RESEARCH CONFERENCES

ESF Conference in Partnership with LFUI

Charge Transfer in Biosystems

Universitätszentrum Obergurgl (Ötz Valley, near Innsbruck) • Austria
17-22 July 2011

Chaired by:
Dr. Rosa Di Felice, Center S3, CNR-NANO, Modena, IT
Co-Chaired by:
Yuri Berlin, Northwestern University, Evanston, US
Marcus Elstner, Karlsruhe Institute of Technology, DE

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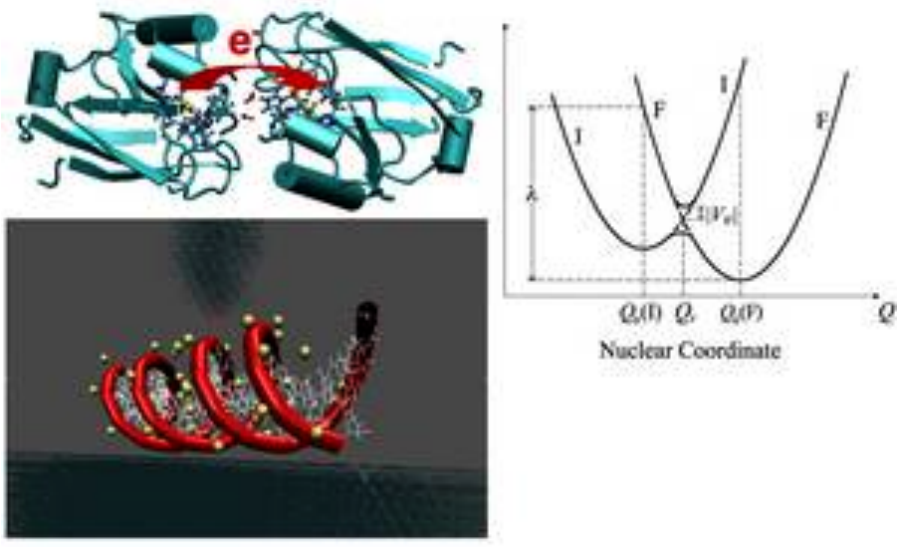

Report

The issue of charge transfer in biosystems is a hot topic in the scientific community since decades, especially due to its relevance in biology and medicine. The advent of nanotechnology and in particular the use of biomolecules in devices has rekindled the interest in this field. This situation has generated the confluence of many different approaches to study the problem.

For instance, traditionally measurements of charge transfer were done on molecular ensembles in solution (chemistry groups), while now one can also measure electrical currents through single molecules between electrodes (physics groups): what is the relation between the transfer rates measured in solution and the electrical currents measured in devices? Theoretical methods are also merging and competing: is it better to compute transfer integrals at a high accuracy level for small frozen fragments or is it better to do simplified semi-empirical simulations of entire fluctuating molecules? What is the role of self-interaction corrections? Is it important to go beyond the two-state approximation? All these problems were debated during the conference.

A particularly relevant aspect, that was repeatedly raised during the plenary and informal discussions, is the relation between theory and experiment: how can the theorists communicate easily to the experimentalists what are the shortcomings of the existing theoretical methods for which the interpretation of experiments is not always clear and unanimous? How can experiments be employed to validate theories? Can we plan benchmark experiments that effectively assess theoretical/computational results? Can we identify small benchmark biosystems on which we can appraise different approximations in the existing methods? I remark the lively dialogue between theorists and experimentalists at the conference.

The conference was successful from several viewpoints:

- It really brought together different communities with diverse expertise and multi-disciplinary background (physics, biology, chemistry, engineering);
- It created an informal atmosphere that enabled unbiased discussions;
- It effectively brought into play early stage researchers, who animatedly participated not only in the oral/poster program but also in the discussions;
- It created new contacts between scientists, likely promoting future collaborative projects;
- There was a very high scientific quality of the presentations;
- The participants were quite satisfied of all the aspects of the conference, including the science, the organization, the venue, the social program, the professional response of the staff to any sudden request.

<u>Conference summary</u>

The first introductory session was devised to set the **basics of charge transfer theory and its relation to the quantum theory of conductivity**. Two invited lectures fulfilled this scope.

- Spiros Skourtis emphasized the role of environmental fluctuations and the need for enhanced sampling techniques: not only time enhanced sampling, but general methods to improved tha statistics and account for rare events. He then discussed an application to bacteria nanowires that are essentially 2-dimensional networks of cytochromes with high packing and high order. These systems were also the topic of an experimental talk later in the program and a lively discussion soon arose.
- Abraham Nitzan talked about current transfer, explaining the relevance of transfer not only of the position but also of the momentum. He introduced magnetic effects and the excitation of circular currents. He presented studies on simple model systems, namely benzene rings.

The two invited lectures were complemented by 2 short talks on applications of theory and computation. The discussion at the end of the session was characterized by the question: “What distinguished electron transfer in biological systems from electron transfer in other systems?” It emerged that model systems can be used to study the basics of charge transfer mechanisms, but different systems have peculiarities.

Two sessions (2 and 7) were devoted to **computational approaches to charge transfer**.

- Nicola Marzari (invited) talked about the relevance of the self-interaction correction. He discussed the oxidation of Fe ions in water and short-range self-interaction in transition-metal chemistry, where he showed that GGA+U theory works.
- Alessandro Troisi (invited) discussed the relation between charge transfer in biosystems and organic electronics. He insisted again on the importance of dynamical effects. He presented work on the charge

separation at organic/inorganic interfaces, relevant for solar-cell applications.

- Gianaurelio Cuniberti (invited) talked about Landauer's theory on charge transport and applications to: molecules at surfaces, bioelectronics, molecular materials.
- Agostino Migliore (invited) presented new theoretical developments to compute thansfer integrals in DFT using non-orthogonal diabatic states.
- Ferdinand Grozema (invited) talked about the electronic structure and excited states in DNA hairpins from computational approaches.
- Jochen Blumberger (invited) presented large-scale molecular simulations of protein systems.

David Bowler presented linear scaling constrained density functional theory (DFT), with examples of scaling for Si and Ge and application to DNA and proteins. Thorsten Hansen's work was based on non-equilibrium Green's functions techniques. Michele Pavanello discussed the relevance of the amount of exact exchange contributions in the DFT computation of transfer integrals with hybrid functionals. Michael Zwolak talked about computational studies of DNA sequencing: he remarked, once again, the paramount importance of structural fluctuations. Tomas Kubar presented a scheme to effectively account for fluctuations in computational investigations, based on SCC-DFTB and QM/MM. Discussion on theory aspects.

- Transfer integrals calculations: need for benchmark systems to validate theories and experimental approaches
- λ, ΔG: need for polarizable force fields.
- Importance of the initial state for the charge-transfer reaction.

Two sessions (3 and 5) were devoted to **charge transfer/transport in proteins and complex biological systems**.

- Leslie Dutton's (invited) work is devoted to understanding elementary processes of oxidation-reduction and diverse biological events coupled to it. He explores biological redox reactions and possibility of engineering photochemistry.
- Paolo Facci (invited) presented experimental work done on single biomolecules with the electro-chemical scanning tunneling microscope.
- Krystof Bobrowski (invited) introduced the radiation-induced electron-transfer in enkephalins. He discussed experimental work on two different kinds of enkephalins, with either Leu or Met at the C terminal. Radiation is an alternative method to induce charge transfer, relative to the widely employed photochemistry.
- Bernd Giese (invited) gave an overview on the significant experimental contribution of his group to elucidate charge transfer in DNA through the years. Then he focused on new work on peptide assays for electron transfer. He discussed through-bond electron transfer, connection to photosystems, water mediation, the role of charges.

Among the short talks in these sessions, I point out the work of Moh El-Naggar on bacteria nanowires, who carried out transport measurements on lithographic electrodes, revealing high currents probably due to the network of cytochromes. Carlo Bortolotti presented a dynamical view of cytochrome C from electrochemistry measurements. Lior Sepunaru presented current measurements in protein layers between electrodes, revealing fingerprints of unfolding by varying the temperature.
The discussion on experiments focused on how to understand the mechanisms of charge transfer through DNA: how does the polaron model match with superexchange? What are good experiments to prove the existence of polarons? Though precise answers did not emerge, these critical issues were identified for future directives.

One session (4) was devoted to **DNA conductance and charge transport in DNA molecular junctions.** The only invited lectures, Danny Porath, reviewed the pioneering work done by him and his collaborators to enable and understand measurements of electrical currents through single DNA molecules between nanoscale electrodes. He then presented new developments on more complex biosystems.

Two sessions (6 and 8) were devoted to **charge migration and excitations in DNA.** All the invited lectures presented experimental work and discussed various methods and systems, including photochemistry and electrochemistry, as well as various DNA modifications with metal inclusion and with photoactive elements. It emerged that, despite the long years of investigation, a clear understanding of the charge transfer mechanisms still deserves attention, especially if DNA is to be exploited for nanotechnologies.

