Eur. Phys. J. D **26**, 111–118 (2003)
DOI: 10.1140/epjd/e2003-00203-9

THE EUROPEAN PHYSICAL JOURNAL D

Control of the Coulomb explosion of I_2

M.J.J. Vrakking[a]

FOM Institute for Atomic and Molecular Physics (AMOLF), Kruislaan 407, 1098 SJ Amsterdam, The Netherlands

Received 6 January 2003 / Received in final form 20 February 2003
Published online 15 July 2003 –

Abstract. We present calculated results for the optimization highly-charged fragment ion formation in the Coulomb explosion of I_2 in an intense laser field. Calculations are performed using a simple genetic algorithm and a classical model for the Coulomb explosion process. We find that at low intensity the production of highly-charged fragment ions is optimized by a Fourier-limited pulse, whereas at higher intensity the Coulomb explosion is optimized by a sequence of pulses, with a time-separation determined by enhanced ionization at the critical internuclear distance. Our calculations provide insight into the sensitivity of adaptive pulse shaping experiments to the parameters and evolutionary approaches used.

PACS. 33.80.Rv Multiphoton ionization and excitation to highly excited states (e.g., Rydberg states) – 82.53.Eb Pump probe studies of photodissociation – 02.60.Pn Numerical optimization

1 Introduction

In recent years femtosecond pulse shaping techniques have substantially extended the means by which ultrashort time dynamics in physics and chemistry can be studied. Traditionally femtosecond dynamics has been studied by performing pump-probe studies, where the response of the system under investigation is initiated by an ultrashort pump pulse and is probed by a second ultrashort probe pulse [1]. Measurements at a variable time delay between the pump and probe lasers, which sometimes can be accompanied by spectral information, then reveal the timescales that play a role in the system. Femtosecond pulse shaping experiments provide an alternative approach, where the experimental result consists of a determination of the optimum pulse leading to the achievement of a preset goal in the experiment [2,3]. An important challenge in pulse shaping experiments is the interpretation of the structure of the optimum pulse in the frequency or time domain. At the same time, an important concern is the ability of the experiment and the optimization algorithm to determine the optimum pulse shape for achieving the target that has been defined. Generally this optimization is performed by making use of a genetic or evolutionary algorithm [4,5], where the problem of finding the optimum solution mimics the process of biological evolution. Clearly, if an interpretation of the optimum pulse found by the experiment is going to be attempted, one has to be confident that the optimum that is determined in the experiment truly corresponds to the actual global optimum.

In this paper we present the results of a synthetic pulse shaping experiment, where we consider the Coulomb explosion of I_2 in an intense laser field, and where we try to optimize the formation of highly charged fragment ions. Following a brief introduction to the Coulomb explosion process and a discussion of the implementation of the genetic algorithm, the optimum pulses obtained by the genetic algorithm in a computer simulation of the Coulomb explosion process are discussed. The results of our calculations are two-fold. On the one hand, the calculations provide a determination of the optimum pulse shape for the formation of highly-charged atomic fragments in the Coulomb explosion, and illustrate the role of the critical internuclear distance where electron localization takes place, in agreement with existing experimental results [6,7]. On the other hand, the calculations provide insight in the sensitivity of adaptive pulse shaping experiments to the parameters and evolutionary approaches used in the genetic algorithm. We show that — unless appropriate measures are taken — the algorithm can easily get stuck on local optima in the optimization process, which correspond to a fundamentally different mechanism for the ionization process.

2 Multi-electron dissociative ionization of a diatomic molecule

In the last ten years our understanding of the intense field ionization of small molecules has progressed significantly [6–8]. The Coulomb explosion of diatomic molecules is now understood as a three-step process, in which the first step involves the formation of a singly-charged molecular ion through field ionization of the ground state molecule, the second step is the dissociation of the molecular ion after the absorption of a few more photons, and the

[a] e-mail: vrakking@amolf.nl

third step is the removal of one or more electrons near the so-called critical distance where localization of the outer electron on one of the atomic fragments takes place. At the critical distance the intensity requirements for removal of an electron from the molecular ion are greatly reduced (typically about one order of magnitude with respect to the intensity that is required at the equilibrium internuclear distance), and therefore the Coulomb explosion preferentially takes place near this point. Evidence for this mechanism has been obtained both in studies of the kinetic energy release of the atomic fragments as a function of the pulse duration and in time-resolved experiments.

In a recent experiment in our laboratory, we have studied the Coulomb explosion of iodine and bromine using the velocity map ion imaging technique [9]. Charged atomic fragments as high as I^{6+} and Br^{4+} were observed and velocity map images were recorded as a function of the pulse duration and pulse energy of the 800 nm pulse used for the explosion. Our experiments clearly revealed the role of dynamic alignment in the explosion process. For relatively short pulse durations ($\sim$100 fs) broad angular distributions were observed, where alignment along the laser polarization axis arises predominantly from geometric alignment in the ionization process, *i.e.* the preferential ionization of molecules whose internuclear axis is aligned along the laser polarization axis. For longer pulse durations (typ. 1−3 ps) a significant narrowing of the angular distribution was observed as a result of dynamic alignment. In this mechanism the strong oscillatory electric field of the laser induces an oscillating dipole in the molecule, whose interaction with the electric field of the laser leads to the formation of a potential energy minimum for molecules that are aligned along the laser polarization axis. Hence the laser provides a force which brings molecules into alignment along the laser polarization axis, provided the pulse duration is long enough for the adaptation of the internuclear axis to the laser field to occur.

