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Adiabatic processes in the ionization of highly excited hydrogen atoms

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Adiabatic and non-adiabatic processes in the dynamics of periodically driven quantum systems are studied employing the Floquet picture of quantum mechanics. The validity of N-niveau approximations in the Floquet theory is investigated. A method is described which allows the separation of fast (periodic) and slow (parametric) time-dependence and which yields a transparent description of the dynamical Landau-Zener mechanism. Using the model of surface-state electrons it is demonstrated that adiabaticity is decisive for the description of ionization experiments on highly excited hydrogen atoms; furthermore, an ionization mechanism based on the sudden onset of Landau-Zener transitions is proposed and shown to yield values for the ionization threshold which are in good agreement with experimental data. The connection to classical mechanics is considered by establishing the semiclassical limit of Floquet dynamics.

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1. Introduction

Although the interaction of atoms and molecules with time-periodic external fields is a very old subject in quantum mechanics, recent experiments in this area have discovered unexpected phenomena which still are not fully understood theoretically. A particularly puzzling example is given by the behaviour of highly excited hydrogen atoms in strong microwave fields which has been investigated experimentally by Bayfield and Koch [1, 2]. In these experiments, one observes ionization although the ionization energy of the initial stationary state corresponds to the energy of up to several hundred microwave photons [2]. Furthermore, the ionization rate depends sensitively on the strength but hardly on the frequency of the microwave field. These results have stimulated many theoretical activities. Since the full solution of the time-dependent Schrödinger equation in 3 space dimensions is beyond present-day abilities one has to rely on simple models. One of the most important models in this context is the model of surface-state electrons (SSE model) in the presence of an oscillating field which has been investigated within the framework of both classical [3, 4] and quantum [5–7] mechanics. Whereas even the first classical numerical simulations [3] took into account the fringe fields of the microwave cavity which in the rest frame of the atom appear as a slow rise and decrease of the external field, the quantum calculations usually rest on the assumption that the effect of the turn-on of the external field can be neglected [7]. As we shall show in this paper, this assumption is, in general, invalid; on the contrary, adiabatic behaviour, which in turn results from the slow turn-on of the field, plays a major rôle in the dynamics of the solutions of Schrödinger's equation. Following the general reasoning of prior investigations [8, 9] where it has been shown that for Hamiltonians periodic in time adiabaticity is intimately connected to the Floquet picture of quantum mechanics, we use the SSE model for a detailed study of those adiabatic processes that govern the response of highly excited hydrogen atoms to the entrance into a microwave cavity. To understand the initial step of the ionization mechanism we restrict ourselves to a discussion of the dynamics in the bound state part of the underlying Hilbert space.

As a main result we show that the Floquet picture is very well suited for describing situations where the amplitude of the external field is not constant in time

since in this picture adiabatic behaviour expresses itself as conservation of the occupation probabilities of the Floquet states when the driving amplitude is varied. For the particular case of the SSE model, we show that Landau-Zener type transitions among Floquet states due to the appearance of multiple avoided crossings of quasienergies above certain critical values of the field strength provide a transparent mechanism for exciting higher Floquet states; these critical values are related to the experimentally observed ionization threshold.

The material of our paper is organized as follows: Chap. 2 contains the basic elements of Floquet theory and mainly serves to establish our notation. In Chap. 3 we show that numerical calculations of Floquet spectra within a finite basis set are subject to certain errors which have to be carefully controlled; these results are applied to obtain stable quasienergy spectra for the SSE model. In Chap. 4, which has to be regarded as the central one of this paper, we present a general discussion of adiabaticity in the Floquet picture; again we use the SSE model to support our theoretical conclusions. Finally we sum up our findings in Chap. 5 and point out how to apply semiclassical quantisation rules to calculate quasienergy spectra. This may be of interest since the classical counterparts of driven quantum systems exhibit, in general, chaotic behaviour.

2. Elements of Floquet theory and notation

Let us consider a Hamiltonian with periodic time dependence

$$H(\mathbf{x}, t)=H(\mathbf{x}, t+T), \tag{2.1}$$

where T is the period and $\mathbf{x}$ denotes all spatial and spin degrees of freedom. According to Floquet's theorem [10] there are solutions of the Schrödinger equation

$$(H(\mathbf{x}, t)-i\partial_t)\,\psi(\mathbf{x}, t)=0 \tag{2.2}$$

that can be written in the form

$$\psi(\mathbf{x}, t)=u(\mathbf{x}, t)\,\mathrm{e}^{-\mathrm{i}\varepsilon t} \tag{2.3}$$

where u is periodic in time

$$u(\mathbf{x}, t)=u(\mathbf{x}, t+T); \tag{2.4}$$

ε is referred to as Floquet index or quasienergy.

In order to obtain such solutions one has to solve the eigenvalue equation

$$(H(\mathbf{x}, t)-i\partial_t)\,u_\alpha(\mathbf{x}, t)=\varepsilon_\alpha u_\alpha(\mathbf{x}, t) \tag{2.5}$$

imposing (2.4) as a boundary condition. Formally, the operator

$$\mathscr{H}:=H(\mathbf{x}, t)-i\partial_t \tag{2.6}$$

acts on a Hilbert space of time-periodic functions [11] with scalar product

$$\langle\langle u|v\rangle\rangle:=\frac{1}{T}\int_0^T \mathrm{d}t\int \mathrm{d}x\, u^*(\mathbf{x}, t)\,v(\mathbf{x}, t); \tag{2.7}$$

the completeness relation in this space reads

$$\sum_\alpha u_\alpha(\mathbf{x}, t)\,u_\alpha^*(\mathbf{x}', t')=\delta(\mathbf{x}-\mathbf{x}')\,T\delta_T(t-t'), \tag{2.8}$$

where δ_T denotes the T-periodic δ-function.

If $u_j(\mathbf{x}, t)$ is a solution of (2.5) with eigenvalue ε_j we immediately obtain a whole class of solutions $\left(\omega=\frac{2\pi}{T}\right)$

$$u_\alpha(\mathbf{x}, t)=u_j(\mathbf{x}, t)\,\mathrm{e}^{\mathrm{i}m\omega t}, \qquad m\in\mathbf{Z}, \tag{2.9}$$

corresponding to the eigenvalues

$$\varepsilon_\alpha=\varepsilon_j+m\omega, \qquad m\in\mathbf{Z}. \tag{2.10}$$

Hence α can be written as an array

$$\alpha=(j, m) \tag{2.11}$$

and the functions $u_j(\mathbf{x}, t)$ form a complete system at each instant of time:

$$\sum_j u_j(\mathbf{x}, t)\,u_j^*(\mathbf{x}', t)=\delta(\mathbf{x}-\mathbf{x}'). \tag{2.12}$$

It easily follows from (2.3) that the solution $\psi(\mathbf{x}, t)$ of Schrödinger's equation is independent of m. Thus the whole class (2.9) corresponds to *one* physical state ψ.

As an instructive example we consider the forced harmonic oscillator in $(1+1)$ space – time dimensions given by the Hamiltonian

$$H(x, t)=\frac{p^2}{2\mu}+\frac{\mu\omega_0^2}{2}x^2+\lambda x\sin\omega t. \tag{2.13}$$

From the well-known solutions of Schrödinger's equation

$$\psi(x, t)=\chi_j(x-y(t))\,\mathrm{e}^{-\mathrm{i}E_j t}\int_0^t L(\tau)\,\mathrm{d}\tau+\mathrm{i}\mu\dot{y}(x-y) \tag{2.14}$$

(χ_j is the oscillator eigenfunction with energy $\mathrm{E_j}=\omega_0(j+\frac{1}{2})$, L is the classical Lagrangian evaluated along the classical periodic trajectory $y(t)$), we obtain the eigensolutions $u_j(x, t)$ by isolating the time-peri-

odic part:

$$\psi(x,t) = \chi_j(x-y(t))\,\mathrm{e}^{\mathrm{i}\left(\int_0^t L\,\mathrm{d}\tau - \frac{t}{T}\int_0^T L\,\mathrm{d}\tau + \mu\dot{y}(x-y)\right)} \cdot \mathrm{e}^{-\mathrm{i}\left(E_j - \frac{1}{T}\int_0^T L\,\mathrm{d}\tau\right)t}$$

$$= u_j(x,t)\,\mathrm{e}^{-\mathrm{i}\varepsilon jt}. \tag{2.15}$$

Hence the Floquet spectrum of the forced harmonic oscillator is given by

$$\varepsilon_\alpha = E_j - \frac{1}{T}\oint L\,\mathrm{d}\tau + m\omega$$

$$= E_j + \frac{\lambda^2}{4\mu\omega^2}\frac{1}{1-\left(\frac{\omega_0}{\omega}\right)^2} + m\omega \tag{2.16}$$

where m is any integer and $j=0, 1, 2, 3, \ldots$.

