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**A quairesonant smoothing algorithm  
for the fast analysis of  
selective vibrational excitation**

# A QUASIRESONANT SMOOTHING ALGORITHM FOR THE FAST ANALYSIS OF SELECTIVE VIBRATIONAL EXCITATION

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**Abstract.** One key problem in modern chemistry is the simulation of the dynamical reaction of a molecule subjected to external radiation. This is described by the Schrödinger equation, which, after eigenfunction expansion, can be written in form of a system of ordinary differential equations, whose solutions show a highly oscillatory behaviour. The oscillations with high frequencies and small amplitudes confine the stepsizes of any numerical integrator – an effect, which, in turn, blows up the simulation time. Larger stepsizes can be expected by averaging these fast oscillations, thus smoothing the trajectories. This idea leads to the construction of a quasis resonant smoothing algorithm (QRS). In QRS, a natural and computationally available splitting parameter  $\delta$  controls the smoothing properties. The performance of QRS is demonstrated in two applications treating the selective excitation of vibrational states by picosecond laser pulses. In comparison with standard methods a speedup factor of 60–100 is observed.

A closer look to purely physically motivated quasis resonant approximations such as WFQRA shows some additional advantages of the above smoothing idea. Among these the possibility of an adaptive formulation of QRS via the parameter  $\delta$  is of particular importance.

**Key Words.** averaging, smoothing, quasis resonant, vibrational excitation, selectivity, laser pulse

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**1. Introduction.** In the last years phrases like *Molecular Modelling* appear in nearly all discussions about the future of chemistry. In most of the processes constructed to model molecules the interaction of light with the considered molecule is a fundamental part. More exactly those processes depend on an exact knowledge how external radiation effects the internal excitation or the dynamical structure of the molecule. The key equation for the description of the dynamical behaviour of the molecule is the time dependent Schrödinger equation

$$(1) \quad i\hbar \partial_t \psi = H\psi$$

where  $H$  is the Hamiltonian of the whole system. For the largest class of problems from real life applications it is reliable to assume that the molecule–light interaction is quasiclassical (i.e.  $H = H_0 + H_{\text{int}}$ ) and that the pure molecular problem (i.e. the eigenproblem  $H_0\Phi = E\Phi$ ) has been solved in a first step (by experimental data or numerical means). In this situation eigenfunction expansion shows (1) to be equivalent to a system of ordinary differential equations (ODE):

$$(2) \quad i \partial_t a = (\Omega + g(t)V) a,$$

with  $a = (a_1, \dots, a_n) \in C$ , a diagonal and possibly complex matrix  $\Omega$ , and a real, but dense one  $V$ , and with  $g$  modelling the external radiation field. In the presented form (with  $\Omega, V$  and  $g$  being optional within the given scope) (2) describes a wide family of problems, whose common property is the highly oscillatory behaviour of the solutions of its members. Let us call (2) the *fundamental equation of motion*.

In nontrivial cases the computational effort of solving (2) is enormous. But fundamental equations should be solvable with utmost efficiency. Many users from physics or chemistry apply simple explicit Runge–Kutta methods with fixed stepsizes to integrate (2). But there are several ideas to gain efficiency: Floquet theory, quasiresonant approximations, ... (see e.g. [6], [9]). They all were invented treating problems with real  $\Omega$  and  $g(t) = E_0 \cos \omega t$ . Their transferability to a wider subclass of (2) is either little investigated or questionable. However, from the point of view of numerical mathematics one is interested in an *efficient tool for solving a sufficiently large subclass of (2)* with an in some sense guaranteed exactness of its results.

Section 2 of this article will give a more detailed derivation of (2) for the special case of the interaction of the vibrational states of single OH– and HOD–molecules with monochromatic light. These two problems will be used as examples to point out the following observations, which can be made in a very vast class of problems from application:

1. The solutions of (2) show oscillations with high frequencies and small amplitudes around average trajectories.
2. These fast oscillations confine the stepsizes of any numerical integrator, which, in turn, blows up the computation times.
3. For all practical means the knowledge of the average trajectories is sufficient.

Hence: Larger stepsizes can be expected by averaging the fast oscillations, thus *smoothing* the trajectories. On this background the *central task* this article deals with is:

*Construct a smoothing algorithm, which increases the efficiency of the numerical integration of (2) by computing the average trajectories only.*

In section 3 I will give a more precise and mathematical formulation of this task. As a first step to a solution a *quasiresonant smoothing algorithm* (QRS) will be motivated and constructed (starting with the smoothing idea). Its usefulness as an efficient solver for a sufficiently large subclass of (2) will be demonstrated.

It was no accident that the interaction of the vibrational structure of OH and HOD with monochromatic light was chosen as the example. Following Paramonov et al. (e.g. [8], [7]) the selective vibrational excitation of single bounds in simple molecules using ultrashort laser pulses is broadly discussed today. A tool for increasing the selectivity in such a process is the optimization of the parameters of the driving laser pulse. In the optimization procedure one must solve (2). Thus, this is a good example for the use of simulation processes based on our fundamental equation of motion. Hence with a little overstatement we can call the OH- and HOD-examples 'real life applications'.

Not for nothing QRS is named *quasiresonant*. Section 4 will introduce and generalize the most common quasiresonant method WFQRA (Weak Field QuasiResonant Approximation). We will see fundamental structural similarities between WFQRA and QRS, in particular with regard to smoothing. But WFQRA was physically motivated as a method giving in some sense approximate solutions of (2). I see no way (apart from 'having physical or chemical experiences') in which this 'in some sense' could guarantee the exactness of the results (an example is given). QRS, in its formulation presented here, works more reliable and more efficient, but cannot give any guarantees, too. But together with the smoothing idea it opens the door for an adaptive formulation via the parameter  $\delta$  – an adaptivity which permits the construction of an error control.

In section 5 the performance of QRS and WFQRA is demonstrated in the OH- and HOD-problems. In these examples a speedup factor of 60-100 is observed for QRS.

## **2. A derivation of the equation of motion for monochromatic radiation.**

The physical systems we consider are samples of dilute gas molecules subjected to strong, monochromatic infrared laser radiation. We are only interested in the population dynamics of a set of discrete states during the interaction of a single molecule with the external laser field. This set of states may be a discrete part of the vibrational or rotational ones.

*The equation of motion.* Then in a standard way (electric dipole approximation), we can write the molecular Hamiltonian in the form

$$(3) \quad H = H_0 + H_1$$

$$(4) \quad H_1 = -\vec{\mu} \cdot \vec{E}$$

where  $H_0$  is the pure molecular Hamiltonian, neglecting the field  $\vec{E}(t)$ .  $\vec{\mu}$  is the molecular dipole moment operator. For monochromatic radiation we can write

$$(5) \quad E(t) = f(t) \cos \omega t$$

with the pulse form function  $f$ , which in comparison to the light oscillations  $\cos \omega t$  is a slowly varying function. We may choose  $f \equiv \text{const}$  to describe a constant light source or  $f$  as the pulse form function in order to model a short laser pulse.

We consider the pure molecular problem to be solved:

$$H_0 \varphi_k = \epsilon_k \varphi_k$$

with discrete and countable eigenvalues  $\epsilon_k$ ,  $k \in J \subseteq N$ . For simplicity let us consider  $J$  as finite, so  $k = 0, \dots, n$ .