Our experimental results were corroborated by a classical model for the Coulomb explosion process, which borrowed heavily from an earlier model developed by Posthumus *et al.* [6]. We extended this model to three dimensions and incorporated the effect of dynamical alignment [10,11]. Semi-quantitative agreement was obtained with the experimentally obtained fragment angular distributions. Since the model was extensively described in reference [11] only a very brief description of it will be presented here. In reference [11] we assumed that molecules were ionized as soon as the laser intensity exceeded an angle-dependent ionization threshold, which was taken to be 6.9×10^{12} W/cm^2 for molecules aligned parallel to the laser field and 9.0×10^{12} for molecules aligned perpendicular to the laser polarization axis. In the present paper a change was made in the way that this initial ionization of the neutral molecules was calculated from their ionization rate. These were calculated according to ADK-theory [12], making use of an angle-dependent ionization limit according to $I_p = I_{\mathrm{mol}} I_{\mathrm{atom}} / \{I_{\mathrm{mol}} + (I_{\mathrm{atom}} - I_{\mathrm{mol}}) \cos^2(\theta)\}$, where I_{mol} and I_{atom} are the ionization potentials of an I_2 molecule and an I atom, respectively, and where θ is the angle of the internuclear axis of the molecule with respect to the laser polarization axis. For molecules that are aligned along the laser polarization axis ($\theta = 0$), $I_p = I_{\mathrm{mol}}$, whereas for molecules aligned perpendicular to the laser polarization axis ($\theta = \pi/2$), $I_p = I_{\mathrm{atom}}$.

Upon ionization the molecules are further excited to a repulsive curve and the dissociation starts. At each subsequent timestep in the calculation an evaluation is made of the combined Coulomb+laser potential surface experienced by the outer electron and it is assumed that ionization proceeds with 100% efficiency when the electron energy exceeds the energy of one of the two saddlepoints on the potential surface. At this point an electron is removed from the molecule and the calculation proceeds on a repulsive potential that depends on the new atomic charges. Throughout the calculation, *i.e.* both before and after the first ionization process, polarization-induced dynamic alignment forces are considered. The calculations lead to a prediction of the final alignment angle and charge state of the atomic fragments of the explosion, which depends on the laser intensity and pulse duration and the initial angle of the molecule with respect to the laser polarization axis.

In the present paper we extend these calculations to arbitrary pulse shapes of the 800 nm laser responsible for the Coulomb explosion. It is assumed that the experiments are performed with a laser pulse with a Gaussian frequency spectrum, where the spectral phase function can be varied by using a pulse shaping device. The spectral phase was typically specified at 64 equidistant frequencies, and a spline interpolation was used for the intermediate frequencies, mimicking the achievable phase control on a practical pulse shaping device [13]. The time structure of the pulse was obtained by a Fast Fourier Transformation (FFT) of the complex spectral distribution and trajectories were calculated for a given initial angle of the internuclear axis with respect to the laser polarization axis and for a given pulse peak intensity (*i.e.* the peak intensity reached in the laser pulse in case of a Fourier Transform-limited pulse). A Monte Carlo sampling of the initial angle and laser intensity was used in order to account for the isotropic nature of the initial molecular sample and the Gaussian focus of the laser beam.

3 Implementation of the genetic algorithm approach

Genetic algorithms are a class of algorithms used in optimization/inversion problems, where one tries to find the optimal solution to a problem by mimicking the process of biological evolution. The algorithm operates on a population of possible solutions, which usually are subject to random initialization. For each of the solutions an evaluation of the response of the system is made and a fitness value is assigned to each solution, depending on how well the solution satisfies a target that has been defined. Next, the process of evolution is initiated, and a new generation of possible solutions is formed, by adapting several mechanisms which occur in biological evolution. In a *crossover*

event, two solutions are picked from the existing population with a probability according to their fitness, and act as parents for two new solutions that use part of the information contained in both parents. In a *mutation* event a random change is made in a solution that is carried from the old population to the new population (or in a solution resulting from a crossover event). Also, one may choose to retain a select group of solutions that have performed well in a previous generation, which are transferred to the next generation without modification ("*elitism*").

A very strong feature of genetic algorithms is the fact that they are capable of performing optimizations under conditions where the dimensionality of the solution space is very large and contains many local optima. Furthermore, within certain limits, the optimization does not depend very strongly on parameters like the probability for crossover or the probability of a mutation, which need to be defined in the algorithm. The performance of genetic algorithms *does* however depend significantly on the fitness function that is used and on the criteria that are used for the selection of parents in a crossover event. This is particularly true for femtosecond pulse shaping experiments, where the result of changing one single parameter in the solution may strongly depend on the values of all other parameters in the solution ("*epistasis*"). This makes it relatively easy for the algorithm to get stuck on a local maximum in the optimization, with the danger that the experiment leads to misleading results and interpretations. To minimize these problems we have implemented a form of *fitness sharing* in our algorithm, which punishes solutions when they become very similar to each other, hence applying pressure on the algorithm to retain a large variety in the population. This large variety is necessary to avoid premature convergence of the algorithm and to maximize the chances of finding the global maximum of the fitness function.