Conference Program

The conference program included 8 oral topical sessions and 1 poster session. The posters stayed on the boards for the duration of the conference. The oral sessions included invited lectures of 40 minutes each and short talks of 20 min each. The latter were selected among the submitted abstract, which were overall of high quality. In the details below, names of invited speakers are in bold characters. Each oral session was concluded with a discussion phase.

The poster session was preceded by a flash presentation of posters, in which the early stage researchers who presented posters could illustrate with one slide the contents of their posters to the audience. There was an excursion that stimulated informal discussions among the participants: it was attended by almost all participants. There was a final Forward Look Plenary Discussion in the evening of the last program day (Thursday July 21), in which we discussed the stat-of-the-art and the challenges for the future, set few goals for the near future and planned a new conference on the same topics, chaired by Rosa Di Felice with co-chairs Bernd Giese and Spiros Skourtis.

Names of invited speakers are in bold in the program table.

Sunday 17 July	
18:00 onwards	**Registration at the ESF Desk**
19.00	**Welcome Drink**
19.30	**Dinner**

Monday 18 July	
9.20 - 9.40	**Welcome Address**
Session 1: Theory of charge transfer and relation to charge transport	Session Chair: Yuri Berlin
09.40 - 10.20	**Spiros Skourtis**, University of Cyprus, CY *Modeling electron transfer and transport from the molecular to the cellular length scales*
10.20 - 10.40	Emilie Cauët, University Libre de Bruxelles, BE *Hole-trapping property of the human telomere sequence*
10.40 - 11.00	**Coffee Break**
11.00 - 11.20	Vladimir Egorov, Russian Academy of Science, RU *Novel theory of charge transfers in condensed matter and its correlation with experiment: Optical line shapes for polymethine dyes and their aggregates*
11.20 - 12.00	**Abraham Nitzan**, Tel Aviv University, IL *Circular currents, current transfer and magnetic field effects in molecular wires*
12.00 - 12.40	Discussion
13.00 - 15.00	**Lunch Break and Informal Discussion**
Session 2: Computational approaches to charge transfer (I)	Session Chair: Rosa Di Felice
15.00 - 15.40	**Nicola Marzari**, Oxford University, UK *Charge transfer from first-principles: challenges and solutions*
15.40 - 16.00	David Bowler, University College London, UK *Charge transfer in large systems with linear scaling constrained DFT*
16.00 - 16.20	Thorsten Hansen, Lund University, SE *Non-equilibrium Green's function theory of 2D electronic spectroscopy*
16.20 - 16.40	**Coffee Break**
16.40 - 17.20	**Alessandro Troisi**, University of Warwick, UK *What can we learn about charge transfer in biosystems from organic electronics?*
17.20 - 17.40	Michele Pavanello, Leiden University, NL *Charge transfer in biological systems studied by subsystem density functional theory*
17.40 - 18.00	Michael Zwolak, Los Alamos National Laboratory, US *Rapid DNA sequencing via transverse electronic transport*
18.00 - 18.20	Tomas Kubar, Karlsruhe Institute of Technology, DE *Non-adiabatic simulation of charge transfer in DNA*
18.20 - 19.00	**Gianaurelio Cuniberti**, TU Dresden, DE *From molecular wires to organic semiconductors and back - some "don't ask, don't tell" of soft electronics*
19.00 - 19.40	Discussion
20.00	**Dinner**

Tuesday 19 July	
Session 3: Charge transfer/transport in proteins and complex biological systems (I) Session Chair: Danny Porath	
09.00 - 09.40	**P. Leslie Dutton**, University of Pennsylvania, US *Molecular engineering of photochemical charge*

	separation
09.40 - 10.00	Nurit Ashkenasy, Ben Gurion University, IL *Charge transfer through, and from, artificial proteins in solid state configurations*
10.00 - 10.20	Samita Basu, Saha Institute of Nuclear Physics, IN *Magnetic field effect on photoinduced electron transfer between calf thymus DNA and ternary copper complex*
10.20 - 10.40	**Group Photo**
10.40 - 11.00	**Coffee Break**
11.00 - 11.40	**Paolo Facci**, CNR-NANO-S3 Modena, IT *ECSTM/STS investigation of single molecules bearing two redox levels*
11.40 - 12.00	Eduardo Della Pia, Cardiff University, UK *Observations of conductance gating for a single-redox engineered protein junction*
12.00 - 12.20	Randall Thomas Irvin, University of Alberta, CA *Spontaneous modulation of the electronic state of stainless steel via a novel synthetic bio-metallic interface*
12.20 - 12.40	Liliana Radu, Ministry of Health Romania, RO *Fluorescence resonance energy transfer in the investigation of normal and tumoral chromatin structure*
12.40 - 13.00	Discussion
13.00 - 15.00	**Lunch Break and Informal Discussion**
Session 4: DNA conductance and charge transport in DNA molecular junctions Session Chair: Abraham Nitzan	
15.00 - 15.40	**Danny Porath**, Hebrew University of Jerusalem, IL *Charge transport and spectroscopy in DNA molecules*
15.40 - 16.00	Daria Brisker-Klaiman, Technion-Israel Institute of Technology, IL *Coherent elastic transport contribution to currents through ordered DNA molecular junctions*
16.00 - 16.20	**Coffee Break**
16.20 - 16.40	Margarita Dimakogianni, University of Athens, GR *On the conductivity behaviour of the DNA double helix*
16.40 - 17.00	Orsolya Ujsághy, Budapest University of Economics and Technology, HU *Conductance of DNA molecules: Effects of decoherence and bonding*
17.00 - 17.20	Erika Penzo, Columbia University, US *Directed biomolecular assembly of integrated single molecule devices: toward reliable transport measurements*
17.20 - 18.30	**Flash Presentations of Posters -** poster presenters will introduce themselves to the audience and illustrate in one slide the contents and message of their poster.
18.30 - 20.00	**Poster Session** - posters can remain on the boards for the duration of the conference
20.00	**Dinner**
21.30 - 23.00	**Roundtable Discussions**

Wednesday 20 July	
Session 5: Charge transfer/transport in proteins and complex biological systems (II) Session Chair: Paolo Facci	
09.00 - 09.40	**Krzysztof Bobrowski**, Institute of Nuclear Chemistry & Technology, PL *Radiation-induced electron transfer in enkephalins*
09.40 - 10.00	Carlo Augusto Bortolotti, University of Modena, IT *Transient open of solvent-accessible cavities in Yeast cytochrome c as a tool for fine-tuning of its redox potential*
10.00 - 10.20	Lior Sepunaru, Weizmann Institute Rehovot, IL *Temperature dependent electron transport in proteins*
10.20 - 10.40	Moh El-Naggar, USC Los Angeles, US *Electron Transfer across the Biotic-Abiotic Interface in Microbial Fuel Cells*
10.40 - 11.00	**Coffee Break**
11.00 - 11.40	**Bernd Giese**, University of Fribourg, CH *Electron hopping through peptides: The role of side chains and the backbone*
11.40 - 12.00	Stefano Corni, CNR-NANO-S3 Modena, IT *Electron transfer proteins on gold surfaces investigated by molecular dynamics simulations*
12.00 - 12.20	Gilbert Nöll, University of Siegen, DE *Electrochemical switching of the flavoprotein dodecin on DNA-monolayers*
12.20 - 12.40	Brotati Chakraborty, Saha Institute of Nuclear Physics, IN *Magnetic field effect corroborated with docking study to explore photoinduced electron transfer in drug-protein interaction*
12.40 - 13.00	Discussion
13.00 - 17.30	**Excursion with lunch box** (lunch will be served as normal for those who will not participate in the excursion)

Session 6: Charge migration and excitations in DNA (I) Chair: Dimitra Markovitsi	
17.40 - 18.20	**Gary Schuster**, Georgia Institute of Technology, US *Radical cation hopping and reaction in DNA*
18.20 - 18.40	Irena Kratochvílová, Academy of Sciences of the Czech Republic, CZ *Charge transport in DNA oligonucleotides with various base-pairing patterns*
18.40 - 19.00	John M. Kelly, Trinity College Dublin, IE *Dipyridophenazine metal complexes which undergo photo-induced electron transfer with DNA*
19.00 - 19.40	**Torsten Fiebig**, Northwestern University, US *Electronic Transfer Processes in Biological and Biomimetic Donor-Acceptor Systems*
19.40 - 20.00	Discussion
20.00	**Drinks Reception and Conference Dinner**