From the point of view of physical applications one encounters Hamiltonians of the form

$$H(\mathbf{x},t) = H_0 + \lambda x \sin\omega t \tag{2.17}$$

where H_0 is the time-independent Hamiltonian of an atomic or molecular system and the second term describes the interaction with a single mode radiation field in the dipole approximation; λ denotes the field strength and ω its frequency. In most cases the spectrum of H_0 contains a continuous part and hence the Floquet spectrum of (2.17) covers the whole real axis, i.e. in a strict mathematical sense there are no normalisable Floquet states [12]. The situation can be seen in close analogy to the static (DC) Stark effect: bound states of H_0 turn into resonances described by complex Floquet indices with a negative imaginary part.

The model we shall mainly use to support our general conclusions is the model of surface-state electrons (SSE model) given by a $(1+1)$-dimensional Hamiltonian of the form (2.17) where

$$H_0 = \tfrac{1}{2}p_x^2 + V(x) \tag{2.18}$$

$$V(x) = \begin{cases} -\dfrac{1}{x}; & x>0 \\ +\infty; & x\leq 0. \end{cases} \tag{2.19}$$

This model had originally been devised in order to describe electrons bound by their image charge to a surface of liquid helium and has meanwhile frequently been used to investigate the microwave ionization of hydrogen atoms in both classical [3, 4] and quantum [5–7] calculations; the reduction to one space dimension has been justified in [6]. Although ionization ultimately involves the coupling to the continuum it has been argued that the initial step of the ionization process must be due to some process taking place in the bound space and therefore it should be sufficient to decouple the continuum and to consider the 'bound space projected' dynamics [7]. This is a reasonable assumption as long as the time scale of decay set by the imaginary part of the Floquet indices is long compared to the time scales of these dynamical processes.

3. *N*-niveau approximations in Floquet theory

In this chapter we are concerned with the numerical solution of the eigenvalue equation (2.5) where $H(\mathbf{x},t)$ is of the form of (2.17). A commonly adopted strategy consists in transforming the Schrödinger equation (2.2) into a matrix equation

$$i\partial_t\psi_n(t) = E_n\psi_n(t) + \lambda\sin\omega t\sum_{m=1}^{\infty} D_{nm}\psi_m(t) \tag{3.1}$$

using an eigenbasis of H_0

$$H_0\varphi_n = E_n\varphi_n, \qquad n=1,2,3,\ldots, \tag{3.2}$$

such that

$$D_{nm} = \langle\varphi_n|x|\varphi_m\rangle \tag{3.3}$$

is the matrix of the dipole operator x. To solve (3.1) on a computer one has to truncate this system to a finite dimensional one, since only a finite basis set

$$\{\varphi_1, \varphi_2, \ldots, \varphi_N\} \tag{3.4}$$

can be handled numerically. Within this N-niveau approximation one calculates the monodromy operator, i.e. the time-developement operator $U^{(N)}(T,0)$ for a complete cycle. From the Floquet theory it follows that diagonalisation of $U^{(N)}(T,0)$ yields the eigenvalues

$$\{\mathrm{e}^{-\mathrm{i}\varepsilon_j^{(N)}T}\}_{j=1,\ldots,N},$$

where the $\varepsilon_j^{(N)}$ are the Floquet indices (determined mod ω) in the N-niveau scheme.

For our investigation of adiabaticity in Chap. 4 we do not only need the Floquet indices for a specific value of the field strength λ but rather we have to know the whole λ-dependence

$$\varepsilon_\alpha = \varepsilon_\alpha(\lambda). \tag{3.5}$$

It is the purpose of the following considerations to show that the N-niveau approximation will lead to systematic errors of the functions

$$\varepsilon_\alpha^{(N)} = \varepsilon_\alpha^{(N)}(\lambda) \tag{3.6}$$

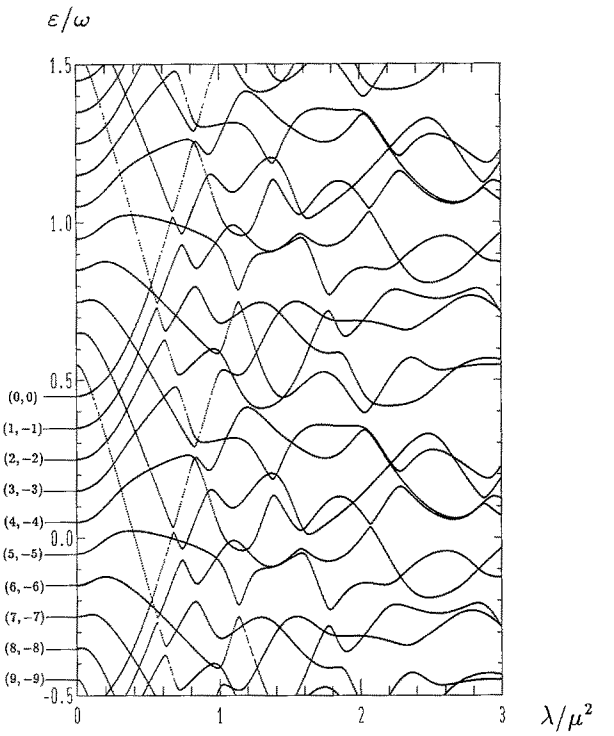

Fig. 1. Quasienergies for the driven oscillator (2.13) calculated within an ($N=10$)-niveau approximation and organized in two Brillouin zones. Parameters chosen are: $\omega=1.0\,\mu$, $\omega_0=0.9\,\mu$. Indices α are chosen such that $\alpha=(j,0)$ denotes the Floquet index continuously connected to $E_j=\omega_0(j+\frac{1}{2})$

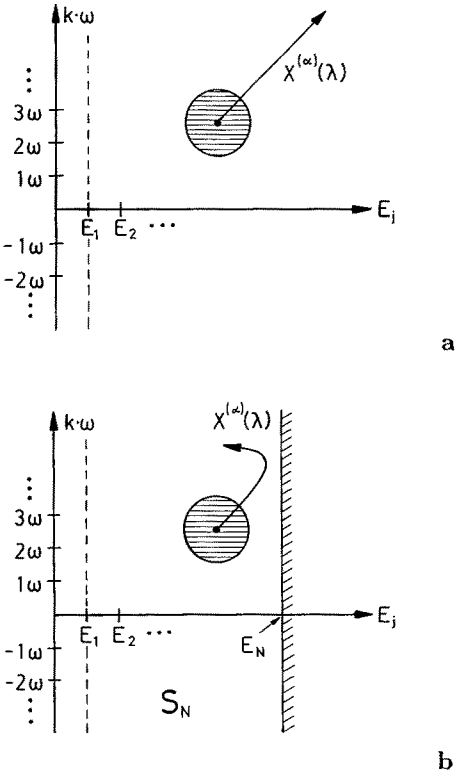

Fig. 2. **a** Flow of the center $X^{(\alpha)}$ of the distribution (3.10) in an infinite dimensional Hilbert space. **b** as **a**, but in a truncated Hilbert space

for *every* finite N which have to be carefully controlled.

A first indication for these errors can be deduced from the trace identity well known from the theory of periodic differential equations [13]

$$\sum_{j=1}^{N} \varepsilon_j^{(N)}(\lambda)=\frac{1}{T}\int_0^T \mathrm{d}t\,\mathrm{tr}(H^{(N)}(t)) \quad (\mathrm{mod}\,\omega). \tag{3.7}$$

The right hand side of this equation is λ-independent for pure harmonic time-dependence and equal to the sum of the first N energy eigenvalues (mod ω) of the static hamiltonian, i.e. we have

$$\sum_{j=1}^{N} \varepsilon_j^{(N)}(\lambda)=\sum_{j=1}^{N} E_j \quad (\mathrm{mod}\,\omega) \tag{3.8}$$

for all λ. This constraint is, however, N-dependent and hence unphysical.