In the implementation of the genetic algorithm that was used in most of the calculations in this paper, every solution consisted of a set of 64 parameters in the interval $[0, 2\pi]$, which, as discussed above, represented the spectral phase at equidistant frequencies within the spectrum of the pulse. An 8-bit binary representation was used for every parameter, so that one complete solution consisted of a 512-bit string. In a crossover event, the strings of two selected parents A and B were cut at two randomly chosen positions along the string, and two new strings were formed by taking the first and third segment from parent A and the second segment from parent B, and *vice versa* [5]. Mutations were performed by changing the value of one parameter in the solution depending on the value of a random number compared to the mutation probability. If a mutation was to be performed, then a random number was added to the value of the parameter, subject to the constraint that the distribution of possible changes in the parameter value was Gaussian. The width of this Gaussian was adapted in successive generations, depending on how well the mutations that were performed contributed to an increase in the fitness function observed [14]. Typically the calculations were performed with a population of 100 solutions, and the best 4 solutions were carried over to the next generation without any change. Under these conditions an optimum mutation probability of 0.02 was found, and an optimum crossover probability of about 0.6 [15].

As mentioned, finding the global optimum of the fitness function required the use of fitness sharing in the calculations. When selecting two parents for a crossover, the probability for two parents to be selected was proportional to a scaled value of their fitness, which was determined as follows. The difference Δ_{ij} between two solutions i and j was defined by taking the sum of the squares of the differences between the parameters $\alpha_{k,i}$ and $\alpha_{k,j}$ in both solutions. Next the uniqueness of a particular solution i was evaluated by taking the sum of the differences Δ_{ij} where j runs over the 50 solutions that had the smallest difference with solution i. Finally the fitness of solution i was then multiplied by its uniqueness. In this fashion, solutions that differed very little from each other were penalized and forced to "share their fitness". Before this form of fitness sharing was introduced into the calculations the algorithm had a large tendency to converge on a local optimum (see below).

In the calculations presented in this paper we focussed on optimizing the formation of highly charged atomic fragments in the Coulomb explosion of I_2, when subjected to shaped laser pulses derived from a pulse with a Fourier Transform-limited pulse duration of 25 fs and a peak intensity of $2-5 \times 10^{14}$ W/cm^2 when the pulse was at the Fourier limit. The formation of highly-charged states was rewarded by augmenting the fitness function with an amount of 2^N for a trajectory where the total charge on both atomic fragments was equal to N. The fitness function of candidate solutions was determined by calculation 100 trajectories for the pulse under consideration, choosing the initial angle of the internuclear axis with respect to the laser polarization axis and the position in the laser focus (and thus the peak intensity experienced by the molecule) through Monte Carlo sampling.

4 Computational results

4.1 Unrestricted optimization of the charge state distribution in multi-electron dissociative ionization

First we present results for the Coulomb explosion of I_2 with a pulse derived from a Fourier-limited laser with a relatively low peak intensity of 2×10^{14} W/cm^2 and a pulse duration of 25 fs, where we let the genetic algorithm evaluate the optimum pulse shape for the formation of highly-charged atomic fragments by means of an unrestricted parametrization with the phase specified at 64 frequencies. Figure 1a shows how in successive generations the average and maximum ("best of population") fitness increase until convergence is reached after about 150 generations. Although the calculation used moderate elitism (4 elite solutions within a population of 100 solutions) the maximum fitness occasionally drops as a result of fitness sharing, which degrades the fitness of solutions that become similar and thus puts them at risk of disappearing

Table 1. Comparison between the maximum fitness observed in the genetic algorithm calculations and results obtained for a Fourier-limited pulse.

Intensity	Unrestricted parametrization[a] (64 parameters)	Restricted parametrization[a] (3 parameters)	Fourier-limited pulse[b]
2×10^{14} W/cm^2	571[c]	761[c]	662.5
3×10^{14} W/cm^2	1093[d,e]	1485[d]	1107.3
4×10^{14} W/cm^2	2185[d]	4957[d]	1557.7
5×10^{14} W/cm^2	4917[d]		2110.5

[a] Best result observed in a genetic algorithm calculation where the fitness is determined on the basis of calculating 100 trajectories. [b] Fitness determined on the basis of a calculation of 1000 trajectories for a Fourier-limited pulse. [c] Single pulse. [d] Multiple pulse. [e] A fitness of 1321 was achieved in a 32 parameter calculation.