Thursday 21 July	
Session 7: Computational approaches to charge transfer (II) Session Chair: Marcus Elstner	
09.00 - 09.40	**Agostino Migliore**, Tel Aviv University, IL *Effective electronic coupling calculation using non-orthogonal diabatic states: application to charge transfer in π-stacks relevant to biochemistry and nano-electronic*
09.40 - 10.00	Andrea Ferretti, CNR-NANO-S3 Modena, IT *Hybrid functional and GW corrections to quantum transport calculations*
10.00 - 10.40	**Ferdinand Grozema**, Delft University, NL *Charges and excited states in DNA hairpins: a theoretical study*
10.40 - 11.00	**Coffee Break**
11.00 - 11.40	**Jochen Blumberger**, University of Cambridge, UK *Electron transfer in cytochromes, oxidase and bacterial `wire'-proteins: Insights from molecular computations*
11.40 - 12.00	George Kalosakas, University of Patras, GR *Electronic parameters for charge transfer along DNA*
12.00 - 12.40	Discussion
13.00 - 15.00	**Lunch Break and Informal Discussion**
Session 8: Charge migration and excitations in DNA (II) Session Chair: Gary Schuster	
15.00 - 15.40	**Thomas Carell**, Ludwig-Maximilians University, DE *Metal-base pairs and metal containing DNA*
15.40 - 16.20	**Dimitra Markovitsi**, CEA Saclay, FR *Electronic excited states and reactivity of DNA*
16.20 - 16.40	**Coffee Break**
16.40 - 17.00	Frank Garwe, IPHT Jena, DE *Long-range energy transfer in DNA after fs laser pulse excitation of silver nanoparticle neighboured to DNA*
17.00 - 17.20	Rudy Schlaf, University of South Florida, US *Electronic structure of self-assembled peptide nucleic acid thin films*
17.20 - 18.00	**Jason Slinker**, University of Texas at Dallas, US *Fundamentals of DNA-mediated electrochemistry*
18.00 - 18.20	Marcos Brown Goncalves, University of Sao Paulo, BR *Theoretical study of metal DNA structures*
18.20 - 19.00	**Hans-Achim Wagenknecht**, University of Regensburg, DE *Photoinduced electron transfer in synthetically modified DNA*
19.00 - 19.40	Discussion and Summary
20.00	**Dinner**
21.30 - 22.30	**Forward Look Plenary Discussion** Coordinated by Bernd Giese

Friday 22 July
Breakfast and Departure

List of participants.

Accepted applicants.

	Surname	Name	sex	Year of Birth	Town	Ctry Residence
2	Ak	Jissy	F	1983	Sreekariyam	IN
4	Amdursky	Nadav	M	1982	Rehovot	IL
6	Artes Vivancos	Juan Manuel	M	1982	Barcelona	ES
7	Ashkenasy	Nurit	F	1967	Beer Sheva	IL
8	Banerjee	Mousumi	F	1983	Kolkata	IN
9	Basu	Samita	F	1959	Kolkata	IN
10	Bende	Attila	M	1973	Cluj-Napoca	RO
11	Berstis	Laura	F	1984	Zurich	CH
12	Borges	Anders	M	1988	Copenhagen	DK
13	Bortolotti	Carlo Augusto	M	1978	Modena	IT
14	Bowler	David	M	1970	London	UK
15	Brazdova	Veronika	F	1975	London	UK
16	Breuer	Marian	M	1987	London	UK
17	Brisker-Klaiman	Daria	F	1980	Haifa	IL
19	Camargo Dalmatti Alves Lima	Filipe	M	1986	São Paulo	BR
20	Cauët	Emilie	F	1980	Brussels	BE
21	Caycedo-Soler	Felipe	M	1980	Ulm	DE
22	Chakraborty	Brotati	F	1983	Kolkata	IN
23	Corni	Stefano	M	1975	Modena	IT
24	Davis	Elisabeth	F	1983	Edmonton	CA
25	Della Pia	Eduardo Antonio	M	1982	Cardiff	UK
26	Di Paolo	Gaia	F	1986	Roma	IT
27	Dimakogianni	Margarita	F	1981	Athens	GR
28	Dorner	Ross	M	1987	London	UK
29	Egorov	Vladimir V.	M	1949	Moscow	RU
30	El-Naggar	Moh	M	1979	Los Angeles	US
31	Èoga	Lucija	F	1986	Ljubljana	SI
32	Ferreiro	Dardo Nahuel	M	1985	Buenos Aires	AR
33	Garwe	Frank	M	1965	Jena	DE
35	Goncalves	Marcos	M	1976	Sao Paulo	BR
39	Hansen	Thorsten	M	1974	Lund	SE
41	Irvin	Randall Thomas	M	1952	Edmonton	CA
42	Kalosakas	George	M	1968	Patras	GR
44	Kelly	John	M	1944	Dublin	IE
45	Kim	Heeyoung	F	1980	Daejeon	KR
47	Kratochvilova	Irena	F	1965	Prague	CZ
48	Kubar	Tomas	M	1980	Karlsruhe	DE
51	Macdonald	John Emyr	M	1959	Cardiff	UK
56	Nöll	Gilbert	M	1972	Siegen	DE
58	Omerzu	Ales	M	1968	Ljubljana	SI
59	Ouahab	Lahcène	M	1953	Rennes	FR
61	Pavanello	Michele	M	1979	Leiden	NL
62	Penzo	Erika	F	1983	New York	US
63	Plasser	Felix	M	1984	Vienna	AT
65	Quinn	Susan	F	1976	Dublin	IE
66	Radu	Liliana	F	1946	Bucharest	RO
68	Sarangi	Manas	M	1981	Kolkata	IN
70	Schlaf	Rudy	M	1964	Tampa	US
71	Sepunaru	Lior	M	1981	Rehovot	IL
73	Solomon	Gemma	F	1980	Copenhagen Ø	DK

76	Torrellas	Germán	M	1988	Colmenarejo	ES
77	Ujsághy	Orsolya	F	1968	Budapest	HU
78	Varsano	Daniele	M	1973	Rome	IT
80	Woiczikowski	Benjamin	M	1983	Karlsruhe	DE
81	Wolter	Mario	M	1986	Karlsruhe	DE
83	Zakrassov	Alexander	M	1972	Haifa	IL
84	Zilly	Matias	M	1979	Duisburg	DE
85	Zwolak	Michael	M	1979	Los Alamos	US
86	Ferretti	Andrea	M		Modena	IT

Invited speakers and chairs.

Surname	Name	Status	Sex	Year of Birth	Ctry Residence
Berlin	Yuri	C	M	1944	US
Blumberger	Jochen	S	M	1976	UK
Bobrowski	Krzysztof	S	M		PL
Carell	Thomas	S	M	1966	DE
Cuniberti	Giovanni	S	M		DE
Di Felice	Rosa	C	F	1967	IT
Dutton	P. Leslie	S	M	1941	US
Elstner	Marcus	C	M		DE
Facci	Paolo	S	M	1964	IT
Fiebig	Torsten	S	M		US
Giese	Bernd	S	M	1940	CH
Grozema	Ferdinand	S	M		NL
Markovitsi	Dimitra	S	F	1954	FR
Marzari	Nicola	S	M	1966	UK
Migliore	Agostino	S	M	1973	IL
Nitzan	Abraham	S	M	1944	IL
Porath	Danny	S	M	1966	IL
Schuster	Gary	S	M	1946	US
Skourtis	Spiros	S	M	1966	CY
Slinker	Jason	S	M		US
Troisi	Alessandro	S	M	1975	UK
Wagenknecht	Hans-Achim	S	M	1968	DE

Abstracts of papers.

(Only the abstracts of short talks are reported. Abstracts were not requested from invited speakers)

Emilie Cauët, University Libre de Bruxelles, BE *Hole-trapping property of the human telomere sequence.*

Today, there is no doubt that electron hole (radical cation) migration in DNA is possible and can occur over long molecular distances [1]. These findings have led to speculation that DNA itself contains sacrificial sites, particularly sites comprising guanine (G) rich sequences that are positioned optimally to absorb holes and thereby protect sensitive regions of the genome from oxidative damage [2]. In this regard, G-rich telomeres found at the end of chromosomes have been proposed as good candidates for "genome protectors" [2]. In humans, the telomeres consist of tracts of TTAGGG sequence repeats, which persist up to 10 kilobase pairs [3]. Although most of the telomeric sequence is double-stranded, a portion of the G-rich strand extends past the duplex as a single-stranded overhang [4]. This overhang is not transcribed and must thus be excised and repaired after oxidation.

