Program
and
Abstracts

17th International Conference on Density-Functional Theory and its Applications

August 21 - 25, 2017

Tällberg, Sweden

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on Density-Functional Theory and its Applications

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and its Applications

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Sponsors

The organizers gratefully acknowledge financial support from the **Swedish Research Council (Vetenskapsrådet)**, the **Royal Swedish Academy of Sciences (Kungliga Vetenskapsakedemien)** and the **Psi-K network.**

We thank the journal **/Computation/** for sponsoring two best poster awards.

Program and Abstracts

This book contains the camera-ready copies of the abstracts as sent by the authors. In some cases layout adjustments were made.

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- Prof. Dr. Levente Vitos, KTH Stockholm, Sweden

Contents

General information

- The Get Together party takes place in the boathouse by lake Siljan (marked on the map).
- The guided church boat excursion on lake Siljan starts near the same boathouse. Life vests can be provided.
- The two lecture halls are called “Oppsittu” and “Rådstuggu” and are located on the first floor and on the ground floor, respectively, in Åkerblads gästgiveri.
- The poster room is called “Storstuga” and is located on the first floor of Åkerblads gästgiveri, next to “Oppsittu”.
- Posters A may be hung from Tuesday 1 pm to Wednesday 1 pm. Posters B may be hung from Wednesday 1 pm to Thursday 1 pm.
- Speakers should plan to bring their presentations on a USB flash drive or similar source. For each session a laptop will be provided and we encourage you to use the provided computers. Your presentation file should then be in PDF or PPT format. You are encouraged to copy your presentation files onto the supplied laptop before your session starts.
- If you prefer to use your own laptop, you need to bring any adaptors necessary to connect to the VGA projector cable provided. International visitors should bring adapters for European electrical outlets type F.

./map/taellberg_2.png

List of presenters and abstract index

Plenary speaker	**Affiliation**	**Page**
Ebert, Hubert	Ludwig Maximilian University of Munich, Germany	171
Engel, Eberhard	Goethe University Frankfurt am Main, Germany	170
Ernzerhof, Matthias	University of Montreal, Canada	123
Helgaker, Trygve	University of Oslo, Norway	76
Levy, Mel	Tulane University, New Orleans, USA	75
Mattsson, Ann E.	Sandia National Laboratories, Albuquerque, USA	24
Röthlisberger, Ursula	Swiss Federal Institute of Technology in Lausanne, Switzerland	25
Perdew, John	Temple University, Philadelphia, USA	40
van Leeuwen, Robert	University of Jyväskylä, Finland	122

Invited speaker	**Affiliation**	**Page**
Amovilli, Claudio	University of Pisa, Italy	136
Armiento, Rickard	Linköping University, Sweden	130
Aryasetiawan, Ferdi	Lund University, Sweden	34
Burke, Kieron	University of California, Irvine, USA	77
Brémond, Éric	CompuNet, Istituto Italiano di Tecnologia, Italy	81
Chioncel, Liviu	Augsburg University, Germany	35
Cohen, Aron	University of Cambridge, UK	78
De Proft, Frank	Free University of Brussels, Belgium	32
Elstner, Marcus	Karlsruhe Institute of Technology, Germany	28
Hermansson, Kersti	Uppsala University, Sweden	33
Hu, Qing-Miao	Institute of Metal Research, Shenyang, China	127
Hyldgaard, Per	Chalmers University of Technology, Sweden	30
Kaupp, Martin	Technical University of Berlin, Germany	83
Kokko, Kalevi	University of Turku, Finland	124
Kong, Jing	Middle Tennessee State University, Murfreesboro, USA	128
Köster, Andreas M.	CINVESTAV, Mexico City, Mexico	84
Landa, Alexander	Lawrence Livermore National Laboratory, USA	132
Maitra, Neepa	Hunter College of the City University of New York, USA	79
Mohn, Peter	Vienna University of Technology, Austria	134
Nakai, Hiromi	Waseda University, Tokyo, Japan	37

Peach, Michael	Lancaster University, UK	80
Richter, Manuel	IFW Dresden, Germany	36
Sancho-Garcia, Juan Carlos	University of Alicante, Spain	82
Sandratskii, Leonid	Max Planck Institute of Microstructure Physics, Halle, Germany	137
Saue, Trond	Université Toulouse III-Paul Sabatier, France	38
Sun, Zhimei	Beihang University, Beijing, China	125
Söderlind, Per	Lawrence Livermore National Laboratory, USA	133
Teale, Andrew	University of Nottingham, UK	39
Tognetti, Vincent	University of Rouen, France	31
Toulouse, Julien	Université Pierre-et-Marie-Curie, Paris, France	26
Ujfalussy, Balazs	Wigner Research Center for Physics, Budapest, Hungary	126
Wills, John M.	Los Alamos National Laboratory, USA	129
Witek, Henryk	National Chiao Tung University, Hsinchu, Taiwan	29
Yang, Weitao	Duke University, Durham, USA	27
Zhao, Jijun	Dalian University of Technology, China	131

Contributed speaker	**Affiliation**	**Page**
Alharbi, Fahhad	Hamad bin Khalifa University, Qatar	139
Aschebrock, Thilo	University of Bayreuth, Germany	47
Berland, Kristian	University of Oslo, Norway	96
Blaha, Peter	TU Vienna, Austria	48
Bokdam, Menno	University of Vienna, Austria	169
Calaminici, Patrizia	CINVESTAV, Mexico	90
Cort Barrada, Luis	University of Jyväskylä, Finland	91
Dharma-wardana, Chandre	National Research Council of Canada, Ottawa, Canada	44
Elliott, Peter	Max-Planck Institute of Microstructure Physics, Germany	93
Fabiano, Eduardo	Italian National Research Council, Lecce, Italy	45
Gattinoni, Chiara	ETH Zuerich, Switzerland	168
Giesbertz, Klaas	Vrije Universiteit Amsterdam, The Netherlands	86
Grabowski, Ireneusz	Nicolaus Copernicus University, Poland	87
Hansen, Andreas	University of Bonn, Germany	165
Huang, Li	China Academy of Engineering Physics, Jiangyou, China	42
Jiao, Yang	Chalmers University of Technology, Sweden	46
Lacombe, Lionel	Hunter College of the City University of New York, USA	92

Lucian, Constantin	Italian Institute of Technology, Italy	166
Ludeña, Eduardo	Escuela Superior Politecnica del Litoral, Guayaquil, Ecuador	138
Matito, Eduard	Donostia International Physics Center, Bilbao, Spain	89
Medvedev, Michael G.	A. N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Moscow, Russia	88
Niehaus, Thomas	Université Lyon, France	85
O'Regan, David	Trinity College Dublin, Ireland	43
Ramos-Cordoba, Eloy	University of California, Berkeley, USA	95
Rubel, Oleg	McMaster University, Hamilton, Canada	167
Savarese, Marika	Italian Institute of Technology, Genova, Italy	164
Stener, Mauro	University of Trieste, Italy	94
Östlin, Andreas	Augsburg University, Germany	41

Short talk presenter	**Affiliation**	**Page**
Al-Zoubi, Noura I.	Tafila Technical University, Jordan	143
Araujo, Moyses	Uppsala University, Sweden	157
Banafsheh, Mojdeh	University of Geneva, Switzerland	161
Cangi, Attila	Sandia National Laboratories, Albuquerque, USA	151
Dale, Stephen G.	Dalhousie University, USA	160
Gierada, Maciej	Cracow University of Technology, Poland	152
Huang, He	China Academy of Engineering Physics, Jiangyou, China	141
Javierre, Guilhem	Ecole Centrale Marseille, France	154
Kabanda, Mwombeki M.	North-West University, Mmabatho, South-Africa	153
Karlsson, Daniel	University of Jyväskylä, Finland	163
Lopez-Acevedo, Olga	Aalto University, Finland	162
Ojamäe, Lars	Linköping University, Sweden	159
Qiu, Ruizhi	China Academy of Engineering Physics, Jiangyou, China	149
Ramanantoanina, Harry	Laboratory for nuclear materials, Villigen, Switzerland	158
Sa, Baisheng	Fuzhou University, China	155
Streltsov, Sergey	Institute of Metal Physics, Ekaterinburg, Russia	145
Thonig, Danny	Uppsala University, Sweden	144
Wang, Cong	Institute of Applied Physics and Computational Physics, Beijing, China	150
Yang, Yu	Institute of Applied Physics and Computational Mathematics, Beijing, China	148

Yu, Huilong	China Academy of Engineering Physics, Jiangyou, China	147
Zaleśny, Robert	Wroclaw University of Science and Technology, Poland	156
Zhang, Hualei	Xi'an Jiaotong University, China	140
Zhang, Ping	Institute of Applied Physics and Computational Mathematics, Beijing, China	146
Zhao, Wenyue	Beihang University, Beijing, China	142

Poster presenter	**Affiliation**	**Page**
Abbasipour, Marjan	Iran University of Science and Technology, Tehran	117
Al-Hamdani, Yasmine S.	University of Luxembourg, Luxembourg	105
Arbuznikov, Alexey	Technische Universität Berlin, Germany	52
Arvidsson, Adam	Chalmers tekniska högskola, Gothenburg, Sweden	67
Brumboiu, Iulia E.	KTH - Royal Institute of Technology, Stockholm, Sweden	101
Casier, Bastien	LCPMR UMR, Paris, France	115
Chermette, Henry	Universté Lyon1, Villeurbanne, France	120
Damas, Giane B.	Uppsala University, Sweden	114
Davidsson, Joel	Linköping University , Sweden	106
Decolvenaere, Elizabeth	University of California, Santa Barbara, USA	60
Dong, Zhihua	KTH - Royal Institute of Technology, Stockholm, Sweden	51
Feldbauer, Gregor	Hamburg University of Technology, Germany	55
Fletcher, Peter	Lancaster University, UK	69
Floris, Franca Maria	University of Pisa, Italy	68
Garcia de la Vega, Jose	Universidad Autonoma de Madrid, Spain	66
Gugler, Johannes	Vienna University of Technology, Austria	57
Huang, Shuo	KTH - Royal Institute of Technology, Stockholm, Sweden	110
Humbert-Droz, Marie	University of Geneva, Switzerland	103
Ji, Zongwei	KTH - Royal Institute of Technology, Stockholm, Sweden	112
Kalai, Cairedine	UPMC, Paris, France	107
Kretschmer, Silvan	Helmholtz-Zentrum Dresden-Rossendorf, Germany	59
Lani, Giovanna	Université Pierre et Marie Curie, Paris, France	72
Levämäki, Henrik	University of Turku, Finland	116
Li, Xiaojie	KTH - Royal Institute of Technology, Stockholm, Sweden	58
Li, Xiaoqing	KTH - Royal Institute of Technology, Stockholm, Sweden	56