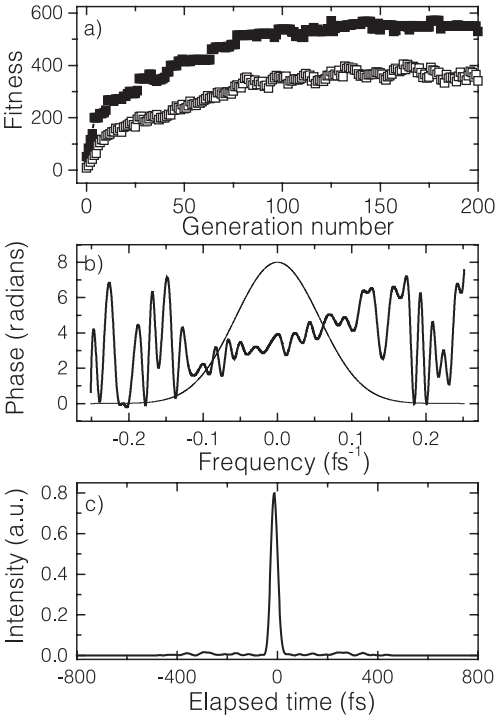

Fig. 1. (a) Increase in the average fitness (□) and the best-of-population fitness (■) as a function of the number of generations, for a calculation using a 25 fs pulse with a peak intensity of 2×10^{14} W/cm^2. The calculation used a population of 100 solutions, where the phase function was varied at 64 discrete values of the frequency, and where the fitness function was evaluated as $F = \sum_{I=1-100} 2^{N(I)}$, where $N(I)$ represents the total fragment charge in calculation I. Further details on the parameter settings of the genetic algorithm are found in the text; (b) phase function (thick curve) of the best solution found by the genetic algorithm after 200 generations. The phase function is nearly linear for frequencies falling within the bandwidth of the laser (thin curve); (c) optimized pulse found by the genetic algorithm after 200 generations. The algorithm has converged towards a Fourier-limited pulse where all the ionization takes place near the equilibrium internuclear distance.

from the elite segment of the population. Nevertheless, as will be discussed below, we have observed fitness sharing to be crucial for eventually achieving the optimum fitness in the calculation.

The optimal phase function found in the calculation described above is shown in Figure 1b. Within the bandwidth of the laser pulse the genetic algorithm has removed most phase variations except for a linear dependence of the phase on frequency. This linear dependence does not affect the temporal shape of the pulse, but merely leads to a displacement of the pulse in time. The laser pulse shape corresponding to the optimal phase function is shown in Figure 1c and corresponds approximately to a Fourier-limited pulse. In fact, when the calculation is performed using a Fourier-limited pulse, a further increase in the fitness of about 20% is observed (see Tab. 1). We conclude that at low peak laser intensities the formation of high charge states is optimized by a concentration of all the available laser energy into a short pulse that ionizes the molecule near the ground-state equilibrium internuclear distance.

In Figure 2 similar results are shown for a calculation where the peak laser intensity of the pulse was equal to 3×10^{14} W/cm^2. As before, Figure 2a shows how the calculation reaches convergence in about 150 generations. However, in this case the optimal phase function (Fig. 2b) shows a pronounced oscillatory structure on top of a linear variation with frequency. The linear phase variation, as before, only influences the timing of the pulse, but not its shape. As a result of the oscillatory component in the phase function, the laser field consists of a dominant pulse that contains about half the available energy and two weaker pulses that share the remaining energy and that are located about 300 fs before and after the main pulse (see Fig. 2c). The interpretation of this pulse structure can readily be understood on the basis of the Coulomb explosion model described in Section 2. Since iodine atoms are heavy, it takes about 300 fs in our model for the iodine molecular ion to dissociate and reach the critical internuclear distance, where the intensity requirements for reaching high charge states are significantly reduced. Hence it is advantageous for the light field to organize itself into a sequences of pulses separated by about 300 fs. Molecules in the central portion of the laser focus or molecules that have their internuclear axis aligned along the laser polarization axis are singly ionized and dissociated by the first pulse and reach the critical internuclear distance at a time corresponding to the dominant second pulse in the laser pulse, whereas molecules in the outer portion of the focus that do not have their internuclear axis aligned along the

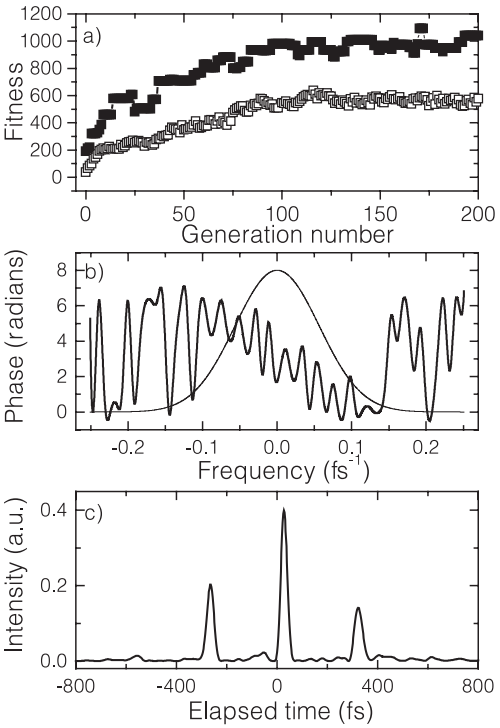

Fig. 2. (a) Increase in the average fitness (□) and the best-of-population fitness (■) as a function of the number of generations, for a calculation using a 25 fs pulse with a peak intensity of 3×10^{14} W/cm^2. The calculation used a population of 100 solutions, where the phase function was varied at 64 discrete values of the frequency, and where the fitness function was evaluated as $F = \sum_{I=1-100} 2^{N(I)}$, where $N(I)$ represents the total fragment charge in calculation I. Further details on the parameter settings of the genetic algorithm are found in the text; (b) phase function (thick curve) of the best solution found by the genetic algorithm after 200 generations. For frequencies falling within the bandwidth of the laser (thin curve), the phase function shows a regular oscillatory pattern on top of a nearly linear slope; (c) optimized pulse found by the genetic algorithm after 200 generations. The algorithm has converged towards a train of three pulses, where the majority of ionization events involves ionization of the ground state molecule by the first or the second pulse, followed by further ionization of the dissociating molecule at the critical internuclear distance by the second or the third laser pulse.

