THE WAVE PACKET - A UNIVERSAL QUANTUM OBJECT[1]

S. Stenholm

The Academy of Finland and Helsinki Institute of Physics,
PL 9, 00014 Helsingin yliopisto, Finland

K.-A. Suominen

Theoretical Physics Division, Department of Physics, University of Helsinki, PL 9,
00014 Helsingin yliopisto, Finland

We summarize the theoretical description of wave packets on molecular energy
levels. We review the various quantum mechanical effects which can be studied
and the models that can be verified on this system. This justifies our claim that
the wave packet constitutes a universal quantum object.

1. Introduction

Quantum Mechanics has turned out to be our most versatile and universal descrip-
tion of microscopic Nature. Its concepts and methods have been applied to ever larger
ranges of microscopic entities and their accompanying phenomena. However, most ap-
plications are based on calculating the stationary energy eigenvalues or the probability
fluxes in scattering situations. The theory predicts a multitude of energy levels in
atoms, molecules, solids, nuclei and elementary particles. Also, the standard approach
to scattering utilizes a steady flow of particles instead of the normalizable wave packets
corresponding more closely to the physical conditions.

Recently the situation has changed considerably. The technical development of well
controlled laser pulses has made it possible to excite non-stationary quantum states and
follow their Schrödinger evolution in real time. Similar experiments were earlier carried
out with nuclear and electronic spins, but their time evolution takes place in a finite
Hilbert space, whereas only experiments on atoms and molecules can address excited
states living on a continuum.

With picosecond laser pulses one can excite wave packets on Rydberg levels and
probe their quantum fate, see [1] and for a review [2]. With the recent development
of femtosecond pulses, one can excite nuclear wave packets on the adiabatic electronic

S. Stenholm, K.-A. Suominen

levels of molecules [3] and follow their motion. Within the Born-Oppenheimer description, this is the ideal laboratory for wave packet experiments [4], and it provides an excellent opportunity to test the validity of much used models in quantum theory; see Ref. [5] where much of our work on wave packets is reviewed. We have also applied time dependent methods to electronic states in semiconductor heterostructures [6], where the potential wells provide an interesting analogy to the energy levels of molecules. Furthermore, these methods have been very useful in studies of cold collisions between laser cooled and trapped neutral atoms [7].

In this paper, we will review the physical formulation of laser-induced processes in molecules (Sec. 2), summarize some of the physical phenomena investigated (Sec. 3), and present some of our most recent results (Sec. 4). These are mainly found in the work [8] being the PhD Thesis of Asta Paloviita.

2. Formulation of the problem

Within the Born-Oppenheimer approximation, we solve for the electronic energy levels with the nuclei localized at their classical positions R. The corresponding eigenvalues $\mathcal{U}_n(R)$ give the potential surfaces for the nuclear motion, and the corresponding eigenfunctions $\varphi_n(r)$ form an orthonormal set in the space of electronic states. This can be utilized as a basis even when the electronic levels are coupled by external laser fields. We thus write for the full state of the system the wave function

$$\Psi(r, R; t) = \sum_n \psi_n(R, t)\, \varphi_n(r),$$ (1)

which is still exact. In the Born-Oppenheimer approximation, we neglect the R-dependence of the electronic states $\varphi_n(r)$, and obtain the equations

$$i\hbar \frac{\partial}{\partial t}\psi_n(R, t) = \left[-\frac{\hbar^2}{2M}\nabla^2 + \mathcal{U}_n(R)\right]\psi_n(R, t)$$
$$+ \sum_m \langle \varphi_n \,|\, \mathbf{D} \,|\, \varphi_m \rangle \cdot \mathbf{E}(t)\, \psi_m(R, t).$$ (2)