Both calculations and oxidative yield experiments have demonstrated that GG and GGG act as shallow hole sinks and that the hole density is favored on the 5'-G [5]. Generally, a strong correlation has been found between the calculated ab initio ionization energy (IE) of guanine in the different stacking environments and the experimentally observed relative oxidative damage [5d]. Hence, in this study, we examined the IE of guanine in the human telomere sequence. For reference, the IE of stacked contiguous guanines (up to six) has also been evaluated. To support the effective protection of the genes against oxidative damage provided by the telomeric overhangs, we report here (i) the prediction that the TTAGGG telomeric repeat sequence is particularly prone to oxidation and can act as a profound hole trap as deep as a sequence of five consecutive guanines and (ii) a simple molecular orbital analysis to explain how modifications in the human telomeric sequence are expected to change the efficiency of the sequence as a hole trap.

[1] (a) Genereux, J. C.; Barton, J. K., Chem. Rev. 2010, 110(3), 1642-1662; (b) Slinker, J. D.; Muren, N. B.; Renfrew, S. E.; Barton, J. K., Nat. Chem. 2011, 3, 230.

[2] Heller, A., Faraday Discuss 2000, 116, 1-13.

[3] Collins, K., Curr. Opin. Cell. Biol. 2000, 12(3), 378-383.

[4] Greider, C. W., Cell 1999, 97(4), 419-422.

[5] (a) Hall, D. B.; Holmlin, R. E.; Barton, J. K., Nature 1996, 382(6593), 731-735; (b) Sugiyama, H.; Saito, I., J. Am. Chem. Soc. 1996, 118(30), 7063-7068; (c) Saito, I.; Takayama, M.; Sugiyama, H.; Nakamura, T., J. Photoch. Photobio. A 1997, 106(1-3), 141-144; (d) Saito, I.; Nakamura, T.; Nakatani, K.; Yoshioka, Y.; Yamaguchi, K.; Sugiyama, H., J. Am. Chem. Soc. 1998, 120(48), 12686-12687; (e) Cauët, E.; Liévin, J., Adv. Quantum Chem. 2007, 52, 121-147; (f) Cauët, E.; Liévin, J., J. Phys. Chem. A 2009, 113(36), 9881-9890; (g) Adhikary, A.; Khanduri, D.; Sevilla, M. D., J. Am. Chem. Soc. 2009, 131(24), 8614-8619.

Vladimir Egorov, Russian Academy of Science, RU *Novel theory of charge transfers in condensed matter and its correlation with experiment: Optical line shapes for polymethine dyes and their aggregates*

Polymethine dyes are the simplest prototypes of biological molecules, which are well in tracing the basic properties of the dynamic self-organization of elementary charge transfer processes in condensed matter. Though theoretical treatment of the optical line shapes for polymethine dyes and their aggregates has been a top problem in physics and chemistry for many decades, it has not been solved conclusively to date [1]. The author proposes a novel theory of charge transfers on the basis of dozy chaos [2–4] that gives insight into the nature of the optical line shapes for polymethine dyes, their dimers, H-, H*-, and J-aggregates. This theory formulates a proper definition of electron- nuclear coupling in the dynamics of the transient state, which is of paramount importance for charge transfers in such organic systems due to their largeness [2]. By dozy chaos the light electron succeeds in controlling the motion of extremely heavy nuclei in the transient state, making it chaotic [2]. Dozy chaos is absent in the initial and final states, and arises in the transient state alone. Dozy chaos was introduced into science at the beginning of the 21st century as a novel physical substance to describe charge transfers in condensed matter [2–4]. The necessity for introducing this substance stems from the presence of inherent singularity in the probability of charge transfers as a result of transit beyond the adiabatic approximation in the quantum mechanics of electron–nuclear motion. Formally, dozy chaos is introduced as an imaginary part in the electron–nuclear coupling in the dynamics of the transient state in charge transfers, and a novel area is the Green function method into which dozy chaos is introduced [2–4]. The physical picture of charge transfers in the presence of dozy chaos is discussed in Refs. [2–4]. Formerly in terms of the novel theory the author clarified the nature of optical line shapes for dye monomers and J-aggregates [3,4]. Now this theory is developed to involve exciton effects that are important in dimers and H-aggregates [1]. Some of the results are in theoretical absorption line shapes fitted by the author to the basic experimental data [5] on dye monomers, dimers, H-, H*-, and J-aggregates [1] and also theoretical curves fitted to the well-known data [5] on the monomer-dimer concentration equilibrium [1].

References:

[1] V.V. Egorov, J. Lumin. 131 (2011) 543. [2] V.V. Egorov, Physics Procedia 2 (2009) 223. [3] V.V. Egorov, J. Chem. Phys. 116

(2002) 3090. [4] V.V. Egorov, Chem. Phys. 269 (2001) 251. [5] T.H. James (Ed.), The Theory of the Photographic Process, Macmillan, N.Y., 1977.

David Bowler, University College London, UK *Charge transfer in large systems with linear scaling constrained DFT*
I will describe the implementation of constrained DFT within the O(N) DFT code, CONQUEST. This will allow the simulation of charge transfer within biomolecules and other large systems with full ab initio accuracy. CONQUEST is capable of plane wave accuracy, and has been shown to scale to millions of atoms and thousands of processors, opening the way to new classes of biosimulation.

Thorsten Hansen, Lund University, SE *Non-equilibrium Green's function theory of 2D electronic spectroscopy*
A novel method for doing nonlinear response theory on the Schwinger-Keldysh contour is presented. Specifically, we obtain the Liouville space pathways of the nonlinear optical response functions. This result unleashes the use of non-equilibrium Green's function techniques in nonlinear optical spectroscopy.
We study exited state quantum dynamics and simulate 2D electronic spectra for comparison with experiment. This work leads towards insights into exciton quantum dynamics, and to how form follows function in the circular LH2 light-harvesting antenna complexes in photosynthetic purple bacteria.

Michele Pavanello, Leiden University, NL *Charge transfer in biological systems studied by subsystem density functional theory*
The subsystem formulation of DFT known as Frozen Density Embedding (FDE) offers an excellent platform for studying charge transfer (CT) reactions in biological systems. We present the necessary theory developments for the calculation of such CT parameters as the solvent reorganization energy, the transfer integral, and the internal energy of reaction carried out in a fully quantum-mechanical fashion. We present preliminary calculations on solvated DNA oligomers radical cations and selected radical anions involved in intervalence CT reactions.

Michael Zwolak, Los Alamos National Laboratory, US *Rapid DNA sequencing via transverse electronic transport*
A rapid and low-cost DNA sequencing method would revolutionize medicine: a person could have their full genome sequenced so that treatments could be tailored to their specific conditions; doctors could know in advance a patient's likelihood to develop a given ailment; cures to major diseases could be developed faster. These goals of "personalized medicine" are hampered today by the high cost and slow speed of DNA sequencing methods. I discuss a sequencing protocol we suggest that uses the measurement of transverse electronic currents during the translocation of single-stranded DNA through nanopores and support our conclusions using molecular dynamics simulations coupled to quantum mechanical calculations of the tunneling current in experimentally realizable systems. Several recent experiments also support our theoretical predictions. In addition to their possible impact in medicine and biology, the above methods offer ideal test beds to study open scientific issues in the relatively unexplored area at the interface between solids, liquids, and biomolecules at the nanometer length scale [1].
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Tomas Kubar, Karlsruhe Institute of Technology, DE *Non-adiabatic simulation of charge transfer in DNA*
Coarse-grained multi-scale method based on DFT for the simulation of charge transfer in complex molecular systems is presented. The fragment-orbital ansatz and the use of an approximative DFT method to compute charge- transfer parameters allow to simulate the dynamics of excess charge on a nanosecond time scale, not having to neglect the important effects of structural fluctuations and solvent. Non-adiabatic schemes to propagate the wave function of the excess charge have been implemented - (i) simultaneous integration of coupled equations of motion for QM and MM within the framework of time-dependent DFT, and (ii) diabatic surface hopping approach. An empirical correction has been introduced to remedy the self-interaction error inherent to DFT, which brings on an exaggerated delocalization of the hole charge.
In the case of DNA, the polarization of solvent is the dominant factor affecting the hole transfer. The hole charge polarizes the surrounding water, which in turn supports a localization of the hole charges - a water polaron is formed, extended dynamically over several nucleobases. The features and rate of the process obtained with the various approaches is discussed. Also, the application to hole transfer in a protein is mentioned briefly.

Nurit Ashkenasy, Ben Gurion University, IL *Charge transfer through, and from, artificial proteins in solid state configurations*
In recent years there is a great interest in the integration of proteins within electronic devices. For best device performance, better understanding of charge transfer through the proteins in solid state configurations and at their interface with inorganic materials should be gained. Furthermore, since proteins did not evolve to perform such tasks, the targeted design of proteins for these specific applications is of great importance. Our research focuses on the development and electronic characterization of simple artificial protein systems for molecular electronics applications. This approach will be presented here by two distinct examples. Our studies demonstrate the great potential of the use of specifically designed proteins as

components of electronic devices. Moreover, I will show that such systems can be used as simple platforms for understanding the role of different charge transfer mechanisms in proteins.
In the first example, the design and characterization of beta-sheet like self-assembled cyclic peptide nanotubes, which can potentially be used as protein based molecular wires, will be demonstrated. Taking advantage of a novel layer by layer deposition approach we have developed, the nanotubes' charge transfer properties have been studied as function of the nanotube length using conductive-atomic force microscopy. These studies reveal a very efficient charge transfer through this supramolecular protein, with an attenuation factor of 0.1 Å-1. Detailed analysis of the current-voltage relations provide evidence that effective charge transfer can occur through hydrogen bonds in proteins, and that hoping may be a dominant charge transfer mechanism even for very short distances.

