arguments, and we shall discuss them next. It should be no surprise that some of the conditions also apply to the validity of the local excitation approach presented in section 2.4.3.

3.1.2. Conditions for instantaneous excitation. We simplify the situation by assuming that the potential surfaces in the curve crossing picture are

$$U_g(R) = \frac{1}{2} mw^2(R - R_0)^2 \quad U_e(R) = -\alpha(R - R_0) + \beta$$

(3.1)
where \( R_0 \) is the ground-state equilibrium position for the molecule. The initial wave-packet is a Gaussian as in (2.19). After entering the excited-state potential surface any part of this wave-packet will feel the acceleration \( \alpha \) imposed by the potential \( \mathcal{U}_e(R) \) (see equation (2.23) in section 2.2):

\[
a = -\frac{1}{m} \left( \frac{\partial \mathcal{U}_e(R)}{\partial R} \right) = \frac{\alpha}{m}.
\]

(3.2)

In this case the acceleration is constant. During a pulse with duration \( \tau \) any excited part of the wave-packet moves roughly the distance

\[
\Delta R \simeq \frac{\alpha}{2m} \tau^2.
\]

(3.3)

This distance is compared with the width \( \sigma \) of the initial ground-state wave-packet in order to obtain the time-scale \( \tau_{ex} \) for the wave-packet evolution.

Once the wave-packet is no longer bound by the harmonic ground-state potential it will disperse as described in section 2.2. If the ground state is very narrow, the unbound excited-state wave-packet has a very large width in momentum; the spreading disperses the wave-packet quite rapidly. We assign the time-scale \( \tau_d \) given in (2.26) to the dispersion. It should be noted that Gaussian wave-packets on linear and flat potential surfaces disperse in the same manner (Stenholm 1983).

If the excitation process is not complete, the wave-packet components remaining on the ground state evolve as the ground-state wave-packet rearranges itself. The time-scale \( \tau_{gr} \) for this process is determined by the frequency \( \omega \). Hence we have three time-scales:

\[
\tau_{ex} \sim \sqrt{\frac{2m\sigma}{\alpha}},
\]

(3.4)

\[
\tau_{gr} \sim \omega^{-1} = \frac{2m\sigma^2}{\hbar}.
\]

(3.5)

\[
\tau_d \sim \frac{2m\sigma^2}{\hbar} = \tau_{gr}.
\]

(3.6)

If all these time-scales are clearly larger than the pulse duration \( \tau \), the local excitation model is valid. This is not yet a sufficient condition for a complete Franck-Condon excitation. As mentioned earlier in this section, the pulse must bring the ground and excited-state potential surfaces into resonance over the whole region of the space that is occupied by the initial wave-packet. However, the large bandwidths of the ultrashort pulses reduce the importance of the resonance requirement.

In section 2.4.3 we showed how to use the time-dependent models to predict wave-packet excitation results when the local excitation approach is valid. We used the Rosen-Zener model with hyperbolic pulse envelope as an example. In figure 7 we show the excited-state populations during a pulse (potentials as in (3.1)) for two cases, (a) one with small \( \alpha \) and (b) one with large \( \alpha \). In figure 7(a) the bandwidth of the pulse is large enough so that we can assume \( \Delta(R) \simeq \Delta(R_0) \) for all \( R \) in (2.70) and (2.71); however, \( \Delta(R_0) \) is still large compared to the bandwidth and full excitation is not achieved even though the pulse area is equal to 5\( \pi \). The Rosen-Zener approach describes the situation well, but when the slope is increased the local excitation approach begins to fail and the accuracy of the prediction from the Rosen-Zener model is lost, as seen in figure 7(b).

3.1.3. Rabi oscillations. The pulse area determines the population distribution between the levels for ultrashort pulses, so only pulses with areas equal to odd multiples of \( \pi \) can deplete
the ground state completely. On the other hand the pulse area affects only the total excited population, so for ultrashort pulses the form of the wave-packet is still preserved. Thus, given that the coupling dominates, the excitation process can be described by a transfer matrix

$$T = \begin{pmatrix} \cos(A/2) & -i \sin(A/2)e^{i\phi} \\ -i \sin(A/2)e^{-i\phi} & \cos(A/2) \end{pmatrix}$$

(3.7)

where $A$ is the pulse area and $\phi$ is the phase of the interaction: $V = |V|e^{i\phi}$; we usually set $\phi = 0$. The transfer matrix describes the net effect of the short pulse and is applied to the initial state vector (which, for example, is in the form of (2.14)). The action of $T$ preserves the norm of the state vector. For the case of excitation by an extremely short pulse we may approximate the pulse envelope by a delta function; $V(t) = V_0\delta(t)$. The transfer matrix (3.7) then applies with $A = V_0$.

If the pulse area is larger than $\pi$ we observe Rabi oscillations in the time evolution of the excited-state populations, as seen in figure 7. (A general account of Rabi oscillations and the Rabi frequency can be found in, for example, Allen and Eberly (1975) or Knight and Milonni (1980). In brief, the oscillations in population occur in multi-level systems when a driving field is able to create coherences amongst the energy levels.) In figure 7(a) Rabi oscillating wave-packet is transferred back and forth between the energy surfaces during the pulse. When this is combined with the breakdown of the local excitation approach some interesting effects arise (Suominen et al 1992). As the wave-packet components appear on the excited state for the first time, they can escape rapidly from the resonance region via acceleration or dispersion. Hence the latter part of the Rabi cycle finds very little resonant population to take back to the ground state. During each cycle more wave-packet components are pumped to the excited-state surface and subsequently accelerated away from $R_0$, so that a row of small wave-packets which move away from the excitation region is created. A good example of such behaviour is shown in figure 8, where both the acceleration and dispersion contribute to the effect. The edges of the dispersed wave-packet are beyond the reach of the Rabi cycling and therefore continue moving in opposite directions. Eventually the repulsive potential slope reflects the part moving towards negative $x$ ($x = 0$ is the equilibrium position for the ground state). As a result the excited-state wave-packet becomes deformed and quite delocalized.
3.2. Processes induced by chirped pulses

A time-dependent change in the laser frequency during the pulse is called chirping or frequency-sweeping (see, for example, Shore 1990). In addition to pulse shaping it is an integral part of finding optimal control of quantum systems using femtosecond pulses (Amstrup et al 1993 and references therein). The chirp in a pulse adds a new, externally controllable degree of freedom to the laser–molecule system. It is usually easier to induce a chirp into a femtosecond pulse, than to obtain a specific pulse shape (Ruhman and Kosloff 1990, Amstrup et al 1993).

A straightforward application of chirping is to increase the maximum obtainable population transfer between two molecular levels. For example, in a simple one-state Morse potential case studied numerically by Chelkowski et al (1990) enhancement of molecular dissociation by chirped pulses was observed. In the Morse potential the energy separation of the vibrational states decreases as the vibrational quantum number increases. A pulse with a decreasing frequency can take the initial ground-state wave-packet to the dissociation limit stepwise: the wave-packet moves upwards in the vibrational state structure as the pulse proceeds. This up-the-ladder excitation induced by chirping has been observed in laser–atom systems (Broers et al 1992).

Frequency chirping is not necessarily the best way to enhance population transfer. By simply making the pulses shorter we can induce full transfer as was seen in the model presented in section 3.1. However, additional potential surfaces may then participate in the excitation because of the broad bandwidth of the pulse and therefore the external control over the molecular process may be reduced. For example, the motivation for the study of chirped excitation by Chelkowski et al (1990) was the need to avoid ionization which becomes dominant in their case at pulse intensities larger than $10^{13}$ W cm$^{-2}$. The stimulated Raman adiabatic passage (STIRAP) is an efficient way to transfer population between two levels using (indirectly) a third level (Shore et al 1992). However, it does not involve wave-packets and so we do not discuss it further here.

Some applications of chirped pulses are the different pump-and-dump schemes. For instance, we can pump the ground-state wave-packet to the excited-state potential surface with one ultrashort pulse and then dump it back with another one. If there is a time delay between the pulses and the wave-packet has time to evolve but not to spread, we end up dumping the original ground-state wave-packet back to the ground-state potential surface. However, since the position of the wave-packet has been shifted, it does not overlap with the original equilibrium position and starts to oscillate. This oscillatory motion of the wave-
Wave-packet dynamics in femto-time

Packet is a manifestation of a coherent superposition of a set of vibrational states. However, instead of two consecutive pulses one might use a single chirped pulse, as proposed by Ruhman and Kosloff (1990). They see the build-up of coherent ground-state superposition of vibrational states in their numerical study. The same phenomenon is also present in the optimal control study by Amstrup et al (1993).

More complex behaviour for the pump-and-dump processes can be seen when the pumping is not complete, and the ground-state wave-packet components that have avoided excitation can interfere with those dumped back again, especially if the pulse introduces phase differences between the components (see section 3.5). Of course, the pump-and-dump schemes are not limited to the creation of vibrational superpositions on the ground-state potential surface. For instance, Gross et al (1992) study a scheme with three potential surfaces, shown in figure 9. Two of the surfaces are very similar looking dissociating ones, which cross each other (the breakdown of the Born–Oppenheimer approximation) near the equilibrium position \( R_0 \) for the third surface, which is a Morse potential. A system which is initially on one of the dissociating states will experience at least partial population transfer to the other one when the wave-packet describing the system evolves and is split at the surface crossing. Thus the final product of the process is a superposition of the populations of the two states. However, in order to obtain final products corresponding to a single populated state one dumps the moving wave-packet onto the third potential surface before it reaches the crossing. By applying a second pulse with suitable time delay and frequency we can transfer the wave-packet back to the original dissociative state. Because of the motion of the wave-packet on the Morse potential during the time delay the second process takes place on the other side of the crossing and the splitting of the wave-packet does not occur.

