SCIENTIFIC REPORT

My name is Ádám Nagy, I am from Budapest, Hungary. I was a visiting guest of Dr. Maurice H. M. Janssen for 15 days with the starting date 28/09/2005 at the Laser Centre and Chemistry Department of Vrije University (LCVU) in Amsterdam, The Netherlands, thanks to the ESF Short Visit Grant with Reference Number 784.

I detail my studies and work during my trip below.

Mechanisms of quantum control by imaging

Discovering and developing of laser instrumentations and techniques is of great interest for almost a half century. The applications estabilished a huge field in natural and other sciences for now, namely in physics, chemistry, biology, pharmaneutical science, *etc.*. Several Nobel prizes and other scientific awards prove that 'the Laser' added more than important informations to our knowledge about the world around us.

One of the aims of my visit was to get an as wide as possible insight of the research work of the European laser community. I can maintain that this purpose of becoming acquainted with these themes, which were novel for me, was successful via two symposiums organized by the LCVU: the LASERNET meeting on 29/09/2005, with subtitle '*New Frontiers in Laser Applications in Biology, Chemistry and Medicine*', and the LASERLAB USER meeting on 30/09/2005. [1] Bunches of interesting lectures of researchers of the world's top laser-user universities and institutes made me believe in the properness of my former decision about planning to start my Ph.D. job in such kind of chemistry instead of my former pure theoretical investigations.

However, there was a probably more important exercise I had to carry out during my short visit. I studied and discussed the theoretical interpretation of a slice of the numerous and wide-ranging experiments currently being done at the LCVU [2] on the understanding of mechanisms in quantum control using advanced imaging techniques. A program written in C programming language I had to test helped me for the sake of this cause. I will talk over the results after an introduction.

It was a great advantage for reaction kinetics, when laser reached the ultrashort domain in the picosecond (1 ps = 10^{-12} s) and femtosecond (1 fs = 10^{-15} s) ranges (nowadays one can generate XUV pulses in the 10^{-18} s, *i.e.* attosecond area). Although the roots of this topic may be traced back to the earliest days of laser developmnet, the technical facilities appeared only nearly 20 years ago. It is especially true for the latter mentioned femtosecond lasers, that their use in photodissociation studies has provided great progress in our fundamental understanding of structure and dynamics in chemical reactions. This is easy to understand, since when one divides a typical bond distance (cca. 10^{-10} m) by a usual speed value (cca. 10^{3} ms^{-1}), the result is somewhere around 100 fs and shorter pulses are necessary to give relevant informations.

Full information on the potential energy surface (PES) can be obtained by combining coincidence imaging with femtosecond lasers, also called time-resolved coincidence imaging. In coincidence imaging experiments both the recoiling photo-electron and the correlated ionic photofragment originating from the isolated dissociation events are detected. Measurement of photo-electron angular distributions can provide a wealth of information on the nature of the molecular orbital that is ionized, the geometry and orientation of the molecule as the electron departs, and the dynamics of the photoionization process. Photo-electron/photo-ion coincidence provides the opportunity to determine the molecular frame photo-electron angular distribution.

In particular, there are very interesting and new opportunities in the field of coherent control of chemical reactions. [3,4,5,6] Current developments in chemistry are towards controlling the outcome of chemical reactions. The detectors used in these experiments are mostly one-dimensional, *i.e.* only the intensity of the mass-signal of the desired fragment can be measured. In the coherent control community there is a great interest in multi-dimensional detectors, like velocity map imaging and coincidence imaging. [7,8,9,10]

There are problems, which involve global optimization over continuous spaces. They are ubiquitous throughout the scientific community. For convenience, a system’s parameters are usually represented as a vector. The standard approach to an optimization problem begins by designing an objective function that can model the problem’s objectives while incorporating any constraints. Ideas borrowed from genetics and evolution theory gave useful optimization programmes using *e.g.* Genetic Algorithms (GA), Genetic Programming (GP), Evolutionary Strategies (ES) or Differential Evolution (DE). [11,12]

The latter method uses generations of individuals of the random generated parameters. From the second generation one can bulid the new parameters randomly or choosing the best previous set(s), and crossing over them (different strategies). There is a feedback control, which provides the best parameter set of the investigated ones. The variable *cvar* is just for monitoring purposes, some others stood in Tables I and II are of no consequence at this very place.