Samita Basu, Saha Institute of Nuclear Physics, IN *Magnetic field effect on photoinduced electron transfer between calf thymus DNA and ternary copper complex*
Application of low magnetic field (MF) of the order of 0.01-0.02 tesla helps enormously in the elucidation of the reaction pathways of photoinduced reactions that involve either geminate radical ion pairs or radical pairs as transient intermediates produced through photoinduced electron transfer and hydrogen abstraction or bond cleavage respectively. The radicals when separated by a certain distance by diffusion where exchange interaction becomes negligible might undergo maximum intersystem crossing by spin flipping in the presence of an internal MF i.e. hyperfine interaction (HFI) present in the system. Application of an external MF which can overcome HFI could reduce the intersystem crossing leading to an increase in recombination product or free ion formation, which is a signature of the initial spin state of the radical ion pairs, either singlet or triplet respectively. Moreover, MF could signify the optimum separation distance that would provide maximum spin flipping and formation of free ions or recombination products. Organized assemblies like micelles, reverse micelles and vesicles have the potential to prolong the lifetime of the radicals to be detected by laser flash photolysis technique and provide sufficient space to maintain the above optimum separation. Biological macromolecule itself provides a confined and restricted environment required to sustain the geminate characteristics of the radical pairs or ion pairs, which has been observed in the interactions of DNA and some model proteins with some biologically relevant molecules. It has been found that transition metal complexes undergo electron transfer with DNA. The 2:1 1,10-phenanthroline (phen)- copper (I) complex is the first synthetic coordination complex, which acts as a˜chemical nuclease with an efficient nucleolytic activity in presence of reducing agents, e.g. thiol or ascorbic acid, and molecular oxygen or hydrogen peroxide. We have studied the mechanism of electron transfer phenomenon occurring between calf thymus DNA and [Cu(phen)2]2+ complex and its amino acid substituted homologues, [Cu(phen)(Htyr)]ClO4 and [Cu(phen)(Htrp)]ClO4 (Htyr: L- tyrosinato and Htrp: L-tryptophanato) on photo-excitation using laser flash photolysis and magnetic field effect. The occurrence of partial intercalation of the complexes within DNA helps in maintaining that proper inter-radical distance between the radical ion pairs generated through photoinduced electron transfer, so that spin correlation exists between them and magnetic field effect could be observed. In organized assemblies, e.g., reverse micelles, magnetic field effects with different amino acid containing complexes are not similar due to their differential solubility in reverse micelles.

Eduardo Della Pia, Cardiff University, UK *Observations of conductance gating for a single-redox engineered protein junction*
Measuring single molecule conductance is a fundamental step in order to realize the basic elements of future electronic circuits. In particular, the next generation of biosensors could be realized of single proteins that have chemical, physical and structural properties ideal for single molecule events recognition. However, technical hurdles still exist for the integration of proteins into semiconductor technology. For example, (i) electrical contact to biomolecules still needs to be fully understood and (ii) modulation of the current through proteins by external signals has not been measured yet.
Here we report measurements of single metal-protein-metal junction conductance achieved by covalently linking the molecule to metallic electrodes. Crucially the proteins' conductance can be modulated by an external potential in a fashion similar to a solid-gate transistor and the tunnelling mechanism through the molecule is consistent with a two- electron transfer theoretical model.
In this study we used the affinity of thiol groups (-SH) for gold to realize good electrical contacts between a protein and two electrodes. Cytochrome b562, a small redox-active protein, was engineered with two cysteine residues (which have thiol-terminated side-chains) at opposite ends of the molecule, both along the long axis and across the short axis of the protein, to facilitate organized assembly on a gold surface. The cytochrome b562 double cysteine mutants can be efficiently anchored to a gold surface in orientations defined by protein engineering while crucially retaining their electron transfer properties as showed by UV-Visible absorption spectroscopy, hemin spectrophotometric titration experiments and electrochemical measurements. A combination of in air and in-situ STM imaging and molecular current-voltage and current-distance measurements was used to probe the conductance of the gold STM tip-cytochrome b562–Au(111) system in both protein orientations. The proteins containing the anchoring groups strongly interact with the two conducting surfaces and have a conductance of ~1 nS. In contrast, the gold-wild type cytochrome b562 junction was both less robust and at least one order of magnitude less conductive. The proteins' conductance can be electrochemically modulated and the molecule has its higher

conductance when its molecular energy levels are aligned within the Fermi energy levels of the electrodes.
Our findings illustrate the possibility of wiring a molecule as complex as a redox protein to two metal conductors and of gating its conductance, opening new perspectives for the realization of biomolecular nanoscale electronics.

Randall Thomas Irvin, University of Alberta, CA *Spontaneous modulation of the electronic state of stainless steel via a novel synthetic bio-metallic interface*
Previously reported electron conducting bacterial nanowires are atypical type IV pili (where the pilin structural protein consists of a single helix) while the classical type IV pili been reported to be non-conducting despite extensive sequence similarity with the N-terminal á-helical domain of the classic pilins. We show that the P. aeruginosa pili in fact function as insulated conducting nanowires. PAK pili bind to stainless steel via a previously unreported type of chemical interaction between a tip displayed receptor binding domain (RBD) in the C-terminal disulfide looped region of the PilA structural protein. A synthetic peptide derived from the native sequence of PilA spontaneously interacted with stainless steel to generate an altered form of the metal we term bioorganic stainless steel. Bioorganic stainless steel has a significantly increased electron work function (4.9+.05eV compared to 4.79+.07eV), decreased material adhesive force (19.4+8.8 nN compared to 56.7+10.5 nN), and is significantly harder than regular 304 stainless steel (~40% harder). A novel formal or semi-formal organo-metallic covalent bond is generated between a pilin receptor binding domain and stainless steel based on XPS analysis which indicates that the electronic state of the surface is altered. We hypothesized that the PilA-derived synthetic peptide formed a direct electrical connection with the steel that could readily transfer electrons from the surface through to the external environment. The EWF of the surface was substantially reduced via the coupling of the RBD to a highly charged random coil. Subsequent formation of a highly charged but with a net neutral charge coiled-coil further altered the electrical properties of the surface. Consistent with these findings, corrosion studies confirmed that electron transfer was substantially enhanced when the coil was fused to the RBD and even further enhanced when the coiled-coil was formed. Subsequent cyclic voltammetry studies demonstrated that receptors fused to the RBD and coupled to steel could function as field effect transistors and serve as a label free biosensor to monitor receptor- ligand interactions. Taken together, these data show that synthetic peptides derived from the P. aeruginosa PilA protein alter the physical and electrical properties of stainless steel establishing their potential use in a variety of bioelectronic applications.

Liliana Radu, Ministry of Health Romania, RO *Fluorescence resonance energy transfer in the investigation of normal and tumoral chromatin structure*
Chromatin is the complex of deoxyribonucleic acid (DNA) with proteins, that exists in eukaryotic cell nuclei. Informations on the chromatin structure from normal tissues and tumoral tissues and also on the chromatin structure modifications produced by fast neutrons were obtained utilising the fluorescence resonance energy (FRET) method. The chromatin was extracted from a normal tissue (liver of Wistar rats) and from a tumoral tissue (Walker carcinosarcoma maintained on Wistar rats). The chromatin samples were irradiated by fast neutrons in doses of 10- 100 Gy. In the FRET method, a donor fluorophore is excited by incident light and if an acceptor is in close proximity, the excited-state energy from the donor can be transferred to it. Double-fluorescent labelling of chromatin was performed with dansyl chloride and acridine orange. The dansyl chloride reacts, under mild alkaline conditions, with the - and -amino groups of the proteins, the cysteine sulphydryl group, the histidine imidazole group and the tyrosine phenolic group. Acridine orange is intercalated between chromatin DNA base pairs. FRET is possible between this pair of fluorescent ligands, because the emission spectrum of dansyl chloride (donor) is superposed on the excitation spectrum of acridine orange (acceptor). The Förster energy transfer efficiency was determined and the Förster critical distance at which 50% of the excitation energy is transferred from the donor to the acceptor and the distance between donor and acceptor were established. The normal chromatin has a more condensed structure than the tumoral chromatin. In the tumoral chromatin the euchromatin/heterochromatin ratio is higher than in the normal chromatin. The energy transfer efficiency decreases with the fast neutrons dose, indicating a more unstable chromatin structure. The increase of the distance between the ligands reflects the enhancement of the distance between chromatin proteins and DNA, which suggests a loosening of the chromatin structure. This distance variation is greater in Walker carcinosarcoma chromatin than in normal liver chromatin. ¸The knowledge of the normal and tumoral chromatin structure and of these chromatin structure modifications in the fast neutron actions are important in improving diagnostics in clinical applications.