Here $\mathbf{E}(t)$ is the external field coupled to the molecular energy levels, and the molecular operator $\mathbf{D}$. Near resonance between two molecular energy levels, we can perform the rotating-wave approximation and reduce the problem to the coupled equations

$$i\frac{\partial}{\partial t}\psi_1 = \left[-\frac{\partial^2}{\partial x^2} + \mathcal{U}_1(x)\right]\psi_1 + V\psi_2$$
$$i\frac{\partial}{\partial t}\psi_2 = \left[-\frac{\partial^2}{\partial x^2} + \mathcal{U}_2(x) - \omega\right]\psi_2 + V\psi_1.$$ (3)

Here ω is the laser frequency, and we have scaled the variables in a way adapted to numerical computations. Most of our work has been based on equations like (3); to introduce one more level is simple, but to add more dimensions strains even up-to-date computer resources. For a discussion of the numerical problems encountered see Ref. [5].

The wave packet - a universal quantum object

Solving the coupled equations (3) directly does not involve the Franck-Condon principle, which, however, is embedded in the local nature of the excitation process. Only for distances satisfying an energy resonance condition, can population transfer between the levels take place. The Condon factors can be made explicitly visible by using an expansion in the nuclear eigenfunctions on the electronic energy surfaces, see e.g. [9].

A straightforward application of the equations (3) is an investigation of the level crossing models introduced by Landau and Zener. By tuning the laser frequency ω, we can move the crossing point given by

$$\mathcal{U}_2(x) - \omega = \mathcal{U}_1(x),$$ (4)

and the coupling strength V is determined by the laser intensity. In this situation we have been able to verify the Landau-Zener theory by integrating the wave packet motion across a laser-induced crossing [10]. In fact, our computations show that it is difficult to find experimentally significant deviations from the simple theory.

3. Physics of wave packet excitation

The ground state of a molecule prepares nearly an exact Gaussian wave packet, which can be lifted to an excited level by a laser pulse, see Fig. 1. Ideally this can take place without distortion, but quantum dynamics distorts the shape for pulses of finite duration [11].
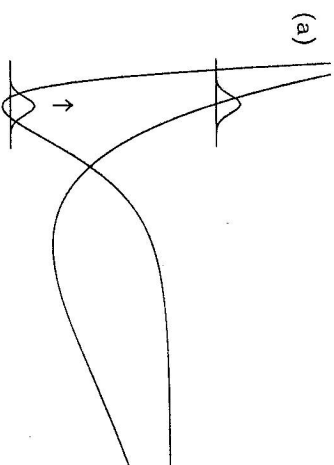

(a)

Fig. 1. The basic model for molecular excitation by ultrashort pulses.

At once upon excitation, the excited wave packet starts to spread, in a manner determined mainly by the initial width of the wave packet. The wings of a broad wave packet are out of resonance, and when the population starts to return back to the ground state, the wings do not participate in the Rabi flopping occurring during the laser pulse. If the wave packet is excited to a potential slope, the situation is less straightforward, and hence the emerging wave packet may assume a rather complicated shape as shown

in [11]. Near the resonance position, we may see the standard Rabi flopping between the two levels.

If the slope on the excited level is steep enough, the excited wave packet is rapidly accelerated and thus it escapes the resonance region. Then it can no longer participate in the flopping and is returned less efficiently to the ground state. By chirping the laser frequency in a propitious way, one may increase the excitation efficiency of the process [12].

When the intensity and the length of the laser pulse are increased, the population on the upper level has not enough time to undergo any quantum dynamics before it is returned to the ground level. Thus on the upper state, the motion appears frozen [13], and only the fraction of the population remaining at the end of the pulse can escape as shown in Fig. 2.