The key for the description of the population dynamics is the time dependent Schrödinger equation:

$$(6) \quad i\hbar \partial_t \psi = H\psi.$$

Expanding the wave function  $\psi$  of the sample in the basis of the molecular eigenfunctions  $\varphi_k$

$$(7) \quad \psi = \sum_k a_k \varphi_k,$$

we can deduce an equivalent ODE-form of Schrödinger's equation:

$$(8) \quad i\hbar \partial_t a = (\Omega + f(t) \cos(\omega t) V) a$$

using the assumption  $\vec{E}(t) \parallel \vec{\mu}$  with  $\vec{\mu} \cdot \vec{E} = f(t) \cos(\omega t) \mu$ .  $a = (a_k)$  is the (complex) vector of the expansion coefficients,  $\Omega$  the real and diagonal matrix of the molecular eigenvalues  $\Omega = \text{diag}(\epsilon_0, \dots, \epsilon_n)$  and  $V = (V_{kl})$  the dipole matrix defined by:

$$(9) \quad V_{kl} = - \langle \varphi_k | \mu | \varphi_l \rangle.$$

In addition, let us assume that the values in  $V$  can be evaluated by use of experimental data or computational results. This is reasonable for all kinds of e.g., pure rovibrational problems. Normally (8) is given in the standard form

$$(10) \quad i \partial_t a = (\Omega + f(t) \cos(\omega t) V) a$$

transformed to *dimensionless units* by the substitutions:

$$(11) \quad \begin{aligned} t &\leftrightarrow \frac{\epsilon_0}{\hbar} t \\ \Omega &\leftrightarrow \frac{1}{\epsilon_0} \Omega \\ V &\leftrightarrow \frac{1}{\epsilon_0} V \\ \omega &\leftrightarrow \frac{\hbar \omega}{\epsilon_0} \end{aligned}$$

For simplicity the old symbols are held, but divergently let us write

$$\begin{aligned} \Omega &= \text{diag}(\omega_0, \dots, \omega_n) \quad \text{with} \\ \omega_k &= \frac{\epsilon_k}{\epsilon_0}. \end{aligned}$$

Physically the expansion coefficients are not observables. Only the populations  $p_k$  of the molecular eigenstates are measurable. They are given by the probabilities

$$(12) \quad p_k(t) = |\langle \varphi_k | \psi \rangle|^2 = |a_k|^2.$$

Hence it is more than sufficient for our task to know the expansion coefficients  $a(t) = (a_k(t))$  or any *unitary* transformed set of coefficients  $\bar{a} = U a$  (unitary  $U$  with  $U^*U = 1$ ). Another important property of equation (10) is the *number conservation*

$$(13) \quad \sum_{k=0}^n |b_k|^2 = \langle \psi | \psi \rangle = 1,$$

which is inherited from the Schrödinger equation.

Equation (10) can be transferred into the interaction picture by

$$(14) \quad b(t) = D(t)a(t)$$

with the unitary diagonal matrix  $D(t) = \exp(i\Omega t)$ . Written in components the result is

$$(15) \quad i \partial_t b_m = f(t) \cos(\omega t) \sum_{k=0}^n V_{mk} b_k \exp(i(\omega_m - \omega_k)t).$$

Equation (10) becomes an initial value problem introducing the initial condition

$$(16) \quad a_k(0) = \frac{1}{2}(1 + i) \delta_{k0}$$

which (by *phase choose*) results from the assumption that at  $t = 0$  all systems occupy the ground state:

$$(17) \quad |a_k|^2(0) = \delta_{k0}$$

*Two application problems.* The two application problems in which the work of the presented algorithm will be demonstrated are

1. the selective excitation of the 5th vibrational state of a single OH-bound with an optimal parameterized picosecond laser pulse and
2. the selective vibrational excitation of the OD-bound in HOD via an analogue process.

For both problems the modelling can be done as explained above with (10) as the equation of motion for the populations. To get the data for  $V$  and  $\Omega$  the oscillating bounds are modelled by Morse potentials (see Fig. 1) and the necessary computations are done in accordance with [4].

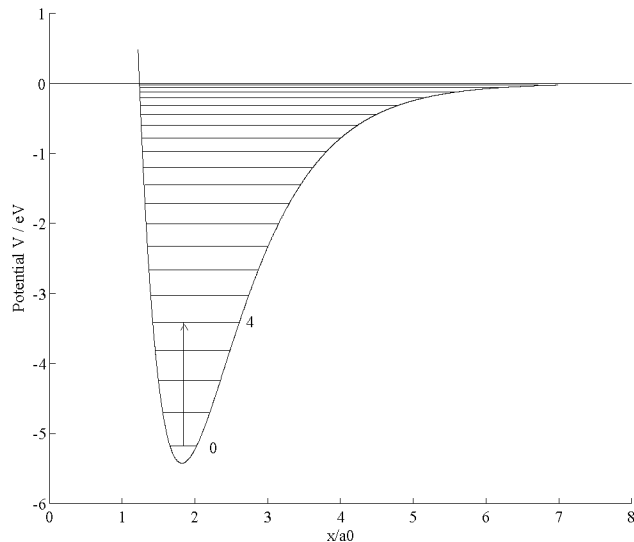


FIG. 1. Morse potential and vibrational eigenstates of an OH-bound

The model for the laser pulses has been  $\sin^2$ -shapes, written in the time coordinate of (10) as:

$$(18) \quad f(t) = E_r \sin^2(\eta t)$$

with  $\eta = \frac{\pi\hbar}{\tau\epsilon_0}$  for pulse length  $\tau = 1\text{ps}$ . Hence physically we have got two free parameters in (10): light frequency  $\omega$  and field strength  $E_r$ . In the second problem (HOD) the coupled vibrational states are numbered in energetic order. In this order the selected quasi pure OD-vibration state with quantum number (0,7) gets the number 23 while the ground state (0,0) is numbered 0. Hence problem 2 can be formalized as: *Find  $\omega$  and  $E_r$  so that  $p_{23}(\tau) = |c_{23}|^2(\tau)$  becomes maximal.* To compute  $|c_{23}|^2(\tau)$  for some pair  $(\omega, E_r)$  one has to solve (10) or an equivalent problem.

*Remarks.* The demand for the spectrum of  $H_0$  to be discrete can be weakened without losing (10) as the equation of motion. According to [10] we can consider the



existence of decay into continua by allowing for complex eigenenergies with decay width  $\gamma_k$

$$\epsilon_k = \Re(\epsilon_k) + i \gamma_k$$

leading to a complex  $\Omega$ . This gives us another link between (10) and its generalized form (2). Naturally we need not confine our derivation of (10) to the case of monochromatic light. This is done for simplicity only. Another possibility of choosing  $g$  in (2) could be

$$(19) \quad g(t) = \sum_k f_k(t) \cos \mu_k t$$

modelling the case of a mixture of several frequencies.