Daria Brisker-Klaiman, Technion-Israel Institute of Technology, IL *Coherent elastic transport contribution to currents through ordered DNA molecular junctions*
The recently reported experimental control of the connectivity between double-stranded DNA and the electrodes in a junction is proposed as a tool for characterizing the mechanisms of charge transport through DNA. In particular, sensitivity of the current-voltage curve to the connectivity strategy can probe the contribution of coherent elastic charge transport to the current through DNA junctions. Landauer transport calculations show that for ordered long DNA sequences, the efficiency of the coherent transport increases by several orders of magnitude, and the calculated currents associated with the purely

coherent transport mechanism become as high as currents measured in transport experiments on DNA junctions. The possibility that coherent transport through long ordered sequences may become as efficient as incoherent transport is raised.

Margarita Dimakogianni, University of Athens, GR *On the conductivity behaviour of the DNA double helix*

The realization of innovative applications in nanotechnology has generated a widespread interest in the transport properties of biological systems, with DNA being one of the most promising candidates. The character of the carriers and the transport mechanisms along with external stimuli, such as finite electric fields and temperature (T) conditions, determine their electrical response.

We investigate the transport mechanism responsible for the measured electrical conductivity of DNA biomolecules taking into account the one-dimensional (1D) character of the system, the possible polaronic character of the carriers and the presence of disorder, resulting from the random base sequences and the randomly positioned counterions along the backbone of the DNA helix. The microscopic transport mechanism is treated within the framework of the generalized molecular crystal model and the Kubo formula, while percolation theoretical arguments lead to analytical expressions for the macroscopic behaviour of the electrical conductivity at high (multi- phonon assisted hopping) and low (few-phonon assisted hopping) temperatures under the influence of finite electric fields. At high temperatures, ignoring the effect of correlations between successive hops, we have obtained analytical expressions for the temperature dependence of the electrical conductivity and the maximum hopping distance. The theoretical results have been successfully applied to experimental data reported for ë-DNA and poly(dA)-poly(dT) DNA, leading to the conclusion that multiphonon-assisted small polaron hopping between neighboring base pairs could be the responsible charge transfer mechanism at high temperatures.

The inclusion of correlations leads to a different T-law and a corresponding maximum hopping distance. Applying our new theoretical results to the most recent experimental data, we have obtained consistently longer maximum hopping distances, supporting the idea of long distance charge migration in DNA. Most recently, we examined the interplay of the electric field and temperature on the non-ohmic behaviour of the small polaron hopping conductivity of 1D systems, ignoring and including correlations. This work pushes our theoretical investigation in 1D systems one step forward and aims to motivate further experimental research on DNA and other biosystems.

Orsolya Ujsághy, Budapest University of Economics and Technology, HU *Conductance of DNA molecules: Effects of decoherence and bonding*

We examine the influence of decoherence and bonding on the linear conductance of single double-stranded DNA molecules by fitting a recently developed phenomenological statistical model (EPJB 68,237 (2009)) to experimental results. The DNA molecule itself is described by a tight binding ladder model with parameters obtained from published ab initio calculations (J.Am.Chem.Soc.127, 14894 (2005)). The good agreement with the experiments on sequence and length dependence gives a hint on the nature of conduction in DNA and at the same time provides a crucial test of the model.

Erika Penzo, Columbia University, US *Directed biomolecular assembly of integrated single molecule devices: toward reliable transport measurements*

DNA has been the focus of attention of chemists and physicists for its potential use in nanoelectronic devices, both as a template for assembling nanocircuits and as an active element of such circuits. Experiments to date measuring DNA conductance have resulted in a wide range of behaviors, from insulating to superconducting. These experiments are quite difficult and they are done under very different conditions. This may account for the inconsistent results observed so far.

In order to obtain a more clear understanding of charge transport in DNA and to establish the underlying mechanisms, a stable device platform is required. We are developing a single molecule device using carbon nanotube (CNT) electrodes to contact the molecule. CNTs offer distinct advantages for this purpose, as they are excellent one-dimensional conductors that are approximately the same size as DNA and other conjugated molecules. Being made of carbon, they also lend themselves to the formation of robust, reproducible carbon bonds to the molecule of interest. In contrast to earlier work in which the molecule was inserted into a gap cut into the CNT, our approach will incorporate CNT-molecule complexes formed in solution. This eliminates the problem of matching the gap size with the molecule length.

The CNT-molecule complexes will be organized on surfaces using lithographically directed biomolecular assembly. We have developed techniques to selectively functionalize lithographically patterned nanodots with a variety of biomolecules. We use these nanodots as anchors for the assembly of different nanomoieties. For example, we have recently been able to monitor thousands of DNA-protein interactions in parallel with single molecule resolution. We are also exploring assembly of electronically functional nanomaterials on DNA origami. By selectively placing the origami scaffolds at lithographically determined locations, we can integrate multiple CNT-molecule devices on a single substrate.

This new approach combines solution-based chemistry, self-assembly and precision lithographic engineering. It may serve as a new paradigm for building well controlled, robust nanoelectronic devices and circuits.

Carlo Augusto Bortolotti, University of Modena, IT *Transient open of solvent-accessible cavities in Yeast cytochrome c as a tool*

for fine-tuning of its redox potential

The dynamic interplay between a protein and the surrounding solvent is fundamental to its structure/function relationship, but its exploration is still experimentally too demanding. By contrast, long (i.e. hundreds of nanoseconds) molecular dynamics simulations can reveal unexpected events even for extensively studied biomolecules . We made use a mix of experimental (electrochemistry) and theoretical (Perturbed Matrix Method, PMM) approaches to investigate the reversible opening of two distinct fluctuating solvent-accessible channels in wild- type Yeast cytochrome c. Both channels allow for water access in proximity to the heme propionates. The resulting conformational hydrated states of the protein feature relatively small but significant shifts in the redox potential, that could be estimated on a theoretical basis. These transient cavities could likely be involved in the modulation of the driving force of the electron transfer between cytochrome c and its physiological partners.

Lior Sepunaru, Weizmann Institute Rehovot, IL *Temperature dependent electron transport in proteins*

Electron transfer (ET) through proteins is a fundamental process in biology. It has been and is studied intensively in solution. Solid state electron transport (ETp) across proteins, sandwiched between two solid electrodes, an evolution of molecular electronics, aims at understanding the extent to which protein features/functions are expressed (and used) in this new configuration. Most studies to date were conducted with one or just a few molecules in the junction.

We show that one can prepare and electrically characterize high quality, large area monolayer junctions with three different families of proteins: Bacteriorhodopsin (bR), a membrane protein-chromophore complex with proton pumping function, Azurin (Az), a blue-copper ET metallo-protein, and Bovine Serum Albumin (BSA) and that we can gain information about their ETp mechanism by applying solid state physics methods, such as current-voltage temperature (I-V-T) measurements to these proteins. We find dramatic changes in the proteins' ETp activation energies and mechanisms, for bR and Az, respectively. Our results shed new light on ETp properties in proteins (mostly they resemble molecular wires, more than insulators) and lead us a step further towards utilizing the functional characteristics of these and related biocomplexes as actual electronically conductive components.

Moh El-Naggar, USC Los Angeles, US *Electron Transfer across the Biotic-Abiotic Interface in Microbial Fuel Cells*

Microbes can be regarded as powerful factories that catalyze a wide array of reactions to meet their energy demands. Understanding and taking advantage of these activities at interfaces presents potentially transformative approaches to bioenergy and biosynthesis of nanomaterials. For example, the ability of certain microorganisms to transfer electrons directly to solid surfaces enables the emerging technology of microbial fuel cells (MFCs), where living cells utilize complex or mixed biofuels to produce electricity. However, despite the overwhelming importance of the biotic-abiotic interface in MFCs, we possess minimal knowledge regarding the role of extracellular nanostructures in direct electron transfer between living cells and MFC electrodes. This talk describes our ongoing work to bridge this knowledge gap using approaches ranging from device-scale electrochemical characterization, to nanoscale electron transport measurements along bacterial nanowires produced by the dissimilatory metal-reducing bacterium Shewanella oneidensis MR-1. Transport along bacterial nanowires was independently evaluated by two techniques: (1) nanofabricated electrodes patterned on top of individual nanowires, and (2) conducting probe atomic force microscopy (CP-AFM) at various points along a single nanowire bridging a metallic electrode and a conductive AFM tip. The S. oneidensis nanowires were found to be electrically conductive along micrometer length scales with electron transport rates up to 10^9/s at 100mV of applied bias and a measured resistivity on the order of 1 ohm·cm. We also show that mutants deficient in genes for c-type decaheme cytochromes MtrC and OmcA produce appendages that are morphologically consistent with bacterial nanowires, but are non-conductive. The measurements reported here suggest that bacterial nanowires constitute a viable microbial strategy for extracellular electron transport. Finally, we summarize our efforts to directly measure the microbial activity under physiological conditions, including in fuel cell environments, using optically accessible microfabricated devices that could shed light on microbe-surface interactions setting the limits to electricity generation.