Another phenomenon disrupting the excitation process is spontaneous decay. When the decay time is of the same order as the exciting pulse, this allows some excitation followed by eventual return to the ground state. We have investigated the dynamics of this situation [14] using the state vector Monte Carlo method. This also gives the statistics of the position where the spontaneous decay occurs; as this determines the central frequency of the emerging photon, we are thus able to provide a picture of the time dependent spectrum too [15].
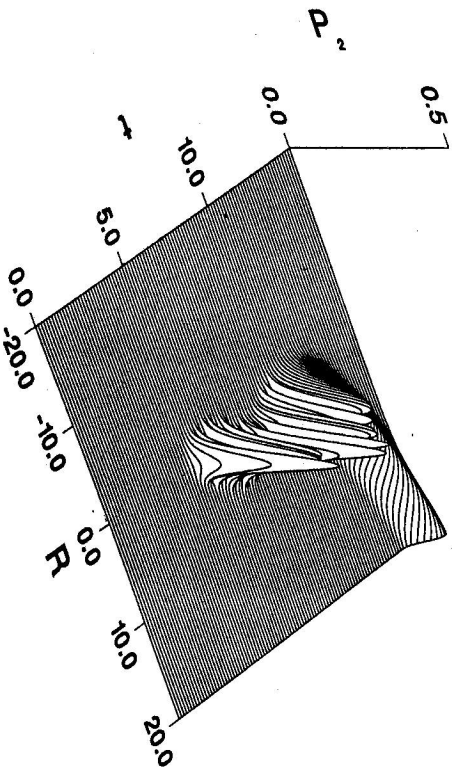

Fig. 2. The excited state wave packet $P_2(R, t)$ during an excitation by a pulse with a Gaussian envelope.

4. Wave packet decay

When the ground state of a molecule is coupled suddenly to the slope of an excited state, its discrete bound energy level becomes coupled to the continuum of the sloping potential. This is exactly the situation treated by Weisskopf and Wigner [16] as a model of exponential decay. Such a model has become the prototype for radiative decay, particle creation and resonances in scattering theory [17]. It is also used for describing non-radiative processes in large molecules [18] and dissipative processes in Quantum Optics [19].

The simple case of a discrete state $|0\rangle$ embedded in a continuum $\{|\epsilon\rangle\}$ and coupled linearly to it, can be described by the model

$$H = H_0 + V$$

$$H_0 = \omega_0|0\rangle\langle0| + \int d\epsilon\, \epsilon\, |\epsilon\rangle\langle\epsilon|$$

$$V = \int d\epsilon \left(V_\epsilon|\epsilon\rangle\langle0| + V_\epsilon^*|0\rangle\langle\epsilon|\right). \tag{5}$$

This system can be solved using the standard methods of quantum theory, and with the initial state $\varphi_0(x) \equiv \langle x|0\rangle$ we find the time evolution of this state to be

$$\psi(x, t) = \exp[-\{i\omega' + \Gamma/2\} t]\varphi_0(x), \tag{6}$$

where ω' is the renormalized frequency ω_0 and Γ is the decay rate; in the weak coupling limit this is given by the Weisskopf-Wigner expression. The wave packet on the continuum levels is found to emerge in the form

$$\Psi(x, t) = \Phi(x, t) - \exp[-\{i\omega' + \Gamma/2\} t]\Phi(x, 0), \tag{7}$$

where $\Phi(x, t)$ is the outgoing wave packet for times much longer than Γ^{-1}. The validity of this result and its correction terms are discussed in Ref. [20].

To test the validity of the expression (6), we have replaced the simple model (5) by one of the type (3) with the potentials

$$U_1(x) = \frac{1}{2}x^2 \tag{8}$$

$$U_2(x) - \omega = \frac{1}{\sqrt{2}} - \alpha x.$$

With this choice, we find the energies of the discrete state to coincide with that of the continuum at $x = 0$, see Fig. 3. When we couple the two, we find that the decayed population emerges on the slope as a localized wave packet, Fig. 4. The probability of remaining on the original level is shown in Fig. 5 on a semilogarithmic scale, and the exponential decay is clearly seen.