**3. Quasiresonant Smoothing.** Let us take the situation in problem 1 as a typical situation for the data  $\Omega, V$  in equation (10). In addition let us assume, that we want to solve this equation by use of a numerical integrator. So our first question is: *How can we find a computationally cheap solution of (10) using integrators.*

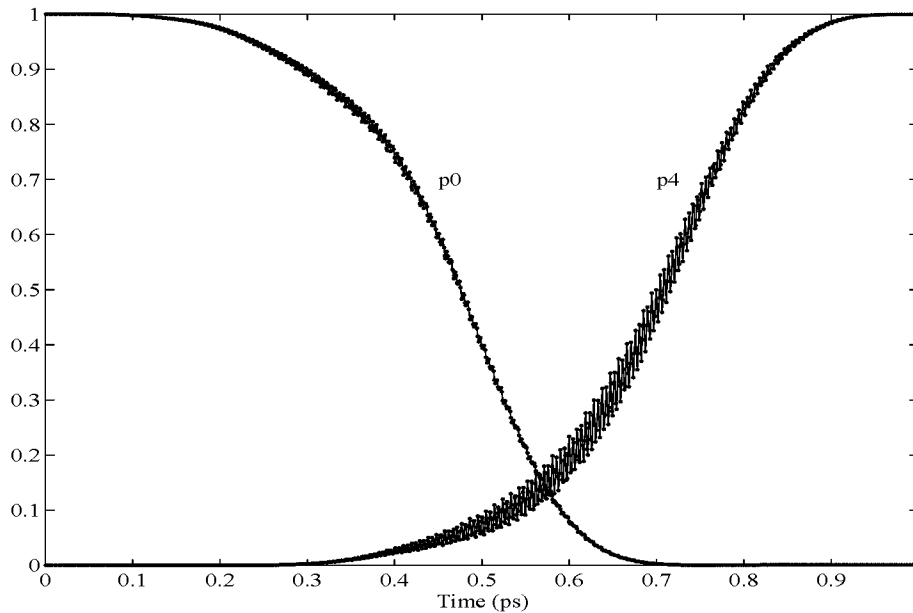


FIG. 2. Population dynamics for states 0 and 4 for OH with optimal laser parameters

To answer this we can take a closer look to Fig. 2, which shows data from the exact solution of (10) with the OH-data from problem 1 using the optimal laser parameters for this process. We see the population  $p_0 = |c_0|^2$  of the ground state dying out and the evolution of the desired full occupation  $p_4(\tau) = 1$ . Most of the high computational

effort of this solution is caused by the oscillations with high frequencies and small amplitudes: they force the integrator to choose very small time steps. At least this becomes clear if we take a look at Fig. 3. The complicated oscillatory time dependence of the populations can be found in the single coefficients  $c_k$ , too.

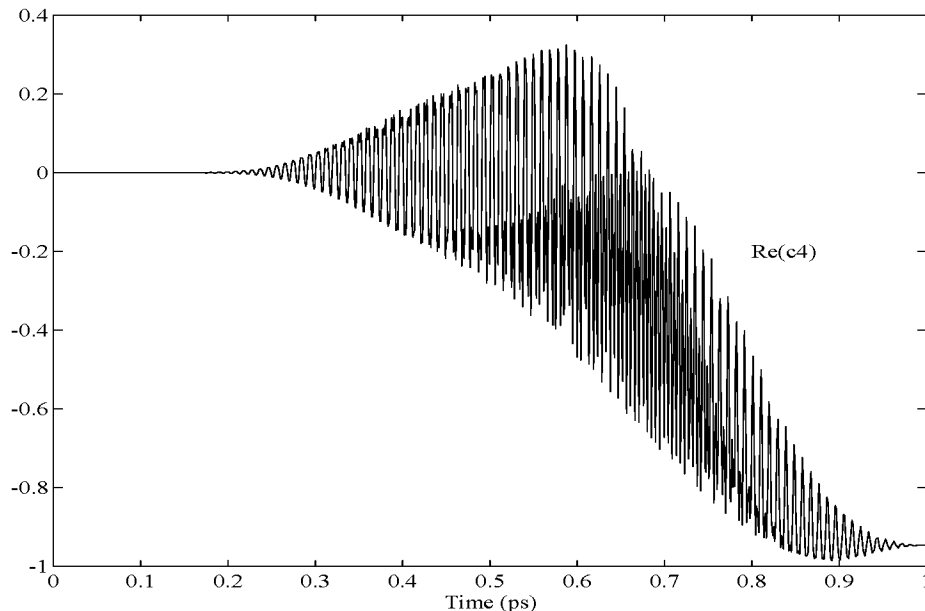


FIG. 3. Dynamics of coefficient  $\text{Re}(c_4)$  for OH. Same parameters as in Fig. 1

Physically, in the most cases, namely for the class of problems above, the knowledge of the averaged trajectories of the populations  $p_k = |c_k|^2$  would be sufficient. The local time average of the populations can be defined introducing an *average-operator* like

$$(20) \quad (\mathcal{A}_T p_k)(t) = \frac{1}{2T} \int_{t-T}^{t+T} |c_k|^2(s) ds$$

with  $T$  big enough in comparison with the fast oscillation's periods. In our OH-example we are getting some behaviour as shown in Fig. 4.

Hence one should reformulate our problem the following way  
*Replace equation (10) by a similar one, whose  $p_k$ -solutions are good approximations of the averaged  $p_k$ -solutions of (10).*

Later on this 'similar one' will be called *smoothed equation*. If this problem could be managed the integrator would make larger time steps and we can expect a gain in efficiency for the simulation. We should call  $q_k$  a good approximation of  $p_k$  if at least for some norm:

$$(21) \quad |\mathcal{A}_T q_k - \mathcal{A}_T p_k| < \text{TOL},$$

with a chosen tolerance  $\text{TOL} > 0$ . In this section I will present a heuristical solution of the reformulated problem. For this purpose a few agreements on some notations should

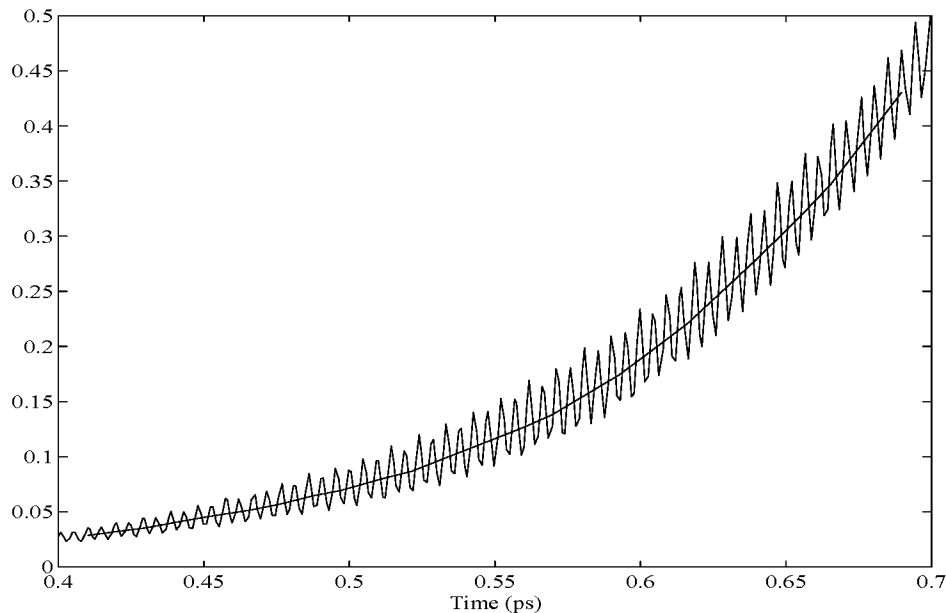


FIG. 4. Section from Fig. 2:  $p_4$  and its local time average

precede.