Lousada, Cláudio M.	KTH - Royal Institute of Technology, Stockholm, Sweden	104
Lu, Song	KTH - Royal Institute of Technology, Stockholm, Sweden	121
Marocchi, Simone	Universidade de São Paulo, Brasil	108
Mirsakiyeva, Amina	KTH - Royal Institute of Technology, Stockholm, Sweden	70
Montero-Campillo, M. Merced	Instituto de Quimica Medica (CSIC), Madrid, Spain	49
Nishimura, Yoshifumi	Research Institute for Science and Engineering, Tokyo, Japan	113
Romanov, Alexander	Lobachevsky State University of Nizhny Novgorod, Russia	102
Schönecker, Stephan	KTH - Royal Institute of Technology, Stockholm, Sweden	54
Seibert, Jakob	University of Bonn, Germany	100
Serobatse, Kemoabetswe R. N.	North-West University, Mmabatho, South-Africa	64
Shenton, Kane	University College London, UK	61
Sipr, Ondrej	University of West Bohemia, Plzen, Czech Republic	65
Śmiga, Szymon	Nicolaus Copernicus University, Torun, Poland	111
Szilva, Attila	Uppsala University, Sweden	98
Steffler, Fernando	Universidade Federal de Minas Gerais UFMG, Belo Horizonte, Brasil	50
TalwelkarShimpi, Mayura	Luleå Tekniska Universitet, Sweden	119
Tian, Liyun	KTH - Royal Institute of Technology, Stockholm, Sweden	118
Valter, Mikael	Chalmers University of Technology, Gothenburg, Sweden	63
Xie, Ruiwen	KTH - Royal Institute of Technology, Stockholm, Sweden	62
Yoshio, Satoshi	Sumitomo Metal Minig Co., Ltd., Minato-ku, Tokyo, Japan	53
Zech, Alexander	University of Geneva, Switzerland	71
Zlatar, Matija	University of Belgrade, Serbia	97

Memorial session	**Affiliation**	**Page**
Daul, Claude	University of Fribourg, Switzerland	73
Schwarz, Karlheinz	Technical University Vienna, Austria	74
Mattsson, Ann E.	Sandia National Laboratories, Albuquerque, USA	74
Levy, Mel	Tulane University, New Orleans, USA	74

Program

Monday, August 21

15.00 - 23.00	Registration at Åkerblads gästgiveri
15.30 - 17.00	Coffee and refreshments at Åkerblads gästgiveri
19.00 - 22.00	Get together barbecue buffet at Lake Siljan Welcome speech by Olle Eriksson (Uppsala University, Sweden)

Tuesday, August 22

Morning Plenary Session
Room: Oppsittu
Chair: Levente Vitos

8.30 - 8.40	Opening (Levente Vitos)
8.40 - 9.20	**Ann E. Mattsson**, Sandia National Laboratories, Albuquerque, USA *A density based Electron Localization Function*
9.20 - 10.00	**Ursula Röthlisberger**, Swiss Federal Institute of Technology in Lausanne, Switzerland *Nature knows best: computational strategies for the design of biomimetic systems*
10.00 - 10.30	Coffee & refreshments break

Morning Invited Session A (parallel)
Room: Oppsittu
Chair: Martin Kaupp

10.30 - 11.00	**Julien Toulouse**, Université Pierre-et-Marie-Curie, Paris, France *Combining density-functional theory and many-body methods*
11.00 - 11.30	**Weitao Yang**, Duke University, Durham, USA *Localized Orbital Scaling Correction for Systematic Elimination of Delocalization Error in Density Functional Approximations*
11.30 - 12.00	**Marcus, Elstner**, Karlsruhe Institute of Technology, Germany *The approximate DFT models 'DFTB': performance and challenges*
12.00 - 12.30	**Henryk, Witek**, National Chiao Tung University, Hsinchu, Taiwan *Automatized parameterization of DFTB*

Morning Invited Session B (parallel)
Room: Rådstuggu
Chair: Juan-Carlos Sancho-Garcia

10.30 - 11.00	**Per Hyldgaard**, Chalmers University of Technology, Sweden *Understanding exchange and correlation in regular and hybrid van der Waals density functionals*
11.00 - 11.30	**Vincent Tognetti**, University of Rouen, France *The DFT-CDFT-QTAIM synergy to investigate chemical reactivity*
11.30 - 12.00	**Frank De Proft**, Vrije Universiteit Brussel, Brussels, Belgium *Chemical Concepts from Density Functional Theory: Theoretical Developments and Applications in Bonding, Chemical Reactivity and Molecular Design*
12.00 - 12.30	**Kersti Hermansson**, Uppsala University, Sweden *DFT-based multi-scale modelling of materials and nanoparticles*
12.30 - 14.00	Lunch at Åkerblads gästgiveri

Afternoon Invited Session A (parallel)
Room: Oppsittu
Chair: Peter Mohn

14.00 - 14.30	**Ferdi Aryasetiawan**, Lund University, Sweden *Hubbard bands vs plasmons in correlated metals: A view from self-consistent GW+DMFT*
14.30 - 15.00	**Liviu Chioncel**, Augsburg University, Germany *Towards multiple-scattering theory for disordered systems with Anderson localization*
15.00 - 15.30	**Manuel Richter**, IFW Dresden, Germany *Quantitative Predictions by Electronic Structure Theory*

Afternoon Invited Session B (parallel)
Room: Rådstuggu
Chair: Kersti Hermansson

14.00 - 14.30	**Hiromi Nakai**, Waseda University, Tokyo, Japan *Relativistic density functional theory with picture-change corrected electron density based on infinite-order Douglas-Kroll-Hess method*
14.30 - 15.00	**Trond Saue**, Université Toulouse III-Paul Sabatier, France *Beyond the electric dipole approximation in simulations of X-ray absorption spectroscopy*
15.00 - 15.30	**Andrew Teale**, University of Nottingham, UK *Density-Functional Theory for Molecules in Strong Magnetic Fields*
15.30 - 16.00	Coffee & refreshments break

Afternoon Plenary Session
Room: Oppsittu
Chair: John Wills

16.00 - 16.40	**John Perdew**, Temple University, Philadelphia, USA *The SCAN Density Functional: Nonempirical, Predictive, and Efficient*

Contributed Session A (parallel)

Room: Oppsittu
Chair: John Wills

16.45 - 17.00	**Andreas Östlin**, Augsburg University, Germany *Green's function-based method for correlated electronic structure calculations*
17.00 - 17.15	**Li Huang**, China Academy of Engineering Physics, Jiangyou, China *Combined semilocal exchange potential with dynamical mean-field theory*
17.15 - 17.30	**David O'Regan**, Trinity College Dublin, Ireland *Optimizing constraints and corrections in approximate DFT*
17.30 - 17.45	**Chandre Dharma-wardana**, National Research Council of Canada, Ottawa, Canada *Finite-T electron-electron, electron-ion and ion-ion xc-functionals, discontinuities in the mean ionization, and phase transitions in low-Z warm-dense matter*

Contributed Session B (parallel)

Room: Rådstuggu
Chair: Kalevi Kokko

16.45 - 17.00	**Eduardo Fabiano**, Italian National Research Council, Lecce, Italy *The interaction-strength interpolation method for main-group chemistry: benchmarking, limitations, and perspectives*
17.00 - 17.15	**Yang Jiao**, Chalmers University of Technology, Sweden *Towards truly nonlocal exchange and correlation functionals: Nonempirical constructions*
17.15 - 17.30	**Thilo Aschebrock**, University of Bayreuth, Germany *Semi-local exchange functionals showing ultranonlocal response: the hope to replace exact exchange*
17.30 - 17.45	**Peter Blaha**, TU Vienna, Austria *A simple way to apply nonlocal van der Waals functionals within all-electron methods*
19.00 - 20.30	Dinner at Åkerblads gästgiveri

Poster Session

Room: Storstuga
Chair: Henry Chermette, Claude A. Daul

20.30 - 22.00	**Posters A** (Poster presenters on p. 19)

Wednesday, August 23

Memorial Session

Room: Oppsittu
Chair: Ágnes Nagy

8.00 - 8.40	**Claude A. Daul, Karlheinz Schwarz, Ann E. Mattsson, and Mel Levy**, *Presentation in memory of Annick Leray-Goursot and Walter Kohn*

Plenary Session

Room: Oppsittu
Chair: Ágnes Nagy

8.40 - 9.20	**Mel Levy**, Duke University, Durham, USA *Exact Constraints for Creating Density Functionals, and Thoughts of Robert G. Parr*
9.20 - 10.00	**Trygve Helgaker**, University of Oslo, Norway *The Four-Way Correspondence of Density-Functional Theory*
10.00 - 10.30	Coffee & refreshments break

Invited Session A (parallel)

Room: Oppsittu
Chair: Weitao Yang

10.30 - 11.00	**Kieron Burke**, University of California, Irvine, USA *Direct extraction of excitation energies from ensemble density-functional theory*
11.00 - 11.30	**Aron Cohen**, University of Cambridge, UK *The Exact Density Functional*
11.30 - 12.00	**Neepa Maitra**, Hunter College of the City University of New York, USA *New Approaches to Memory-Dependent Functionals in Time-Dependent Density Functional Theory*
12.00 - 12.30	**Michael Peach**, Lancaster University, UK *Triplet Emission Processes in Platinum Complexes*

Invited Session B (parallel)

Room: Rådstuggu
Chair: Hiromi Nakai

10.30 - 11.00	**Éric Brémond**, CompuNet, Istituto Italiano di Tecnologia, Italy *Single and Double Hybridization Schemes in Density-Functional Theory*
11.00 - 11.30	**Juan Carlos Sancho-Garcia**, University of Alicante, Spain *Benchmark and Applications Studies of Double-Hybrid Density Functionals Based on the Adiabatic Connection Model*
11.30 - 12.00	**Martin Kaupp**, Technical University of Berlin, Germany *Recent Progress on Local Hybrid Functionals*
12.00 - 12.30	**Andreas M. Köster**, CINVESTAV, Mexico City, Mexico *Hybrid Functionals in Auxiliary Density Function Theory*

12.30 - 14.00	Lunch at Åkerblads gästgiveri

Contributed Session A (parallel)
Room: Oppsittu
Chair: Paola Gori-Giorgi

14.00 - 14.15	**Thomas Niehaus**, Université Lyon, France *The budget way to quasiparticle and exciton binding energies*
14.15 - 14.30	**Klaas Giesbertz**, Vrije Universiteit Amsterdam, The Netherlands *Invertibility of the retarded response functions for initial mixed states: application to one-body reduced density matrix functional theory*
14.30 - 14.45	**Ireneusz Grabowski**, Nicolaus Copernicus University, Poland *Optimized Effective Potential Method based on the Scaled-Opposite-Spin Second-Order Correlation*
14.45 - 15.00	**Michael G. Medvedev**, A. N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Moscow, Russia *Accuracy of DFT self-consistent electron densities*
15.00 - 15.15	**Eduard Matito**, Donostia International Physics Center, Bilbao, Spain *DFT functional assessment from quasi-exact energies and densities at different correlation regimes*
15.15 - 15.30	**Patrizia Calaminici**, CINVESTAV, Mexico *On the Structure Determination of U_2C_79: U_2CC_{78} or $U_2C_3C_{76}$? Insight from a DFT Study*

Contributed Session B (parallel)
Room: Rådstuggu
Chair: Miguel Marques

14.00 - 14.15	**Luis Cort Barrada**, University of Jyväskylä, Finland *Time-dependent density-functional theory for strongly interacting electrons*
14.15 - 14.30	**Lionel Lacombe**, Hunter College of the City University of New York, USA *Modeling the exact time-dependent exchange-correlation potential*
14.30 - 14.45	**Peter Elliott**, Max-Planck Institute of Microstructure Physics, Germany *Ultrafast Charge and Spin Dynamics with TDDFT*
14.45 - 15.00	**Mauro Stener**, University of Trieste, Italy *A New Efficient Time Dependent Density Functional Algorithm for Large Systems: Theory, Implementation and Plasmonics Applications*
15.00 - 15.15	**Eloy Ramos-Cordoba**, University of California, Berkeley, USA *Excited states for orbital-optimized second-order perturbation theory*
15.15 - 15.30	**Kristian Berland**, University of Oslo, Norway *An assessment of hybrid functionals for transport and excited-state properties of bulk semiconductors*