We shall next present a basic wave-packet model for excitation by a chirped pulse, which is very similar to the model presented in section 2.4. For a hyperbolic secant pulse the first Demkov–Kunike provides a chirped equivalent to the Rosen–Zener model:

\[
V(t) = V_0 \text{sech}(t/T)
\]

\[
\frac{d\phi(t)}{dt} = F \text{tanh}(t/T).
\]

Here \( V \) is the pulse envelope and \( \phi \) is the phase factor in the pulse which produces the chirp in the frequency in respect to its mean frequency. The hyperbolic tangent form for the chirp becomes, in practice, a linear change in time when the chirp amplitude \( F \) is much

![Figure 9. The three-surface model for bypassing the crossing of two dissociating states.](image-url)
The excited-state population $P_2$ as a function of the chirp parameter $F$ (given in scaled units) as calculated by Paloviita et al. (1995). In (a) the pulse duration corresponding to the full curve is four times larger than the one corresponding to the broken curve, and in (b) the pulse duration ratio corresponding to full, broken and dotted curves is 10:5:1. Also, in (b) the slope of the excited state is 20 times larger than in (a). In (a) the standard pulse area $2\pi V_0\tau$ has been equal to $\pi$ and in (b) equal to $2\pi$. In (b) only the dotted curve corresponding to a very short pulse follows the area theorem, and the role of the effective area is clearly seen: $P_2$ is zero only for $F = 0$. For longer pulses the resonance points play a role and $P_2$ is asymmetric in respect to $F$.

It has been shown that this model gives good predictions for the wave-packet excitation process (Paloviita et al. 1995) in the same manner and under the same conditions as the Rosen–Zener model for the non-chirped case. The time-dependent local detuning is related to the parameters of the first Demkov–Kunike model in (2.74) by the expression

$$\Delta(R, t) = U_2(R) - U_1(R) + F \tanh(t/T) = 2\tilde{E}(R) + 2E_0 \tanh(t/T).$$

(3.10)

For short pulses the surfaces appear as uniformly resonant over the whole initial wave-packet. Then we can ignore the spatial dependence of the local detuning and set $\tilde{E} = 0$. The final population of the excited-state surface is then

$$P_2 = \begin{cases} 
\frac{1 - \cosh^2\left[\pi T \sqrt{(F/2)^2 - V_0^2}\right]}{\cosh^2(\pi TF/2)} & \text{if } |F/2| > V_0 \\
\frac{\cosh^2\left[\pi T \sqrt{V_0^2 - (F/2)^2}\right]}{\cosh^2(\pi TF/2)} & \text{if } |F/2| < V_0 
\end{cases}$$

(3.11)

obtained from (A.6). In the area theorem, the normal pulse area must be replaced by an effective one, which takes into account the fact that the true resonance is only present at $t = 0$ (Hioe 1984). In systems where the pulse shape and duration are for some reason fixed, we can still strongly affect the area theorem behaviour of the excitation process by changing the effective pulse area with a frequency chirp.

The numerical results presented in figure 10 for the Demkov–Kunike pulse and potential surfaces of section 3.1 show that excitation enhancement by chirping is quite possible. In figure 10(a) the pulse area is equal to $\pi$ when $F = 0$, but because of the relatively long pulse duration the excitation is not complete. When the pulse is chirped, the spatial positions of the field-induced resonance points move during the pulse, so that the initial wave-packet is brought into resonance more efficiently than in the absence of the chirp. For large $F$ this process becomes fast and hence the population transfer eventually diminishes as $F$ increases. For short pulses (broken curve) the large bandwidth makes the role of the resonance points
less important, but for long pulses a non-zero optimum value for $F$ can be found, as seen in figure 10(a).

If we allow the wave-packet to evolve during the pulse, a clear dependence on the chirp direction can be observed (Ruhman and Kosloff 1990, Paloviita et al 1995), as shown in figure 10(b). The direction of the chirp is determined by the sign of $F$; when $F < 0$ we have a red-shifted pulse, i.e. positive chirping, and vice versa. In the curve-crossing picture the excited-state potential surface moves upwards in the energy scale during the pulse when $F > 0$ and downwards when $F < 0$. (Alternatively, one can imagine the ground-state potential surface moving into the opposite direction.)

The asymmetry of population transfer with $F$ is typical for cases where the excited-state potential surface is very steep near $R_0$ (large $|\alpha|$). Then the excited wave-packet components experience a strong accelerating force, and the spatial locations of the resonance points (in the case where there are two of them) appear in a very asymmetric way around the equilibrium position. When $\alpha > 0$ the point which lies towards larger $R$ contributes most to the excitation. The wave-packet components enter the excited-state potential surface near this resonance point and then accelerate towards increasing $R$. For a negative chirp, the resonance point moves in the same direction as the wave-packet components, so the effective time they spend in the interaction region is increased. For a positive chirp the resonance point and the components move in opposite directions. Then at each new location of the resonance point the excited-state potential surface appears empty and the excitation is more efficient than it would be if population already existed on the excited state surface (the case of negative chirp). Such behaviour was also observed in the early study by Ruhman and Kosloff (1990), in which for negative chirp the final excited-state population was $P_2 \sim 46\%$ and for positive chirp $P_2 \sim 77\%$.

### 3.3. Pump-probe schemes

The concept of the pump–probe scheme is simple. First, one applies a pump pulse to excite a wave-packet (as described in section 3.1); this is the wave-packet preparation step. Then there is a time interval during which the excited-state wave-packet evolves. In some schemes the motion of the ground-state wave-packet is also important; it evolves because the excitation process leaves behind a packet which is not in an equilibrium position. After a pause, the probe pulse is applied and information is gained about the wave-packet motion. The type of information varies between the experiments. Sometimes the term femtosecond transition state spectroscopy (FTS) is used because the experiments reveal information about the transition from one state of a molecule to another via one or more ‘transition states’. Whilst short pulses are desirable in order to resolve vibrational motions on a femtosecond time-scale, there is a constraint on extremely short pulses. The bandwidth theorem, $\Delta \nu \Delta t \sim 1$, means that there is an energy spread for the applied pulse of $\Delta E = h/\Delta t$. For a 1 fs pulse this has a value of about 4 eV. As a result if the wave-packet has a significant energy spread then time resolution is gained at the expense of energy resolution for extremely short pulses.

One of the early experiments was performed in the group of Shank (Fragnito et al 1989). Wave-packet motion was deduced from a pump–probe experiment on the dye nile blue. Very short laser pulses of only 6 fs duration were used. This results in a large bandwidth for the pulse, which has a spectrum ranging from 580–700 nanometers. The experimental results can be accounted for with a theory based on only two electronic levels (Pollard et al 1990a, b). The pump pulse promotes a wave packet from the ground state to an excited level, but in this experiment the motion of the wave-packet that is left on the
ground state is significant. When the probe pulse is applied the frequencies of light that are absorbed by the ground state depend on where the wave-packet is, or, more precisely, on its shape (because the motion on the ground state is small). Figure 11 shows the ripples in the time-dependent spectrum that result from the wave-packet motion. In a classical model the absorption of a particular frequency would depend on the amount of wave-packet to be found at the exact position where the energy difference between the two levels matches the frequency and the dipole moment at the point. In this way the vibrational period of 55 fs is revealed from the time-dependent absorption spectra. As a first approximation the dipole moment is usually assumed to be constant over the spatial extent of the wave-packet. The theory should also include the stimulated emission that results from the probe pulse being absorbed by the excited-state wave-packet which is also moving on its potential (Pollard et al 1990a, b). If the pump pulse is weak this is a smaller effect leading to probe absorption over a range of frequencies. However, experimentalists usually find the probe difference absorption spectrum, that is, the absorption spectrum without a pump pulse is subtracted from the absorption spectrum with the pump pulse. Then there are seen to be two contributions to the spectrum; one from the excited-state wave-packet, and one from a ground-state ‘hole’. The hole is formed in the ground-state wave-packet when the excited-state wave-packet is removed by the pump pulse. The role of the wave-packet hole in pump–probe spectroscopy has been discussed by Yan et al (1989), Yan and Mukamel (1990) (who refer to the related concepts of a doorway state and a window state), and by Pollard et al (1990a, b), Banin et al (1994). An attempt to distinguish these wave-packets has been made by Hong et al (1993).

The absorption spectrum for the experiment of Fragnito et al (1989) was calculated in Pollard et al (1990a, b) by using time-dependent perturbation theory, and this has been the approach taken by theorists in many of the descriptions of pump–probe experiments (Walmsley et al 1988, Yan et al 1989, Lee et al 1989, Kono and Fujimara 1989, Hartke et al 1989, Bosma et al 1990, Pollard et al 1990a, b, Yan and Mukamel 1990, Engel 1991, Stock and Domcke 1992, Cho et al 1993, Ziegler et al 1994). The perturbation method can be applied to just a few vibrational levels and is valid for relatively weak applied fields; a situation found in many experiments. An advantage gained in this regime is that because just a few vibrational levels are considered it is possible to include dissipative effects such as $T_2$ dephasing (we will discuss non-perturbative approaches to dissipative wave-packet dynamics in section 4).