*Cutting smoothers.* Let us denote the set

$$(22) \quad L := \{f : R \rightarrow R \mid f(t) = \sum_k \alpha_k \exp(i\eta_k t) \text{ with } \eta_k \in R, \alpha_k \in C\}.$$

For simplification of the heuristical reasoning let us assume that in the following the functions we want to smooth are such sums of  $\exp(i\cdot)$ -terms from  $L$ . For  $\mu > 0$  the operation

$$G_\mu : L \rightarrow L$$

$$(23) \quad \begin{aligned} f(t) = \sum_k \alpha_k \exp(i\eta_k t) & \mapsto \\ (G_\mu f)(t) & = \sum_{\substack{k \\ |\eta_k| \leq \mu}} \alpha_k \exp(i\eta_k t) \end{aligned}$$

can be called a 'cutting smoother'.

*Heuristical smoothing.* Using  $\cos \omega t = \frac{1}{2}(e^{i\omega t} + e^{-i\omega t})$  and the definition

$$\Delta_{mk} := \omega_m - \omega_k$$

one can rewrite our dynamical equation (15) (interaction picture):

$$(24) \quad i \partial_t b_m = \frac{1}{2} f(t) \sum_{k=0}^n V_{mk} b_k \left( e^{i(\Delta_{mk} + \omega)t} + e^{i(\Delta_{mk} - \omega)t} \right).$$

Hence a simple choice of a good class of equations for searching a 'smoothed equation' is

$$(25) \quad i \partial_t d_m = \frac{1}{2} f(t) \sum_{k=0}^n \left( A_{mk}^+ e^{i(\Delta_{mk} + \omega)t} + A_{mk}^- e^{i(\Delta_{mk} - \omega)t} \right) d_k.$$

If we assume  $d_k \in L$ ,  $d_k(t) = \sum_l \alpha_l^{(k)} \exp(i\eta_l t)$ , one obtains from (25) by integration:

$$(26) \quad d_m(t) = d_m(t_0) + \frac{f(t)}{2} \sum_{k=0}^n \sum_l \alpha_l^{(k)} \left( A_{mk}^+ I_{mk,l}^+ + A_{mk}^- I_{mk,l}^- \right)$$

with

$$(27) \quad I_{mk,l}^\pm(t, t_0) = -\frac{i}{\eta_l + \Delta_{mk} \pm \omega} \exp(i(\eta_l + \Delta_{mk} \pm \omega)t) \Big|_{t_0}^t.$$

If the  $d_m$  should have smooth trajectories, i.e. if  $d_m = G_\mu d_m$  should hold for some small  $\mu$ , all  $I_{mk,l}^\pm$  with  $\Delta_{mk} \pm \omega \gg \mu$  must vanish. The simplest choice in order to realize this is

$$(28) \quad A_{mk}^\pm(\delta) = \begin{cases} V_{mk} & : |\Delta_{mk} \pm \omega| < \delta \omega \\ 0 & : \text{otherwise} \end{cases}$$

where  $\delta \geq 0$  is a free parameter.

This observation already gives the rather simple idea of the QRS( $\delta$ ) algorithm (Quasi-Resonant Smoothing):

- Choose  $\delta$  heuristically by physical insight (see below).
- For this  $\delta$  compute a smooth solution  $d$  of (25) with data (28).
- take  $d$  as an approximation for  $G_\mu b$  and take  $|d_m|^2$  as an approximation for the smoothed populations  $|b_m|^2 = |c_m|^2$  to be computed from (10).

*Interpretation.* Choosing a small  $\delta \in (0, 1)$  the matrices  $A^\pm(\delta)$  only consist of the *quasi-resonant* elements in  $V$ : For those  $\delta$  we can interpret the condition

$$(29) \quad |\Delta_{mk} \pm \omega| < \delta \omega$$

as a choice of pairs of states  $(m, k)$  between which the light field  $\omega$  can induce a quasi first order transition. Therefore the effect of the pulse form function  $f$  (which is slowly varying in comparison to  $\cos \omega t$ ) can be understood as the effect of a splitting of the inducing light frequency  $\omega$ . This splitting causes a softening of the hard first order transition condition

$$|\Delta_{mk}| \simeq \omega$$

to a condition like (29). Hence only those elements  $V_{mk}$  have to be considered, which belong to interactions fulfilling (29).  $\delta$  has to be chosen in a way which reflects these connections. Let us write

$$B(\delta) := \{(m, k), \quad |\Delta_{mk} \pm \omega| < \delta \omega\}.$$

*Remarks.* In addition to the given smoothing heuristics one can try to take equation (24) and operate with integral smoothers (see (21)) on it. Together with some heuristical assumptions one gets a result for the 'smoothed equation' very similar to (25). Naturally these assumptions forbid the cases of neglecting too big dipole elements in  $V$ , i.e. there must not be states  $(j, l) \notin B$  with  $V_{jl} \gg \max_{(m,k) \in B} V_{mk}$ .

**4. Quasiresonant Approximations.** The quasiresonant approximation (often called *rotating wave approximation*) has been attacked by many authors. I only mention [9] and [10], where it is called more exactly *weak field quasiresonant approximation* (WFQRA), and the references cited herein. It was discussed as an efficient method for the solution of equation (10) in the case of pure coherent, monochromatic light, i.e. for constant  $f(t) \equiv E_r$ . Here, after a short introduction to WFQRA, a proposal will be made how it can be generalized in order to use it as an approximative algorithm for solving (10) with time-dependent  $f$ .

*Standard WFQRA.* Let us rewrite equation (15) as

$$(30) \quad i \partial_t b_m = \frac{1}{2} f(t) \sum_{k=0}^n V_{mk} b_k \exp(i D_{mk} t) (1 + \exp(2i \operatorname{sgn}(\Delta_{mk}) \omega t)),$$

using the notion

$$D_{mk} := \Delta_{mk} - \operatorname{sgn}(\Delta_{mk}) \omega.$$

From this we come to

$$(31) \quad i \partial_t b_m = \frac{1}{2} f(t) \sum_{k=0}^n V_{mk} b_k \exp(i D_{mk} t),$$

neglecting the high frequency term  $\exp(2i \operatorname{sgn}(\Delta_{mk}) \omega t)$ . According to [10] this is valid (in the sense of getting a 'good approximation') if the two conditions

$$(32) \quad f(t) V_{mk} \ll \omega,$$

$$(33) \quad D_{mk} \ll \omega$$

are fulfilled.