15.30 - 16.00	Coffee & refreshments break

Excursion

16.00 - 19.00	Guided church boat excursion on lake Siljan *or* guided tour to Digerberget (Diger summit)
19.30 - 21.00	Conference dinner at Åkerblads gästgiveri Presentation about Dalarna by Börje Johansson (KTH - Royal Institute of Technology, Stockholm, Sweden)

Poster Session

Room: Storstuga
Chair: Jose Garcia de la Vega, Paul Geerlings

21.00 - 22.30	**Posters B** (Poster presenters on p. 21)

Thursday, August 24

Plenary Session

Room: Oppsittu
Chair: Kieron Burke

8.40 - 9.20	**Robert van Leeuwen**, University of Jyväskylä, Finland *The density-potential mapping in time-dependent density-functional theory*
9.20 - 10.00	**Matthias Ernzerhof**, University of Montreal, Canada *Constructing exchange-correlation functionals using the strong-interaction limit and the correlation factor ansatz*
10.00 - 10.30	Coffee & refreshments break

Morning Invited Session A (parallel)

Room: Oppsittu
Chair: Leonid Sandratskii

10.30 - 11.00	**Kalevi Kokko**, University of Turku, Finland *Quasi non-uniform approximation, flexible exchange-correlation functional for alloys and compounds*
11.00 - 11.30	**Zhimei Sun**, Beihang University, Beijing, China *Electronic and topological properties of MXenes: a first-principles study*
11.30 - 12.00	**Balazs Ujfalussy**, Wigner Research Center for Physics, Budapest, Hungary *Superconducting order parameter in layered systems*
12.00 - 12.30	**Qing-Miao Hu**, Institute of Metal Research, Shenyang, China *Applications of Density Functional Theory on Design of Advanced Titanium Alloys*

Morning Invited Session B (parallel)

Room: Rådstuggu
Chair: Trond Saue

10.30 - 11.00	**Jing Kong**, Middle Tennessee State University, Murfreesboro, USA *Density Functional for Computing the Strong Nondynamic Correlation*
11.00 - 11.30	**John M. Wills**, Los Alamos National Laboratory, USA *Automatic generation of pseudopotentials by an all-electron methods*
11.30 - 12.00	**Rickard Armiento**, Linköping University, Sweden *Semi-Local Functionals with Non-vanishing Asymptotic Potentials: Beyond the AK13*
12.00 - 12.30	**Jijun Zhao**, Dalian University of Technology, China *Which is the best exchange-correlation functional for describing atomic and molecular clusters?*
12.30 - 14.00	Lunch at Åkerblads gästgiveri

Afternoon Invited Session A (parallel)

Room: Oppsittu
Chair: Balazs Ujfalussy

14.00 - 14.30	**Alexander Landa**, Lawrence Livermore National Laboratory, USA *Alloying-Driven Phase Stability in Group-VB Transition Metals Under Compression*
14.30 - 15.00	**Per Söderlind**, Lawrence Livermore National Laboratory, USA *Phase stability, elasticity, and phonons for plutonium from electronic-structure theory*
15.00 - 15.30	**Peter Mohn**, Vienna University of Technology, Austria *Ab initio calculation of spin lattice relaxation of NV^- centers in diamond*

Afternoon Invited/Contributed Session B (parallel)

Room: Rådstuggu
Chair: Henryk Witek

14.00 - 14.30	**Claudio Amovilli**, University of Pisa, Italy *Properties of electron density in weak binding conditions*
14.30 - 15.00	**Leonid Sandratskii**, Max Planck Institute of Microstructure Physics, Halle, Germany *The insight into the Dzyaloshinskii-Moriya interaction through first-principles study of chiral magnetic structures*
15.00 - 15.15	**Eduardo Ludeña**, Escuela Superior Politecnica del Litoral, Guayaquil, Ecuador *The power series representation of the Pauli kinetic energy functional, shell structure and the Sturm-Liouville problem*
15.15 - 15.30	**Alharbi Fahhad**, Hamad bin Khalifa University, Qatar *Axiomatically Derived Kinetic Energy Density Functionals*

15.30 - 16.00	Coffee & refreshments break

Short talk Session A (parallel)
Room: Oppsittu
Chair: Karlheinz Schwarz

16.00 - 16.10	**Hualei Zhang**, Xi'an Jiaotong University, China *Ab initio investigation on high-entropy alloys*
16.10 - 16.20	**He Huang**, China Academy of Engineering Physics, Jiangyou, China *Phase stability of CrCoNi ME alloys and CRSS for twinning nucleation in CrCoNi M-HE alloys*
16.20 - 16.30	**Wenyue Zhao**, Beihang University, Beijing, China *Tuning the plasticity of Ni-Mo solid solution in Ni-based superalloys by ab initio calculations*
16.30 - 16.40	**Noura I. Al-Zoubi**, Tafila Technical University, Jordan *First-principles study of the structural and elastic properties of* Au_xV_{1-x} *and* Au_xNb_{1-x} *alloys*
16.40 - 16.50	**Danny Thonig**, Uppsala University, Sweden *Existence of Topological Nontrivial Surface States in Strained Transition Metals: W, Ta, Mo, and Nb*
16.50 - 17.00	**Sergey Streltsov**, Institute of Metal Physics, Ekaterinburg, Russia FeO_2*: a possible novel magnetic constituent of Earth's lower mantle*
17.00 - 17.10	**Ping Zhang**, Institute of Applied Physics and Computational Mathematics, Beijing, China *First-principles studies of plutonium oxides and their surface interaction with gaseous molecules*
17.10 - 17.20	**Huilong Yu**, China Academy of Engineering Physics, Jiangyou, China *Adsorption, dissociation and diffusion of hydrogen on* PuO_2 *(110) surface: A DFT study*
17.20 - 17.30	**Yu Yang**, Institute of Applied Physics and Computational Mathematics, Beijing, China *Structural and electronic properties of* U_nO_m $(n = 1-3, m = 1-3n)$ *clusters: A theoretical study using screened hybrid density functional theory*
17.30 - 17.40	**Ruizhi Qiu**, China Academy of Engineering Physics, Jiangyou, China *Orbital-free density-functional theory models for radiation damage in Al*
17.40 - 17.50	**Cong Wang**, Institute of Applied Physics and Computational Physics, Beijing, China *First principle molecular dynamics studies of warm dense matter*
17.50 - 18.00	**Attila Cangi**, Sandia National Laboratories, Albuquerque, USA *First-principles Stopping Power in Warm Dense Matter*

Short talk Session B (parallel)
Room: Rådstuggu
Chair: David Tozer

16.00 - 16.10	**Maciej Gierada**, Cracow University of Technology, Poland *Computational Insights into Reactivity of the Supported* CrO_x/SiO_2 *(Phillips) Catalyst Towards Ethylene*
16.10 - 16.20	**Mwombeki M. Kabanda**, North-West University, Mmabatho, South-Africa *A DFT Study on the Preferred Hydrogen Atom Transfer Pathway for the Reaction between Diethylthiourea and* $^{\bullet}OH$
16.20 - 16.30	**Guilhem Javierre**, Ecole Centrale Marseille, France *Transesterification mechanism in alkyl hydrogeno-phenylphosphinates*
16.30 - 16.40	**Baisheng Sa**, Fuzhou University, China *Design of Flexible Anodes for Lithium-Ion Batteries using vdW Heterostructures*
16.40 - 16.50	**Robert Zaleśny**, Wroclaw University of Science and Technology, Poland *Practical hints on the selection of functionals for optical band shapes simulations:* BF_2*-carrying compounds as test cases*
16.50 - 17.00	**Moyses Araujo**, Uppsala University, Sweden *Photocatalytic power of graphitic carbon nitride from first-principles theory: band alignment, excitonic effects and dispersive interactions*
17.00 - 17.10	**Harry Ramanantoanina**, Laboratory for nuclear materials, Villigen, Switzerland *A non-empirical calculation of 2p core-electron excitation by Ligand-Field and Density Functional Theory (LFDFT)*
17.10 - 17.20	**Lars Ojamäe**, Linköping University, Sweden *Computational-chemistry modelling of surface reactions and CVD growth*
17.20 - 17.30	**Stephen G. Dale**, Dalhousie University, USA *Interrogating the "B05" density functional for non-locality information*
17.30 - 17.40	**Mojdeh Banafsheh**, University of Geneva, Switzerland *Analytically inverted non-additive kinetic potential functional at small density overlaps*
17.40 - 17.50	**Olga Lopez-Acevedo**, Aalto University, Finland *On the transferability of a parametrized kinetic functional for orbital-free density functional theory calculations*
17.50 - 18.00	**Daniel Karlsson**, University of Jyväskylä, Finland *Systems with disorder, interactions, and out of equilibrium: The exact independent-particle picture from density functional theory*
19.00 - 20.30	"Kräftskiva" (crayfish party/buffet) at Klockargården hotel

Friday, August 25

Contributed Session A (Parallel)

Room: Oppsittu
Chair: Per Hyldgaard

8.30 - 8.45	**Marika Savarese**, Italian Institute of Technology, Genova, Italy *Development and application of theoretical models for the characterization of complex reactions*
8.45 - 9.00	**Andreas Hansen**, University of Bonn, Germany *The new GMTKN55 database: comprehensive and state of the art benchmarking of various density functional methods including newly developed robust "high-speed" approaches*
9.00 - 9.15	**Constantin Lucian**, Italian Institute of Technology, Arnesano, Italy *Semiclassical atom theory applied to solid-state physics*

Contributed Session B (Parallel)

Room: Rådstuggu
Chair: Manuel Richter

8.30 - 8.45	**Oleg Rubel**, McMaster University, Hamilton, Canada *Electronic Localization in Semiconductor Alloys*
8.45 - 9.00	**Chiara Gattinoni**, ETH Zuerich, Switzerland *Defect chemistry and size effects in* $SrRuO_3$
9.00 - 9.15	**Menno Bokdam**, University of Vienna, Austria *Challenges and solutions for the description of hybrid perovskites with first principles methods*

Early Morning Plenary Session

Room: Oppsittu
Chair: Per Hyldgaard

9.20 - 10.00	**Eberhard Engel**, Goethe University Frankfurt am Main, Germany *Exact Exchange Plane-Wave-Pseudopotential Approach to Non-Jellium Slabs*
10.00 - 10.30	Coffee & refreshments break

Late Morning Plenary Session

Room: Oppsittu
Chair: Manuel Richter

10.30 - 10.35	Announcement of two best poster prizes
10.35 - 11.15	**Hubert Ebert**, Ludwig Maximilian University of Munich, Germany *Spin and orbital currents in magnetic solids*
11.15 - 11.20	Closing (Karlheinz Schwarz / Levente Vitos)
11.20 - 13.20	Lunch at Åkerblads gästgiveri

Posters A (Tuesday, August 22)