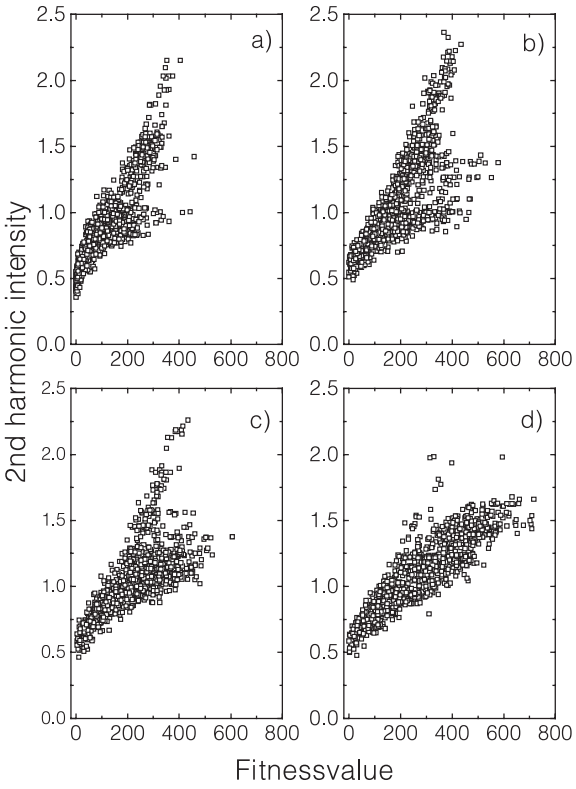

Fig. 3. Evolution in the type of solutions used by the genetic algorithm, in a calculation starting from a 25 fs pulse with a peak intensity of 3×10^{14} W/cm^2. The four panels show the fitnessvalue (calculated as $F = \sum_{I=1-100} 2^{N(I)}$, where $N(I)$ represents the total fragment charge in calculation I) and the time-integral of the squared intensity (*i.e.* the 2nd harmonic intensity) at four stages during the optimization: (a) calculations 1−1000; (b) calculations 1001−2000; (c) calculations 2001−3000; (d) calculations 3001−4000. Eventually, after about 8000 calculations, the genetic algorithm reaches a fitness of 1093 (see Fig. 2). In the calculation, the initial optimization is towards a Fourier-limited pulse where all the energy is concentrated in a single peak. However, due to the implementation of fitness sharing the population retains sufficient diversity for the algorithm to be able to branch out into solutions where the laser field consists of several pulses, that optimize the efficiency of ionization at the critical internuclear distance where electron localization takes place.

laser polarization axis are ionized by the more intense second pulse and reach the critical internuclear distance at the time of the third, weaker pulse, where limited further ionization is seen to take place.

The results shown in Figure 2 are very sensitive to the implementation of fitness sharing in the genetic algorithm. As shown in Figure 3, in the course of the optimization large fitness values are observed involving two qualitatively different types of laser pulses, which differ by the extent that the increase of the fitness function is accompanied by an increase in the time integral of the square of the laser intensity (corresponding to the signal that would be measured in a 2nd harmonic generation experiment), that we will call the SHG-value. In the initial stages of the optimization (Fig. 3a), laser pulses are mostly observed where the increase in the fitness value is accompanied by a corresponding increase in the SHG-value. This means that initially the optimization proceeds towards a Fourier-limited pulse, as in the earlier calculation for a peak intensity of 2×10^{14} W/cm^2. However, in the present calculation the Fourier-limited pulse represents only a local maximum in the fitness function, and the global optimum in the fitness function is obtained for a more complicated pulse. As a result of the implementation of fitness sharing there is an incentive for the algorithm to maintain a large diversity in the population, and therefore after about 10 generations the algorithm starts to include trials where the ionization involves multiple pulses. Here,

part of the ionization takes place at the critical internuclear distance and a high fitness value is obtained even though the SHG-value remains relatively low (Figs. 3b and 3c). In later generations the multiple-pulse solutions dominate at the expense of the single-pulse solutions and lead to fitness values that are beyond the fitness value that is obtained for a Fourier-limited pulse (Fig. 3d). At this stage, the algorithm proceeds by fine-tuning the amplitude and period of the oscillatory phase function, in order to achieve the optimum result shown in Figures 2b and 2c. Importantly, these optimum results are only found if the genetic algorithm is operated with fitness sharing. All in all, four calculations were performed at an intensity of 3×10^{14} W/cm^2, using different random initializations of the initial population and different initialization of the Monte Carlo sampling of the experimental conditions on each occasion. In three of these four tests, the algorithm managed to find the multiple pulse solution due to fitness sharing, whereas in one case the algorithm still got stuck on the Fourier-limited solution.