As an example we consider the driven oscillator (2.13) within an ($N=10$)-niveau approximation, i.e. we solve (2.5) numerically in the space spanned by the 10 lowest lying oscillator eigenfunctions. The resulting Floquet indices $\varepsilon_\alpha^{(10)}(\lambda)$ are displayed in Fig. 1 which has to be contrasted to the exact solution given by (2.16). According to this formula all the exact indices $\varepsilon_\alpha(\lambda)$ show the same quadratic λ-dependence, a fact which is incompatible with (3.8) for any finite N.

The relevance of (3.8) can be clearly seen from the figure: Whereas for small λ the quasienergies corresponding to the lower lying states are approximately correct, i.e. quadratically increasing for the parameters chosen, the other indices must decrease in order to satisfy (3.8). Obviously the 'correct' and the 'wrong' levels influence each other and produce a pronounced avoided crossing structure such that, for higher field strength, Fig. 1 has nothing to do with the exact solution in the infinite Hilbert space.

This potentially dangerous effect of basis truncation becomes more transparent from the following argument: Decomposing

$$u_\alpha(x,t)=\sum_{j,k} a_{j,k}^{(\alpha)}\,\varphi_j(x)\,\mathrm{e}^{-\mathrm{i}k\omega t}, \tag{3.9}$$

a Floquet state u_α can be characterised by a normalised distribution

$$(E_j, k\omega)\to|a_{j,k}^{(\alpha)}|^2. \tag{3.10}$$

Projected onto the $E_j-k\omega$ plane (see Fig. 2a), this mapping can be visualised as a distribution with

center

$$X^{(\alpha)}(\lambda)=\begin{pmatrix}\Sigma_{j,k}E_j|a_{j,k}^{(\alpha)}|^2\\ \Sigma_{j,k}k\omega|a_{j,k}^{(\alpha)}|^2\end{pmatrix}\equiv\begin{pmatrix}\langle\langle u_\alpha|H_0|u_\alpha\rangle\rangle\\ \langle\langle u_\alpha|i\partial_t|u_\alpha\rangle\rangle\end{pmatrix}. \tag{3.11}$$

Obviously, for $\lambda=0$ the eigensolutions are given by

$$u_\alpha(x,t)|_{\lambda=0}=\varphi_{j_0}e^{-ik_0\omega t},\qquad \alpha=(j_0,k_0), \tag{3.12}$$

with a delta-function like distribution and center

$$X^{(\alpha)}(\lambda=0)=\begin{pmatrix}E_{j_0}\\ k_0\omega\end{pmatrix}. \tag{3.13}$$

With increasing λ the corresponding distribution obtains a finite width (schematically depicted by patches in Fig. 2) and its center moves in the above constructed plane.

By repeated use of the Hellman-Feynman theorem we derive the following equation for the 'parameter-velocity' (for all hamiltonians of the general form (2.17)):

$$\frac{d}{d\lambda}X^{(\alpha)}(\lambda)=\begin{pmatrix}\frac{\partial}{\partial\lambda}\langle\langle u_\alpha|H_0|u_\alpha\rangle\rangle\\ \frac{\partial}{\partial\lambda}\langle\langle u_\alpha|H_0|u_\alpha\rangle\rangle+\lambda\frac{\partial^2}{\partial\lambda^2}\varepsilon_\alpha\end{pmatrix}. \tag{3.14}$$

This equation, of course, is valid for both the exact solution and the N-niveau-approximation. Whereas, however, in the infinite Hilbert space the λ-flow given by (3.14) is unhindered (see Fig. 2a), in the truncated case it is restricted to a strip

$$S_N:=\{(x,y)|E_1\leqq x\leqq E_N\} \tag{3.15}$$

which necessarily changes the global properties of the flow (see Fig. 2b). If a center $X^\alpha(\lambda)$ reaches the truncation induced boundary of S_N the velocity vector must considerably change its direction which according to (3.14) gives rise to a large curvature term $\lambda\partial^2\varepsilon_\alpha/\partial\lambda^2$. Taking this as a signal for avoided crossings of Floquet eigenvalues we conclude that truncation of the basis set inevitably leads to the occurence of 'wrong' avoided crossing structures.

Needless to say, the mathematical cause underlying our discussion is the fact that the closed unit sphere in the infinite Hilbert space is non-compact whereas it is compact in the finite dimensional approximating subspaces.

We remark that our argumentation may also serve as a starting point to investigate the appearance of *real* avoided crossings, since there are physical constraints, for example the 'boundary' defined by the ground state energy of H_0.

Let us now illustrate this general discussion using the SSE model reviewed in Chap. 2. In atomic units

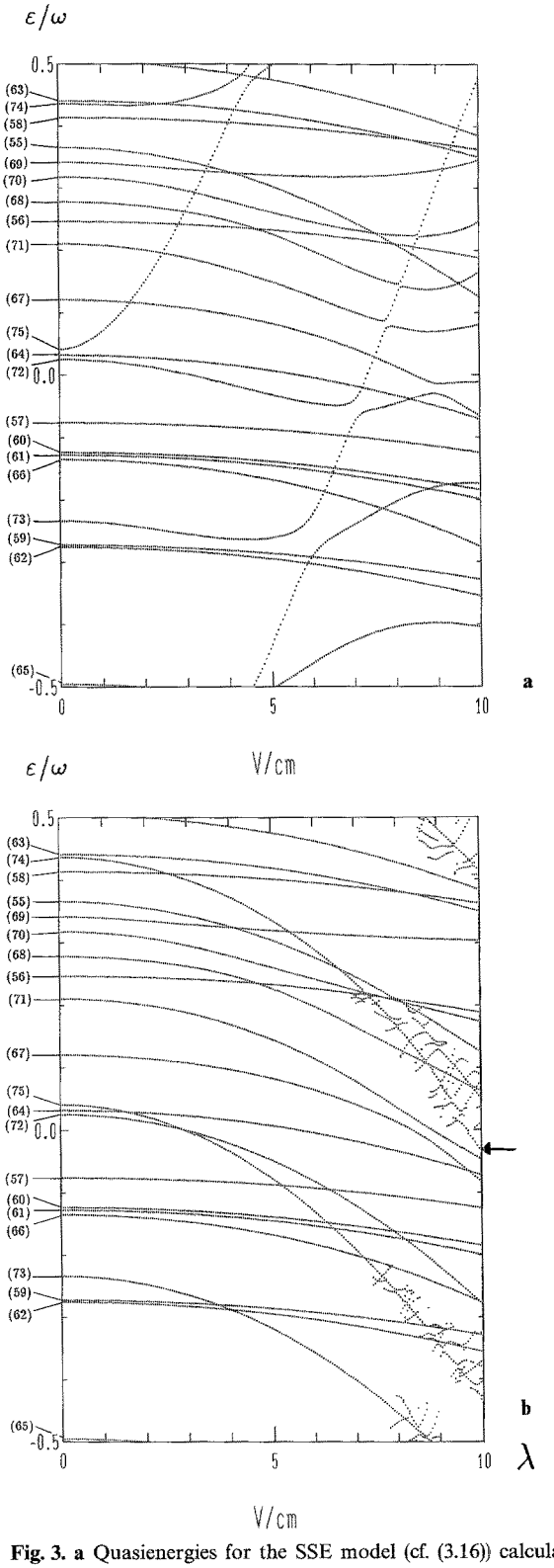

Fig. 3. a Quasienergies for the SSE model (cf. (3.16)) calculated in a basis of 21 states ($N_{\min}=55$, $N_{\max}=75$). The frequency corresponds to 9.92 Ghz. Levels are marked by principal quantum numbers of H_0. **b** as **a**, but using a basis of 101 states ($N_{\min}=55$, $N_{\max}=155$). Only the levels corresponding to those in **a** are plotted. The arrow marks a state used in Chap. 4 to demonstrate Landau-Zener transitions

the time-dependent Schrödinger equation is given by [5–7]

$$i\partial_t \psi_n(t) = -\frac{1}{2n^2}\psi_n(t) + \lambda \sin\omega t \sum_{m=N_{\min}}^{N_{\max}} D_{nm}\psi_m(t), \qquad (3.16)$$

where the dipole matrix D_{nm} is known analytically. It should be noted that the basis set employed in (3.16) is obtained from a twofold truncation at $n = N_{\min}$ and $n = N_{\max}$.