A1 **M. Merced Montero-Campillo**, Instituto de Quimica Medica (CSIC), Madrid, Spain
Trapping CO_2 *by Adduct Formation with Azole-Based Carbenes*

A2 **Fernando Steffler**, Universidade Federal de Minas Gerais UFMG, Belo Horizonte, Brasil
A TDDFT study of Keggin Polyoxometalates

A3 **Zhihua Dong**, KTH - Royal Institute of Technology, Stockholm, Sweden
Thermal spin fluctuation effect on the elastic constants of paramagnetic Fe from first-principles

A4 **Alexey Arbuznikov**, Technische Universität Berlin, Germany
On the Performance of Local Hybrid Functionals: Effects of Advanced Calibration Functions

A5 **Satoshi Yoshio**, Sumitomo Metal Minig Co., Ltd., Minato-ku, Tokyo, Japan
Analysis of optical properties of solar control materials

A6 **Stephan Schönecker**, KTH - Royal Institute of Technology, Stockholm, Sweden
Thermal surface free energy and stress of iron

A7 **Gregor Feldbauer**, Hamburg University of Technology, Germany
The acetone/TiO_2 *(110) rutile hybrid interface: A DFT study on the geometry, energetics, and vibrational modes*

A8 **Xiaoqing Li**, KTH - Royal Institute of Technology, Stockholm, Sweden
Anomalous ideal tensile strength of ferromagnetic Fe and Fe-rich alloys

A9 **Johannes Gugler**, Vienna University of Technology, Austria
Ab initio calculation of spin lattice relaxation of NV^- *centers in diamond*

A10 **Xiaojie Li**, KTH - Royal Institute of Technology, Stockholm, Sweden
Ab initio calculations of mechanical properties of reduced activation steels

A11 **Silvan Kretschmer**, Helmholtz-Zentrum Dresden-Rossendorf, Germany
Structural transformations in two-dimensional transition-metal dichalcogenide MoS_2 *under electron beam: insights from first-principles calculations*

A12 **Elizabeth Decolvenaere**, University of California, Santa Barbara, USA
Improving DFT for Transition Metal Alloys: The V/DM-17 Test Set

A13 **Kane Shenton**, University College London, UK
Effects of the Hubbard U on density functional-based predictions of $BiFeO_3$ *properties*

A14 **Ruiwen Xie**, KTH - Royal Institute of Technology, Stockholm, Sweden
Generalized stacking fault energy of C-alloyed γ*-Fe: A study at paramagnetic state*

A15 **Mikael Valter**, Chalmers University of Technology, Gothenburg, Sweden
Electrochemical dehydrogenation of glycerol and metanol on Au(111) with DFT

A16	**Kemoabetswe R. N. Serobatse**, North-West University, Mmabatho, South-Africa *A DFT Study on the Reaction between Thiourea and* $^{\bullet}$*OH*
A17	**Ondrej Sipr**, University of West Bohemia, Plzen, Czech Republic *Importance of Madelung potential for magnetism of alloys: FePt studied via CPA and via supercells*
A18	**Jose Garcia de la Vega**, Universidad Autonoma de Madrid, Spain *Performance of SIE and Dispersion in DFT Calculations Involving Ionic Liquids*
A19	**Adam Arvidsson**, Chalmers tekniska högskola, Gothenburg, Sweden *Investigating metal dimer sites in ZSM-5 zeolites with electronic structure calculations and micro-kinetic modelling*
A20	**Franca Maria Floris**, University of Pisa, Italy *Shannon entropy and correlation energy for electrons in atoms*
A21	**Peter Fletcher**, Lancaster University, UK *Quantifying the Accuracy of Molecular Excited State Emission Calculated with TDDFT*
A22	**Amina Mirsakiyeva**, KTH - Royal Institute of Technology, Stockholm, Sweden *The geometrical and optical investigations of PEDOT and its selenium and tellurium derivatives from the density functional theory perspective*
A23	**Alexander Zech**, University of Geneva, Switzerland *A Reliability Parameter for FDET Calculations*
A24	**Giovanni Lani**, Université Pierre et Marie Curie, Paris, France *Spatial and temporal non-locality in approximate exchange-correlation kernels for TDDFT*

Posters B (Wednesday, August 23)

B1	**Matija Zlatar**, University of Belgrade, Serbia *Rational Design of Single Molecule Magnets — Density Functional Perspective*
B2	**Attila Szilva**, Uppsala University, Sweden *Theory of non-collinear interactions beyond Heisenberg exchange; applications to bcc Fe*
B3	**Jakob Seibert**, University of Bonn, Germany *Thermochromism of Ferrocene*
B4	**Iulia E. Brumboiu**, KTH - Royal Institute of Technology, Stockholm, Sweden *The Electronic Structure of CoPc from an Optimally Tuned Range-Separated Hybrid Functional*
B5	**Alexander Romanov**, Lobachevsky State University of Nizhny Novgorod, Russia *Time-dependent density functional theory applied to calculation of electron current excited during atom ionization by intense two-color laser pulses*
B6	**Marie Humbert-Droz**, University of Geneva, Switzerland *Modelling the* π *conjugation length in aromatic antenna: A simple predictive tool for the synthesis of functional material*
B7	**Cláudio M. Lousada**, KTH - Royal Institute of Technology, Stockholm, Sweden *Adsorption of oxygen onto aluminum — Performance of the density functionals: PBE, PBE0, M06, and M06-L*
B8	**Yasmine S. Al-Hamdani**, University of Luxembourg, Luxembourg *Properties of the water to boron nitride interaction: from zero to two dimensions with benchmark accuracy*
B9	**Joel Davidsson**, Linköping University , Sweden *High-thoughput search for defects in SiC*
B10	**Cairedine Kalai**, UPMC, Paris, France *Combining Density-functional Theory And Wave-function Methods: The RS*λ*H + MP2 Scheme*
B11	**Simone Marocchi**, Universidade de São Paulo, Brasil *Quantum mechanics in metric space: distances between exchange-only correlations*
B12	**Shuo Huang**, KTH - Royal Institute of Technology, Stockholm, Sweden *Thermal expansion in FeCrCoNiGa high-entropy alloy from theory and experiment*
B13	**Szymon Śmiga**, Nicolaus Copernicus University, Torun, Poland *Accurate Kohn-Sham Ionization Potentials from Scaled-Opposite-Spin Second-Order Optimized Effective Potential Methods*
B14	**Zongwei Ji**, KTH - Royal Institute of Technology, Stockholm, Sweden *Plastic deformation modes in lamellar TiAl alloys beyond the Schmid's law*

B15	**Yoshifumi Nishimura**, Research Institute for Science and Engineering, Tokyo, Japan *A linear-scaling approximate DFT method for quantum mechanical molecular dynamics simulations of large systems*
B16	**Giane B. Damas**, Uppsala University, Sweden *Electrochemical Reduction of Carbon Dioxide in Sn-based Electrodes: A mechanistic study*
B17	**Bastien Casier**, LCPMR UMR, Paris, France *Study of the Keto-Enol Tautomerism in Acetylacetone, in Gas Phase and in Solvent*
B18	**Henrik Levämäki**, University of Turku, Finland *The Becke Fuzzy Cells Integration Scheme for Exchange-Correlation in GPAW Density Functional Program*
B19	**Marjan Abbasipour**, Iran University of Science and Technology, Tehran *Modification of Material Surface by plasma*
B20	**Liyun Tian**, KTH - Royal Institute of Technology, Stockholm, Sweden *Density functional theory study of the formation energies of Cu-Au system*
B21	**Mayura TalwelkarShimp**, Luleå Tekniska Universitet, Sweden *Some Hydrated Molecular Complexes of 4-Cyanophenylboronic acid: Significance of Water in the Structure Stabilization by Theoretical Investigations*
B22	**Henry Chermette**, Universté Lyon1, Villeurbanne, France *First helical Zn(II) complex based on N4-Schiff base: Experimental and theoretical approach*
B23	**Song Lu**, KTH - Royal Institute of Technology, Stockholm, Sweden *First-principles study of the semicoherent interface between TiC and Fe*

Presenters' abstracts

A density based Electron Localization Function

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Abstract

The subsystem functional scheme (SSF) for constructing Density Functional Theory (DFT)[1] functionals uses two types of ingredients: a) one specialized functional for every type of subsystem that we want to accurately treat with the final functional, and b) an interpolation index that decides how much of each specialized functional is used in a point in the real system. The SSF was successfully used to create the AM05[2] exchange-correlation functional, where a) the uniform electron gas (UEG) and Airy gas (AG) surface systems provided the specialized functionals, and b) the interpolation index was based on the dimensionless gradient of the density, s. At small values of s, a functional based on the UEG (LDA) is used, while for large s the specialized functional created from the AG surface system is successively used more.

In our current work of creating an exchange-correlation functional accurate also for systems with a mix of localized and itinerant electrons[3], we will add a) a specialized functional for confined systems based on the harmonic oscillator (HO) gas[4], and b) use the Electron Localization Function (ELF)[5] as interpolation index. Since the ELF is using the kinetic energy density, this will result in a meta-GGA type functional. In this presentation I will discuss our efforts to parametrize the ELF as a function of s and the dimensionless Laplacian, q, see Figure 1, to instead obtain an ordinary GGA type functional.

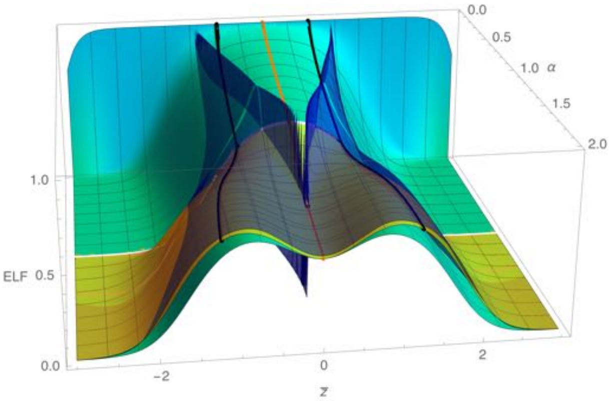

Figure 1: The exact ELF for HO gases (yellow) ranging from large confinement at low α, to less confinement at larger α. The ELF of systems with $\alpha \leq 1$ can be exactly described with an HO based parameterization in s and q (cyan), while the ELF for $1 < \alpha < 2$ systems gradually are better described by an AG based parameterization (blue). The lines on the exact surface, indicate $q = 0$ (black) and $s^2 = 0$ (orange).

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Keywords: *Exchange-Correlation, Kinetic Energy, Electron Localization Function (ELF), Subsystem Functional Scheme*

Nature knows best: computational strategies for the design of biomimetic systems

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Abstract

The design of biomimetic systems that can act in similar ways as their natural counter parts is a long-sought goal in many research areas. In particular, the engineering of catalytically active systems that can copy the natural 'green chemistry' of enzymes has attracted a lot of attention. In spite of this, the number of functional biomimetic systems and re-engineered proteins tailored for specific functions is still limited. From a computational point of view artificial enzyme design is a highly challenging problem that involves the choice of appropriate targets and structural templates and requires efficient ways to explore the enormous space of possible sequences as well as a reliable prediction of their three-dimensional structure and function.