We can introduce the *level scheme integer*  $N_k$  by defining it as that integer which fulfills

$$(34) \quad \omega_k = N_k \omega + x_k \quad \text{with} \quad -\frac{\omega}{2} < x_k \leq \frac{\omega}{2}.$$

Hence equation (31) gets the form

$$(35) \quad i \partial_t b_m = \frac{1}{2} f(t) \left( \sum_{\substack{k \\ |N_m - N_k| = 1}} V_{mk} b_k e^{i(x_m - x_k)t} \right. \\ + \sum_{\substack{k \\ |N_m - N_k| = 0, 2}} V_{mk} b_k e^{i(x_m - x_k)t} e^{\pm i \omega t} \\ \left. + \text{terms with } e^{\pm m i \omega t}, m = 2, 3, \dots \right).$$

Now a second approximation is made by removing all terms with  $|N_m - N_k| \neq 1$ . Following [10] again this shall be valid approximately if the conditions (32) are fulfilled. However this may be, let us do this approximation and write

$$(36) \quad i \partial_t b_m = \frac{1}{2} f(t) \sum_{k=0}^n B_{mk} b_k \exp(i(x_m - x_k)t)$$

with the sparse dipole matrix

$$(37) \quad B_{mk} = \begin{cases} V_{mk} & : \quad |N_m - N_k| = 1 \\ 0 & : \quad \text{otherwise} \end{cases}.$$

At least this can be brought into an interesting form by defining

$$(38) \quad X := \text{diag}(x_1, \dots, x_n)$$

$$(39) \quad a := \exp(-i X t) b.$$

We finally obtain a system

$$(40) \quad i \partial_t a = \left( X + \frac{1}{2} f(t) B \right) a$$

which in the case  $f(t) \equiv E_r$  becomes a system with constant coefficients. Originally this property was the main success of this form of WFQRA: If the approximation is valid one can answer questions for  $|c_m|^2(\tau) = |b_m|^2(\tau) = |a_m|^2(\tau)$  for a certain  $\tau$  by solving (40) directly:

$$(41) \quad a(\tau) = \exp(-i(X + \frac{1}{2} E_r B)\tau) a(0),$$

The right side of (41) can be computed very efficiently by diagonalization, because  $X + \frac{1}{2} E_r B$  is real and symmetric.

In our case of time dependent  $f$  the most efficient direct evaluation of (36) or (40) can be done by integrators.

A generalization of WFQRA. Starting from (35) we can enlarge the WFQRA algorithmic idea, getting the family of methods WFQRA(M):

- Choose an index  $M$ .
- Find an approximation by solving

$$(42) \quad i \partial_t b_m = \frac{1}{2} f(t) \sum_{\substack{k \\ ||N_m - N_k| - 1| \leq M}} V_{mk} b_k e^{i(x_m - x_k)t} e^{i(N_m - N_k)\omega t}.$$

Then the effective dipole matrix is

$$B^{(M)} = \begin{cases} V_{mk} & : \quad ||N_m - N_k| - 1| \leq M \\ 0 & : \quad \text{otherwise} \end{cases}$$

with  $B^{(0)} = B$  from the original WFQRA equation. The form in which the sparse matrix  $B^{(M)}$  is given shows a wide structural similarity of WFQRA to the QRS smoothing algorithms.

*Remark.* Obviously in the case of usual rovibrational spectra and infrared radiation the second condition in (32) can never be fulfilled. In [10] this point is discussed. Therein the result is: Only (32.1) is useful and that only as an *advice* for the usefulness of WFQRA as an approximation method.

**5. Numerical experiments.** Now, let me demonstrate the performance of QRS and WFQRA in the two application problems from section 2:

- Excitation  $0 \rightarrow 4$  for OH (dimension of the ODE–system: 44)
- Excitation  $0 \rightarrow 23$  for HOD (dimension: 120)

As integrator for calculations leading to the exact solutions I have already used the extrapolation code DIFEX (for details of implementation and availability see [3]) with adaptive control of order and stepsize (for numerical details see [1] and [2]). Looking at the figures you will remark dots at some trajectories. They serve as marks for each single time step of the integrator.

In the following figures the exact trajectories for some populations and coefficients are compared with their counterparts computed with  $\text{QRS}(\delta)$ . In the most cases the optimal data for  $\omega, E_r$  are chosen as laser parameters (OH:  $\omega = 0.8866, E_r = 3.641$ ; HOD:  $\omega = 0.8975, E_r = 7.55$  in the dimensionless units given above). The  $\delta$ –values have been  $\delta = 0.4$  (for OH) and  $\delta = 0.7$  (for HOD).

In addition, exact data will be given for a comparison of the computational effort of the different algorithms presented above. Two tables embody the effort observed by the solution of the OH– (Table 1) and the HOD–problem (Table 2). The effort is measured by

- the needed number of evaluations of the right hand side of the solved ODE,
- the time the computation needs on a SUN sparc station IPX.

Measured in realtime the speedup factor of QRS compared with DIFEX is about 100 (OH) and 60 (HOD), respectively. Measured in the number of evaluations it is 20 and 6. The difference is caused by the fact that QRS uses a sparsed dipole matrix, which decreases the effort of each evaluation of the right hand side in comparison with the original situation. The effort of the respectively 'right' WFQRA(M) is always a factor 2–3 higher as that of QRS.

### 5.1. The OH–example.

*Results for QRS in the OH–example.* In Fig. 5 and Fig. 6 the exact and the QRS–trajectories basing on the OH–data are plotted. Comparing them you can observe the QRS–integrator choosing much bigger stepsizes. For  $\text{QRS}(0.4)$ , compared with an efficient exact solver, a speedup of about a factor 100 is obtained. For more information about the computational effort see Table 1 below.

*Results of WFQRA in the OH–example.* Taking the data of the OH example even the original WFQRA(0) gives about the same solutions for the populations  $p_k$  as  $\text{QRS}(0.4)$  does. In particular you can take Fig. 6 as the graphical output of WFQRA(0) in this case. Thus both, WFQRA(0) and QRS, compute a smoothed solution via a quasiresonant sparsing of the dipole matrix. But the computational effort for WFQRA(0) is about a factor 2 higher than that of  $\text{QRS}(0.4)$ .



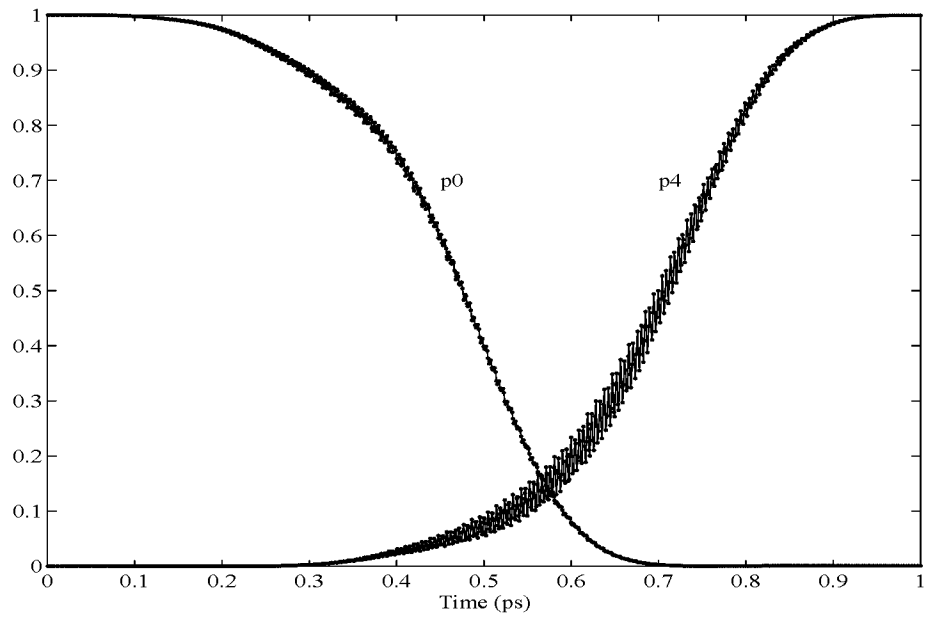


FIG. 5. Population dynamics for states 0 and 4 for OH with optimal laser parameters