Further calculations were performed for laser pulses with peak intensities of 4×10^{14} W/cm^2 and 5×10^{14} W/cm^2. Two calculations were performed at both intensities, and in all cases the optimum solution consisted of a double pulse, where the fitness function was dominated by trajectories where the first pulse led to a single ionization of the iodine molecule, followed by the removal of 2−7 more electrons by the second pulse at the critical internuclear distance. The results of these calculations are shown in Table 1. At intensities of 4×10^{14} W/cm^2 and 5×10^{14} W/cm^2 the two pulse solutions found by the genetic algorithm have a fitness that is substantially higher than the fitness of a calculation with a Fourier-limited pulse.

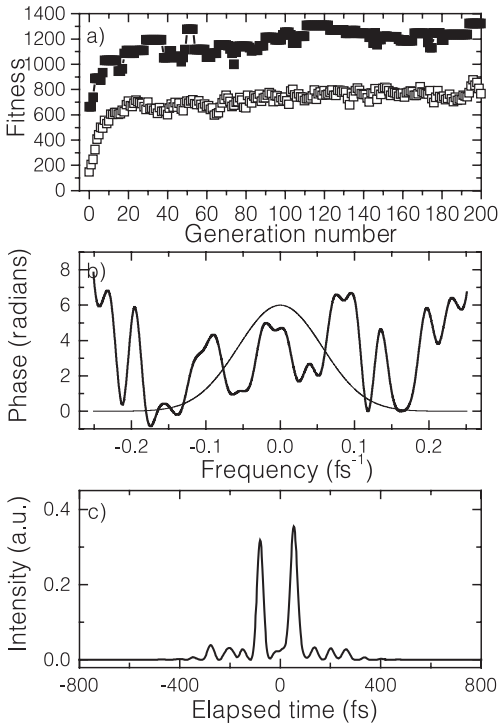

Fig. 4. (a) Increase in the average fitness (□) and the best-of-population fitness (■) as a function of the number of generations, for a calculation using a 25 fs pulse with a peak intensity of 3×10^{14} W/cm^2. The calculation used a population of 100 solutions, where the phase function was varied at 32 discrete values of the frequency, and where the fitness function was evaluated as $F = \sum_{I=1-100} 2^{N(I)}$, where $N(I)$ represents the total fragment charge in calculation I. Further details on the parameter settings of the genetic algorithm are found in the text; (b) phase function (thick curve) of the best solution found by the genetic algorithm after 200 generations. For frequencies falling within the bandwidth of the laser (thin curve), the phase function shows a regular oscillatory pattern, with a period that is about double the period found in the 64 parameter calculation shown in Figure 2; (c) optimized pulse found by the genetic algorithm after 200 generations. The algorithm has converged towards a sequency of two pulses, where the fitness function is dominated by trajectories where the first pulse leads to a double ionization of the ground state molecule and where the second pulse, which comes 135 fs later, leads to further ionization at the critical internuclear distance.

4.2 Influence of the number of free parameters used by the genetic algorithm

At a peak intensity of 3×10^{14} W/cm^2 a limited number of calculations were performed where the phase function was described by 32 or 128 parameters. Two calculations were performed where the phase function was parameterized at 32 frequencies. In this case, it was no longer possible for the genetic algorithm to generate an oscillatory phase function with a period corresponding to the formation a pulse train with a separation of 300 fs. However, in both cases the algorithm found an interesting way to circumvent this problem, one of which is shown in Figure 4. In this calculation the algorithm converged to a phase function where the oscillation frequency of the phase function is significantly slower than the one in Figure 2, resulting in a laser pulse where the individual sub-pulses are only 135 fs apart. However, at the same time the algorithm has arranged the phase function in such a way that the output pulse consists of two equally intense pulses, the first of which is now intense enough to lead to a double ionization of many of the ground state molecules in the laser focus. As a result many molecules in the laser focus dissociate following an $I^+ + I^+$ curve, rather than an $I^+ + I$ curve, and reach the critical internuclear distance already after about 135 fs, coinciding with the appearance of the second pulse. In the second 32 parameter calculation the algorithm took an alternative approach. Again a phase function was generated leading to a pulse train with a period of approximately 150 fs, but in this case the relative amplitudes of the pulses were such that the pulse was dominated by two sub-pulses which were 300 fs apart, mimicking the result of the 64 parameter calculation shown in Figure 2.

In both calculations involving 32 parameters it was clear that convergence towards an optimal result was significantly faster than in the earlier 64 parameter calculations. In Figure 4 the fitness value reaches a maximum

after only 40−50 generations, whereas in the 64 parameter calculations shown in Figures 1 and 2 convergence set in after about 100−150 calculations. Calculations with a 128 parameter phase function representation thus far did not lead to a satisfactory convergence and performed significantly inferior to the results of the 64 parameter calculations.