The program I investigated solves the following polynomial fitting problem using the DE. [11,13]

Let us consider a polynomial,

$$f(\mathbf{a},x)=\sum_{n=0}^{D-1} a_n x^n \quad , \quad \text{with } D\in \mathbf{Z}>1.$$

The boundary conditions are

$$f(\mathbf{a},x)\in[-1,1] \qquad \text{for } x\in[-1,1] \ ,$$

and

$$f(\mathbf{a},x)\geq T_8(1.2) \qquad \text{for } x=\pm 1.2 \ ,$$

with

$$T_8(x)=1-32x^2+160x^4-256x^6+128x^8$$

being the Chebychev polynomial of degree eight.

This optimization problem of the *D* parameters is transformed into an objective function to be minimized (*cmin*), which consists of the weighted sum of squared errors along *S* sample points distributed in the interval of [-1,1]U{±1.2}.

Results of the runnings are shown in Tables I and II.

Table I. Results of the general investigations of the program.[a]

Type of strategy	Max. no. of iterations = Max. no. of generations–1	No. of parents (*NP*) = Individuals	No. of parameters (*D*)	Interval of pars.	Output refresh cycle no.	Seed no.	Weighting factor (*F*)	Crossover constant (*CR*)	No. of function evaluations (*NFE*) = 'time'	Weighted sum of squared errors (*cmin*)	Cost-variance (*cvar*)	No. of sample points (*S*)
1 (DE/best/1/exp)	**3000**	**60**	**9**	**[–100., 100.]**	**100**	**3**	**0.9**	**1.0**	**16080 (0:01)**	**0 (<1.0E–06)**	**0 (<1.0E–06)**	**62**
1 (DE/best/1/exp)	3000	60	9	[–100., 100.]	100	3	**0.8**	1.0	**11160 (0:01)**	0	0	62
1 (DE/best/1/exp)	3000	60	9	[–100., 100.]	100	3	0.9	**0.9**	**32880 (0:01)**	0	0	62
1 (DE/best/1/exp)	3000	60	9	[–100., 100.]	100	3	**0.8**	**0.9**	**21060 (0:01)**	0	0	62
1 (DE/best/1/exp)	3000	60	**35**	[–100., 100.]	100	3	**0.8**	1.0	**6000 (0:01)**	0	**6.25E+00**	62
1 (DE/best/1/exp)	3000	**500**	9	[–100., 100.]	100	3	**0.8**	1.0	**121500 (0:02)**	0	**4.80E–06**	62
1 (DE/best/1/exp)	3000	60	**640**	[–100., 100.]	100	3	**0.8**	1.0	**180060 (2:03)**	**4.35E+02**	0	62
1 (DE/best/1/exp)	3000	**100**	**640**	[–100., 100.]	100	3	**0.8**	1.0	**70100 (0:46)**	0	**3.65E–06**	62
1 (DE/best/1/exp)	3000	60	**1280**	[–100., 100.]	100	3	**0.8**	1.0	**180060 (4:03)**	**1.31E–01**	**2.85E–06**	62
1 (DE/best/1/exp)	3000	**100**	**1280**	[–100., 100.]	100	3	**0.8**	1.0	**16400 (0:22)**	0	**9.93E–02**	62
1 (DE/best/1/exp)	3000	**100**	**1280**	[–100., 100.]	100	3	0.9	1.0	**300100 (6:29)**	**6.89E+02**	0	62
1 (DE/best/1/exp)	3000	**100**	**1280**	[–100., 100.]	100	3	0.9	**0.9**	**300100 (5:10)**	**1.07E+04**	**4.50E+09**	62
1 (DE/best/1/exp)	3000	60	9	[–100., 100.]	100	3	0.9	1.0	**180060 (1:14)**	**2.33E–05**	0	**3002**
1 (DE/best/1/exp)	3000	**100**	**1280**	[–100., 100.]	100	3	**0.8**	1.0	**terminated by user at 10200 (7:30)**	-	-	**3002**
1 (DE/best/1/exp)	3000	**100**	**1280**	[–100., 100.]	100	3	**0.8**	1.0	**20400 (0:40)**	0	**2.01E–02**	**102**
1 (DE/best/1/exp)	3000	**100**	**1280**	[–100., 100.]	100	3	**0.8**	1.0	**300100 (16:45)**	**1.08E–01**	0	**202**
2 (DE/rand/1/exp)	3000	60	9	[–100., 100.]	100	3	**0.7**	**0.5**	**180060 (0:02)**	**8.90E+01**	**7.36E+05**	62
3 (DE/rand-to-best/1/exp)	3000	60	9	[–100., 100.]	100	3	**0.85**	1.0	**11100 (0:01)**	0	0	62
4 (DE/best/2/exp)	3000	60	9	[–100., 100.]	100	3	**0.5**	**0.6**	**180060 (0:02)**	**5.54E–02**	**3.81E–02**	62

[a] Bold values denotes the columns which differ from the first line of the table. One can find further relevant informations in the text of this report.