Stefano Corni, CNR-NANO-S3 Modena, IT *Electron transfer proteins on gold surfaces investigated by molecular dynamics simulations*

Investigation of electron transfer (ET) proteins via Electrochemical Scanning Tunneling Microscopy can provide new insight in the basic electron transfer processes taking place in the protein [1]. Moreover, the potential of ET proteins as active elements in electronic devices have also been evaluated [2]. Such experimental studies can be effectively accompanied by atomistic simulations. These can provide a picture of the basic phenomena taking place in the ECSTM setup at a level of detail not yet accessible in the experiments. We have simulated by classical molecular dynamics simulations entire ET proteins (azurin and cytochrome C) immobilized on gold surfaces in water. Thanks to these simulations, we could study the effects of the ECSTM apparatus on the protein orientation on the surface and, in turn, how this orientation affects the ECSTM signal [3]. Moreover, we could rationalize ET trends that have been measured for mutants of cytochrome C on gold electrodes [4]. In particular, we show that structural rearrangements taking place for proteins at the interface can have profound effects on the protein ET ability, even when the folding of the protein is conserved.

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Gilbert Nöll, University of Siegen, DE *Electrochemical switching of the flavoprotein dodecin on DNA-monolayers*

Dodecin from Halobacterium salinarum is a dodecameric, hollow-spherical flavoprotein which contains six flavin binding sites. In each binding site, two flavins are arranged in an aromatic tetrade between two tryptophan residues. Dodecin binds not only native but also artificial flavins with high binding affinities. Reduction of the flavin ligand induces the dissociation of the holocomplex into apododecin and free flavin. Inspired by the binding mode and the redox characteristics of dodecin, we are developing electrochemically active flavin modified electrode surfaces (electrode – molecular wire - flavin) which are able to bind or release dodecin apoprotein triggered by the redox potential. Possible applications range from the control or transport of single molecular assemblies containing dodecin apoprotein, up to the development of bioelectrochemical data storage devices with an electrochemical input (write) and an optical (fluorescence sensitive) output (read). In a first series of studies we examined ds-DNA as possible molecular wire-like unit. When flavin and disulfide modified ds DNA of 20 base pairs was directly adsorbed on gold, it was possible to bind and release apododecin depending on the applied redox potential. For comparison a stepwise surface modification protocol, which included the adsorption of thiol-modified ss-DNA followed by the release of non-specifically adsorbed DNA by addition of a mercaptoalcohol solution, and hybridization with complementary flavin-modified ss-DNA subsequently, was applied. By this protocol, a more densely packed protein monolayer could be obtained after addition of apododecin, but the release of apododecin upon electrochemical reduction was not possible any more. In control experiments up to 70% of the previously adsorbed apododecin could be released by chemical reduction using sodium dithionite. Also after minimizing the length of the linkers between thiol and DNA or DNA and flavin, it was not possible to release apododecin upon electrochemical reduction. As an important result of these studies, different surface modification protocols should be compared when electron transfer through DNA monolayers on electrodes is investigated.

Brotati Chakraborty, Saha Institute of Nuclear Physics, IN *Magnetic field effect corroborated with docking study to explore photoinduced electron transfer in drug-protein interaction*

Conventional spectroscopic tools like UV-vis absorption, fluorescence, and circular dichroism spectroscopy used in the study of photoinduced drug-protein interactions can yield useful information about ground-state and excited-state phenomena. However, photoinduced electron transfer (PET) may be a possible phenomenon in the drug-protein interaction, which may go unnoticed if only conventional spectroscopic observations are taken into account. Although PET reactions in proteins have already been reported by a number of workers, especially intramolecular PET, relatively little is known about PET in drug-protein interaction. An applied magnetic field (MF) can alter the fate of a PET reaction by influencing this spin evolution in spite of contributing nothing to the chemical energy. Actually, the radicals or radical ions, formed in the due course of PET, when separated by a certain distance by diffusion where exchange interaction becomes negligible may undergo maximum intersystem crossing by spin flipping in the presence of an internal MF i.e. hyperfine interaction (HFI) present in the system. Application of an external MF which can overcome HFI may reduce the intersystem crossing leading to an increase in recombination product or free ion formation, which is a signature of the initial spin state of the radical ion pairs, either singlet or triplet respectively. In the study of interaction of the model protein HSA with acridine derivatives, Acridine Yellow (AY) and Proflavin (PF+), conventional spectroscopic tools along with docking study have been used to decipher the binding mechanism and laser flash photolysis technique with an associated MF has been used to explore PET. The results of fluorescence study indicate that fluorescence resonance energy transfer takes place from the protein to the acridine-based drugs. Docking study unveils the crucial role of Ser 232 residue of HSA in explaining the differential behavior of the two drugs towards the model protein. Laser flash photolysis experiments help to identify the radicals/radical ions formed in the due course of PET and the application of an external MF has been used to characterize their initial spin-state. Owing to its distance dependence, MF effect gives an idea about the proximity of the radicals/radical ions during interaction in the system and also helps to elucidate the reaction mechanism. A prominent MF effect is observed in homogeneous buffer medium owing to the pseudo-confinement of the radicals/radical ions provided by the complex structure of the protein.

Irena Kratochvílová, Academy of Sciences of the Czech Republic, CZ *Charge transport in DNA oligonucleotides with various base-pairing patterns*

We combined various experimental (scanning tunneling microscopy and Raman spectroscopy) and theoretical (density functional theory and molecular dynamics) approaches to study the relationships between the basepairing patterns and the charge transfer properties in DNA 32-mer duplexes that may be relevant for identification and repair of defects in base pairing of the genetic DNA and for DNA use in nanotechnologies. Studied were two fully Watson-Crick (W-C)-paired duplexes, one mismatched (containing three non-W-C pairs), and three with base pairs chemically removed. The results show that the charge transport varies strongly between these duplexes. The conductivity of the mismatched duplex is considerably lower

than that of the W-C-paired one despite the fact that their structural integrities and thermal stabilities are comparable. Structurally and thermally much less stable abasic duplexes have still lower conductivity but not markedly different from the mismatched duplex. All duplexes are likely to conduct by the hole mechanism, and water orbitals increase the charge transport probability.

John M. Kelly, Trinity College Dublin, IE *Dipyridophenazine metal complexes which undergo photo-induced electron transfer with DNA*

Dipyrido[3,2-a:2',3'-c]phenazine (dppz) complexes are well known to bind to DNA though intercalation of the hetero-aromatic ligand between the base-pairs of the polynucleotide. Considerable attention has been paid to the effect of this intercalation process on the photophysics of complexes such as [Ru(phen)2(dppz)]2+, which are non-emissive in water, but which luminesce when bound to DNA.[1]

Our interest is in complexes such as [Ru(TAP)2(dppz)]2+,[2] and [Cr(phen)2(dppz)]3+, [3] (TAP = 1,4,5,8- tetraazaphen-anthrene; phen = 1,1-phenanthroline) which are luminescent in solution but whose emission is quenched upon binding to DNA, due to reduction of the metal complex excited state by a nucleobase (especially guanine). In the case of [Ru(TAP)2(dppz)]2+ this process has been attributed to proton-coupled electron transfer partly on the basis of the differing rates of both the forward and back reaction in D2O compared to those in H2O. [2] Unpublished data on the photo-induced electron transfer behaviour of the pure enantiomeric pure complex will be presented.

The binding of both the delta and lambda enantiomers of [Cr(phen)2(dppz)]3+ and its 11,12 –substituted derivatives [Cr(phen)2dppzR2]3+ (R = F or Me) with DNA has been probed by a number of spectroscopic techniques. To gain an understanding of the electron transfer photophysics in DNA a detailed transient spectroscopic study of the quenching of [Cr(phen)2(dppz)]3+ by guanosine monophosphate using steady state and time resolved absorption and photoluminescence spectroscopy been carried out.[3]

Finally we would like to report on recent findings with fac-[Re(CO)3(dppz-F2)(py)]+., where there is evidence, through monitoring the formation of the reduced rhenium complex and the oxidation of the guanine for electron transfer proceeding on both a sub-picosecond and 35 ps timescale.