In Fig. 3a we show the Floquet spectrum obtained in a relatively small basis of 21 states ($N_{\min} = 55$, $N_{\max} = 75$). Even at very low values of the field strength λ the index ε_{75} behaves different from the rest of the spectrum, at slightly larger values ε_{74} changes its monotonic behaviour, then ε_{73} and so on. This is a typical indication of truncation errors fully in agreement with the naive picture of Fig. 2b since the corresponding centers $X^{(75)}$, $X^{(74)}$, $X^{(73)}$ etc. succesively reach the critical boundary zone of the strip (3.15). In fact, a repetition of the calculation within a slightly larger basis set ($N_{\min} = 55$; $N_{\max} = 85$) already leads to the disappearance of all the avoided crossings of Fig. 3a. In Fig. 3b we plot the quasienergies $\varepsilon_{55} - \varepsilon_{75}$ which result from an extended calculation ($N_{\min} = 55$; $N_{\max} = 155$). For small λ, all the indices decrease monotonically; above certain values of λ the quasienergies ε_{75}, ε_{74} and ε_{73} are seen to undergo several very narrow avoided crossings with levels resulting from higher lying states. This result turns out to be stable with respect to further increase of $N_{\max}$.

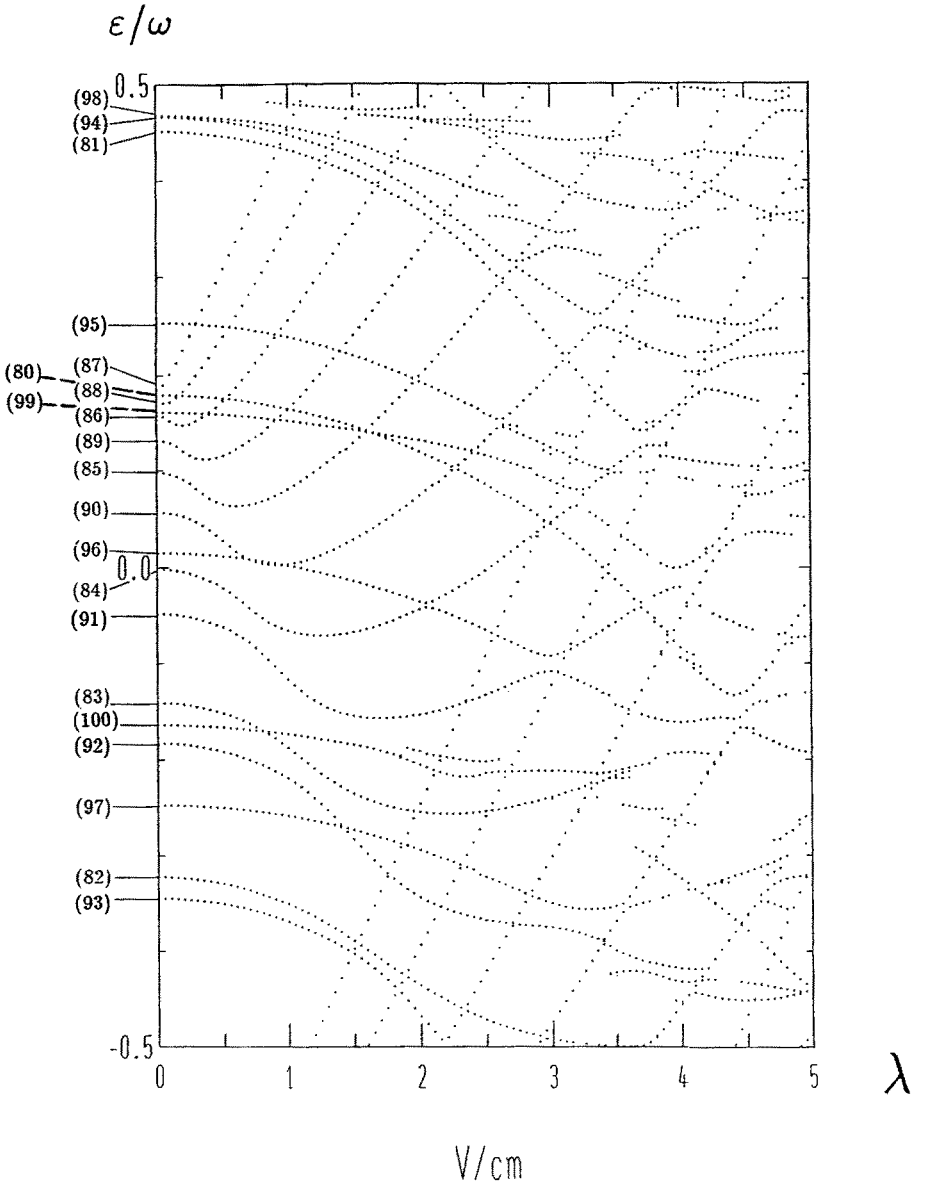

Fig. 4. Stable quasienergies for the SSE model ($\omega/2\pi = 9.92$ GHz) originating from the stationary states with principal quantum numbers $n = 80, \ldots, 100$

Naturally, stability (i.e. truncation independence) is a minimal requirement on a physical model. The lesson to be learned from the preceeding discussions may be summarized as follows:

(*i*) Any numerical calculation within a finite basis set is subject to the trace identity (3.8) and yields at least some wrong levels which have to be identified and discarded.

(*ii*) Stability of the remaining levels with respect to the basis size must be guaranteed.

(*iii*) Special care has to be taken in order to distinguish artificial, i.e. truncation induced, avoided crossings from possible real ones, since the latter, as we know from previous work [8, 9], dominate non-adiabatic effects.

It is a non-trivial fact that this procedure which demands a certain amount of skill actually yields stable results.

Our next question concerns the occurence of real avoided crossings in the quasienergy spectra of the SSE model. Again, an important clue can be guessed from the oscillator formula (2.16): If ω is less than the level spacing ω_0, all quasienergies decrease with increasing λ whereas they increase for $\omega > \omega_0$. For the hydrogen atom and a microwave frequency of 9.92 GHz the levels with principal quantum numbers $n = 87, 88$ are approximately at resonance, for lower levels the spacing between adjacent levels is bigger than ω. Therefore it can be expected from the oscillator formula that levels with $n < 87$ move 'down' which is confirmed in Fig. 3b. On the other hand, for $n > 88$