In the model (8), we can calculate the decay rate in the Weisskopf-Wigner limit including an analytic expression for the Condon factor. In the limit of a steep slope, the reflection principle gives the decay rate

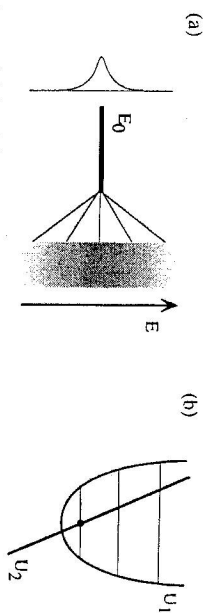$$\Gamma = 2\pi \frac{V^2}{\alpha\,(2\pi^2)^{1/4}}; \tag{9}$$

Fig. 3. The basic model for (a) a discrete state coupled to a continuum, and for (b) a molecular representation of the same situation. In (b) the discrete state is the lowest vibrational state of the harmonic potential, and the eigenstates of the linear potential form the continuum.
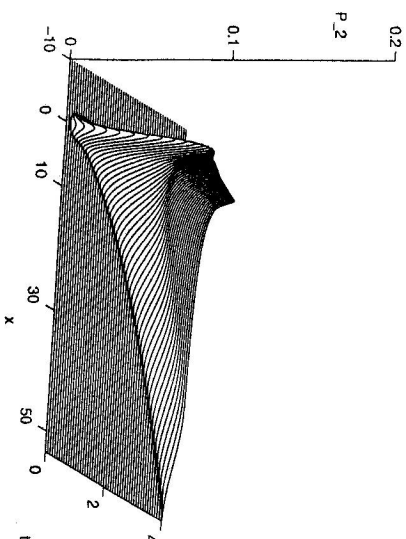

Fig. 4. The excited state wave packet $P_2(x,t)$ for $\Gamma \simeq 0.26$.

this limit of large α is the perturbative regime, and we have found that the exponential decay can be found for values

$$\Gamma \leq 1. \qquad (10)$$

Fig. 4 is computed at $\Gamma \simeq 0.26$, which is well into the perturbative regime. In our paper [21], we show that the initial wave packet is found to decay exponentially with a decay rate given by

$$\Gamma = 2\pi V^2 |S|^2, \qquad (11)$$

where S is the Franck-Condon factor, as long as (10) is satisfied. For larger values of Γ, the decay acquires oscillational features, the behaviour goes over into the Rabi-type oscillations described above.

Even when the decay is no longer exponential, the emerging state on the slope still has a main component shaped like a wave packet, Fig. 6 where we have $\Gamma \simeq 2.4$, well above the perturbative regime. Here we can also see the Rabi oscillations between the ground state and the excited one. This displays the freezing effect discussed above, which can also be looked upon as wave packet trapping in the adiabatic potential wells
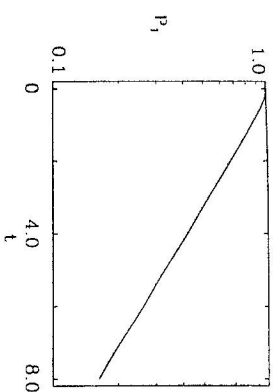
Fig. 5. The ground state population $P_1(t)$ as a function of time t. It shows the exponential nature of the excitation process.
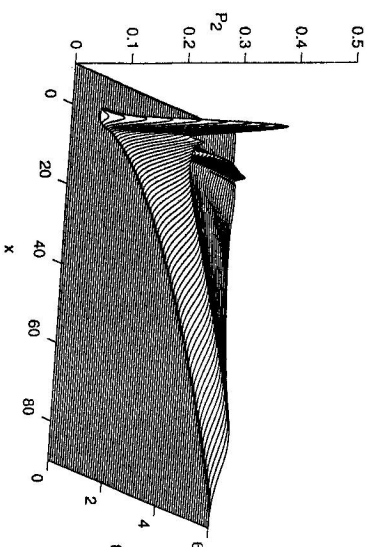

Fig. 6. The excited state wave packet $P_2(x,t)$ for $\Gamma \simeq 2.4$.

formed by the two intersecting levels; see also [10]. This probability sloshes around in the metastable well and oozes out as a long tail of probability clearly visible in Fig. 6. For a detailed discussion of the behaviour, we refer to Ref. [21].