The pump–probe experiments of Walkup et al (1990, 1991) also used the absorption
Wave-packet dynamics in femto-time

spectrum of a probe pulse as a signal, though in a scheme which involves three electronic levels. The early experiments were performed with thallium iodide in which a wave-packet was excited by a pump pulse of 160 fs at 308 nm. Thereafter the ground state plays no further role in the experiment. The excitation is to a dissociating energy level leading to the breakup of the molecule in about 500 fs. During and after this breakup the probe pulse is applied. The probe connects the travelling wave-packet to a third energy level which, given the kinetic energy of the packet, also leads to dissociation. The probe pulse is quite lengthy at about 20 ps, but because it is chirped it only comes into resonance for very short times (of the order of 60 fs). Thus the simplest theory can consider the excitation to be of the impulsive delta-function-type of section 3.1. The most general theory given (Walkup et al 1991) accounts for multiple excitations that can occur as well as the finite resonance time of the chirped pulse. After each excitation a dipole moment is created, which, in a classical picture, oscillates at the instantaneous frequency determined by the energy difference between the two excited states. As the wave-packet moves out and the molecule dissociates this frequency changes with the changing shape of the potentials. Over time-scales which are long compared with the dissociation, this frequency change manifests itself as a phase change \( \eta \) in the dipole radiation at the frequency of the well separated atoms:

\[
\eta = \int_{t^*}^{\infty} [\omega(\tau) - \omega_0] \, d\tau.
\]

(3.12)

The time \( t^* \) is the point at which the chirped pulse excites the system and \( \omega(\tau) \) describes the frequency difference between the two levels as a function of time; \( \omega(\infty) = \omega_0 \). Because this dipole radiation has acquired a phase change it produces interference when mixed with the Fourier components of the chirped probe pulse. The interference means that the absorption profile near \( \omega_0 \) can change from a Lorentzian to a dispersive profile. A simple argument gives an absorption coefficient (Walkup et al 1990, 1991)

\[
\alpha \propto d(R^*)d_0[\cos \eta L(\Delta) + \sin \eta D(\Delta)]
\]

(3.13)

where \( d(R^*) \) and \( d_0 \) are the dipole moment at the point of excitation and when the atoms are well separated. The functions \( L \) and \( D \) are the Lorentzian and dispersive profiles, and the spectrum is measured from the centre absorption frequency of the separated atoms: \( \Delta = \omega - \omega_0 \). As can be seen from (3.13) the absorption can be negative (Misewich et al 1988). This is because (3.13) is a simplification which neglects the absorption when the chirp is resonant. More detailed calculations have shown that the spectrum has a long tail on the red side leading to net overall absorption (Walkup et al 1991).

The dissociation is much like a half collision with phase interruption of the radiation. Information is deduced about the molecule by fitting a combination of Lorentzian and dispersive line shapes to the absorption curve. This gives the phase shift \( \eta \) as a function of the probe delay which tells us about the classical trajectory. The early results could not go much beyond a phase shift of 2\( \pi \) because of the wide range of classical trajectories encompassed by the wave-packet. This was because the excitation by the pump pulse is to a very steep repulsive potential. The same kind of experiment has been performed on GaCl (Glownia et al 1993).

example is the experiment on I$_2$ (Dantus et al 1989, Dantus et al 1990) where 300 fs laser pulses were used to raise the ground-state wave-packet to an excited level with a period of about 300 fs. The vibrational motion then proceeds until the arrival of the probe pulse which lifts the wave-packet to a second excited level if the packet is near the inner turning point. Then the fluorescence from this third level is monitored to give an indication of how much of the packet was near the turning point on the second level. The results from changing the pump–probe delay time clearly showed the vibrational period over tens of cycles as well as a beating due to the anharmonic nature of the potential. By Fourier transforming the results for the fluorescence it was deduced that in this experiment only two vibrational frequencies were significant. Rotational effects could be eliminated by careful use of polarized pulses, but their presence could be clearly seen by revivals in the fluorescence on a much longer time-scale of about 500 ps.

A notable experiment on NaI used a 60 fs pump pulse to create the wave-packet in a shallow well (Rose et al 1989, Mokhtari et al 1990); see figure 12(a). This well arises from an avoided crossing of two electronic energy levels. One is covalent in character and the other is ionic. The vibrational motion of the wave-packet is sufficiently large to result in the wave-packet travelling over the crossing. Whilst a very slow packet would simply avoid the crossing by switching from one curve to the other there is, in general, some leakage at the crossing. This kind of problem will be discussed in much more detail in section 3.4. Here we will simply note that part of the trapped packet leaks out of the crossing at every traversal. These pieces of packet result in a dissociation in steps. As one of the molecular constituents is sodium, this step-wise dissociation can be confirmed by monitoring the fluorescence of the sodium D-line with a probe pulse close to 590 nm. The fluorescence detected after the probe pulse increases in a sequence of steps as a function of the delay time (figure 12(b)); this indicates the accumulation of sodium atoms. If the probe frequency is changed slightly then the position of the resonance is shifted from the dissociating part of the potential to a part of the well. This time the fluorescence shows a sequence of spikes as a function of the pump–probe delay time as may be seen in figure 12(b). Each spike indicates that the wave-packet was in the resonant position at the time of the probe pulse. The same molecular system has now been used to demonstrate femtosecond control over

![Figure 12](image.png)

Figure 12. Wave-packets trapped in a shallow well in NaI. The energy levels in (a) show the wave-packet trapped between the ionic and covalent surfaces. The wave-packet can be probed in the well (resulting in the lower curves in (b)) or it can be probed as it leaks out of the crossing (upper curve in (b)) leading to dissociation. From Rose et al (1989).

The experiments of Scherer et al (1991, 1992) are of the pump–probe-type, though it might also be described as an experiment with two pump pulses, or as a pump-and-dump scheme. A weak pump pulse of about 60 fs carries out the excitation process and creates a wave-packet with a period on the excited state of about 300 fs (see figure 13). However, the ‘probe’ pulse is almost identical to the pump and to a first approximation will promote a similar wave-packet to the excited state. In general this would create two wave-packets, but the possibility of wave-packet interference plays a central role in this experiment. It is the fluorescence from the excited level and after the probe pulse that is monitored in this experiment. If the second wave-packet interferes destructively with the first one there will be no subsequent fluorescence. If the second packet interferes constructively the fluorescence is enhanced above the level found from two separate packets on the excited state. For interference to take place the first wave-packet must have returned to its point of excitation, i.e. the pump–‘probe’ delay time should be close to a multiple of the vibrational period. The kind of interference that takes place depends on two types of phase. Firstly, it depends on the phase relationship between the two pulses. For this reason the pulses should be phase-locked. (Though some of the matter wave interference is still observed in the envelope of the signal if there is no repeatable phase difference between the pulses.) Secondly, the interference depends on the phase of the matter waves, or the phase acquired by the de Broglie waves during the wave-packet motion. This yields information about the molecule in addition to the vibrational period. An example interferogram is shown in figure 13 (inset). The interference is displayed using the independent packet case as a reference level. Each of the spikes shows the time when the excited-state wave-packet returned to its excitation point. The sign of the spikes indicates the effect of wave-packet interference and changes because of the change of de Broglie phase. The interferogram becomes less clear for large delay time because of wave packet dispersion. Wave-packet interference and the nature of the de Broglie phase is discussed further in section 3.5.

3.4. Wave-packet splitting at crossings

The probing of evolving wave-packets described above can often be treated as a surface crossing problem when the wave-packet moves across a probing region. If we use a probe laser, the information is then obtained either from the absorption spectrum of the probe or from the measurement of the population transferred to a potential surface which leads to specific, measurable final products. For example, we can measure the rates for probe-induced dissociation. The probing process can alternatively involve a naturally occurring crossing between the pumped potential surface and a suitable probing channel; in this case the presence of a laser field is not necessary, though there is less control over the outcome.

3.4.1. Simple semiclassical splitting. We presented in section 2.4.4 the classical trajectory approach to the wave-packet splitting at curve crossings. It was based mainly on a combination of the Landau–Zener model with the classical motion of the wave-packet. This is an old and well known result, given in the basic textbooks such as that of Levine and Bernstein (1987) and tested against the exact quantum propagation of a wave-packet by Garraway and Stenholm (1991). An early, fully quantum mechanical calculation of wave-packet propagation across a curve crossing was made by Alvarellos and Metiu (1988). It
Firave wave-packet interference schemes as applied to $I_2$ by Scherer et al. (1991). This is a two pulse scheme where a wave-packet promoted by the first pulse interferes with the wave-packet from a second pulse. The interference depends on the phase acquired by the wave packet as well as the phase of the two pulses. Results for in-phase pulses are shown inset.

has also been successfully applied to the interpretation of experimental results, see, for example, Rose et al. (1988, 1989) (natural crossings), and Bali et al. (1994) and Marcassa et al. (1994) (laser-induced crossings). The basic conditions for the approach were discussed in section 2.4.4, and next we look into some additional aspects.

The wave-packet has a width both in momentum and position. In the case of spatially wide wave-packets and steep potential surfaces the spatial slices of the wave-packet can evolve very differently, depending on their initial location. Hence these components of a pulse-generated wave-packet can reach a level crossing at significantly different times, and with different velocities. This means that the velocity dependence of the Landau–Zener expression (2.77) becomes important in an analysis based on wave-packet 'slicing'. In figure 14 the mean momentum of a Gaussian wave-packet on a flat potential surface is seen to change as it traverses a linear surface crossing. The fast components reach the crossing first and the mean momentum drops as these components are partly transferred away. However, eventually the slow components also reach the crossing and since the transfer favours them according to (2.77), the final result is an increase in the mean momentum ($p$).