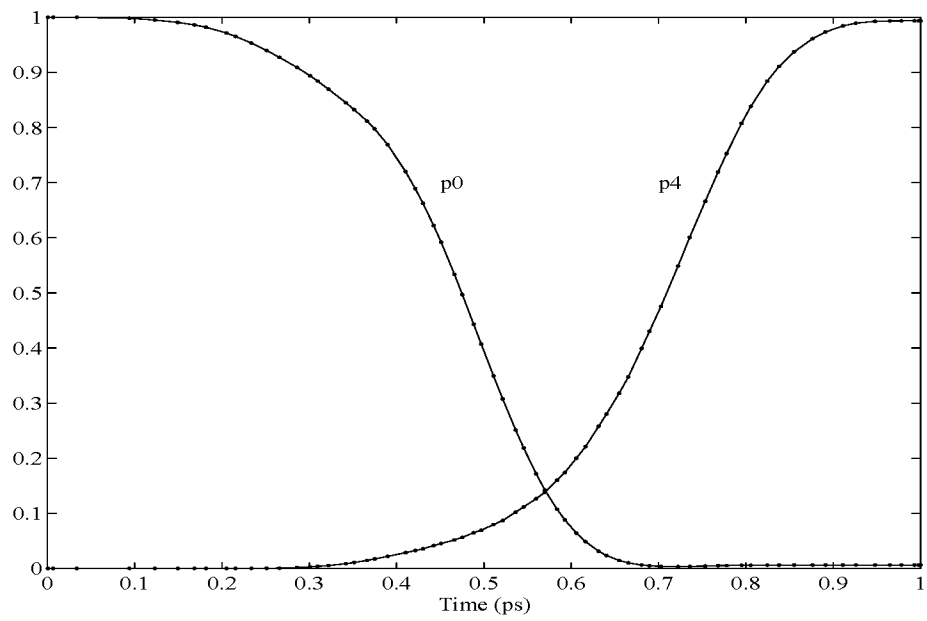


FIG. 6.  $QRS(0.4)$  population dynamics for states 0 and 4 for OH with optimal laser parameters

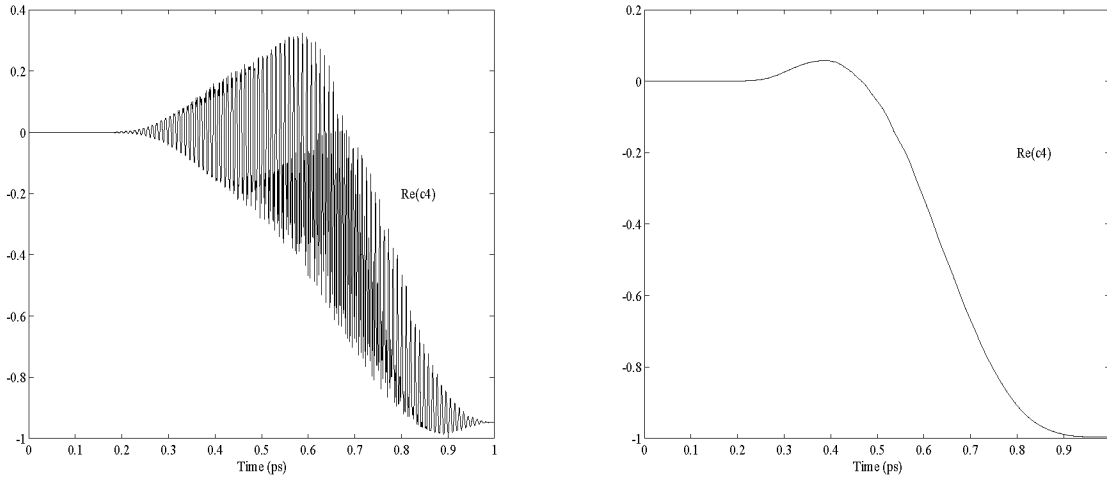


FIG. 7. Exact and QRS(0.4) dynamics of coefficient  $Re(c_4)$  for OH.

## 5.2. The HOD-example.

*Results for QRS in the HOD-example.* In this example QRS(0.7), if compared with an efficient exact solution, decreases the computational effort by a factor 60 (see Table 2). Fig. 8 and Fig. 9 show the plotted exact and QRS results. Obviously QRS works as a smoothing algorithm in the sense of equation (21). Again an increase in the chosen stepsizes can be observed.

*Results of WFQRA(M) in the HOD-example.* While WFQRA still works well in the OH-case, let us have a look at the WFQRA(M) approximations of the populations in our HOD example (Fig. 11).

Here the solutions of standard WFQRA(0) are *simply wrong*, while WFQRA(1)

Algorithm	no. of evaluations	time effort	relative effort
Exact	19774	122 sec	1
WFQRA(0)	2258	2.5 sec	0.02
WFQRA(1)	5221	8 sec	0.06
QRS	1087	1.2 sec	0.01

TABLE 1  
Computational effort for the solution of the OH-problem

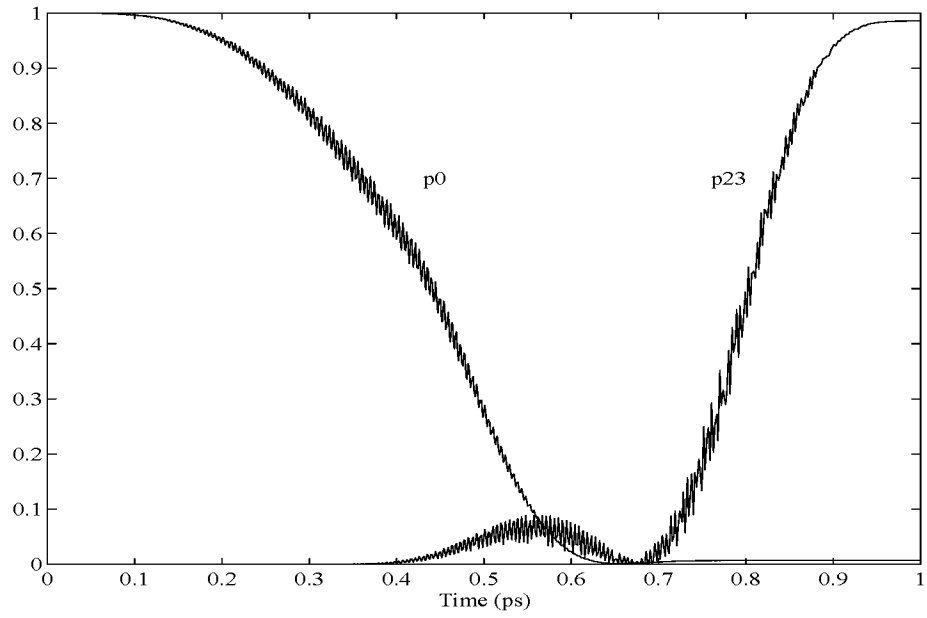


FIG. 8. Population dynamics for states 0 and 23 for HOD with optimal laser parameters