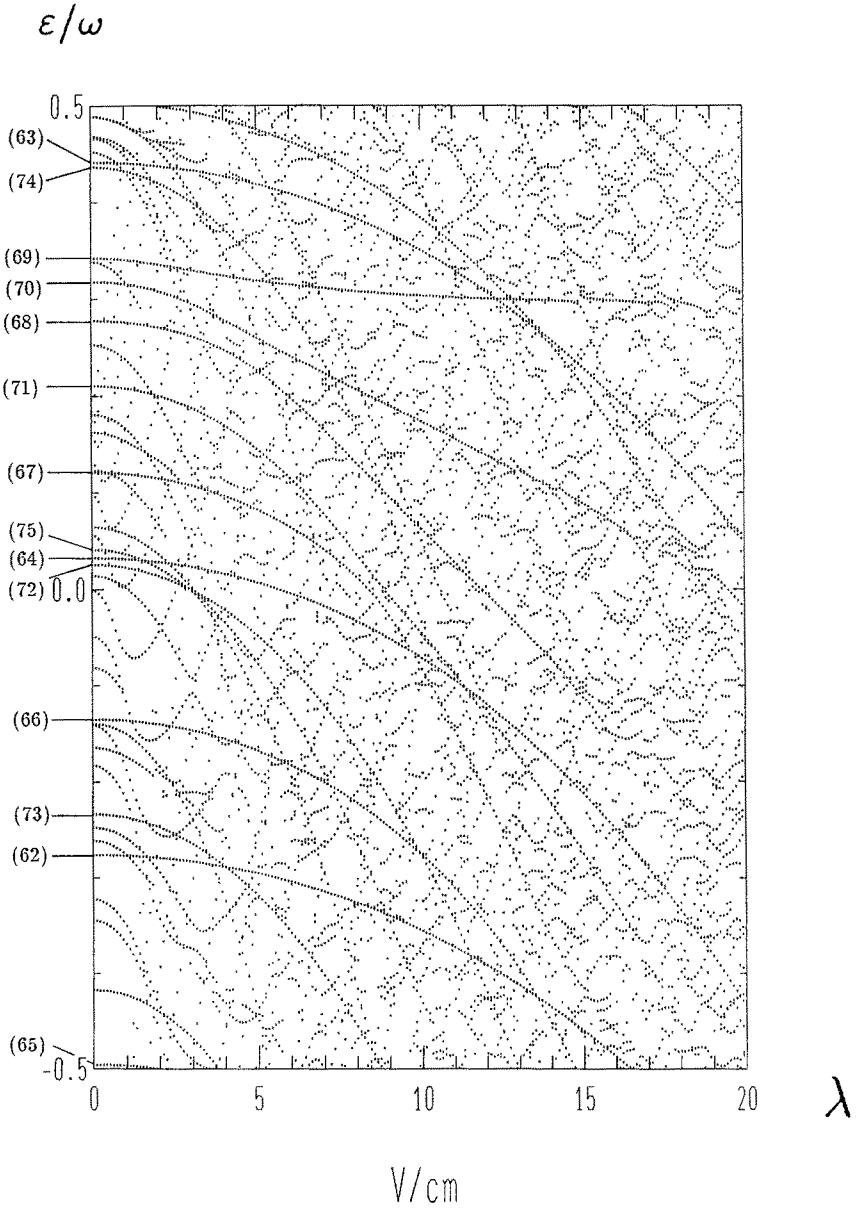

Fig. 5. Stable quasienergies for the SSE model ($\omega/2\pi = 9.92$ GHz). For testing adiabaticity in Chap. 4 the states $n = 64, 74$ have been used as initial states

the level spacing is less than the frequency and the levels should move 'up'. Hence the 'resonance point' is of special interest, since in its neighbourhood there are both types of levels which is a necessary condition for an avoided crossing. This simple argument is confirmed in Fig. 4 where the quasienergies originating from the stationary states with quantum numbers $n=80$ to $n=100$ are plotted. These indices result from a calculation employing 101 basis functions and have been found to be stable; in particular, the avoided crossing structure is correct.

To give an impression of the actual complexity of the quasienergy spectra in the experimentally relevant interval of field strength we plot in Fig. 5 the stable result of a 101 state calculation (the upper 50 and lower 7 indices have been removed). Whereas the 'lower' quasienergies behave regular the 'upper' ones undergo many avoided crossings on a very narrow scale.

We remark that these calculations are far more demanding than solving the initial value problem for the SSE model: Even without counting diagonalisations the numerical effort to obtain Fig. 5 is equivalent to propagating an initial state over 10^4 cycles within a basis of 101 functions.

4. Adiabatic and non-adiabatic behaviour in time periodic external fields

The adiabatic theorem [14] is one of the most important tools for the investigation of the time-dependent Schrödinger equation in the limit of slow time variation of a Hamiltonian $H(\tau)$. Considering the time-interval $0 \leqq \tau \leqq T_a$ and introducing the dimensionless time-parameter

$$s := \frac{\tau}{T_a} \tag{4.1}$$

Schrödinger's equation reads

$$i\partial_s \psi_{T_a}(s) = T_a H(s) \psi_{T_a}(s), \tag{4.2}$$

where

$$\psi_{T_a}(s) := \psi(s T_a) \tag{4.3}$$

and

$$0 \leqq s \leqq 1. \tag{4.4}$$

Assuming the system to be initially in a non-degenerate eigenstate of $H(0)$

$$\psi_{T_a}(0) = \varphi(0), \qquad H(0)\varphi(0) = E(0)\varphi(0), \tag{4.5}$$

the adiabatic theorem states that the solution of (4.2) converges in the limit $T_a \to \infty$ to an eigenstate of $H(s)$

$$\psi_{T_a}(s) \to \mathrm{e}^{-\mathrm{i}T_a \int_0^s \mathrm{d}s' E(s')} \varphi(s), \tag{4.6}$$

where

$$H(s)\varphi(s) = E(s)\varphi(s). \tag{4.7}$$

The eigenvectors $\varphi(s)$ are supposed to be normalised

$$\langle \varphi(s) | \varphi(s) \rangle = 1 \tag{4.8}$$

and their phases have to be chosen such that [14]

$$\left\langle \varphi(s) \middle| \frac{\partial}{\partial s} \varphi(s) \right\rangle = 0. \tag{4.9}$$

The fact that this requirement can, in general, not be satisfied globally in a higher dimensional parameter space leads to the well-known Berry-phases [15, 16].

The adiabatic theorem is valid even if the spectra of the one-parameter family $H(s)$ are unbounded or contain a continuous part and it can be extended to the case of degeneracies [17]. The degree of adiabaticity, i.e. the magnitude of T_a necessary to guarantee adiabatic behaviour, depends sensitively on details of the spectra and the smoothness of the parameter variation [18].

There is an extension of the adiabatic theorem to the Floquet picture of quantum mechanics which has been formally proven in [19]. To make our assertions more transparent we should like to proceed along different lines.

We start from the fact that strict periodic time-dependence is not what is encountered in real experiments. For example, Rydberg atoms entering a microwave cavity see a slowly rising field which has to be described by a time-dependent field strength

$$\lambda = \lambda\left(\frac{\tau}{T_a}\right). \tag{4.10}$$

Now the Schrödinger equation

$$\{H(\lambda(\tau/T_a); \tau) - i\partial_\tau\} \psi(\tau) = 0 \tag{4.11}$$

contains two different time scales set by the laser- or maser-period $T = 2\pi/\omega$ and the switching-on time T_a. Assuming that the amplitude $\lambda(\tau/T_a)$ changes negligibly during one period of the external field we treat both time-dependencies separately:

First we determine the Floquet-eigenstates $u_\alpha(\lambda)$ for each fixed λ-value in the range of the function

$\lambda=\lambda(\tau/T_a)$ as the solutions of the eigenvalue equation

$$\mathscr{H}(\lambda;t)\,u_\alpha(\lambda;t)=\varepsilon_\alpha(\lambda)\,u_\alpha(\lambda;t)$$
$$u_\alpha(\lambda;t+T)=u_\alpha(\lambda;t), \tag{4.12}$$

where

$$\mathscr{H}(\lambda;t)=H(\lambda;t)-i\partial_t. \tag{4.13}$$

This corresponds to integrating out the fast, oscillating time-dependence which is denoted by t in (4.12).

Secondly we include the slow, parametric time-dependence of $\lambda=\lambda(\tau/T_a)$ which is determined by the adiabatic evolution equation

$$\mathscr{H}(\lambda(\tau/T_a);t)\,\Phi(\tau;t)=i\partial_\tau\Phi(\tau;t). \tag{4.14}$$

From $\Phi(\tau;t)$ the solution $\psi(\tau)$ of the original Schrödinger equation (4.11) can easily be recovered by equating t and τ

$$\psi(\tau)=\Phi(\tau;t)|_{t=\tau}, \tag{4.15}$$

since

$$\begin{aligned} i\partial_\tau\psi(\tau)&=i(\partial_\tau\Phi)(\tau;\tau)+i(\partial_t\Phi)(\tau;\tau)\\ &=(\mathscr{H}\Phi)(\tau;\tau)+i(\partial_t\Phi)(\tau;\tau)\\ &=H\Phi(\tau;\tau)\\ &\equiv H\psi(\tau). \end{aligned} \tag{4.16}$$

The main advantage of (4.14) lies in the fact that it is a Schrödinger equation precisely of the form of (4.2), Floquet-eigenstates u_α play the role of the stationary eigenstates φ. Therefore, the conventional adiabatic theorem can be applied: Assuming the initial value

$$\Phi(\tau;t)|_{\tau=0}=u_\alpha(\lambda(0);t), \tag{4.17}$$

the solution of (4.14) converges for $T_a\to\infty$ to

$$\Phi(\tau;t)=\mathrm{e}^{-i\int_0^\tau d\tau'\,\varepsilon_\alpha(\lambda)}\,u_\alpha(\lambda(\tau/T_a);t). \tag{4.18}$$

Equating t and τ now proves the adiabatic theorem of the Floquet picture.