The wave-packet experiences momentum filtering (Suominen and Garraway 1993). This would happen if, for instance, a spatially narrow wave-packet is excited near the crossing. The new form of the wave-packet in the momentum representation after filtering is then given by (assuming that $T$ is the time it takes to traverse the crossing)

$$W(p, T) = (1 - P^{\text{dia}}_2(p))W_0(p, 0)$$  \hfill (3.14)

where $P^{\text{dia}}_2$ is the Landau–Zener transition probability from (2.77) and $W_0(p, 0)$ is the
wave-packet in the momentum representation just before it enters the crossing (assuming the classical relation $p = mv$, where $m$ is the reduced mass and $v$ is the velocity). In the situation described in figure 14 the final mean momentum given by this expression is roughly the same as observed in the numerical result.

3.4.2. Non-classical behaviour at simple crossings. In many cases the Landau–Zener expression on its own is quite adequate, with $p$ replaced by the mean momentum $\langle p \rangle$ for the wave-packet. This is especially true when $p$ is large compared with $\Delta p$, the width of the wave-packet in the momentum representation. Garraway and Stenholm (1991) have studied the wave-packet dynamics at linear surface crossings and verified the ability of the Landau–Zener expression to correctly predict the wave-packet splitting ratio as such crossings are traversed. They also studied some special cases. For instance, the initial potential surface can be tilted so much that the wave-packet is clearly slowed down as it approaches the crossing. If its kinetic energy in the classical picture is too small to permit it to reach the crossing, the Landau–Zener approach with classical trajectory cannot be used; population transfer at the crossing becomes energetically forbidden. However, the population transfer takes place within an interaction region rather than only at the crossing point. If we look at the wave-packet evolution in terms of adiabatic potential surfaces, the level coupling pushes the barrier down and the crossing can be reached classically, even if it is ‘shielded’ in the diabatic picture.

When the initial kinetic energy is not large enough to allow the wave packet to reach the crossing even in the adiabatic basis, transfer can still occur, as seen in figure 15(a). This is a sort of tunnelling effect. In the adiabatic basis the process is seen as follows. The non-adiabatic coupling is small but still exists, and it is effective in a region surrounding the crossing point. If the turning point for the incoming wave-packet is close enough to this region, part of the wave packet is transferred to the upper adiabatic surface, where it remains trapped for a brief moment, as shown in figure 15(b). It oscillates in the adiabatic well and leaks back to the lower adiabatic surface. This leaking can take place on either side of the crossing. Similar periodic leakage due to wave-packet oscillations has been experimentally observed by Rose et al (1988, 1989).

A wave-packet can also be placed directly into a laser-induced adiabatic trap where it can oscillate back and forth on the upper surface whilst spreading near the turning points. The leakage is small for a large enough coupling. These light-induced wells could be useful
Figure 15. In (a) we show the wave-packet transfer probability between the diabatic states in a tilted linear crossing as a function of coupling $V$. The potential surfaces have equal slopes except for a different sign, i.e. $dU_2/dr = -dU_1/dr$. For $V \leq V_0$ the wave-packet, initially on surface 1, cannot reach the crossing classically even in the adiabatic picture. In (b) we show how the wave-packet component trapped in the upper adiabatic potential surface oscillates and diminishes as it slowly leaks to the lower adiabatic surface. The parameters correspond to the situation where it is classically forbidden to reach the crossing point in both the diabatic and adiabatic formulation. Both figures are taken from Garraway and Stenholm (1991).

for delaying wave-packets, a process which has already been observed in above-threshold dissociation (see, for example, Giusti-Suzor et al 1990, Zavriyev et al 1990, Yang et al 1991, Zavriyev et al 1993, Atabek et al 1994). These experiments and calculations belong to a different regime (of very high intensities) where multiphoton processes are important. Zavriyev et al (1993) have suggested that delays in the dissociation of $D_2^+$ are due to the trapping of the wave-packet in a three-photon avoided crossing. This has been termed bond-hardening, because trapping makes dissociation difficult. Bond-softening is the reverse process where increasing the coupling at an avoided crossing lowers the barrier on the lower surface and makes it easier for a wave-packet to pass through (Bucksbaum et al 1990, Miret-Artés and Atabek 1994).

3.4.3. Splitting at parabolic crossings. When the potential surfaces merely touch they have equal tangents at that point and the derivative of the potential difference is zero. Then the Landau–Zener approach necessarily fails, though a parabolic model can be used under certain conditions. It has limited use, however, as no general analytic solutions for it are known. The $R^2$ potential structure is also more likely to introduce dynamical changes into the wave-packet motion within the interaction region than the linear structure of section 3.4. In figure 16 we show a simple comparison between some results calculated from the purely time-dependent parabolic model (full curve) and a corresponding wave-packet situation (full circles). The wave-packet initially moves along a flat ground-state potential surface, and passes a point where the harmonic excited-state potential surface touches the ground one. In the figure the population transferred to the excited state is presented. The conditions for the validity of the parabolic model with mean momentum are met, as $\Delta p/(\langle p \rangle) = 0.1$ and the momentum loss on the excited state is only 1.3% as the edge of the interaction region is reached.

The parabolic model predicts an interesting result: as the coupling strength is increased ($\epsilon$ decreases in figure 16) the excited-state population $P_2$ increases at first, but eventually
reaches a maximum and then decreases again. In the Landau-Zener case $P_z$ merely increases and approaches unity. The DDP treatment shows that there is a clear double-crossing character in the parabolic model even when it is missing from the original diabatic formulation of the problem. In a double-crossing situation strong transfer at the first crossing is accompanied by a subsequent strong transfer back to the original state at the second crossing, so full transfer cannot be achieved by simply increasing the coupling strength. When the surfaces cross twice, the situation can be viewed as two consecutive Landau-Zener crossings (Suominen 1992b). However, in that case the phase changes which may take place at the crossings must be considered. We will discuss this in section 3.5.

3.5. Wave-packet interference

Wave-packet dynamics can exhibit quantum mechanical interference of the matter wave (of the nuclear coordinate). That is, the internal motion of a wave-packet can take place through two routes, or electronic configurations, with resulting interference that is analogous to the Young’s two slit experiment with light. However, in the molecular case the interference takes place, not with light, but with the nuclear matter wave which may take the form of a wave-packet. In the molecular case we do not have two slits, but two paths along different electronic states. The two routes generate different phases for the matter wave so that when the waves are combined an interference manifests itself in, for example, the populations. This interference takes place in each single molecule and can manifest itself in an optical signal if that signal depends on the final populations.

A simple configuration of energy levels given by Garraway and Stenholm (1992) in a theoretical study is illustrated in figure 17(a). Here a wave-packet (initially on level 2) passes through two regions where it interacts with a laser coupling. If part of the wave-packet is transferred to level 1 at $x_a$ it can be returned to level 2 at $x_b$ and interfere with the original packet which remained on level 1. This configuration of energy levels and coupling lasers is equivalent to a double crossing through which a wave-packet passes having started on one electronic level away from the crossing regions. The first crossing acts to split the wave-packet into the two routes between the crossings and the second crossing recombines the two wave-packets to produce the interference in the final population. Several theoretical approaches were presented in Garraway and Stenholm (1992) including the fully quantum mechanical treatment. The most simple, semiclassical, analysis replaces the wave-packet by a single trajectory and the two crossings by Landau-Zener idealizations of the type presented in sections 2.4 and 3.4. However, in this case it is necessary to consider the phase change that
Figure 17. Two schemes that can exhibit wave-packet interference. In (a) we show two energy levels that are coupled by a laser at two points ($x_a$ and $x_b$). The initial wave-packet $\psi_1$ (created by a short pulse at the position $x_0$) can form $\psi_2$ by two routes: by passing through $\psi_H$, or via $\psi_{II}$. This creates the possibility of interference. (Taken from Garraway and Stenholm 1992.) In (b) we show a configuration of two oscillators used to demonstrate wave packet interference using two pump pulses in (3.18). The displacement between the oscillators is $R_0$ and the energy separation is $\Delta U$. This is an idealization of the experiment of Scherer et al. (1991) which is discussed in sections 3.3 and 3.5, and illustrated in figure 13.

...takes place at the Landau-Zener crossing (see equations (A.13) and (A.14)) as the resultant interference is sensitive to all changes in phase between the crossings and at the crossings. The phase change between the crossings can be approximated from the semiclassical action $S$ on each electronic level (between the crossing points at $R_a$ and $R_b$) which changes the wavefunction phase by a factor

$$\exp \left[ iS_a(R_b, R_a) \right] = \exp \left[ i \int_{R_a}^{R_b} dR' \sqrt{E - E_a(R')} \right].$$

(3.15)

The symbol $E$ stands for the total (kinetic and potential) energy of the trajectory and $E_a(R)$ represents the spatially-dependent potential energy of one of the two electronic energy levels. We found that the best results are obtained with propagation on the adiabatic surfaces for which

$$E_\pm(R) = (U_1(R) + U_2(R))/2 \pm \sqrt{\Delta U(R)^2/4 + V^2}.$$  

(3.16)

Thus the total phase difference is given by $S_+(R_b, R_a) - S_-(R_b, R_a)$ between the crossings and has to be added to the phase changes at the crossings. In Garraway and Stenholm (1992) the bare surfaces, $U_1$ and $U_2$, were, however, still used for the calculation of the crossing velocity in the Landau-Zener adiabaticity parameter $\Lambda$ (equations (2.76) and (2.77)).

For the examples studied in Garraway and Stenholm (1992) the simple analysis presented above proved insufficient to obtain good agreement with the quantum mechanical results; the modulation of the interference pattern in the simple analysis is too deep. However, a good agreement was obtained by ensemble averaging over a distribution of energies $E$ obtained from the initial wave-packet. That is, it proved necessary to include an ensemble of trajectories. This probably shows how sensitive interferometric arrangements can be; in the case of a single crossing a single trajectory works very well unless subtle changes in momentum distributions are being considered (section 3.4).