4.3 Restricted optimization of the charge state distribution in multi-electron dissociative ionization: dependence of the fitness value on the amplitude and period of an oscillatory function

The unrestricted optimizations discussed in the previous section showed that — apart from a linear term which does not affect the pulse shape — the optimum phase function for forming highly-charged ions in multi-electron dissociative ionization is a flat phase function at low intensities and an oscillatory phase function at higher intensities. Therefore in both cases the optimum phase function was a function that could have been represented in terms of only 3 parameters as $\varphi(\omega) = \alpha_1 \cos(\alpha_2\omega + \alpha_3)$.

In Figure 5 results are shown for evaluations of the fitness value as a function of parameters α_1 and α_2, keeping α_3 fixed at zero. Results are shown both for peak intensities of 2×10^{14} W/cm^2 and 3×10^{14} W/cm^2. When $\alpha_1 = 0$ radians (zero amplitude of the phase oscillation) or when $\alpha_2 = 0$ fs (infinite period of the phase oscillation) the pulse is Fourier-limited and a large fitness value is observed. However, there are additional islands in the contourplot where a specific combination of α_1 and α_2 leads to the observation of a large fitness value. For $\alpha_1 \approx 1$ radian and $\alpha_2 \approx 300$ fs an optimum is observed in the fitness value which corresponds to the optimum observed in Figure 2, while for $\alpha_1 \approx 1.2$ radians and $\alpha_2 \approx 135$ fs an optimum is observed corresponding to the second 32 parameter calculations discussed in Section 4.2. In the calculation performed at an intensity of 2×10^{14} W/cm^2 both of these optima lie below the fitness value that is obtained for a Fourier-limited pulse, while in the calculation performed at an intensity of 3×10^{14} W/cm^2 the maximum fitness in the contourplot is 1613, which exceeds both the result for a Fourier-limited pulse and the result found by the genetic algorithm.

A limited number of genetic algorithm optimizations using $\alpha_1 - \alpha_3$ defined above as optimization parameters were performed for peak intensities of $2-4\times10^{14}$ W/cm^2. The results of these calculations are shown in the third column of Table 1, and illustrate that with this parametrization higher fitness values are observed than in the unrestricted parametrization discussed in Section 4.1. Of course, the price paid for these higher fitness values is the fact that the optimization in this case took place in a much more restricted search space and made extensive use of *a priori* knowledge on the ionization process and results of the unrestricted optimization.

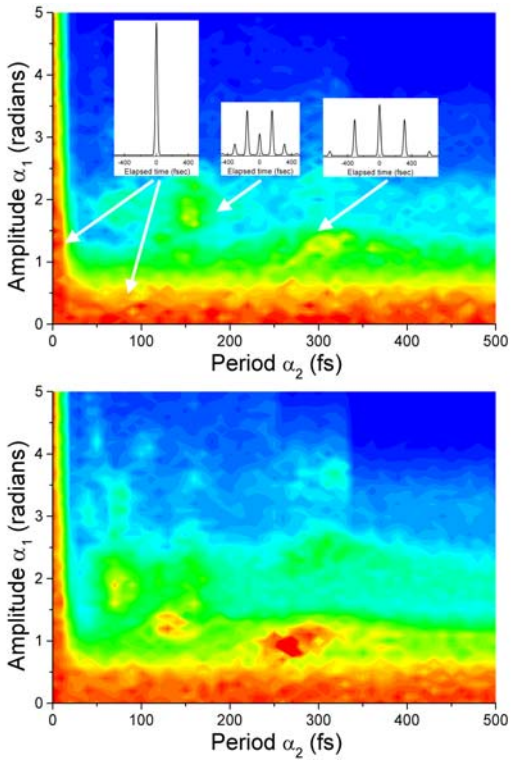

Fig. 5. Dependence of the fitness value $F = \sum_{I=1-100} 2^{N(I)}$ (where $N(I)$ represents the total fragment charge in calculation I) on parameters α_1 and α_2 that describe the spectral phase function according to $\varphi(\omega) = \alpha_1 \cos(\alpha_2\omega)$. The top panel shows a calculation with a laser peak intensity of 2×10^{14} W/cm^2, while the laser peak intensity in the bottom panel is 3×10^{14} W/cm^2. Both calculations show that a high fitness value can not only be achieved by a Fourier-limited pulse ($\alpha_1 = 0$ or $\alpha_2 = 0$), but also in limited regions where the laser pulse breaks up into a pulsetrain where the separation between the pulses matches the time interval needed for dissociation from the equilibrium internuclear distance to the critical internuclear distance, which is about 300 fs in the case of I_2.

5 Conclusions

In this paper results have been presented for the optimization of the formation of highly charged fragment ions in the multi-electron dissociative ionization of I_2 molecules, by performing calculations with a model for the ionization process within a genetic algorithm. The result of these calculations is that at low intensity the formation of high charge states is optimized by a Fourier-limited pulse, whereas at higher intensities the formation of high charge states is optimized by a sequence of an ionization pulse, that ionizes the neutral molecule and initiates the dissociation of the molecular ion, and a second pulse which further ionizes the molecule near the critical internuclear distance where localization of the outer electron on one of the two iodine atoms takes place. However, the more important result of these calculations is the fact that they illustrate the potential sensitivity of the outcome of femtosecond pulse shaping experiments on the details of the

implementation of the genetic or evolutionary algorithm used. In the model system that we have discussed here, the implementation of fitness sharing in the genetic algorithm turned out to be a vital step to help ensure that the algorithm proceeded towards the global optimum in the fitness function, without getting stuck on a local maximum corresponding to a Fourier-limited pulse.