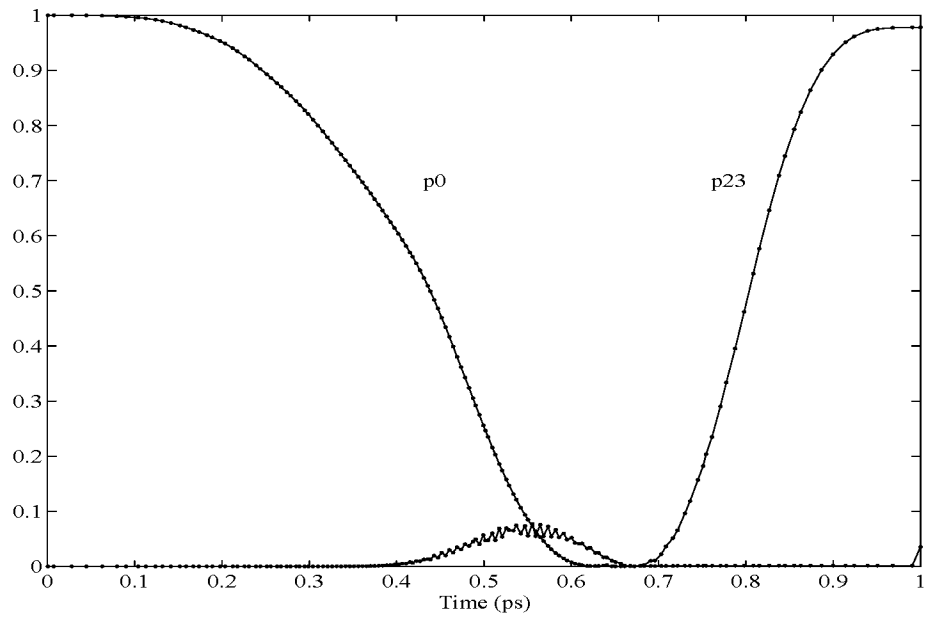


FIG. 9.  $QRS(0.7)$  population dynamics for states 0 and 23 for HOD with optimal laser parameters

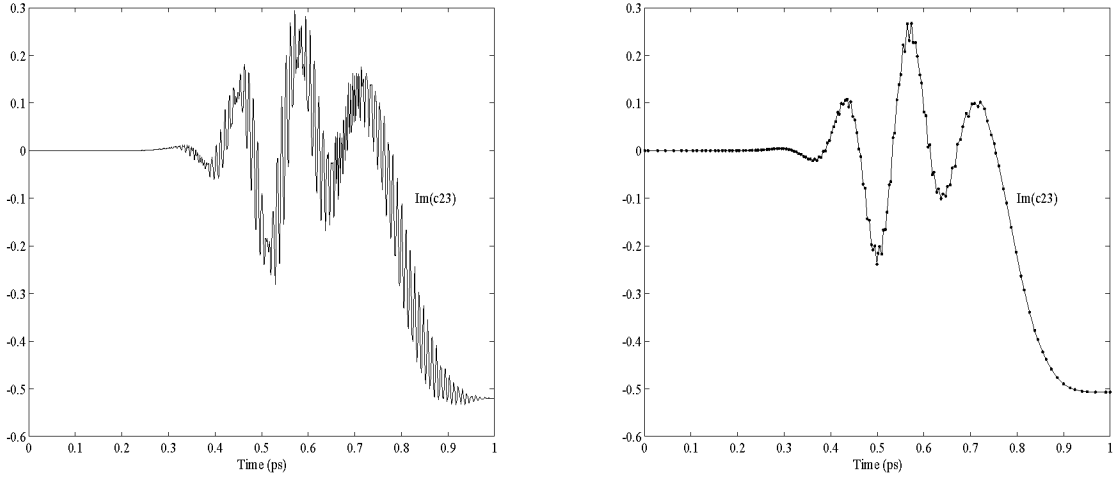


FIG. 10. *Exact and QRS(0.7) dynamics of coefficient  $Im(c_{23})$  for HOD.*

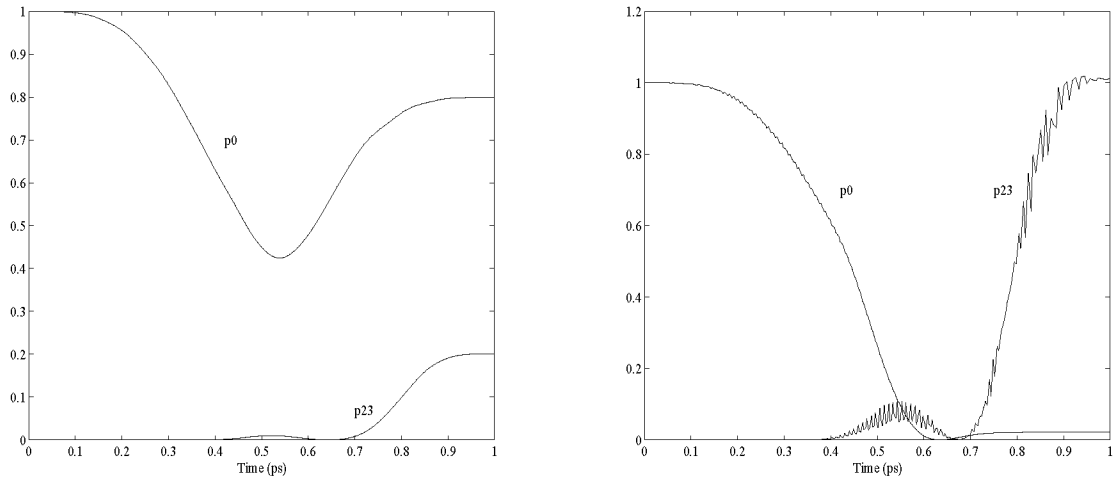


FIG. 11. *WFQRA(0) (left) and WFQRA(1) (right) results for the populations of states 0 and 23 for HOD with optimal parameters. Compare the exact solution shown in Fig. 8*

gives a more or less usable approximation (compare Fig. 11 with Fig. 8 and Fig. 9 – WFQRA(1) computes a probability  $|c_{23}| > 1!$ ). But unfortunately the computational effort of WFQRA(1) is again about a factor 2 higher than that of QRS(0.7). In addition WFQRA(1) cannot seriously be called a smoothing method.

Algorithm	no. of evaluations	time effort	relative effort
DIFEX	18023	17 min	1
WFQRA(0)	Fail	Fail	Fail
WFQRA(1)	6521	62 sec	0.06
QRS	3125	18 sec	0.02

TABLE 2  
*Computational effort for the solution of the HOD-problem*

**5.3. Nonmonochromatic radiation.** Let us have a look at the case of non-monochromatic radiation. If we consider a superposition of several single frequencies QRS can be extended to this case in a trivial way. In test runs this extended version works well and efficient as well for constant light sources as for laser pulses. The case of two superposed laser pulses with different frequencies is important for work on the field ‘selective vibrational excitation’ (see [5] as an example).