The only wave-packet experiments that we are aware of which exhibit this kind of interference effect directly are those reported in Scherer et al. (1991, 1992, 1993). We have
already introduced these experiments in section 3.3, however, whilst they differ from the double-crossing interference scheme described above they are of a similar type. The two crossings are, in effect, replaced by two ultrashort pump pulses. The first pulse acts as the splitter (promoting a wave-packet to an excited electronic state) and the second pump pulse is the mixer that creates the interference (which in this case is best detected from the excited-state fluorescence). The matter wave phase difference comes principally from one wave-packet; the excited state packet which performs an integer number of oscillations on the excited state energy surface.

To illustrate the kind of interference seen in the experiment of Scherer et al. (1991) we will construct a very simple analysis based on their theory. We simplify our model of a molecule to two oscillators which are displaced from each other as shown in figure 17(b). These oscillators will be coupled by the short pump pulses. The action of the pump pulses can be described by transfer matrices $T_a$ and $T_b$. For example, we have (using (3.7) for the first pulse)

$$T_a = \begin{bmatrix} t_a & r_a e^{-i\phi} \\ -r_a e^{i\phi} & t_a \end{bmatrix}$$

where $t_a$ and $r_a$ are coefficients that describe the coherent transfer between the two levels and $\phi$ describes a pump phase. For extremely short pulses $T_a$ is given in (3.7). Note the similarity with the form of the Landau-Zener transfer matrix (A.13) which is used in each of the crossings described at the start of this section. For our first pump pulse we choose the phase $\phi$ to be zero and $r$ to be real to provide a reference, so that for the second pulse $\phi$ describes the relative phase of the two pulses. This implies phase locking of the pulses as discussed in section 3.3. Thus, when we include the free evolution between two pump pulses the state vector after the second pulse is

$$\begin{bmatrix} \Psi_1(r,t) \\ \Psi_2(r,t) \end{bmatrix} = \begin{bmatrix} t_b & r_b e^{-i\phi} \\ -r_b e^{i\phi} & t_b \end{bmatrix} \begin{bmatrix} e^{-iH_1t} & 0 \\ 0 & e^{-iH_2t} \end{bmatrix} \begin{bmatrix} t_a & r_a \\ -r_a & t_a \end{bmatrix} \begin{bmatrix} \Psi_0(r,0) \\ 0 \end{bmatrix}$$

(3.18)

where $H_1$ and $H_2$ describe the free evolution of the two oscillators and $\Psi_0$ is the initial wavefunction (packet) assumed to be the lowest vibrational state of the ground-state oscillator. The frequencies of the two oscillators will be assumed to be equal with the value $\omega$ and they will have a separation $R_0$ in space and $\Delta U$ in energy (see figure 17(b)). The sequence (3.18) has a logical interpretation: a pump pulse is followed by free evolution, followed by another pulse. As a result the final population on the excited state is

$$\Pi_2 = (r_a t_b)^2 + (r_b t_a)^2 + 2 r_a r_b t_a t_b \text{Re}[e^{-i\phi} \langle \Psi_0 | e^{iH_1 t} e^{-iH_2 t} | \Psi_0 \rangle]$$

(3.19)

We calculate $\Pi_2$ because it is proportional to the fluorescent signal. The Hamiltonian $H_1$ has no effect on the ground-state wavefunction, but for $H_2$ the wave-packet $\Psi_0$ is displaced by $R_0$ and so a coherent state $e^{-i\Delta U | R_0 e^{-i\omega t} \rangle}$ (Glauber 1963, Sudarshan 1963) is generated. Thus the final population depends crucially on the overlap $\langle R_0 | R_0 e^{-i\omega t} \rangle$ and we obtain (setting $t_a = t_b, r_a = r_b$)

$$\Pi_2 = 2(r_a t_a)^2 \{1 + \text{Re} \exp[-i\Delta t - i\phi - R_0^2(1 - e^{-i\omega t})]\}$$

(3.20)

$$= 2(r_a t_a)^2 \{1 + \exp[R_0^2(\cos \omega t - 1)] \cos[\Delta t + \phi + R_0^2 \sin \omega t]\}$$

(3.21)

This equation from a very simple model illustrates important parts of the Scherer interference method. The exponential factor depends essentially on the overlap of the two wave-packets promoted by the pump pulses; it is unity whenever the first packet returns to its starting position. The major cosine factor determines the sign of the interference when the wave-packets overlap.
4. Spontaneous emission

4.1. Importance of spontaneous emission

Wave-packets in molecules may be subjected to dissipative processes with different kinds of mechanisms. The term dissipative is used to indicate a process that results in an irreversible loss of energy from the system. Typical dissipative processes for vibrations of molecules include: spontaneous emission, coupling to other vibrational modes, effects of collisions and the influence of solvent molecules. We focus here only on the first of these, namely, spontaneous emission. It may be expected that spontaneous emission could be the only significant relaxation mechanism for small molecules in the gas phase, whereas for large molecules, or in liquids, the other types of relaxation may be important. For wave-packet experiments which are of a very short duration it can be expected that spontaneous emission has a negligible effect. However, for longer periods of wave-packet motion in excited electronic states, spontaneous emission will be important and can be a source of information about the molecule.

The coupling between an (applied) electromagnetic field that we have considered so far has been completely conservative; if a photon is lost from the mode of a laser the energy is gained by the molecule and vice versa. However, an excited state can couple to a state with lower energy by radiating into the vacuum, or free space modes of vibration of the electromagnetic field. This results in irreversible decay. A common approach to describe the combined effects of spontaneous emission and coherent pumping effects (in the absence of internal, e.g. wave-packet, dynamics) is to use the Bloch equations (see, for example, Allen and Eberly 1975, Stenholm 1984):

\[
\begin{align*}
\frac{d}{dt} r_1 &= -2(U_2 - U_1)r_2 - \gamma r_1 \\
\frac{d}{dt} r_2 &= 2(U_2 - U_1)r_1 - 2V r_3 - \gamma r_2 \\
\frac{d}{dt} r_3 &= 2V r_2 - \gamma (r_3 + 1)
\end{align*}
\]

(4.1)

where the Bloch components are \( r_1, r_2 \) and \( r_3 \). The component \( r_3 \) represents the energy of the two-level system, and the components \( r_1 \) and \( r_2 \) represent coherence between the levels. We use \( \gamma \) for the decay rate of energy and set the transverse decay rate (the decay of coherence, or \( T_2^{-1} \)) to half the longitudinal relaxation rate (or energy decay rate \( \gamma = T_1^{-1} \)). The coupling of the two levels (if present) is \( V \) and the energy difference is given by \( U_2 - U_1 \). In the absence of a coupling (\( V = 0 \)), the Bloch vector (comprised of the Bloch components \( r_1, r_2 \) and \( r_3 \)) would simply relax down along the 3-axis from the excited state \( (r_2 = 1) \), until \( r_3 = -1 \) and the other Bloch components are zero; the system is then at rest in the lower state. The presence of the coupling tends to cause precession about a direction determined by the relative sizes of the detuning \( (U_2 - U_1) \) and the coupling. If the coupling is stationary, the system settles down to a steady state. Further details of the Bloch vector approach can be found in Allen and Eberly (1975).

We may also describe spontaneous emission by the use of the density matrix. For a pure state \( \Psi \) the density matrix \( \rho \) is simply \( |\Psi\rangle \langle \Psi| \). However, during a typical relaxation process a pure state evolves into a statistical mixture of states. For a two-level system the density matrix is related to the Bloch components by

\[
\begin{align*}
r_1(t) &= \rho_{12} + \rho_{21} \\
r_2(t) &= i(\rho_{12} - \rho_{21}) \\
r_3(t) &= \rho_{22} - \rho_{11}
\end{align*}
\]

(4.2)
and the time evolution of $\rho(t)$ is then given by a master equation (see, for example, Louisell 1973, Agarwal 1974, Cohen-Tannoudji et al 1992)

$$\frac{d}{dt} \rho = -i[(U_2 - U_1)\sigma_3 + V\sigma_1, \rho] - L(\rho)$$  \hspace{1cm} (4.3)

where $\sigma_1$, $\sigma_2$, and $\sigma_3$ are the Pauli spin matrices (with $\sigma_{\pm} = \sigma_1 \pm i\sigma_2$) and the Liouville operator $L$ is

$$L(\rho) = \frac{1}{2} \gamma(\sigma_+\sigma_-\rho - 2\sigma_-\sigma_+ + \rho\sigma_+\sigma_-).$$  \hspace{1cm} (4.4)

The density matrix equation of motion can be derived rigorously from the coupling of a quantum system to many modes of the radiation field. Then, because we are not interested in knowing the precise state of all the radiation modes that the system couples to, we can express our ignorance of the radiation field by using the density matrix for the quantum system (rather than a state vector). That is, by using the density matrix, rather than a state vector, we are able to describe the average value of system observables without knowing about the corresponding environment state.

When we consider quantum mechanical wave-packet motion, we must include in the master equation the kinetic operator $T_N$ so that

$$\frac{\partial}{\partial t} \rho = -i[T_N + U(R), \rho] - L(\rho)$$  \hspace{1cm} (4.5)

where $U(R)$ is given in (2.33). The presence of the kinetic term means that the density matrix becomes off-diagonal in the spatial coordinate. This has several consequences. Firstly, we cannot use Bloch equations such as (4.2) above. Secondly, if we wish to use numerical techniques based on discretization of the density matrix the problem becomes very large because the discretized matrix is proportional to the square of the number of spatial points. We will describe methods for solving (4.5) in section 4.2 and in section 4.3 we show two ways which make it possible to circumvent the problems caused by the large size of the density matrix.