In the last few years the implementation of femtosecond pulse shaping techniques making use of a genetic or evolutionary algorithm to direct the search towards the global maximum in the fitness function has become a very popular endeavour. In particular, it is regarded as a promising method in situations where a lack of knowledge about the system under investigation precludes a first-principles approach, and where the system under investigation essentially forms a black box. Thus far, the implementation of the search algorithms reported often involves no more than the standard operations of reproduction, crossover and mutation. The model calculations presented in this paper illustrate that one has to be very concerned about the ability of these algorithms to find the global optimum in the experiment. Needless to say, the consequences of a failure to find the global optimum can be very serious. If fitness sharing had not been implemented in our algorithm then we would have been tempted to conclude that the formation of highly charged fragment ions in multi-electron dissociative ionization is optimized by a Fourier-limited pulse, regardless of the peak intensity of the pulse. It is only because of our earlier experience with the Coulomb explosion model that we were fairly confident that better solutions than the Fourier-limited pulse should exist, and as a result tried to improve the search algorithm until it was able to recover these solutions. In this sense, the work reported in this paper and particularly the exploration of the sensitivity of the outcome of the optimization to the genetic algorithm implementation used only represents the initial step of an effort to improve the quality and robustness of the optimization algorithms used in femtosecond pulse shaping experiments. It is extremely likely that the algorithms can be further improved. Besides, this is also very much a necessity. In the present case, the algorithm found a pulse that qualitatively resembles the pulse that we believe to correspond to the global optimum after fitness sharing was introduced, but the algorithm did fail on one of four occasions in the calculations with a peak intensity of 3×10^{14} W/cm^2, and for large numbers of parameters the algorithm had difficulty converging to the optimum fitness value that was observed when a lower number of parameters was used or when a parametrization in terms of "perfect" oscillatory phase functions was used. We hope to be able to report further progress in this area in the future.

This work is part of the research program of the "Stichting voor Fundamenteel Onderzoek der Materie (FOM)", which is financially supported by the "Nederlandse organisatie voor Wetenschappelijke Onderzoek (NWO)". Dr. Sebastien Zamith, Dr. Serguei Asseev and Drs. Yongfeng Ni are acknowledged for useful discussions in the course of this work.

References

1. A.H. Zewail, J. Phys. Chem. A **104**, 5660 (2000), and references therein
2. R.S. Judson, H. Rabitz, Phys. Rev. Lett. **68**, 1500 (1992)
3. A. Assion, T. Baumert, M. Bergt, T. Brixner, B. Kiefer, V. Seyfried, M. Strehle, G. Gerber, Science **282**, 919 (1998)
4. D.E. Goldberg, *Genetic Algorithms in search, optimization and machine learning* (Addison-Wesley, 1989)
5. D. Beasley, D.R. Bull, R.R. Martin, Univers. Comp. **15**, 58 (1993); D. Beasley, D.R. Bull, R.R. Martin, Univers. Comput. **15**, 170 (1993)
6. J.H. Posthumus, A.J. Giles, M.R. Thompson, W. Shaikh, A.J. Langley, L.J. Frasinski, K. Codling, J. Phys. B **29**, L525 (1996); J.H. Posthumus, A.J. Giles, M.R. Thompson, K. Codling, J. Phys. B **29**, 5811 (1996)
7. E. Constant, H. Stapelfeldt, P.B. Corkum, Phys. Rev. Lett. **76**, 4140 (1996)
8. T. Seideman, M.Yu. Ivanov, P.B. Corkum, Phys. Rev. Lett. **75**, 2819 (1995); M. Ivanov, T. Seideman, P.B. Corkum, F. Ilkov, P. Dietrich, Phys. Rev. A **54**, 1541 (1996)
9. F. Rosca-Pruna, E. Springate, H.L. Offerhaus, M. Krishnamurthy, C. Nicole, N. Farid, M.J.J. Vrakking, J. Phys. B **34**, 4919 (2001)
10. S. Banerjee, D. Mathur, G. Ravindra Kumar, Phys. Rev. A **63**, 045401 (2001)
11. E. Springate, F. Rosca-Pruna, H.L. Offerhaus, M. Krishnamurthy, M.J.J. Vrakking, J. Phys. B **34**, 4939 (2001)
12. M.V. Ammosov, N.B. Delone, V.P. Krainov, Sov. Phys. JETP **91**, 1191 (1986)
13. A.M. Weiner, Rev. Sci. Instrum. **71**, 1929 (2000)
14. D. Zeidler, S. Frey, K.-L. Kompa, M. Motzkus, Phys. Rev. A **64**, 023420 (2001)
15. These optimum parameters were found in test calculations, where a fitness function was defined directly based on the time dependence of the laser pulse. This fitness function consisted of a superpostion of an autocorrelation term and a convolution term, similar to the dependence of the fitness function on the structure of the laser pulse in the Coulomb explosion calculation