In this talk, I will present a computational approach to enzyme engineering that is based on an efficient combination of the traditional tools of computational chemistry in the form of classical and mixed quantum mechanical/molecular mechanical molecular dynamics simulations with algorithms from artificial intelligence. The performance of this joint approach is illustrated with the example of a computationally designed, catalytically active and structurally highly robust artificial metalloenzyme based on the B1 domain of streptococcal protein G.

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[2] E. Bozkurt, M. A. S. Perez, R. Hovius, N. J. Browning and U. Rothlisberger (submitted)

Keywords: *QM/MM molecular dynamics, genetic algorithms, biomimetic systems, protein engineering*

Combining density-functional theory and many-body methods

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Abstract

Nowadays, a major strategy for improving approximations in density-functional theory (DFT) is to combine DFT with many-body methods such as many-body perturbation theory. Range separation of the electron-electron interaction provides a practical way of performing such a combination by using a (semi)local-density approximation for the short-range part and an explicit many-body approximation for the long-range part. It combines the best of both worlds: an accurate and compact description of short-range interactions by DFT approximations and an accurate description of long-range nonlocal interactions by many-body approximations, while avoiding any double counting of electron correlations.

After giving an overview of such approaches, I will present some recent advances concerning:
- Range-separated hybrid methods for describing ground-state correlations in molecular and solid-state systems, based on second-order perturbation theory and random-phase approximations [1, 2, 3, 4];
- Range-separated hybrid methods for calculating excitation energies in molecular systems, based a long-range frequency-dependent second-order Bethe-Salpeter correlation kernel [5].

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Keywords: *range-separated hybrids, many-body theory, perturbation theory, random-phase approximation*

Localized Orbital Scaling Correction for Systematic Elimination of Delocalization Error in Density Functional Approximations

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Abstract

The delocalization error of popular density functional approximations (DFAs) leads to diversified problems in present-day density functional theory calculations. For achieving a universal elimination of delocalization error, we develop a localized orbital scaling correction (LOSC) framework, which unifies our previously proposed global and local scaling approaches. The LOSC framework accurately characterizes the distributions of global and local fractional electrons, and is thus capable of correcting system energy, energy derivative and electron density in a self-consistent and size-consistent manner. The LOSC-DFAs lead to systematically improved results, including the dissociation of cationic species, the band gaps of molecules and polymer chains, the energy and density changes upon electron addition and removal, and photoemission spectra.

References

[1] Chen Li, Xiao Zheng, Neil Qiang Su, Weitao Yang, "Localized Orbital Scaling Correction for Systematic Elimination of Delocalization Error in Density Functional Approximations", arXiv:1707.00856

Keywords: *delocalization error, localized orbital scaling correction, band gap, fractional charges*

The approximate DFT models 'DFTB': performance and challenges

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Abstract

The DFTB1[1]/DFTB2[2]DFTB3[3] models can be derived from DFT by a first/second/third order expansion of the DFT total energy functional with respect to the charge density. This leads to an energy expression, where the zero order term can be approximated by a sum of pairwise potentials, which are fitted wrt suitably chosen reference data. Introducing a minimal atomic orbital basis set, the first order terms are described by Hamilton matrix elements, which can be pre-computed in a two-center approximation using neutral atoms and their dimers, and therefore no integral evaluation is necessary during the runtime of the program. DFTB2/DFTB3 applies a monopole approximation for the density fluctuations, leading to tight-binding energy expression which makes use of the chemical hardness values (Hubbard paramter) of the atoms. In third order, the chemical hardness derivative is used to model the change of atomic electron density wrt to the charge state of the atom. Up to now, the DFTB2 and DFTB3 models have been parametrised based on DFT/GGA functionals, thereby incorporating the well known DFT/GGA shortcomings. Therefore, several approaches have been applied to improve the description of non-bonded interactions due to the use of minimal basis sets and GGA-functionals [5]. Recently, range-separated functionals have been implemented, now also allowing to compute a wider range of excited states properties, leading to a description of excitation energies comparable to full DFT[6]. To improve accuracy further, machine learning approaches are used to train the DFTB repulsive protentials, which allows for a more flexible way to integrate large sets of (computed) data.

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Keywords: *DFTB, range separated functionals, weak interactions, excited states.*

Automatized parameterization of DFTB

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Abstract

The talk reviews an automatized parameterization process for the density-functional tight-binding (DFTB) method recently developed in our group. The DFTB family of methods became a popular way of treating large molecular and solid systems in approximate fashion. The optimization of the Slater-Koster files, replacing the standard basis sets in the DFTB formalism, is performed using a stochastic optimization method known as particle swarm optimization (PSO). Main advantages of selecting such a way of optimization are: avoiding the necessity of computing gradients in the parameter space, insensitivity to the domain restrictions in the parameter space, and great robustness of the optimization process. Details of the optimization process are discussed along with the details of the implementation. Initial results illustrating the capabilities of the method and performance of DFTB with the PSO optimized parameters are presented.

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Keywords: *density-function tight-binding (DFTB) method, automatized parameterization, particle swarm optimization (PSO) algorithm, approximate methods for large systems*

Understanding exchange and correlation in regular and hybrid van der Waals density functionals

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Abstract

The adiabatic connection formula (ACF) provides an exact specification of the exchange correlation (XC) energy functional E_{xc} from knowledge of the coupling-constant variation in the electron response. The van der Waals density functional (vdW-DF) method [1] is an ACF-based approach to design computationally efficient XC functionals that are systematic extentions of the local-density approximation (LDA) and the generalized gradient approximation (GGA), capturing general nonlocal-correlation effects in a correction term $E_{\mathrm{c}}^{\mathrm{nl}}$. The construction reflects physics insight on how to best approximate the electron-gas response and thus heighten the transferability of the vdW-DF versions [1, 2]. For example, the emphasis on current conservation in the description of dielectric functions enables $E_{\mathrm{c}}^{\mathrm{nl}}$ to account for dispersion interactions across regions with a sparse or even absent electron concentration [2]. At Chalmers, we focus on developing consistent-exchange vdW-DF [3] for which the functional versions, like vdW-DF-cx, effectively represents a mean-value evaluation of the ACF [2]. In an Oslo-Berkeley-Chalmers collaboration we also pursue development of ACF-based hybrid vdW-DFs that are kept deliberately free of parameters [4].

My talk reports recent formal and numerical analysis detailing mechanisms that makes consistent-exchange and hybrid vdW-DF versatile and robust: vdW-DF-cx (hybrid vdW-DF-cx) seems to deliver the same level of accuracy as constraint-based GGA for traditional hard materials [1, 5] (as GGA-based hybrids for molecules [4]), while also being useful in predicting structure and cohesion in sparse matter, like molecular systems [6]. A key point is how semilocal-correlation effects (that are an essential part of GGA) are designed to emerge in $E_{\mathrm{c}}^{\mathrm{nl}}$, even if the vdW-DF-cx input is strictly limited to the many-particle physics results leading to LDA and gradient-corections for screened exchange. The analysis also includes a mapping of the coupling constant scaling of vdW-DFs and of the many-particle corrections to the kinetic energy. The former is useful for discussion of the hybrid vdW-DF construction, the latter allows a refined discussion of the relation between covalent and dispersive interactions.

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Keywords: *van der Waals density functionals, coupling-constant scaling, hybrid vdW-DF.*

The DFT-CDFT-QTAIM synergy to investigate chemical reactivity

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Abstract

The electron density is the fundamental quantum real space observable at the heart of three complementary theories: density functional theory (DFT),[1] conceptual DFT (CDFT),[2,3] and Bader's atoms-in-molecules theory (QTAIM).[4]

In this talk, I will show how that they can enter a fruitful dialogue that leads to the design of new energetic descriptors,[5-8] derived from known properties of Kohn-Sham exchange-correlation functionals, of energy derivatives and of the electron density gradient field.

Noticeably, these new physical features can be used to rationalize chemical bonding (unraveling for instance the nature of noncovalent interactions and the origin of trans effect in organometallics),[9] to predict chemical reactivity at the atomic level (for example, the electrophilicity of carbocations),[10] or to follow the electronic reorganization along a reaction path.[11]

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Keywords: *Kohn-Sham DFT, conceptual DFT, atoms-in-molecules theory, chemical reactivity, chemical bonding*

Chemical Concepts from Density Functional Theory: Theoretical Developments and Applications in Bonding, Chemical Reactivity and Molecular Design

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Abstract

Quantum chemistry provides the opportunity to introduce a number of chemical concepts of utmost importance to interpret structural, stability and chemical reactivity data. In this lecture, I will give an overview of recent activities of our research group in the theoretical development and application of some of these concepts, mainly within the framework of Density Functional Theory (Conceptual Density Functional Theory, also known as DFT based reactivity theory or chemical DFT) [1].

In a first part, aspects of bonding are considered. In a recent contribution, we expressed the change of the electron density from reactants towards the transition state of a chemical reaction as a linear combination of the so-called state-specific dual descriptors of the corresponding reactant complexes. We show that these quantities bear important resemblance to the so-called Natural Orbitals for Chemical Valence, introduced as the orbitals that diagonalize the deformation density matrix of interacting molecules. We thus highlight that these indices computed for reactant complexes provide important information about charge transfer interactions during a chemical reaction [2]. Next, the bonding and reactivity properties of a series of divalent compounds of Sn are scrutinized. Calculations of the DFT reactivity descriptors reveal that the investigated stannylones [Sn(0)] are soft compounds with a higher basicity and nucleophilicity than the stannylenes [Sn(2)] [3]. Next, bonding in a representative set of E(0) (E = C, Si, Ge, Sn, Pb) compounds is scrutinized using valence bond theory and the recently developed maximum probability domains [4]. In a final part, we assess the linear response function from conceptual DFT to probe bonding and explore its link with the transmission properties in molecular electronic devices [5].

In a second part, two applications are presented focusing on chemical reactivity. First, we investigate two classical organic chemistry reaction mechanism, electrophilic and nucleophilic aromatic substitution, through a metadynamics approach, assessing, among others, the important role of the solvent on the reaction mechanism and the chemical reactivity [6]. Next, we discuss the properties and catalytic activities of so-called frustrated Lewis pairs (FLPs); these are “associations” of a Lewis acid and a Lewis base that are hindered by steric factors from forming strong, datively bound classical adducts. We prove the earlier proposed lack of dative bonding between donor and acceptor centres in these acid-base complexes [7]. In addition, through structural and electronic analyses of the transition states corresponding to H_2 splitting of various Lewis pairs, we establish that classical Lewis pairs split H_2 through a combination of electron donating and withdrawing mechanisms, whereas FLPs split H_2 through a dominantly withdrawing process facilitated by strong polarization [8].

Finally, we will highlight two applications of the so-called inverse design methodology, using the reactivity indices to design molecules with optimal reactivity properties. This approach will be used to construct radicals with unprecedented stabilities [9] and modified diamondoids with improved electronic properties [10].

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Keywords: *Conceptual Density Functional Theory, Chemical reactivity, Bonding, Molecular Design*

DFT-based multi-scale modelling of materials and nanoparticles

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Redox-active metal oxide surfaces and interfaces – such as electrodes, catalysts, and sensors – play crucial roles in our society and in the development of new materials and greener technologies. In the scientific literature, a full arsenal of experimental methods are being used to help to characterize such materials interfaces. Simultaneously, the (ever-increasing) theoretical materials studies in the literature provide structural and mechanistic information at a detail that is difficult to beat by experiments – but are the models accurate enough? There are at least two major challenges in materials modelling: (i) how to build structural models that capture the complexity and imperfections of the real systems, and (ii) how to find good enough interaction models (say a DFT functional [1] or a force-field). Here mimicking the interactions and chemical properties of materials *without explicit electrons* present is a formidable task, especially when the transfer of electrons is closely coupled to the material's functionality, as is the case for redox-active metal oxides.