Fig. 12 shows the exact and QRS solutions of

$$i \partial_t a = (\Omega + g(t)V) a$$

with data  $\Omega, V$  from our OH-example and

$$g(t) = E_1 \sin^2 \eta t \cos(\mu_1 t) + E_2 \sin^2 \eta t \cos(\mu_2 t)$$

(i.e. the superposition of two picosecond laser pulses).  $E_1$  and  $\mu_1$  are the optimal laser parameters for the  $0 \rightarrow 4$  transition in OH from above,  $E_2 = 0.275 E_1$  and  $\mu_2 = 0.96 \mu_1$ . Comparing QRS(0.4) and DIFEX one measures a speedup factor of 90. For structural reasons WFQRA *cannot* be extended to those situations, in particular not to the case of very different frequencies.

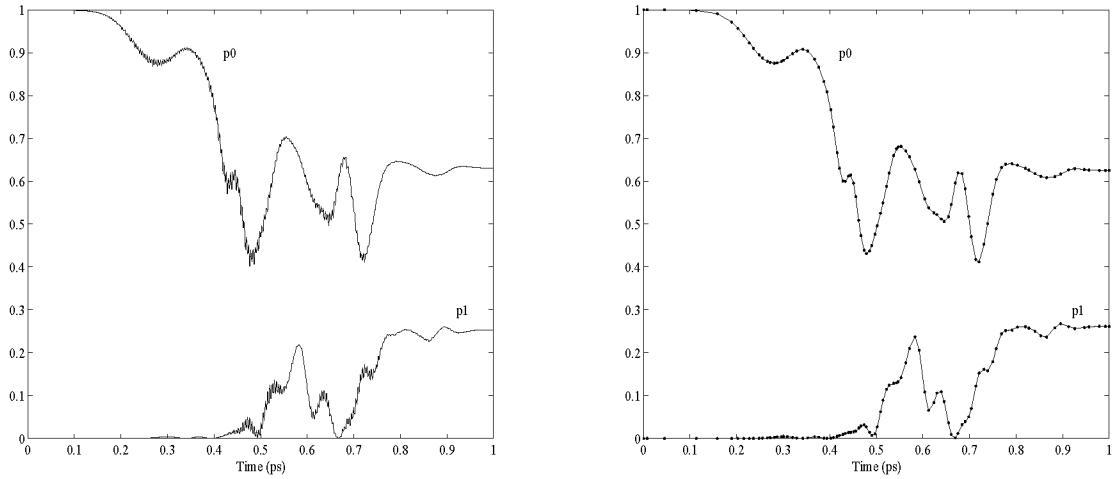


FIG. 12. *Exact and QRS(0.4) dynamics of the populations of states 0 and 6 of OH for a nonmonochromatic laser pulse.*

**5.4. QRS and nonoptimal laser parameters.** This is the place to remark that the well-working of QRS isn't bounded to the use of the optimal laser parameters. Fig. 13 shows exact and smoothed population dynamics for parameters slightly different from the optimal ones. In general I have found that QRS works well for all tried parameter values, while  $E_r$  doesn't get too large (in this case one has to increase the  $\delta$ -value).

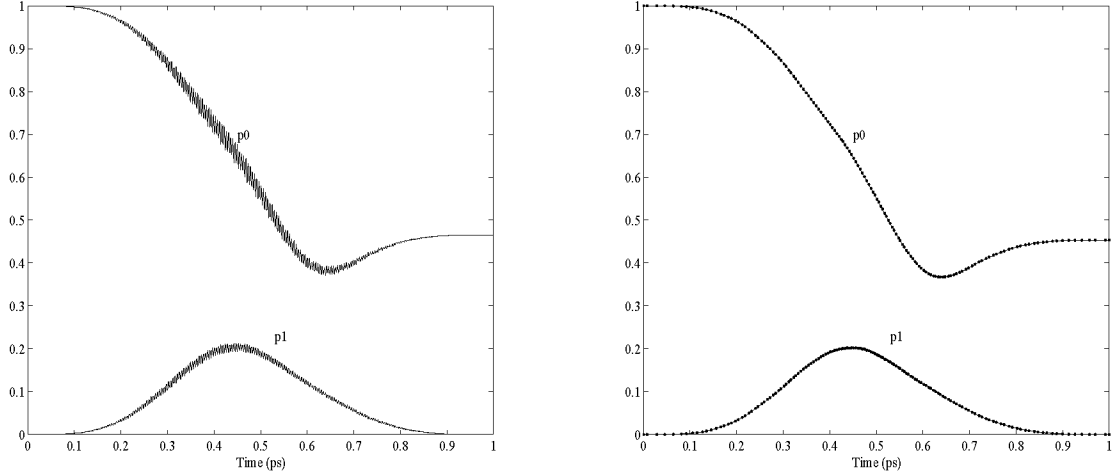


FIG. 13. *Exact and QRS(0.7) dynamics for the populations for nonoptimal laser parameters for HOD. For a change the populations of states 0 and 1 are shown.*

Looking at the whole process of searching the optimal laser parameters for given target-state  $L$  and given data  $V$  and  $\Omega$  the following observation is of special importance:  $p_L(\tau)$  reaches its maximal value at the same parameter point  $(\omega, E_r)$  as  $p_L^{QRS}(\tau)$  does (if  $\delta$  is not too small).

**6. Conclusion.** The above derivation and numerical results lead to the following main observations:

Up to now, quasideviant approximation methods like WFQRA were the most efficient solvers for problems of type (2). However, as we have seen, WFQRA has been constructed for the case of monochromatic radiation with constant intensity ( $f(t) = \text{const}$ ). The inventions in short time laser physics brought up the time-dependent case ( $f(t) = E_r \sin^2 \mu t$ ), where the major advantage of WFQRA (derivation of a system with constant coefficients (see (40)) and solution in one step via diagonalization) can no longer be exploited. Therefore a generalization of the method to this new class of problems is necessary. The results presented herein show that this cannot be done with satisfactory efficiency. In addition there seems to be no possibility to extend WFQRA to cases of polychromatic radiation. Thus, looking for an efficient solution technique applicable to a sufficiently large subclass of (2), WFQRA will not be the method of choice. Therefore an alternative approach called QRS has been developed herein. This approach has proved its robust applicability and reliability for both optimal and nonoptimal laser parameters and for cases of polychromatic radiation. Thus it can be used within optimization routines as well. In all these cases QRS yielded a relative speedup with respect to the exact solution of the order of magnitude  $10^2$ .

A crucial role in the version of QRS presented herein is played by the smoothing parameter  $\delta$ , which must be chosen externally. This can be done satisfactorily with some physical insight from the presented interpretation or by just setting  $\delta = 1$  (a choice that is still of high efficiency and has worked in all test runs). On the other hand this smoothing parameter is one of the big advantages of QRS, since it can successfully be used for an *adaptive* formulation, within which  $\delta$  is chosen automatically in the course of the integration process. This will be a topic of further investigation.

**Acknowledgement.** I am pleased to thank J. Manz and P. Deuffhard for calling my attention to this challenging class of applications. Especially I want to thank B. Just and G.H. Paramonov. They kindly supplied the used 'real life' dipole matrices  $V$  for OH and HOD to me. I really appreciate some useful discussions with M. Quack about the generalization of WFQRA.

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