Table II. Results of the direct investigations of dependencies of time of the number of sample points and parameters.[a]

No. of sample points (*S*)	No. of parameters (*D*)	No. of function evaluations (*NFE*) = 'time'	Weighted sum of squared errors (*cmin*)	Cost-variance (*cvar*)
62	**10**	**25000 (0:01)**	**0 (<1.0E–06)**	**0 (<1.0E–06)**
62	**20**	**12300 (0:01)**	0	**1.01E+01**
62	**50**	**13200 (0:01)**	0	**5.34E–02**
62	**100**	**13200 (0:02)**	0	**6.86E+00**
62	**200**	**15200 (0:04)**	0	**1.52E–01**
62	**300**	**15200 (0:05)**	0	**1.38E+00**
62	**500**	**16800 (0:09)**	0	**4.82E–02**
62	**700**	**14900 (0:11)**	0	**7.79E–01**
62	**1000**	**15700 (0:17)**	0	**4.05E+00**
62	**1300**	**15600 (0:22)**	0	**7.21E–01**
62	**1600**	**14000 (0:24)**	0	**7.74E+00**
62	**2000**	**15800 (0:33)**	0	**3.85E–02**
102	**10**	**25600 (0:01)**	0	0
102	**20**	**9800 (0:01)**	0	**6.78E+01**
102	**50**	**14500 (0:01)**	0	**3.28E+01**
102	**100**	**19000 (0:03)**	0	**8.14E+00**
102	**200**	**16700 (0:06)**	0	**6.43E–03**
102	**300**	**19900 (0:09)**	0	**3.33E–01**
102	**500**	**17000 (0:13)**	0	**3.20E–02**
102	**700**	**23000 (0:25)**	0	**1.75E–01**
102	**1000**	**300100 (7:24)**	**2.72E–01**	0
152	**10**	**23800 (0:01)**	0	0
152	**20**	**10100 (0:01)**	0	**3.79E+01**
152	**50**	**58500 (0:06)**	0	**2.20E-04**
152	**100**	**16000 (0:05)**	0	**5.82E+00**
152	**200**	**300100 (2:04)**	**6.10E+01**	0
202	**10**	**24100 (0:01)**	0	0
202	**20**	**10100 (0:01)**	0	**3.53E+01**
202	**50**	**14400 (0:03)**	0	**1.04E+00**
202	**100**	**20900 (0:06)**	0	**2.56E–03**
202	**200**	**16900 (0:10)**	0	**5.12E–02**
202	**300**	**300100 (3:58)**	**1.57E–01**	0
302	**10**	**25700 (0:01)**	0	0
302	**20**	**11100 (0:01)**	0	**9.30E+01**
302	**50**	**17200 (0:04)**	0	**3.33E–01**

[a] Type of stategy: 1, max. no. of iterations: 3000, *NP*: 100, interval of pars.: [-100.,100.], output refresh cycle no.: 100, seed no.: 3, *F*: 0.8, *CR*: 1.0. See also footnote [a] of Table I.

One can ask the question: why is this program and datas have been just discussed interesting for laser experimentalists? As I mentioned before, pulse shaping can be useful for understanding the nature of light and can provide possibilities to full quantum control of a chemical reaction. Besides many more, one of the best opportunities for femtosecond pulse shaping is the use of a Liquid Crystal Display (LCD). [10] A new lab is to be built in the LCVU is going to make use of a two-layer LCD device with 640×2 = 1280 pixels. The first future task will be to make short pulses with putting different voltages on each of these pixels and modifying an incoming laser pulse this way. The program detailed above is good for modelling the LCD plate as a set of parameters.

The feedback control comes out by detecting interferemetric autocorrelation curves of the second order. [14] Fourier transforming the signs one can get three peaks and when the output pulse is enough short, the rate of these peaks is approaching 0.3:1:0.3.

Tables show, that increasing the variables *D* and *S* near eachother raise CPU time very significant, which seems not so shiny for the first sight. However, there are possibilities to reduce the number of the parameters, because one can describe the autocorrelation curves with a few parameters and/or 'build up' the LCD as larger groups of pixels. So DE through the investigated program is a useful tool for checking the length and/or other properties of laser pulses at the new LCVU laboratory in the future.

In summary I can declare, that my visit to Amsterdam was especially serviceable for me. I was allowed to inspect the research life of a very powerful laser lab and some other European institutes. Further collaboration with LCVU in the form of my Ph.D. studies is a subject to consider from both the university and my side yet.

References

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