I will discuss some of our efforts in the development of a multiscale modelling approach for surfaces and interfaces of metal oxides (e.g. CeO_2, ZnO, MgO) – with and without interacting molecules (e.g. O_2 and water).

In summary, we combine a range of theoretical methods including DFT [2], tight-binding-DFT [3], and reactive force-field simulations [4] in a consistent multi-scale approach to examine the properties of oxide nanosystems. We generate images and spectra to make direct comparisons with the experimental counterparts (e.g. IRRAS spectra [5]), but we also generate properties that cannot be measured by experiments such as the water dipole moment enhancement on a surface (often much larger [1] than in liquid water!). I will also inform about the European Materials Modelling Council (https://emmc.info/), and our efforts to promote the use and quality of materials modelling in industry; the EMMC is open to everyone interested.

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Hubbard bands *vs* plasmons in correlated metals: A view from self-consistent GW+DMFT

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Abstract

The spectral function or density of states of a typical correlated metal is usually characterised by a three-peak structure: a quasiparticle peak around the Fermi level sandwiched by two satellite features below and above it. For many years these satellite features have been interpreted as Hubbard bands, which within the atomic picture are understood as arising from a strong onsite Coulomb interaction. We have studied the spectral functions of $SrVO_3$, which is a prototype of correlated metals, as well as $SrMoO_3$ using a newly developed fully self-consistent GW+DMFT scheme. Analysis of the results reveals that the satellite features are better understood as collective plasmon excitations. This conclusion is reached by the finding that after self-consistency is achieved the impurity Hubbard U is substantially screened by the non-local Coulomb interaction and is much smaller than the energy separation between the two satellites, making the conventional Hubbard-band interpretation untenable. We have also studied a model sodium in which the lattice constant is artificially increased to mimic correlation strength. Indeed, the collective-plasmon picture also applies until the lattice constant reaches 1.5 the equilibrium value, at which stage the system turns into a Mott-Hubbard insulator. The present study suggests that the Hubbard-band picture should be revised in favour of the plasmon picture for a much larger range of correlation strength than was assumed before.

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Keywords: *GW+DMFT, Hubbard bands, plasmons, correlated metals, non-local Coulomb interaction*

Towards multiple-scattering theory for disordered systems with Anderson localization

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Abstract

The basic concepts involved in the physics of localization in disordered systems are discussed on an elementary level. To make possible first-principle electronic structure calculations for substitutionally disordered alloys including the effect of Anderson localization we discuss recent developments including the typical medium, and its dynamical cluster extension. These theories can easily be combined with dynamical mean-field approaches to strongly correlated electrons, thus opening an attractive avenue for a genuine non-perturbative treatment of the interplay of strong interactions and strong disorder.

Keywords: *Effective medium theories of disorder, Coherent Potential Approximation, Typical Medium Dynamical Cluster Approximation*

Quantitative Predictions by Electronic Structure Theory

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Abstract

It is a common but bad practise to call every result obtained by a density functional calculation a "prediction". In many cases, this refers to a result, for example a lattice constant, which is already known experimentally or has been "predicted" in another, earlier calculation. Such cases clearly violate the logical meaning of the word: a prediction should precede the experimental confirmation and it should not be repeated with incremental modification. Moreover, a prediction should be interesting enough to encourage experimentalists to perform the check.

Here, I will present a number of predictions that preceded the experimental confirmation or are still unconfirmed. They are of qualitative nature in the sense that a non-trivial effect is considered. They are quantitative in the sense that specific conditions (chemical composition, atomistic structure, pressure, magnetic field, electric field) for the effect are announced. The considered cases comprise the spin reorientation in $\mathrm{GdCo_5}$ in an external magnetic field [1], the magneto-elastic lattice collapse in $\mathrm{YCo_5}$ under external pressure [2], metamagnetic transitions in $\mathrm{La(Fe;\,Si)_{13}H_x}$ under pressure and magnetic field [3], the tunability of strain along the fcc-bcc Bain path in FePd films [4], magnetic elements by epitaxial stretching [5], electro-chemical tuning of the surface magnetic anisotropy of $\mathrm{L1_0}$ compounds [6], the topological character of $\mathrm{Bi_{14}Rh_3I_9}$ [7], electronic topological transitions in fcc aluminum [8], and first-order martensitic transitions in strained epitaxial films [9].

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Keywords: *external magnetic field, external pressure, epitaxial strain, external electric field, topological phases, magneto-elastic coupling, electronic topological transitions*

Relativistic density functional theory with picture-change corrected electron density based on infinite-order Douglas-Kroll-Hess method

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Abstract

The author's group has developed the efficient two-component relativistic method based on the infinite-order Douglas-Kroll-Hess (IODKH) method.[1,2] The first key technique is the local unitary transformation (LUT) scheme,[3,4] which achieves the linear-scaling computational cost for the unitary transformations for one- and two-electron operators. Reiher and coworkers[5,6] independently proposed a similar local technique for one-electron operator. The second is the combination with the linear-scaling divide-and-conquer (DC)-based electron-correlation theories,[7] which have been developed for the nonrelativistic calculations of the second-order Møller–Plesset (MP2),[8] coupled cluster theories with single and double excitations (CCSD),[9] and its perturbative triple excitations (CCSD(T))[10] methods in addition to the Hartree-Fock (HF) method and density functional theory (DFT).[11,12]

In this presentation, I will explain a novel relativistic DFT treatment at the two-component IODKH level, in which the exchange-correlation energy and potential are calculated using the picture-change corrected (PCC) electron density.[13] Furthermore, the locality of the relativistic effect enables us to limit the region to evaluate the PCC density, which might improve the efficiency of the present PCC-DFT computation. Numerical results of the present method will be given from the viewpoints of efficiency and accuracy.

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Keywords: *picture-change corrected electron density, relativistic two-component theory, infinite-order Douglas-Kroll-Hess method, local unitary transformation, divide-and-conquer method*

Beyond the electric dipole approximation in simulations of X-ray absorption spectroscopy

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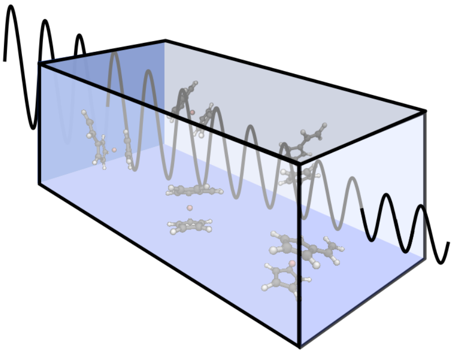
Abstract



X-ray absorption spectroscopy excites core orbitals, which are typically local, element-specific, yet sensitive to the chemical environment. A new generation of light sources, such as the free-electron laser, allows the extension of numerous spectroscopies to the X-ray domain.
The general expression for the absorption cross section is

$$\sigma_{n\leftarrow 0}\left(\omega\right)=\frac{\pi\omega}{\varepsilon_0\hbar c}\left|\langle n|\hat{T}\left(\omega\right)|0\rangle\right|^2 f\left(\omega,\omega_{n0},\gamma_{n0}\right),$$

where $\hat{T}\left(\omega\right)$ represents light-matter interaction and $f\left(\omega,\omega_{n0},\gamma_{n0}\right)$ a lineshape function. Two equivalent methods for the simulation of NEXAFS spectra are restricted excitation window (REW) TDDFT[1] and the complex polarization propagator (CPP) method[2]. Whereas in the first method lineshapes have to be added by hand, they come out automatically in the latter method.
In the UV/Vis domain the electric dipole approximation is generally employed. In the X-ray domain, its validity is less obvious , since the wave length of the radiation is on the order of molecular dimensions. The usual extension of theory is to include terms beyond zeroth order in the wave vector in the interaction operator $\hat{T}\left(\omega\right)$. However, this leads to origin-dependence of absorption cross-sections. In a seminal paper Bernadotte *et al.* showed that this problem is avoided by rather expanding the absorption cross-section $\sigma\left(\omega\right)$ in orders of the wave vector[3]. We have investigated an alternative approach which simply employs the full light-matter interaction[4]. In both approaches rotational averaging has to be considered for isotropic media[5]. In this contribution we consider the extension of these approaches to the relativistic domain.

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Keywords: *X-ray spectroscopy, restricted excitation windon TDDFT, complex response, relativistic molecular quantum mechanics, electric dipole approximation*

Density-Functional Theory for Molecules in Strong Magnetic Fields

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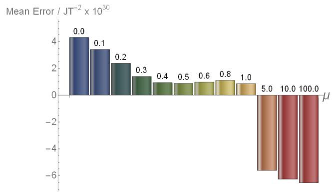
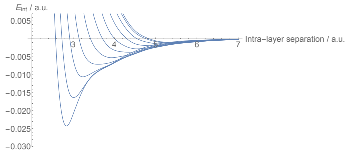
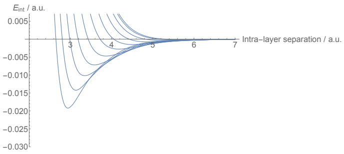
Abstract

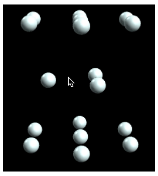
An implementation of current-density-functional theory is presented that allows for the description of molecular systems in strong magnetic fields. Recent work on the evaluation of molecular integrals over London atomic orbitals [1] has allowed for calculations to be performed on larger systems than previously possible, particularly when combined with density-fitting techniques. The development of range-separated methods in this context [2] is discussed and a range-separated analogue of the current dependent version of the TPSS functional [3, 4] (cTPSS) is used to explore the range of electronic interactions that are important in the description of systems in the presence of strong magnetic fields.

Applications will be presented for field strengths ranging from those important for molecular properties such as magnetizabilites and NMR shielding constants through to fields approaching 1 a.u. (235 k Tesla), which are of the magnitude found on stellar objects [5]. The ability of current-density-functional theory to describe both weak and strong field phenomena is assessed by comparison with traditional *ab initio* methods and the high accuracy of meta-GGA functionals in the strong field regime is demonstrated. These functionals provide a good description of the recently proposed perpendicular paramagnetic bonding mechanism [6] and can be applied to larger systems that exhibit strongly anisotropic interactions and chemical behaviour as a result of the anisotropy of the applied field [7].









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Keywords: *Current-density-functional theory, molecular integrals, range-separation, functional development, magnetism*

The SCAN Density Functional: Nonempirical, Predictive, and Efficient*

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The SCAN (strongly constrained and appropriately normed) meta-generalized gradient approximation was constructed [1] to satisfy all 17 known exact constraints that a semi-local functional can satisfy (compared to 11 for the PBE GGA). SCAN is further fitted to appropriate norms, non-bonded systems for which a semi-local functional can be accurate for exchange and correlation separately. SCAN recognizes and provides different GGA-like descriptions for covalent single bonds, metallic bonds, and van der Waals (vdW) bonds. Here I will review the functional itself, along with its long-range vdW extension SCAN+rVV10 [2]. I will also review applications to properties of diversely-bonded systems [3], including ferroelectricity [4], density and structure of liquid water [5], crystal structure stability [6], surface properties of transition metals [7], and critical pressures for structural phase transitions of semiconductors [8]. The accuracy of SCAN is often comparable to or better than that of a hybrid functional, at lower computational cost and without any fitting to bonded systems.