The same method of separating fast (t) and slow (τ) time-dependence has to be employed to calculate deviations from adiabaticity. To be specific, let us consider an adiabatic parameter-variation of the form

$$\lambda(\tau)=\begin{cases}0, & \tau<0\\ \text{smoothly monotonically increasing}, & 0\leqq\tau\leqq T_a\\ \lambda_f=\text{const.}, & \tau>T_a.\end{cases} \tag{4.19}$$

Let the system be initially in an eigenstate of H_0

$$\psi(\tau=0)=u_j(\lambda(0)=0;\tau=0)=\varphi_j. \tag{4.20}$$

After stationarity is reached for $\tau>T_a$, because of the completeness relation (2.12) the solution $\psi(\tau)$ of Schrödinger's equation (4.11) can be decomposed

$$\psi(\tau)=\sum_i a_i\,u_i(\lambda_f;\tau)\,\mathrm{e}^{-i\varepsilon_i(\lambda_f)\tau},\qquad \tau>T_a, \tag{4.21}$$

with τ-independent amplitudes a_i.

Calculations of the transition probabilities

$$P_{j\to i}\equiv|a_i|^2=|\langle u_i(\lambda_f;t)|\psi(\tau)\rangle|^2 \tag{4.22}$$

enables one to measure deviations from the full adiabatic behaviour characterised by $|a_i|^2=\delta_{ij}$. The solution of the evolution equation (4.14) corresponding to $\psi(\tau)$ is now given by

$$\Phi(\tau;t)=\sum_i a_i\,u_i(\lambda_f;t)\,\mathrm{e}^{-i\varepsilon_i(\lambda_f)\tau},\qquad \tau>T_a, \tag{4.23}$$

and hence the τ-independent probabilities (4.22) may be written

$$|a_i|^2=\frac{1}{T}\int_0^T dt\,|\langle u_i(\lambda_f;t)|\Phi(\tau;t)\rangle|^2, \tag{4.24}$$

and from Parseval's theorem we obtain the identity

$$|a_i|^2=\sum_m|\langle\!\langle u_{(i,m)}(\lambda_f;t)|\Phi(\tau;t)\rangle\!\rangle|^2,\qquad \tau>T_a. \tag{4.25}$$

Each term in this sum may be interpreted as a transition probability in the *extended* Hilbert space (cf. Chap. 2); summing over all members of the same class (cf. (2.9)) of a Floquet state yields the *physical* transition probability into this class.

It is (4.25) which contains the extended scalar product that is appropriate for generalizing well known formulae from standard theory [20] to the Floquet picture. For example, to first order in $1/T_a$ (not in λ!) we obtain

$$|a_i|^2\approx\sum_m\left|\int_0^\tau d\tau'\,\dot\lambda(\tau')\left\langle u_{(i,m)}(\lambda)\left|\frac{\partial}{\partial\lambda}u_j(\lambda)\right\rangle\right.\right.\cdot$$
$$\left.\left.\exp\left(i\int_0^{\tau'}d\tau''\{\varepsilon_{(i,m)}(\lambda)-\varepsilon_j(\lambda)\}\right)\right|^2. \tag{4.26}$$

As we have shown in previous work [8, 9] deviations from the adiabatic approximation mainly occur at avoided crossings of the Floquet–eigenvalues $\varepsilon_\alpha=\varepsilon_\alpha(\lambda)$ and can be understood in close analogy to the well-known Landau-Zener mechanism.

Let us therefore assume that there is an isolated avoided crossing at $\lambda_c < \lambda_f$. Since

$$\dot{\lambda}(\tau)\left\langle\!\left\langle u_{(i,m)}\left|\frac{\partial}{\partial\lambda}u_j(\lambda)\right\rangle\!\right\rangle \tag{4.27}$$

is a slowly varying function of τ, the main contribution to $|a_i|^2$ arise from those summands in (4.26) for which the oscillations of the exponential are minimal. In particular, at the avoided crossing there is one term, m_0 say, for which both the frequency $(\varepsilon_{(i,m_0)} - \varepsilon_j)$ is smallest and the overlap (4.27) largest; this term suffices to saturate the sum in (4.26). Hence we see that in this case the transition probability is determined by the energy gap within one Brillouin-zone at an avoided crossing

$$\delta\varepsilon := |\varepsilon_i + m_o\omega - \varepsilon_j| = \min_{m\in\mathbf{Z}} |\varepsilon_i + m\omega - \varepsilon_j|. \tag{4.28}$$

It is important to note that $\delta\varepsilon$ may be substantially smaller than the difference between those representatives that are continuously connected to the eigenvalues of H_0. Therefore the 'excitation energy' measured as the difference between static eigenvalues becomes irrelevant as has been discussed in detail in [9].

A quantitative description of the dynamics at an avoided crossing can be obtained from a two Floquet-state approximation. Again separating fast and slow time-dependence, the usual Landau-Zener calculations can be carried out and yield for the transition probability at an avoided crossing

$$P_{j\to i} = \mathrm{e}^{-\frac{\pi}{2}\eta} \tag{4.29}$$

where the dimensionless parameter η is given by

$$\eta = \left.\frac{\delta\varepsilon\,\delta\lambda}{\dot{\lambda}}\right|_{\lambda_c}, \tag{4.30}$$

and $\delta\lambda$ denotes the λ-interval in which the distance between the levels is enlarged by a factor of $\sqrt{2}$ (see Fig. 6). As could be expected the transition probability $P_{j\to i}$ is determined by a combination of spectral properties $\delta\varepsilon\cdot\delta\lambda$ and the velocity $\dot{\lambda}$; again the appearance of $\delta\varepsilon$, i.e. the spacing of Floquet indices within one Brillouin-zone, is decisive for a Landau-Zener transition among Floquet states [8, 9].

Let us now turn to the problem of highly excited hydrogen atoms entering a microwave cavity. Obviously, the time scale T_a necessary to ensure adiabaticity is of central importance. To estimate the order of magnitude of T_a, we again use the SSE model and model the slowly rising field 'seen' by the atom by

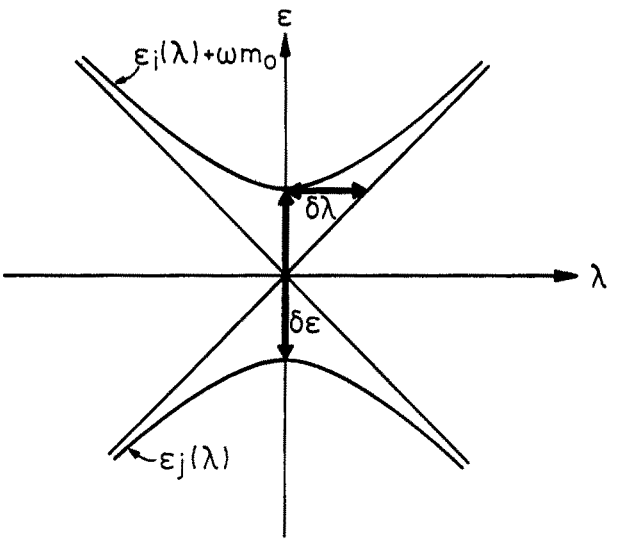

Fig. 6. Geometrical meaning of the parameters $\delta\varepsilon$, $\delta\lambda$ characterizing the $\varepsilon-\lambda$ hyperbolae

a gaussian

$$\lambda = \lambda(\tau) = \begin{cases} \lambda_f \exp\left(-\dfrac{\tau^2}{2T_a^2}\right), & \tau < 0, \\ \lambda_f, & \tau \geqq 0. \end{cases} \tag{4.31}$$

We then assume that for $\tau \to -\infty$ the stationary state with principal quantum number n_0 is populated and solve the Schrödinger equation (4.11); for $\tau = 0$, when the turn-on is completed, we perform a Floquet decomposition according to (4.21).

For a first application of this procedure we choose $\omega/2\pi = 9.92$ GHz, $n_0 = 64$ and $\lambda_f = 15$ V/cm. This is an example of an 'uncritical" case: From Fig. 5 we see that ε_{64} does not undergo an avoided crossing for $0 \leqq \lambda \leqq \lambda_f$. However, the level $n_0 = 64$ exhibits a substantial AC-Stark shift (in other terminology, the corresponding state is strongly 'dressed') and hence the Floquet state u_{64} at λ_f is considerably different from the initial stationary eigenstate φ_{64}. The result of the above described procedure for estimating T_a is shown in Fig. 7a where we have plotted $|a_{64}|^2$, the occupation probability of the Floquet state continuously connected to the initial stationary state, as a function of T_a.