Spontaneous emission plays an important role in the experiment of Dunn et al (1993) on the sodium dimer. A pump pulse is used to create a wave-packet on an excited state. The wave-packet then oscillates on the excited-state surface. Subsequently there is no probe pulse because the experiment proceeds by monitoring the frequency-resolved fluorescence. A simple argument is that the frequency of the spontaneous emission from the wave-packet depends (to a first approximation) on the energy difference between the excited and ground states as the wave-packet moves about on the excited surface. If the fluorescence is monitored by a spectrometer with short time resolution there is a pulse whenever the wave-packet passes over that part of the energy surface that has an energy difference matching the spectrometer frequency (see figure 18). The time-separation of the pulses indicates, for example, the closeness of the selected energy difference to turning points of the wave-packet. More theoretical details can be found in Kowalczyk et al (1990).

4.2. Numerical solution by density matrix methods

In section 4.1 we discussed the role of spontaneous decay in wave-packet dynamics, and presented the density matrix formalism, which replaces the standard Schrödinger equation approach. Here we show how the master equation (4.5) can be treated with numerical methods.
Figure 18. Energy levels (a) (from Kowalczyk et al 1990) and time-dependent fluorescence (b) from the experiment of Dunn et al (1993) on Na₂. Spontaneous emission following excitation has a wavelength that depends on time. The time-dependent fluorescent signal (b) is frequency resolved and in general shows pairs of peaks when the selected energy difference is close to a turning point of the wave-packet. The left-hand part of (b) shows experimental results whilst the right-hand part of (b) shows a theoretical result.

We represent the spatial variable \( R \) by a grid of \( N \) points labelled by suitably scaled variables \( \{ x_i \} \). In solving the master equation (4.5) for a two-state system we replace the density matrix by a four-component vector

\[
 f(x, x', t) = \begin{bmatrix} 
 \langle x | \rho_{11} | x' \rangle \\
 \langle x | \rho_{12} | x' \rangle \\
 \langle x | \rho_{21} | x' \rangle \\
 \langle x | \rho_{22} | x' \rangle 
\end{bmatrix} . \tag{4.6}
\]

It is clear that we must evaluate the components of \( f \) over a two-dimensional spatial grid of size \( N \times N \). This fact makes the numerical treatments of the master equation computationally very demanding. It can be done, just as two-dimensional studies of the Schrödinger equation can be done, but the grid sizes available with current computers, as discussed in section 4.4, only allow studies of very simple problems. A master equation study of a truly two-dimensional problem would require a four-dimensional grid and is obviously beyond the capabilities of modern computers for any practical wave-packet models.

With the definitions above, the master equation (4.5) takes the new form

\[
i \frac{\partial}{\partial t} f(x, x', t) = [K(x, x', t) + U(x, x', t)] f(x, x', t) \tag{4.7}
\]

where

\[
 K(x, x', t) = \left(-\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial x'^2}\right) \mathcal{I} \tag{4.8}
\]
Wave-packet dynamics in femto-time

is the kinetic energy operator in scaled units (\(h^2/2m = 1\)) and

\[
U(x, x', t) = \begin{bmatrix}
U_x^1 - U_x^2 & -V_x & V_x & i\gamma \\
-V_x & U_x^1 - U_x^2 - i\gamma/2 & 0 & V_x \\
V_x & 0 & U_x^2 - U_x^1 - i\gamma/2 & -V_x' \\
0 & V_x & -V_x' & U_x^2 - U_x^1 - i\gamma
\end{bmatrix}
\]  \hspace{1cm} (4.9)

is the combined potential energy and spontaneous decay operator; \(\mathcal{I}\) is the \(4 \times 4\) unit matrix. Here \(U_x^1\) and \(U_x^2\) are the potential energy surfaces for states 1 and 2, respectively, and \(V_x\) is the coupling between them, all evaluated at the position point labelled by \(x\) in the spatial lattice chosen to represent the spatial continuum \(R\).

The new form (4.7) of the master equation resembles the two-dimensional Schrödinger equation. The main difference is that in (4.8) we have the difference rather than the sum of the one-dimensional kinetic terms. Also, instead of a two-component state vector we have a density matrix represented as a four-component vector. However, in a closed system \(\text{Tr}(\rho) = \rho_{11} + \rho_{22} = 1\), and since \(H\) is Hermitian we have \(\rho_{21} = \rho_{12}^*\). These two constraints can be used to reduce the number of coupled equations. In any case (4.7) can be solved numerically using the same techniques as in section 2.3.

If we adapt the split-operator method with Fourier transforms for this particular problem (Lai et al. 1993) we have

\[
f(x, x', t + \Delta t) = U_{V}^{1/2} U_{T} U_{V}^{1/2} f(x, x', t) .
\]  \hspace{1cm} (4.10)

Here we have introduced the unitary time evolution operators

\[
U_{V} = \exp(-iU(x, x')\Delta t)
\]

\[
U_{T} = \exp(-iK(x, x')\Delta t)
\]

\[
= \mathcal{F}^{-1} \left[ \mathcal{I} \exp[-i(k^2 - k'^2)\Delta t] \right] \mathcal{F}
\]  \hspace{1cm} (4.12)

where \(\mathcal{F}\) is the two-dimensional Fourier transform which maps the spatial \((x, x')\) grid to the discrete momentum space \((k, k')\). Hence we avoid the discretization of the spatial derivatives in \(K\), which would be necessary if we choose the Crank–Nicholson method instead of Fourier transforms. Because of the Hermiticity of the density matrix we need to transform only those components of \(f(x, x', t)\) which correspond to \(\rho_{11}, \rho_{22}\) and \(\rho_{12}\). Thus a single operation with \(U_T\) requires a total of six two-dimensional FFT computations per time step.

In order to implement the potential propagator \(U_V\), we diagonalize the matrix \(U\) in (4.9). The matrix is local in the \(x\)-variables, and, due to the Hermiticity of the density matrix, the diagonalization needs to be done only for \(x \geq x'\). The same applies when we operate with \(U_V\) on \(f(x, x', t)\). If there is no explicit time dependence in the coupling \(V\) the evaluation of \(U_V\) needs to be carried out only once. If we have \(V = V(t)\) the diagonalization should then be done for each time step. This can have a notable effect in the total time consumption of the density matrix calculation. However, as proposed by Lai and Stenholm (1994), one can reduce the number of the diagonalization operations. We can rewrite (4.9) as three separate matrices:

\[
U(x, x', t) = UA(x, t) - UB(x', t) + iL
\]  \hspace{1cm} (4.13)

where

\[
L = \begin{bmatrix}
0 & 0 & 0 & i\gamma \\
0 & -i\gamma/2 & 0 & 0 \\
0 & 0 & -i\gamma/2 & 0 \\
0 & 0 & 0 & -i\gamma
\end{bmatrix}
\]  \hspace{1cm} (4.14)
We can apply the split-operator technique to (4.13) to separate the $L$ contribution, and since

\[ [uA(x,t), uB(x',f)] = 0 \]  

(4.17)

we have the exact relation

\[ \exp[-iAt\{U_a(x, t) - U_x(x', t)\}] = \exp[-iAtU_a(x, t)\exp[iAtUg(x', t)] \]  

(4.18)

which can be used to separate the two contributions $A$ and $B$. So, instead of diagonalizing (4.9) $N^2$ times (for each $x$ and $x'$ combination) for each time step, we need to do it only $N$ times for the two matrices ($A$ and $B$) for each time step. This speeds up the numerical process, as described by Lai and Stenholm (1994), and makes it numerically feasible.

The methods described above have been used by Lai et al. (1993), Suominen and Garraway (1993), and Lai and Stenholm (1994) for the study of wave-packet dynamics. A related approach has been developed and applied to a pump-probe scheme in the presence of dissipation in Bermana/ (1992) and Banin et al. (1994). However, a different approach can be taken for systems with low excitation, as is often found in pump-probe schemes. Rather than expressing the density matrix in terms of the vibrational coordinate, it is possible to expand it in the vibrational basis, if this is known. This is a very suitable approach for harmonic oscillator models such as used by May et al. (1993).

4.3. Numerical solution by simulation methods

The simulation methods make it possible to solve the master equation problem numerically (4.5) with less demands on computer memory and with greater speed. This can be achieved at the expense of some statistical uncertainty in the results. The principle that underlies the method is unravelling of the master equation (Carmichael 1993) in which the time evolution of a state vector is calculated during a history of events which often correspond to the detection of photons. The measurement interpretation of the unravelling does not mean that photons have to be counted in an actual experiment, because the loss of photons is actually described by the master equation (4.5). Rather, the history of detection events is a possible route that a photon counting experiment might have taken. From such a simulation of events the master equation results may be generated by repeating the time evolution of many different histories of pure states and averaging the observables. Although each of the histories has a quantum measurement interpretation the complete process after averaging can be regarded as simply a computational method for solving (4.5). We show below the process involved in two simulation methods. In each case we treat a simple two-state problem, however, the method easily generalizes to multi-level systems and other forms of dissipation which can be cast in the Lindblad form used in (4.3) (Lindblad 1976).