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Keywords: density functional theory. exchange-correlation energy, meta-generalized gradient approximation, exact constraints, ferroelectrics, liquid water, phase stability

Green's function-based method for correlated electronic structure calculations

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Abstract

We present a new charge self-consistent scheme that combines Density Functional and Dynamical Mean Field Theory, which uses Green's function of multiple scattering-type. In this implementation the many-body effects are incorporated into the Kohn-Sham iterative scheme without the need for the numerically ill-posed analytic continuation of the Green's function and of the self-energy. This is achieved by producing the Kohn-Sham Hamiltonian in the sub-space of correlated partial waves and allows to formulate the Green's function directly on the Matsubara axis. The spectral moments of the Matsubara Green's function enable us to put together the real space charge density, therefore the charge self-consistency can be achieved. Our results for the spectral functions (density of states) and equation of state curves for transition metal elements, Fe, Ni and FeAl compound agree very well with those from several variants of Hamiltonian-based LDA+DMFT. Our current implementation improves on numerical accuracy, requires a minimal effort besides the multiple scattering formulation and can be generalized in several ways that are interesting for applications to real materials.

Keywords: *correlated electron systems, method development, dynamical mean field theory, transition metals*

Combined semilocal exchange potential with dynamical mean-field theory

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Abstract

The modern semilocal exchange potential is an accurate and efficient approximation to the exact exchange potential of density functional theory. We tried to combine it with the dynamical mean-field theory to derive a new first-principles many-body approach for studying correlated electronic materials. As a paradigm, this approach was employed to investigate the electronic structures and optical properties of strongly correlated ionic insulator YbS. Compared to the regular density functional theory plus dynamical mean-field theory which surprisingly failed to give reasonable electronic structures, the new approach correctly captured all of the important characteristics of YbS. Not only an indirect gap between fully occupied Yb-4f state and an unoccupied conduction band, but also an absence of Drude peak in the optical conductivity $\sigma(\omega)$ were successfully reproduced.

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Keywords: *dynamical mean-field theory, semilocal exchange potential, electronic structures, optical conductivity, YbS*

Optimizing constraints and corrections in approximate DFT

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Abstract

We develop the connection between constrained density functional theory (cDFT) energy derivatives and response functions, assessing of the uniqueness and character of cDFT stationary points while accounting for interactions and screening. We provide a non-perturbative proof that stable stationary points occur only at energy maxima with respect to their Lagrange multipliers. We demonstrate that multiple solutions, hysteresis, and energy discontinuities may occur in cDFT; we provide the necessary conditions for multi-constraint cDFT optimizability, and we show that concave regions of the energy-density landscape cannot be explored using constraints [1].

In approximate DFT, the self-interaction error (SIE) exhibits a predominantly quadratic energy-density profile amenable to correction using efficient, constraint-resembling methods such as DFT + Hubbard U (DFT+U). The use of cDFT to automate SIE correction is a compelling possibility, but we show that non-linear constraints are incompatible with cDFT. We circumvent this using separate linear and quadratic correction terms, leading to the development of a generalized DFT+U method termed DFT+U_1+U_2. This approach enables a simultaneous correction of the total energy and the enforcement of Koopmans condition, and we outline a practical, approximate scheme by which the required pair of Hubbard parameters may be calculated from first principles [2].

Finally, we discuss how constrained DFT may be used to put conventional DFT+U on a more first-principles footing by generating Hubbard U parameters that are properties of the ground-state density, but not referenced to the Kohn-Sham eigensystem. These parameters may be made self-consistent with DFT+U according to a number of plausible criteria, and we demonstrate that the simplest self-consistency scheme is sufficient to recover the correct dissociated limit of the binding curve of H_2^+, a canonical benchmark system for SIE [3].

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Keywords: *constrained DFT, Koopmans' condition, self-interaction error, DFT+U, consistent Hubbard U*

Finite-T electron-electron, electron-ion and ion-ion xc-functionals, discontinuities in the mean ionization, and phase transitions in low-Z warm-dense matter (WDM).

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Abstract

DFT calculations and MD simulations show that low-Z elements like C, H, O, N etc., form transient chemical bonds even at temperatures as high as 8-10 eV [1]. However, the study of these systems and their mixtures using DFT+MD, especially at higher temperatures (T) is quite prohibitive. The neutral-pseudo-atom (NPA) model which solves finite-T Kohn-Sham-Mermin equations is a rigorous DFT method where three XC-functionals F_{xc}^{ee}, F_{xc}^{ei}, and F_{c}^{ii} appear [2]. Spurious discontinuities in the mean-ionization $\bar{Z}$ are suppressed via F_{xc}^{ei} and self-interaction (SI) effects. Methods which seek to introduce broadening of Kohn-Sham levels to avoid discontinuities in the mean ionization are argued to be without foundation. Unlike popular ion-sphere average atom models, the NPA model [2] provides (a) an unequivocal value for the mean-ionization $\bar{Z}$ that satisfies the Friedel sum rule, and (b) captures transient C-C covalent bonding even though it is a "single-center" calculation. It also reveals the existence of phase transitions in complex liquids like WDM carbon. In liquid carbon the strongly correlated fluid undergoes a transition to an uncorrelated mono-atomic fluid characterized by a weakly-coupled pair-distribution function typical of a gas. The existence of similar phase transitions in other low-Z WDM systems of astrophysical interest can be currently addressed easily only by this method.

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Keywords: finite-T density functional theory, warm dense matter, exchange-correlation functionals, discontinuities in ionization, phase transitons

The interaction-strength interpolation method for main-group chemistry: benchmarking, limitations, and perspectives

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Abstract

The interaction-strength-interpolation (ISI) exchange-correlation functional [1] is an advanced non-local functional based on an interpolation between the weak and strong coupling limits. It includes a high degree of sophistication and entails the potential for the development of accurate future tools in DFT. However, benchmarking of this approach has been restricted so far only to simple or model systems. In this contribution instead we present a summary of recent work targeted at assessing the properties and drawbacks of the ISI functional in real applications [2]. In particular, we have applied the functional in different standard tests in computational chemistry (e.g. atomization and reaction energies, barrier heights, non-covalent interactions) and we have analyzed in detail the dependence of the ISI functional, on the basis set and on the ground-state orbitals as well as the influence of the size-consistency problem. In this way, we show and explain some of the limitations of the ISI functional (i.e. for atomization energies), but also unexpectedly positive results, such as the good performance for the interaction energy of dispersion-bonded complexes.

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Keywords: *XC functional, adiabatic connection, interaction-strength interpolation*

Towards truly nonlocal exchange and correlation functionals: Nonempirical constructions

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Abstract

The van der Waals density functional (vdW-DF) method represents an attractive framework for systematically approximating the exchange correlation (XC) energy in both sparse and traditional dense matter. The consistent exchange version vdW-DF-cx [1] provides accurate descriptions of the structure and binding energies in both large-molecules structures and other extended systems. Many molecular properties are dominated by exchange. The nonlocal functionals vdW-DFs therefore often lead to too much hole confinement as they are still anchored in a formulation with gradient-corrected exchange. We explore constraint-based, truly nonlocal density functional by a hybrid of vdW-DF and Fock exchange.

An elegant and robust hybrid formulation of regular constrained-based functionals emerge by using the adiabatic connection formula (ACF) to balance the exchange and correlation. We analyse coupling-constant scaling of the vdW-DF method, including the non-local correlation energy functional, which enables us to use a two-legged hybrid construction, termed vdW-DF-tlh, by adopting the original PBE-based analysis [2]. The Fock-exchange mixing is explicitly asserted for each system and property of interest.

Results for covalent bonding and noncovalent bonding in molecules are presented. While lacking of self-consistency, we still find that the vdW-DF-tlh is accurate. The small Fock mixing scatter gives us confidence that the one mixing design vdW-DF-cx0 [3] launched recently is able to provide a good description of the set of investigated molecular properties. Also systems having Fock mixing away from the averaged value are discussed.

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Keywords: *vdW-DF, hybrid functional, adiabatic connection formula (ACF)*

Semi-local exchange functionals showing ultranonlocal response: the hope to replace exact exchange

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Abstract

The widespread success of Density Functional Theory (DFT) is based on a favorable ratio of accuracy to computional cost, especially with semi-local approximations to the exchange-correlation energy. However, functionals such as the local density approximation (LDA), generalized-gradient approximations (GGA) or meta-generalized-gradient approximations (meta-GGA), typically miss important exact exchange features related to the derivative discontinuity. These are essential for accurately describing long-range charge transfer processes. The electrical response of molecular chains, which is dramatically overestimated by local and semi-local density functionals, is a prime example. The key to its correct description is a term in the Kohn-Sham exchange potential that counteracts the external field and has been named "ultranonlocal". We here present how these field-counteracting properties can be incorporated into semi-local DFT on the meta-GGA level. Thereby we show that by utilizing the kinetic-energy-density, it is possible to model ultranonlocal effects in the Kohn-Sham potential by virtue of a semi-local energy expression.

Keywords: *meta-GGA, semi-local DFT, functional development, field-counteraction, charge transfer, molecular chains*

A simple way to apply nonlocal van der Waals functionals within all-electron methods

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Abstract

The method based on fast Fourier transforms proposed by Roman-Perez and Soler [1], which allows for a computationally fast implementation of nonlocal van der Waals (vdW) functionals [2,3], has significantly contributed in making the vdW functionals popular in solid-state physics. However, the Roman-Perez-Soler method relies on a plane-wave expansion of the electron density, therefore it can not be applied readily to all-electron densities for which an unaffordable number of plane waves would be required for an accurate expansion. In this work, we present the results for the lattice constant and binding energy of solids that were obtained by applying a smoothing procedure to the all-electron density calculated by the linearized-augmented plane-wave method as implemented in the WIEN2k code [4]. The smooth density is given by

$$\rho_s(r) = \begin{cases} \rho(r) & \rho(r) < \rho_c \\ \dfrac{\rho(r) + \rho_c(\rho(r) - \rho_c)^n}{1 + (\rho(r) - \rho_c)^n} & \rho(r) > \rho_c \end{cases}$$

and tests have shown that fast and universal convergence can be obtained with n=1 and $\rho_c = 0.3$ bohr^{-3}. Typically this choice requires a plane wave cutoff of 15-25 bohr^{-3}. This procedure has the advantages of being very simple to implement, basis-set independent, and to allow also the calculation of the vdW-potential. It is also shown that the results agree very well with those from literature that were obtained with the projector augmented-wave method [5,6].

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Keywords: nonlocal van der Waals functionals, all-electron densities, APW+lo method

Trapping CO_2 by Adduct Formation with Azole-Based Carbenes

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Abstract

CO_2 forms stable compounds with nitrogen heterocyclic carbenes (NHC’s) through non-covalent interactions or by covalent bonding. In most cases, exothermic reaction profiles towards the covalently bound form were found, reaching stabilization enthalpies up to -77 kJ·mol-1. Stationary points along the reaction coordinate were identified at the G4MP2 level. There is a narrow dependence between the preference for covalent or non-covalent bonding and the carbene structure, as revealed by a series of physicochemical descriptors.