5. Conclusions

We have considered the nuclear wave packet on an electronic energy level in a molecule as a prototype laboratory for wave packet investigations. The initial state is well defined, it can be excited and manipulated in a well controlled manner, and the time scales are such that the evolution can be followed in real time. We can combine numerical and analytic investigations to explore a multitude of quantum effects in the dynamic regime, and compare the results with well known quantum models.

We have investigated level crossings, pulsed excitation, metastable trapping, Rabi flopping, state freezing, wave packet decay, and the effects of spontaneous decay. In all these cases fundamental concepts of Quantum Mechanics are involved. This justifies calling the molecular wave packet a universal quantum object.

Finally a word of warning is needed. If we look at the freezing effect shown in Fig. 2, we may be tempted to think that the passing of the wave packet back to the ground state, constitutes a measurement if it is still there; thus the process would be an instance of the Zeno effect in Quantum Mechanics. However, no recording has been made, no information has been gathered, and the process is not a measurement. The freezing effect is only a dynamical consequence of the harmonic ground state to return the wave packet to its center. By visiting this potential frequently, the state is prevented from spreading or sliding on the upper level, and the freezing ensues as a purely dynamical effect.

References

[1] M. Nauenberg, C. Stroud, J. Yeazell: *Sci.Am.* **270**, No.6 (1994) 44

[2] G. Alber, P. Zoller: *Phys.Reports.* **199** (1991) 231

[3] M. Gruebele, A.H. Zewail: *Physics Today* **43**, No.5 (1990) 24

[4] B.M. Garraway, K.-A. Suominen, S. Stenholm: *Physics World* **6**, No.4 (1993) 46

[5] B.M. Garraway, K.-A. Suominen: *Rep. Prog. Phys.* **58** (1995) 365

[6] S. Stenholm, M. Kira: *Acta Physica Slovaca* **46** (1996) 325

[7] K.-A. Suominen: *J. Phys. B* **29** (1996) 5981

[8] A. Paloviita: *Ph.D. Thesis* (University of Helsinki, 1997)

[9] S. Stenholm: in *Quantum Dynamics of Simple Systems*, ed. by G.-L. Oppo, S.M. Barnett, E. Riis, M. Wilkinson (IOP, Bristol, 1996) p. 267

[10] B.M. Garraway, S. Stenholm: *Opt. Commun.* **83** (1991) 349

[11] K.-A. Suominen, B.M. Garraway, S. Stenholm: *Phys. Rev. A* **45** (1992) 3060

[12] A. Paloviita, K.-A. Suominen, S. Stenholm: *J. Phys. B* **28** (1995) 1463

[13] A. Paloviita, K.-A. Suominen: *J. Phys. B* **28** (1995) 1463

[14] W.K. Lai, S. Stenholm: *Opt. Commun.* **104** (1994) 313

[15] T.J. Dunn, J.N. Sweetser, I.A. Walmsley, C. Radzewicz: *Phys. Rev. Lett.* **70** (1993) 3388

[16] V. Weisskopf, E. Wigner: *Z. Physik.* **63** (1930) 54

[17] M.L. Goldberger, K.M. Watson: *Collision Theory*, Chapter 8 (J. Wiley & Sons, New York, 1964)

[18] J. Jortner, S.A. Rice, R.M. Hochstrasser: in *Advances in Photochemistry* **7**, ed. by J.N. Pitts, Jr., G.S. Hammond, W.A. Noyes, Jr. (Interscience, New York, 1969) p. 149

[19] C.W. Gardiner: *Quantum Noise* (Springer-Verlag, Berlin 1991)

[20] S. Stenholm, A. Paloviita: *J. Mod. Opt.*, to appear in the Special Issue on State Preparation

[21] A. Paloviita, K.-A. Suominen, S. Stenholm: *J. Phys. B*, to appear in June 1997