The state vector Monte Carlo method corresponds to the direct detection of photons (see Dalibard et al. 1992, Mølmer et al. 1993, Carmichael 1993, and the related work of Mollow 1975, Dum et al. 1992a, b, Gardiner et al. 1992). To show how the simulation proceeds we consider a state vector at time $t$ and consider the two possibilities for advancement of the
wavefunction over a very short time interval $\Delta t$; there may be a quantum jump because of the detection of a photon in $\Delta t$, or there may be no detection of a photon. If at a time $t$ the state vector representing a two-level system is

$$\Psi(R, t) = \begin{bmatrix} \Psi_1(R, t) \\ \Psi_2(R, t) \end{bmatrix}$$  \hspace{1cm} (4.19)$$

and a photon is 'detected', the principles of quantum mechanics require that the state vector becomes

$$\frac{1}{N_j} \sigma_- \Psi(R, t) = \frac{1}{N_j} \begin{bmatrix} \Psi_2(R, t) \\ 0 \end{bmatrix}.$$  \hspace{1cm} (4.20)

The Pauli operator $\sigma_-$ represents the action of the measurement which transfers the wavefunction directly from the excited state 2 to the ground state 1, given that a photon is known to be detected at the given point in time. The factor $N_j$ is required to preserve the normalization of the state after the 'jump' and

$$N_j = \langle \Psi_2(R, t) | \Psi_2(R, t) \rangle.$$  \hspace{1cm} (4.21)

It is important to consider the probability for the detection (jump) process to take place as in the computer simulation a decision is taken as to whether or not there will actually be a detection event at a specific point in the simulated history. This decision must be balanced by the correct probabilities of the two options in a time $\Delta t$. For the state vector (4.19) that probability is simply

$$P_j = \gamma \Delta t \langle \Psi(R, t) | \sigma_+ \sigma_- | \Psi(R, t) \rangle = \gamma \Delta t N_j$$  \hspace{1cm} (4.22)

which is essentially the square of the expectation value of the dipole moment and is seen to be proportional to the normalization in (4.20).

Having considered the jumps, we now consider the other option, that there is no detection event in a time-step $\Delta t$; this occurs with a probability $1 - P_j$ at time $t$ in the simulation. In that case we might suppose that we simply obtain a time evolution with the Hamiltonian $H = T_N + U(R)$. However, this is incorrect. The system always has a possibility to emit photons and whilst the emission of a photon reveals information about the state vector (giving the collapse in (4.20)) we also gain information about the system when there is no jump. This is because the absence of photons is suggestive of the quantum system being in the ground state rather than in the excited state. The correct evolution operator over the no-detection process in time $\Delta t$ is the non-Hermitian Hamiltonian

$$H_{\text{eff}} = H - i\frac{1}{2} \gamma \sigma_+ \sigma_- = H - i\frac{1}{2} \gamma \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}.$$  \hspace{1cm} (4.23)

This propagation can be achieved with one of the standard methods such as the split-operator Fourier transform method, or Crank–Nicholson (section 2.3). However, the non-Hermitian character of $H_{\text{eff}}$ does mean that the state vector will shrink and it should be renormalized prior to the calculation of the next jump probability (4.22) at time $t + \Delta t$.

A single history is generated by a repetition of the above process. The result is smooth evolution with the operator $H_{\text{eff}}$ which is interrupted by the jumps. The observables (e.g. populations) show the same behaviour with discontinuities at the positions of the jumps. However, when simulations are repeated the jumps occur in different places and the discontinuities become less obvious as the master equation result is realized.

and Wilkens 1994) partly for intrinsic interest (e.g. its interpretation), but also as a tool for solving computationally large problems where direct integration of a density matrix would be prohibitive because of the memory requirement. There are only a few examples of the method being used in wave-packet calculations (though we believe the method has much to offer in the future). The scheme has been implemented in quantum mechanical calculations of wave-packets traversing crossings (Lai et al 1993) in the presence of spontaneous emission and in a treatment of the excitation process in the presence of spontaneous emission (Lai and Stenholm 1994). The state vector Monte Carlo method has also been used for wave-packets that describe atoms during cold collisions (Holland et al 1994a, b, Suominen et al 1994, Band et al 1994).

A second simulation method is quantum state diffusion (Gisin and Percival 1992, Gisin and Percival 1993a, b, Percival 1994). In this method the (pure) state vector evolves stochastically, but, as with the state vector Monte Carlo method, when an average over many histories is performed the density matrix results are reproduced. Quantum state diffusion may be regarded as purely another computational tool for the solution of (4.5) although it arose from attempts to understand the 'collapse' process in quantum mechanics. Recently the method has been interpreted as a quantum history during a heterodyne measurement (Wiseman and Milburn 1993, Garraway and Knight 1994b), rather than the direct photon counting of the state vector Monte Carlo method.

The governing equation in quantum state diffusion is a nonlinear stochastic differential equation (Gisin and Percival 1993a, b) which for wave-packets would be of the form

\[ d\Psi(R, t) = \gamma \left[ \langle \Psi(R, t) | \sigma_+ | \Psi(R, t) \rangle \sigma_- - \frac{1}{2} \sigma_+ \sigma_- \right. \\
\left. - \frac{1}{2} \langle \Psi(R, t) | \sigma_+ | \Psi(R, t) \rangle \langle \Psi(R, t) | \sigma_- | \Psi(R, t) \rangle \right] \Psi(R, t) \, dt \\
+ \sqrt{\gamma} \left[ \sigma_- - \langle \Psi(R, t) | \sigma_- | \Psi(R, t) \rangle \right] \Psi(R, t) \, d\xi_t \]

(4.24)

where \( d\xi_t \) is a random complex Wiener variable, or Gaussian noise term. It varies randomly between each time step and for each sample run so that when averaged:

\[ \overline{d\xi_t} = 0 \quad \overline{d\xi_t \, d\xi_t'} = 0 \quad \overline{d\xi_t ^* \, d\xi_t'} = \delta_{t,t'} \, dt . \]

(4.25)

This equation has attracted interest in the field of quantum optics (Gisin and Percival 1992, 1993a, b, Goetsch and Graham 1993, Garraway and Knight 1994a, b). Tests in quantum optics have shown that the method is competitive with the state vector Monte Carlo approach (Garraway and Knight 1994a). An early application to wave-packet dynamics (Alber et al 1995) has used the quantum state diffusion approach in conjunction with the semiclassical trajectories of a wave-packet in a Paul trap.

4.4. Dynamical effects of spontaneous emission on wave-packets

After excitation of a wave-packet has taken place, spontaneous emission transfers the excited-state wave-packet gradually back to the ground state (by spontaneous decay). In the time-dependent picture this decay takes place exponentially, i.e. the total excited-state population diminishes as \( \exp(-\gamma t) \), assuming that the decay process does not interfere with the excitation process itself. Further, if the wave-packet has a classical trajectory \( R(t) \) as a function of time, we can directly relate the position of the wave-packet to its decay \( \exp(-\gamma t) \) as measured from the time and place where the wave-packet was created. Hence the probability to reach, e.g. a resonance region for the probing process, can be estimated. In theoretical studies of cold collisions (Holland et al 1994b, Suominen et al 1994) a good agreement with wave-packet results and estimates given by such a semiclassical approach has been found. In this case there is no dynamical effect of spontaneous emission.
The intermediate case, where the spontaneous decay is non-negligible, but not too strong, has been studied by Lai and Stenholm (1994) using the methods described in sections 4.2 and 4.3. In figure 19 we show their result for a pulse which features several Rabi flops. The full and open squares in figure 19(a) show the role of ensemble sizes in the Monte Carlo approach. The main result, however, is that the decay clips the peaks of the time-dependent oscillatory structure in the excited-state population on both the upper and lower tips. This is because the decay stops the excited-state population from reaching its highest possible values (i.e. the no-decay values featured by the chain curve), and also prohibits any sizable depopulation of the ground state.

When decay is weak the excited-state wave-packet component can move towards large $R$ before it decays back to the ground state. As a result a statistical mixture of the vibrational states of the ground-state potential surface is created, in contrast to the creation of a coherent superposition by a chirped pulse or two pulses separated in time (see section 3.2). In the quantum jump picture it is possible to calculate the averaged position of the excited-state wave-packet prior to the jump, and in figure 19(b) a distribution of these positions is shown. Their average is clearly shifted from the equilibrium position of the ground state towards larger $R$ (or $(x)$ in the figure). Similarly one can calculate the average energy for the spontaneously emitted photon by taking the average of the spatial distribution of the excited-state population prior to the jump with the position-dependent potential energy difference $\Delta U(R) = U_2(R) - U_1(R)$.

A wave-packet can change its kinetic energy if it is excited to an energy level by a laser and it then decays by spontaneous emission back to the original level. If the spontaneously emitted photons have frequencies which differ from the laser frequency then necessarily energy exchange has taken place. Since energy is conserved the frequency difference must appear as a change in the kinetic energy of the wave-packet. The quantum jump picture of the decay shows this explicitly: when a quantum jump takes place, the excited-state component of the state vector becomes the new ground-state component, without any changes in phase. Hence after a quantum jump, the ground-state component has the same kinetic energy and momentum that the excited-state component possessed just prior to the jump. If the obtained increase in the kinetic energy is large enough, the decay may lead to dissociation of the molecule.
These dynamical effects induced by spontaneous decay are very important in cold collisions, where the time spent by the wave-packet traversing a laser-induced crossing is comparable to the time-scale of the decay (Suominen and Garraway 1993, Holland et al 1994b). The excited-state wave-packet can then either accelerate (radiative heating) or decelerate (optical shielding), as shown schematically for the linearized case in figure 20. In femtochemistry similar effects can arise if a wave-packet moving on the ground state is excited to another state with a very short lifetime. This can happen either during an excitation process or a probing process. As a result the ground-state wave-packet may obtain an average momentum which is very different from the original one. However, the exponential nature of spontaneous decay tends to lead to a situation where the changes in the mean momentum of a wave-packet are accompanied by momentum diffusion. This is clearly seen in figure 21 where the increase in the slope of the excited state (figure 20(a)) enhances deceleration, but the momentum distribution of the wave-packet loses its original narrow Gaussian form and a tail towards small values of momentum emerges. It is difficult to create clear shifts in wave-packet momentum using excitation-decay cycles, and at the same time keep the width of the momentum distribution relatively small. Moreover, if the excitation of the wave-packet is only partial, the difference between wave-packet evolution on each potential surface can increase the spatial separation of the two components so that after the decay has taken place, the spatial width of the ground-state wave packet goes well beyond the natural spreading.