We see that a switching-on time of only a few cycles results in almost complete adiabaticity and an almost *pure Floquet state* propagates for $\tau > 0$. Since even the very fast hydrogen atoms used in the experiments [21] see the fringe field for some 40 to 80 periods, adiabaticity can be taken for granted. Therefore, any model which neglects the effects of the fringe fields leads to definitively wrong results: A sudden turn-on of the field described by a θ-function determines the

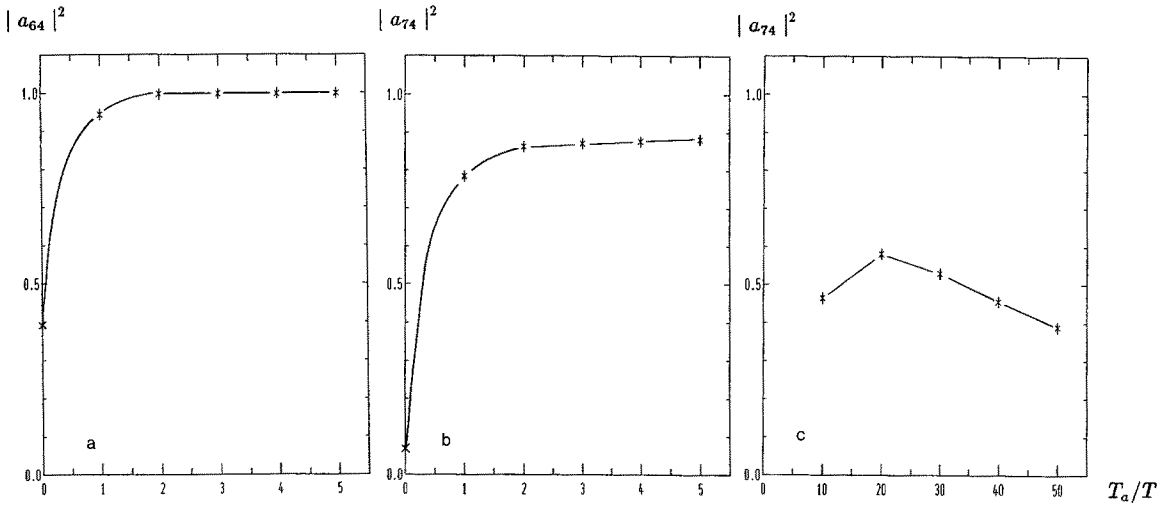

Fig. 7. a Occupation probability of the Floquet state continuously connected to the stationary initial state $n_0=64$ as a function of the switching-on time T_a (cf. (4.31), $T_a=0$ means a sudden, θ-function like turn-on) in units of the maser period T; $\lambda_f=15$ V/cm. **b** as **a**, but $n_0=74$ and $\lambda_f=7$ V/cm. **c** Occupation probability of the state marked by an arrow in Fig. 3b which seems to continue the initial state $n_0=74$ after several avoided crossings; $\lambda_f=9.95$ V/cm

amplitudes a_i in the decomposition (4.21) as the projections of the initial state on the final Floquet states at the moment of switching-on and hence the resulting wavefunction is a *superposition* of many Floquet states. The fact that this is not just a small error can be clearly seen from Fig. 7a: Whereas the initial state stays in its continuously connected Floquet state with probability $|a_{64}|^2>0.995$ for $T_a=2T$, a sudden turn-on yields $|a_{64}|^2\approx 0.39$.

We stress that the simple adiabatic behaviour shown in Fig. 7a becomes visible only as a result of the Floquet decomposition (4.21) and is completely obscured when decomposing with respect to stationary eigenstates of H_0.

However, the dynamics becomes more complicated when the field strength λ_f is enhanced: Above a critical value $\lambda_c(n_0)$, the quasienergy originating from the stationary state n_0 starts to exhibit *many* avoided crossings. For example, from Fig. 3b we read off $\lambda_c(74)\approx 8$ V/cm. Obviously, now many Landau-Zener transitions occur when, during the entrance into the cavity, $\lambda(\tau)$ exceeds $\lambda_c(n_0)$.

To illustrate this phenomenon, we perform calculations analogous to those leading to Fig. 7a for $n_0=74$ and $\lambda_f=7$ V/cm $<\lambda_c(74)$ (see Fig. 7b). Again, the steep rise of $|a_{74}|^2$ demonstrates the importance of adiabaticity; this time, however, convergence to 1.0 is not as rapid as in Fig. 7a since the final state already 'feels' the influence of other Floquet states close by in the Brillouin zone.

Next, we repeat this calculation using the same initial state $n_0=74$ but choose for the final field strength $\lambda_f=9.95$ V/cm $>\lambda_c(74)$ and plot the occupation probability of that state that seems to continue the initial one after several avoided crossings (marked by the arrow in Fig. 3b). In fact, this state has to be denoted by the principal quantum number $n=74$ since, after an avoided crossing, the Floquet states behave as if they had ignored the latter [22]. In Fig. 7c we observe a strong depopulation of that level: At each avoided crossing the jumping-probability (4.29) is diminished with increasing T_a. Therefore at each avoided crossing the wavefunction tends to stay on the continuously connected branch of the $\varepsilon-\lambda$ hyperbola, it has time to change and to take on the structure of the other Floquet state engaged in the avoided crossing. *Thus, it follows that adiabatic processes are responsible for transitions to higher states.*

5. Conclusions

The experimentally observed microwave ionization of highly excited hydrogen atoms poses serious problems to perturbative quantum mechanics: Since a conventional perturbative expansion in the field strength λ would require the inclusion of about 100 orders, a non-perturbative ansatz is needed.

A viable scheme is provided by the Floquet picture since it incorporates the external field in a non-

perturbative manner and furthermore allows for a clear description of adiabatic evolution. Any discussion of adiabatic dynamics has to start from an investigation of the spectral properties of a whole one-parameter family of quasi-hamiltonians

$$\mathscr{H}(\lambda), \quad 0 \leqq \lambda \leqq \lambda_f .$$

As our calculations show, up to certain critical values of the field strength adiabaticity completely determines the solution of Schrödinger's equation and holds down to time scales which are even shorter than those relevant for the experiments.

For a discussion of the ionization mechanism a restriction to the space spanned by the localized bound states seems to be insufficient, since there are no normalizable Floquet states. It is, however, possible to include continuum effects in a qualitative manner since it is plausible that the imaginary part of the complex Floquet indices describing the actual Floquet-resonances is larger for resonances originating from higher bound states of H_0. Hence we now regard our numerically calculated quasienergies for the SSE model as an approximation to the real part of the indices describing resonances and have to keep in mind an additional imaginary part determining their life-time.

Thus, the following picture of the microwave ionization of highly excited atoms finally emerges: A hydrogen atom prepared in a Rydberg state (with main quantum number n_0, say) which enters a microwave cavity sees a field which rises sufficiently slowly to guarantee adiabaticity to a very high degree. As long as the instantaneous field strength $\lambda(t)$ stays below a critical value $\lambda_c(n_0)$ which marks the onset of multiple avoided crossings, the initial state is adiabatically shifted into the continuously connected Floquet-resonance:

$$\varphi_{n_0}(x)\, e^{-iE_{n_0}t} \to u_{n_0}(x,t)\, e^{-i\varepsilon_{n_0}t}. \tag{5.1}$$

If the final field strength within the cavity is less then $\lambda_c(n_0)$, nothing happens: When the atom leaves the cavity, it is adiabatically shifted back into the initial state. The situation changes abruptly when, during the entrance into the cavity, the field strength $\lambda(t)$ reaches $\lambda_c(n_0)$: As described in Chap. 4, Landau-Zener type transitions among Floquet states take place. It is a characteristic feature of the SSE spectra that the first avoided crossings are not isolated but are followed in a rapid succession by further ones. Hence, if the final field strength λ_f is larger than $\lambda_c(n_0)$, the atom undergoes many Landau-Zener transitions already when entering the cavity. In this way Floquet states are populated which originate from higher lying stationary states and therefore have quasienergies with larger imaginary parts. Thus, as soon as these Landau-Zener transitions set in the Schrödinger wavefunction ψ becomes fast delocalizing, i.e. the atom ionizes.