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George Kalosakas, University of Patras, GR *Electronic parameters for charge transfer along DNA*

We present electronic parameters pertinent to charge transfer along DNA. The pi molecular structure of the four DNA bases is investigated by using the linear combination of atomic orbitals method with a recently introduced novel parametrization. The HOMO and LUMO wavefunctions and energies of DNA bases are discussed and then used for calculating the corresponding wavefunctions of the two B-DNA base- pairs. The obtained HOMO and LUMO energies of the bases are in good agreement with available experimental values. Our findings are also compared with existing calculations from first principles. These results are then used for estimating the complete set of charge transfer parameters between neighboring bases and also between successive base-pairs, considering all possible combinations between them, for both electrons and holes. The calculated microscopic quantities can be used in theoretical models of electron or hole transfer along the DNA double helix, as they provide the necessary parameters for a phenomenological description based on the pi molecular overlap. Taking advantage of such a description, at a mesoscopic level, the temporal and spatial evolution of electron or hole transport along DNA can be examined in experimentally relevant time and length scales. Thus, relative reaction rates for charge transfer between donors and acceptors within DNA segments can be calculated and compared with relevant experiments. As an example, hole transfer between guanine radical cations and GGG traps separated by short (AT)n bridges, showing an exponential dependence of the charge transfer rate on the length of the bridge for n=1-3, is currently under investigation.

Frank Garwe, IPHT Jena, DE *Long-range energy transfer in DNA after fs laser pulse excitation of silver nanoparticle neighboured to DNA*

Excitation of metallic nanoparticles with nanosecond- or picosecond laser pulses results already during the pulse duration in an electron-phonon relaxation process and in an increased temperature in the proximal dielectric surrounding. In contrast, resonant femtosecond laser pulses with high electrical fields do not result in similar temperatures [1], since the pulses are too short. However, highly excited electrons in the particles can easily overcome the metal's work function by absorption of three to four photons. These electrons and the amplified electric near field interact directly with the dielectric surrounding [2]. To study the interaction of femtosecond laser pulses with silver nanoparticles attached at stretched DNA-bundles, we used - as

an indirect detection method - the UV photon and electron sensitivity of an underlying Poly methylmethacrylat (PMMA) layer. We ensured that both the DNA itself and the PMMA layer were not affected by femtosecond laser pulses. When the stretched DNA bundle with attached silver nanoparticles was irradiated with the same laser parameters as in the control experiment, these DNA structures showed a quit impressive change [3]: The DNA disappeared over the length of several micrometers, i.e. the length of the original DNA, and only a negative trace in the PMMA remained visible in AFM images as dark structures with a depth of 3-4 nm. These grooves followed the original DNA structure. Two possible mechanisms to explain the transfer of energy from the particle to the DNA seem reasonable. One possibility, electrons overcoming the work function of the nanoparticle, transfer their kinetic energy to the electrons of the PMMA and the DNA bundle or the very high electric field (108-109 V/m) in the nanoparticle surrounding accelerate electrons in PMMA or DNA. This could result in removal of PMMA side groups (radical formation) at a random position nearby the nanoparticle and the DNA position and thus in a main chain scission of PMMA bonds. In DNA, momentum or electron transfer over π stacked DNA base pairs mediated by molecular vibration of the backbone could also take place and result in breaking of DNA bonds. Another hypothesis to be discussed is that nonlinear excited electrons in the metallic nanoparticles, which were created by two-photon excitation via femtosecond pulse laser irradiation (localized surface plasmon resonances), can be seen as light on the nanoscale far below the diffraction limit. Regarding the DNA bundles as a subwavelength optical fiber, a light coupling of the localized surface plasmons in the nanoparticle onto the nearest DNA bundles could occur. The light could propagate through the DNA bundle as quasi-particles, called phonon polaritons caused by electron polarization. These new phenomena could have applications in fields such as lithography, nanoplasmonics or molecular electronics.

Rudy Schlaf, University of South Florida, US *Electronic structure of self-assembled peptide nucleic acid thin films*

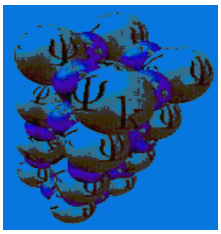
Peptide nucleic acids (PNA) are a promising alternative to DNA for bio-sensing applications as well as for strategies for self assembly based on nucleic acid hybridization. This potential is a result of the PNAÕs neutral pseudopeptide backbone, which eliminates inter-strand electrostatic repulsion. In recent years charge transfer through PNA molecules has been a focus of research due to potential applications in self-assembled molecular circuits. This makes it interesting to investigate the electronic structure of PNA interfaces to electrode materials. A widely used strategy to ÔconnectÕ PNA molecules to metallic electrodes is through thiol-Au bonds using a terminal cysteine appended to PNA oligomers. This motivated the here presented research where the electronic structure of self- assembled PNA monolayers on Au substrates was investigated. Cys-appended PNA 7-mers of thymine (Cys-T7) were incubated on Au substrates in a nitrogen glove box attached to a photoemission spectrometer. Ultraviolet and x-ray photoemission spectroscopy (UPS and XPS) measurements on the resulting SAMs revealed the hole injection barrier at the interface and the interface dipole. Electronic structure calculations based on molecular dynamics sampling of the PNA structure yielded the band gap and the electronic density of states for PNA. Combined with the UPS data, the theoretical calculation enabled the estimate of the electron injection barrier at the interface, as well as he assignment of individual UP spectral features to specific molecular orbitals. Control measurements on Cys- appended, abasic PNA backbone 7-mers allowed the identification of the emissions related to the PNA backbone in the UP spectra. The orbital line-up at the interface between the Au substrate and the Cys-PNA indicates a significant interface dipole resulting in the alignment of the Au Fermi level near the center of the PNA HOMO-LUMO gap. This alignment causes large charge injection barriers for both holes and electrons, and thus impedes charge transfer from Au into the Cys-PNA SAM.

Marcos Brown Goncalves, University of Sao Paulo, BR *Theoretical study of metal DNA structures*

Auto-organization, auto-recognition and selectivity are desirable features for new nanotechnological materials. Biological systems like proteins and DNA are candidates to technological devices. The possible applications range from biological sensors to electronic devices. The electronic transport though DNA have been studied from decades. It is known that some features have still to be improved in the electronic transport in DNA like those related with the chain hardness, substrate interaction and \pi-\pi orbital overlap [1]. In the last years modified DNA structures were developed towards improving these features. One class of these bases is the Cu-hydroxypiridone which is complexed with Cu [2] where EPR studies have shown ferromagnetic interactions among the Cu centers [2]. We study the electronic structure of a monomer and dimer Cu-hydroxypiridone with a theoretical approach in the Kohn- Sham scheme of the Density-Functional Theory using the CP-PAW code [3] including a non-collinear spin formulation. We show the differences in the magnetization in three approaches: influence of charge effects, backbone effects and in plane and inter-plane Cu coordination. We also discuss the magnetic interaction including up to five Cu-hydroxipiridone modified bases.

[1] Porath et al, TCC 237 183 (2004)
[2] Tanaka et al, JACS 124 12494 (2002)
[3] P. Blöchl, PRB 50, 17953 (1994)

Psi-k Network : Towards Atomistic Materials Design



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PSI-K WORKSHOP FINANCE REPORT

Title of the Workshop	
Workshop Organisers	
Location of the Workshop	
Dates of the Workshop	
Total Grant from Psi-k	

EXPENDITURE

(Please complete the tables using numbers ONLY in the amounts fields - the spreadsheet will calculate the totals for you)

WORKSHOP DELEGATES / SPEAKERS			
Name and Country of Claimant	**Travel**	**Accommodation**	**Total (€'s)**
Rosa Di Felice		€ 870.00	€ 870.00
Yuri Berlin		€ 870.00	€ 870.00
Marcus Elstner		€ 870.00	€ 870.00
Nadav Amdursky	€ 140.00	€ 380.00	€ 520.00
Danny Porath		€ 870.00	€ 870.00
			€ -
			€ -
			€ -
			€ -
			€ -
		Total Travel & Accommodation	**€ 4,000.00**

WORKSHOP REFRESHMENTS / CONFERENCE DINNERS			
Date	**Tea / Coffee**	**Lunch / Dinner**	**Total (€'s)**
			€ -
			€ -
			€ -
			€ -
			€ -
		Total Refreshments	**€ -**

MISCELLANEOUS EXPENDITURE	
Details	**Total (€'s)**
Total Miscellaneous	**€ -**

Total Travel & Accommodation	**€ 4,000.00**
Total Refreshments	**€ -**
Total Miscellaneous	**€ -**
TOTAL EXPENDITURE	**€ 4,000.00**

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