5. Conclusions

In this review we have presented an overview of wave-packets and their applications within the areas of physics of which we have some experience. Unfortunately, our presentation has had to be necessarily narrow in some places, and so we wish to apologise to those authors whose work we may not have included. Nevertheless, we have strived to cover a wide range of material. We started with the basics of the electronic states on which molecular
wave-packets reside. We have explored some of the numerical and semiclassical tools which enable simple theoretical modelling of various physical wave-packet problems. We have not tried to cover all the experimental work in femto-time physics and chemistry, but rather by using specific examples we have illustrated the connection between some experimental and theoretical studies.

Since we regard dissipation in the form of spontaneous emission to be an important challenge to both theory and experiment, we have devoted a fairly large section of this review to that subject. This is also the direction in which our own interests currently lie.

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Appendix A. Summary of exactly solvable two-state models

The known set of analytically solvable two-state models is quite limited. Here we present the relevant details for some of these models, as well as the details of two additional models which have approximate solutions. The general Hamiltonian is set as

\[ H = \begin{pmatrix} \alpha(t) & V(t) \\ V(t) & -\alpha(t) \end{pmatrix} \]  

(A.1)

In figure A1 we show the level configuration for the models of this appendix.

The Rosen–Zener model. Although this model first presented by Rosen and Zener (1932) is a special case of the first Demkov–Kunike model, it is important enough to deserve a separate presentation. We have

\[ \alpha = \Delta/2 \quad V = V_0 \text{sech}(t/T). \]  

(A.2)

Here \( T \) defines the pulse time-scale and \( V_0 \) the strength. If \( P_1^{\text{dis}}(-\infty) = 1 \), then

\[ P_1^{\text{dis}}(t) = |F(V_0 T/h, -V_0 T/h; 1/2 - i\Delta T/(2h); z(t))|^2 \]  

(A.3)

Figure A1. The level configurations of the models discussed in this appendix. The full curves are diabatic energy levels, broken ones are the adiabatic ones, and dotted curves feature the couplings in cases where they are not constant. The models are: (a) Rosen–Zener, (b) first Demkov–Kunike, (c) second Demkov–Kunike, (d) the extended Demkov–Kunike, (e) the Landau–Zener, and (f) the parabolic model.
where $F$ is the hypergeometric function and $z(t) = [\tanh(t/T) + 1]/2$. This gives the asymptotic result

$$P_2^\text{dis}(\infty) = \sin^2(\pi V_0 T/h) \sech^2(\pi \Delta T/(2h)). \tag{A.4}$$

**The Demkov–Kunike models.** We use the abbreviations DK1 and DK2 for the first and second Demkov–Kunike models:

DK1: \[
\begin{align*}
\alpha &= \tilde{E} + E_0 \tanh(t/T) \\
V &= V_0 \sech(t/T)
\end{align*}
\]

DK2: \[
\begin{align*}
\alpha &= \tilde{E} + E_0 \tanh(t/T) \\
V &= V_0
\end{align*}
\]

The complicated solutions are expressed in terms of hypergeometric functions and exponentials (Demkov and Kunike 1969, Suominen and Garraway 1992). The solutions are obtained in the non-crossing adiabatic basis, and are ($P_1^\text{dis}(-\infty) = 1$)

**DK1:** \[
P_2^\text{dis}(\infty) = \begin{cases} 
\frac{\sinh \pi T(E_0 + \sqrt{E_0^2 - V_0^2}) \sinh \pi T(E_0 - \sqrt{E_0^2 - V_0^2})}{\cosh \pi T(\tilde{E} + E_0) \cosh \pi T(\tilde{E} - E_0)} & |\tilde{E}| \geq |E_0| \\
\frac{\cosh \pi T(\tilde{E} + \sqrt{E_0^2 - V_0^2}) \cosh \pi T(\tilde{E} - \sqrt{E_0^2 - V_0^2})}{\cosh \pi T(\tilde{E} + E_0) \cosh \pi T(\tilde{E} - E_0)} & |\tilde{E}| < |E_0|
\end{cases} \tag{A.6}
\]

**DK2:** \[
P_2^\text{dis}(\infty) = \frac{\sinh \left[\pi T(E_a - E_a + 2E_0)/2\right] \sinh \left[\pi T(E_a - E_a + 2E_0)/2\right]}{\sinh \pi T E_a \sinh \pi T E_a} \tag{A.7}
\]

where

$$E_a = \sqrt{(\tilde{E} - E_0)^2 + V_0^2} \quad E_c = \sqrt{(\tilde{E} + E_0)^2 + V_0^2}. \tag{A.8}$$

(See also a related problem in Hioe 1984.) It should be noted that for the second Demkov–Kunike model, the levels do not decouple when $t \to \pm\infty$, so there is little sense in defining the initial conditions in the diabatic basis. If we set $\tilde{E} = 0$ then

**DK1:** \[
P_2^\text{dis}(\infty) = \frac{\cosh^2 \pi T \sqrt{E_0^2 - V_0^2}}{\cosh^2 \pi T E_0} = \frac{\cos^2 \pi T \sqrt{V_0^2 - E_0^2}}{\cosh^2 \pi T E_0} \tag{A.9}
\]

**DK2:** \[
P_2^\text{dis}(\infty) = \frac{\sinh^2 \pi T E_0}{\sinh^2 \pi T \sqrt{E_0^2 + V_0^2}}. \tag{A.10}
\]

The Demkov–Kunike models with $\tilde{E} = 0$ are interesting from the point of view of the DDP method (section 2.4.2): they have an infinite series of zero points $t_k$ in the complex plane, and if the DDP results from all of them are summed, one obtains the correct analytic result for $P_2$ (Suominen 1992a).

**The extended Demkov–Kunike model.** This model, unfortunately not solvable analytically, reduces in certain limits to the Rosen–Zener model and both Demkov–Kunike models. It is obtained by putting different time-scales into the DK1 model with $\tilde{E} = 0$:

$$\alpha = E_0 \tanh(t/T_1) \quad V = V_0 \sech(t/T_2). \tag{A.11}$$

Here the basic characteristics of the various models coexist and compete for dominance in different regions of the parameter space. For some parameter values the DDP method can be used (Suominen and Garraway 1992).
Wave-packet dynamics in femto-time

The Landau-Zener model. We have

\[ \alpha = \lambda t \quad V = V_0 \]  

(A.12)

where \( \lambda \) and \( V_0 \) are positive constants.

The Schrödinger equation can be solved in terms of parabolic cylinder functions, also known as Weber functions, (Zener 1932, Shore 1990). With arbitrary initial conditions one gets (Crothers 1989, Kazantsev 1990)

\[
\begin{bmatrix}
  a_1(\infty) \\
  a_2(\infty)
\end{bmatrix} = \begin{bmatrix}
  \sqrt{1 - R^2} e^{-i\phi} & R \\
  R & \sqrt{1 - R^2} e^{i\phi}
\end{bmatrix} \begin{bmatrix}
  a_1(-\infty) \\
  a_2(-\infty)
\end{bmatrix}
\]  

(A.13)

where the Landau-Zener factor (Landau 1932, Zener 1932) is \( R = \exp[-\pi \Lambda/2] \) and \( \Lambda = V_0^2/\lambda \). The phase factor is (Crothers 1971, Crothers 1972, Crothers 1989)

\[
\phi = \frac{\pi}{4} + \frac{\Lambda}{2} \ln \frac{\Lambda}{2e} + \arg[\Gamma(1 - i\Lambda/2)]
\]  

(A.14)

which disappears in the adiabatic limit.

With the initial conditions \( P_1^{\text{dia}}(-\infty) = P_2^{\text{dia}}(-\infty) = 1 \) and \( P_2^{\text{dia}}(-\infty) = P_1^{\text{dia}}(-\infty) = 0 \) one gets the famous result

\[
P_1^{\text{dia}}(\infty) = P_2^{\text{dia}}(\infty) = R^2 = e^{-\pi \Lambda}
\]  

(A.15)

The diabatic and adiabatic levels coincide as \( t \to \pm \infty \), except for a flip of labels.

The parabolic model. This model is the next step after linearization:

\[ \alpha = \alpha t^2 - b \quad V = v \]  

(A.16)

For large positive values of \( b \) the model can be linearized and solved using the Landau-Zener model. When the linearization fails \( \alpha \approx 0 \), the model may be used for cases where the Landau-Zener approximation is useless. Such systems are especially the limiting cases where \( \alpha(t_0) = \alpha'(t_0) = 0 \). The parabolic model also provides information about the phases that need to be taken into account for multiscrossing problems. The approximations for \( P_2(\infty) \), obtained by combining the DDP method with the results from the Landau-Zener model, for the cases \( b < 0, b = 0 \) and \( b > 0 \) are discussed by Suominen (1992b).

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