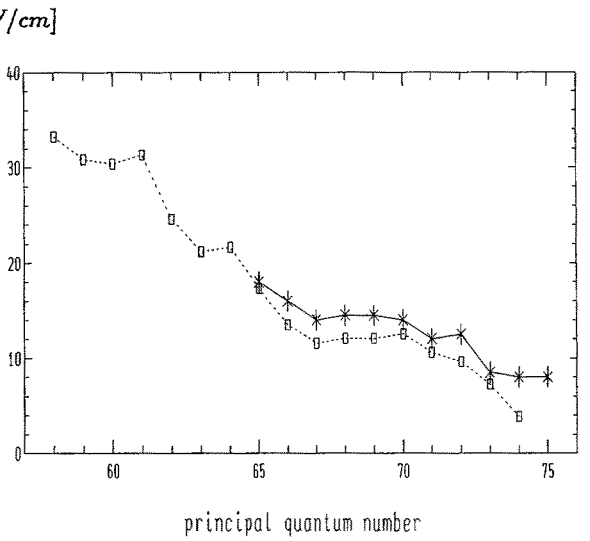

Fig. 8. Stars: Calculated critical field strength $\lambda_c(n)$ for the SSE model marking the onset of multiple avoided crossings ($\omega/2\pi = 9.92$ GHz). Boxes: Experimentally found 10%-ionization field strength (no static field superimposed); data taken from Fig. 2 in [21]

It should be emphasized that those transitions are non-perturbative and their probabilities are determined by the Brillouin-zone distance $\delta\varepsilon$ which is only a small fraction of the frequency ω. In contrast, time-dependent perturbation theory would demand the absorption of a huge number of photons to account for the ionization energy ΔE.

In order to treat the above discussed effects of the continuum in a mathematically consistent way one could employ the method of complex scaling introduced into the Floquet theory in [23].

However, there are implications of the above suggested ionization mechanism which can be checked even within our simple model: The occurence of the first avoided crossings must be related to the ionization threshold. Indeed, plotting the values $\lambda_c = \lambda_c(n)$ from our calculations we obtain Fig. 8 which shows that these critical values are remarkably close to the experimentally found 10%-ionization field strength [21]. Besides being a strong argument in favour of our Landau-Zener mechanism this fact a posteriori justifies the ansatz of concentrating on the bound state dynamics.

We stress that these Landau-Zener transitions occur during the rise of the external field which therefore

is essential for the preparation of the state that actually ends up in the cavity. Hence, to model the entrance into the microwave cavity by a time-dependence of the form

$$\lambda(t)=\lambda_f\,\theta(t)\sin(\omega t+\delta) \tag{5.2}$$

is too crude an approximation: First of all, (5.2) implies that an initial state φ_0 propagates as

$$\psi(x,t)=\sum_i a_i u_i\left(x,t+\frac{\delta}{\omega}\right)e^{-i\varepsilon_i t},\qquad t>0, \tag{5.3}$$

where the amplitudes

$$a_i=\left\langle u_i\left(x,\frac{T}{2\pi}\delta\right)\middle|\varphi_0\right\rangle \tag{5.4}$$

contain a rather unphysical dependence on the phase δ which expresses the fact that they are solely determined by the moment $t=0$ of switching-on. Needless to say, this artificial problem does not occur in an adiabatic approach.

Secondly, we have shown that excitation of higher Floquet states results from adiabatic evolution at avoided crossings. This important feature is completely ignored in approaches based on (5.2).

Notwithstanding these facts, the 'width function' approach of Blümel and Smilansky [7] has been shown to yield values for the ionization threshold which are in agreement with experimental data although the fringe fields are not taken into account. This is quite easy to understand: The width function measures the extent of Floquet states taken at fixed time $t=0$ (assuming an external field $\lambda\sin\omega t$). Obviously, the appearance of many avoided crossings is reflected in the structure of the instantaneous Floquet states and, hence, in the width function. Thus, critical field strengths can be determined from the width function as well as from the quasienergy spectrum. However, the underlying physical mechanism that we suggest is very different from that of Blümel and Smilansky: From their point of view, ionization should occur after population of high lying eigenstates of H_0 ('window states') and a Floquet state corresponding to a fixed field strength λ_f should serve to connect both the initial and the window states; the fringe fields play no rôle at all. In contrast, from our calculations we have to conclude that an initial state is adiabatically turned into a Floquet state when entering the fringe fields, at avoided crossings fast decaying Floquet states are populated.

The detailed investigation of the dynamics of highly excited hydrogen atoms in the fringe fields of a microwave cavity yields new physical insights, in particular, we expect measurable effects: Since the Landau-Zener 'jumping' probabilities (4.29) are affected by the precise form of the fringe fields, different fringe fields may lead to different occupation probabilities of the final Floquet states in the cavity and hence to different structures in the ionization signal. It will be very interesting to study the results of future experiments, where the fringe fields will be under control [24], from this point of view.

It is worthwhile to note that the simple expression (5.1) is essentially the quantum mechanical formulation of the 'stabilization mechanism' conjectured by Jensen [25] on the basis of classical calculations. Since this formula (5.1) is based on the adiabatic theorem of quantum mechanics it is valid for *any* value of the scaled frequency $n_0^3\omega$; however, the time scales necessary for full adiabatic behaviour are longer in near-resonant cases than in non-resonant ones.

Finally we should like to compare the quantum mechanical SSE model with its classical counterpart. It is well known that the classical SSE model exhibits chaotic behaviour above certain values of the coupling strength which furthermore coincide astonishingly well with the observed ionization threshold [21]. From our quantum calculations we conclude that this same threshold corresponds to a change in the quasienergy spectra from regular to irregular, i.e. from smooth λ-dependence to an irregular avoided crossing structure. Hence we see that there is a deep connection between the character of the classical trajectories and the structure of the quantum mechanical quasienergy spectra.

Such a connection has often been found for time-independent hamiltonians and in particular been verified for the case of a hydrogen atom in a static magnetic field [26]; our investigations indicate that it is also true in the Floquet picture for periodically time-dependent hamiltonians. (For a discussion of this subject, see also [27].)

Again, it is instructive to study the harmonic oscillator in this context: Of course the classical version is integrable and the Floquet spectrum (2.16) exhibits no avoided crossings.

In order to understand the role of the classical orbits we construct the classical analogue of the quasi-hamiltonian $\mathscr{H}=H(t)-i\partial_t$. As we have seen, within the Floquet picture $-i\partial_t$ has to be regarded as the momentum p_t conjugated to the time coordinate t. Hence we write for the classical quasi-hamiltonian:

$$\mathscr{H}_{cl}=H(t)+p_t. \tag{5.5}$$

Since periodicity is imposed on the time t, the dimensionless quantity ωt must be interpreted geometrically as angle coordinate with period 2π. Thus the

phase space of the system is the cotangent bundle of an infinite cylinder.

After transforming (5.5) to action-angle coordinates the usual EBK quantisation rules [28] can be applied to yield the semi-classical Floquet indices.

As an example for this procedure we consider the classical counterpart of the driven oscillator

$$\mathscr{H}_{cl}=\frac{1}{2\mu}p_x^2+p_t+\frac{\mu\omega_0^2}{2}x^2+\lambda x\sin\omega t. \tag{5.6}$$

Performing a canonical transformation to action-angle-variables

$$(p_x, x; p_t, t)\to(I_0, \varphi_0; I, \varphi) \tag{5.7}$$

we obtain

$$\mathscr{H}_{cl}=\omega_0 I_0+\omega I+\frac{\lambda^2}{4\mu}\frac{1}{\omega^2-\omega_0^2}. \tag{5.8}$$

Quantising the libration

$$I_0=n+\tfrac{1}{4}\alpha_l$$

with Maslov-index $\alpha_l=2$ and the rotation

$$I=m+\tfrac{1}{4}\alpha_r$$

with Maslov-index $\alpha_r=0$ we immediately recover the exact quantum mechanical formula (2.16).

This method may serve as a viable procedure for investigating the semi-classical limit of periodically driven quantum systems. It should be clear that anharmonicities in the potential of H_0 produce formidable difficulties, i.e. chaos in the classical case and avoided crossings originating from a resonance point as in Fig. 4 in the quantum case.

As a concluding remark we stress the generality of our results. Although we use the model of Rydberg atoms in strong microwave fields to support our considerations they are also relevant for other periodically driven quantum systems, for instance matter interacting with strong laser fields.

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