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Keywords: *carbenes, carbon dioxide, reactivity, G4MP2, Interacting Quantum Atoms*

A TDDFT study of Keggin Polyoxometalates.

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Abstract

Polyoxometalates are a sub group of inorganic compounds characterized by polyhedral formation and they are building blocks for large nanostructures formation. Keggin polyoxometalates are the most studied and enigmatic of the polyoxometalates. Some of them have a bandgap in the ultraviolet and blue region, known as polyoxometalates blue, and they are useful for photoelectrochemistry applications.[1] Recently, a new class of Keggin polyoxometalates were discovered: the polyoxoniobates. This class has different features like high negative charge (-15 or -16) and different electron density behavior.[2] The Time Dependent Density Functional Theory (TDDFT) is an extension of DFT, giving accurate electronic density and energies of excited states.[3] Keggin polyoxometalates $X[M_{12}O_{40}]^{y-}$ with different principal metals (M=Mo, W and Nb) and heteroatoms (X= P, As, Si and Ge) were calculated using the PBE XC functional on Gaussian 09 program. The polyoxoniobates were protonated on their external oxygens (decreasing their high negative charge), with *a posteriori* removal of these protons. Frequency analyses were performed to assure that a minimum in the potential energy surface was found. For TDDFT procedure, Cam-B3LYP and PBE0 XC functional were chosen. The first one is long range corrected energy functional, known to provide more accurate excitation energies. The number of calculated states was 90. Structural properties are in a good agreement with the experimental data. However the external oxygen atoms of polyoxoniobates show deviation of 0.2 Å, probably due to their high negative charges. The excitation energies for Polyoxomolybdates using Cam-B3LYP functional is around 309.79 nm, near of experimental UV-Vis Spectra (309.57 nm). Polyoxotungstates present deviation with respect to the experimental data (~265.56nm) of about -5 nm for Cam-B3LYP and +8 nm for PBE0. Polyoxoniobates are set on peculiar deviation where Cam-B3LYP presents a wavelength 334.91 nm and for PBE0 433.85 nm. In this case, the UV-Vis spectra have a noise or less probable excitations give this huge deviation. The NTO analysis shows a delocalization of HOMO and LUMO orbitals on group 6 polyoxometalates. On the other hand polyoxoniobates do not have any delocalization of HOMO and LUMO. The main differences on the geometry, electron density and UV-Vis spectra between the 6- and 5-Keggin polyoxometalates will be presented in details.

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Keywords: *Polyoxometalates, Photoelectrochemistry, Time Dependent Density Functional Theory, UV-Vis spectra.*

Thermal spin fluctuation effect on the elastic constants of paramagnetic Fe from first-principles

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Abstract

We investigate the impact of longitudinal thermal spin fluctuations on the temperature dependence of the elastic constants of paramagnetic body-centered cubic (bcc) and face-centered cubic (fcc) Fe. Based on a series of constrained local magnetic moment calculations, the spin fluctuation distribution is established using Boltzmann statistics with involving the Jacobian weight, and a temperature-dependent quadratic mean moment is introduced which accurately represents the spin fluctuation state as a function of temperature. We show that with increasing temperature, c' and c_{44} for the fcc phase and c_{44} for the bcc phase decrease at different rates due to different magneto-elastic coupling strengths. In contrast, c' in the bcc phase exhibits relatively high thermal stability. Longitudinal thermal spin fluctuations diminish the softening of both elastic constants in either phase and have comparatively large contributions in the fcc phase. In both bcc and fcc Fe, c_{44} has a larger temperature factor than c'. On the other hand, c' is more sensitive to the longitudinal thermal spin fluctuations, which balance the volume-induced softening by 21.6 % in fcc Fe.

Keywords: *paramagnetic Fe, elastic constants, spin fluctuation, temperature*

On the Performance of Local Hybrid Functionals: Effects of Advanced Calibration Functions

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In local hybrid functionals (local hybrids) [1, 2] the admixture of the exact-exchange energy density is position-dependent (governed by the so called local mixing function (LMF)). This provides these functionals with higher accuracy and flexibility compared to traditional (global) hybrids (e. g. B3LYP, PBE0, TPSSh) A main obstacle to the further development of local hybrids has been the ambiguity in the definition of the exchange-energy density ("gauge problem"): any energy density can be modified ("calibrated") by a so called calibration function (CF) which upon integration over the whole space yields zero [3, 4]. CF and LMF are two of the four building blocks of a local hybrid, with semi-local exchange and semi-local correlation being the other two: the quality of a local hybrid is a matter of a very subtle balance ("compatibility") between all of these factors.

Recently we have constructed simple and transparent CFs based on semi-local ingredients only and thus managed to improve the overall performance of several local hybrids [5, 6]. While in Ref. [5] we constructed CFs in an *ad hoc* manner (taking into account a number of exact constraints that a proper CF should obey), in Ref. [6] we have found a natural and systematic way to produce semi-local CFs from GGA/meta-GGA corrections to the exchange energy density by partial integration (dubbed "pig": partial integration gauge). Repeating such a procedure leads to correction terms of increasing order, resulting in more complicated but also more flexible CFs.

In this work we present a systematic study of the effects of first- and second-order "pig" calibration functions on the overall performance of local hybrids (several subsets of the GMTKN30 database [7] have been selected for that purpose). While restricting ourselves to the so-called "t-LMF" (a scaled ratio of the von Weizsäcker kinetic energy density to the Kohn-Sham kinetic energy density [1, 2]), we considered several combinations of semi-local exchange and correlation with a particular emphasis on the B95 correlation functional [8] in both its original form and a modified one which we introduce for its better compatibility with the t-LMF. Encouraging results open a new avenue for creating local hybrids.

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Keywords: *Local hybrid functional, local mixing function, calibration function, partial integration gauge, B95 correlation*

Analysis of optical properties of solar control materials

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Abstract

Materials that transmit visible light and shield near-infrared light are called solar control materials and are used for window glasses of automobiles and buildings. As the solar control materials, fine particles of ITO, LaB_6, $Cs_{0.33}WO_3$, etc. are known. In particular, LaB_6 and $Cs_{0.33}WO_3$ are excellent solar control materials having both high transmittance of visible light and high absorption of near-infrared light at little doze. We have analyzed the optical properties of these materials by first-principles calculation in order to elucidate the mechanism underlying these unique optical properties.

Regarding LaB_6, the dielectric functions were obtained by considering the Drude term and using the screened exchange method which calculates the band gap with high accuracy. They were found to reproduce the measured ones with good precision [1]. The near-infrared absorption is due to localized surface plasmon resonance, and the high transparency is attributed to the specific hybridization of La5d-B2p orbitals in the basically wide bandgap.

In $Cs_{0.33}WO_3$, from the results of ellipsometric permittivity measurement and EELS analysis it is suggested that polaron absorption is overlapped on plasmon absorption in $Cs_{0.33}WO_3$ [2], but the mechanism by which polaron absorption occurs is not clear. Therefore, we analyzed the itinerantity and localization of electrons in $Cs_{0.33}WO_3$ using first-principles calculation. The dielectric functions obtained by calculation reproduced measured values except for the polaron absorption. By introducing oxygen defects, however, electrons are localized, with a formation of a new absorption in the infrared that agrees well with the measured polaron peak. It became clear that polaron absorption is caused by oxygen defects. Moreover, the polaron absorption increases with increasing amount of oxygen defect, which was confirmed by experiment. Absorption at low energy is concluded to be caused by both free electrons and localized electrons.

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Keywords: *polaron, optical properties, dielectric functions, tungsten oxide*

Thermal surface free energy and stress of iron

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Abstract

Absolute values of surface energy and surface stress of solids are hardly accessible by experiment. We investigated [1] the temperature dependence of both parameters for the (001) and (110) surface facets of body-centered cubic Fe from first-principles modeling taking into account vibrational, electronic, and magnetic degrees of freedom. The found monotonic decrease of the surface energies of both facets with increasing temperature is mostly due to lattice vibrations and magnetic disorder. The surface stresses exhibit non-monotonic behaviors resulting in a strongly temperature dependent excess surface stress and surface stress anisotropy.

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Keywords: *surface energy, surface stress, iron, temperature, DFT*

The acetone/TiO_2 (110) rutile hybrid interface: A DFT study on the geometry, energetics, and vibrational modes

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Abstract

Titanium dioxide draws significant attention because of its potential in catalytic, particularly photocatalytic, processes. [1] Moreover, it promises to be useful in the design of hybrid materials consisting of organic and inorganic components which allow for excellent mechanical properties. Acetone is commonly present in chemical reactions during the formation of hybrid interfaces as a containment or as a part in many catalytic processes. [2] Thus, the role of acetone at TiO_2 surfaces is of high interest, e.g., as a potential competitor to coupling agents like carboxylic acids. Therefore, we studied the adsorption geometry and energetics of acetone molecules on the TiO_2 (110) rutile surface with density functional theory (DFT) employing dispersion-corrected methods. Several exchange-correlation functional are tested. The focus lies on identifying and quantifying differences between molecular and dissociated adsorption modes. Saturation coverage is reached at 0.5 molecules per undercoordinated surface Ti atom. Furthermore, η-acetone binds ≈ 0.23 eV stronger than η-enolate, and 0.70 eV weaker than acetic acid. Vibrational spectra of various adsorption modes are calculated employing density functional perturbation theory (DFPT) [3] and compared to IR spectroscopy experiments. [4]

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Keywords: *titanium dioxide, acetone, adsorption, density functional theory, van der Waals corrections, vibrational spectra*

Anomalous ideal tensile strength of ferromagnetic Fe and Fe-rich alloys

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Abstract

Within the same failure mode, iron has the lowest ideal tensile strength among the transition metals crystallizing in the body-centered cubic structure. Here, we demonstrate that this anomalously low strength of Fe originates partly from magnetism and is reflected in unexpected alloying effects in dilute Fe(M) ($M =$ Al, V, Cr, Mn, Co, Ni) binaries. We employ the structural energy difference and the magnetic pressure to disentangle the magnetic effect on the ideal tensile strength from the chemical effect. We find that the investigated solutes strongly alter the magnetic response of the Fe host from the weak towards a stronger ferromagnetic behavior, which is explained based on single-particle band energies.

Keywords: *Ideal tensile strength, Fe-based alloys, Density-functional simulations*

Ab initio calculation of spin lattice relaxation of NV^- centers in diamond

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Abstract

This poster is complementing the contribution to the corresponding talk with the same title and is showing the details of both the theoretical derivation of the spin-lattice relaxation time and the methods used for the *ab initio* calculation thereof. We investigate on the fundamental mechanism of spin phonon coupling in the negatively charged nitrogen vacancy center (NV^- center) in diamond in order to calculate the spin lattice relaxation time T_1 and its temperature dependence. Starting from the dipolar spin-spin interaction between two electrons, we couple the spins of the electron to the movements of the ions and end up with an effective spin-phonon interaction potential $V_{\mathrm{s-ph}}$. Taking this time dependent potential as a perturbation of the system leads to Fermi's golden rule for transition rates which allows to calculate the spin lattice relaxation time T_1. We simulate the color center with the Vienna *Ab Initio* Simulation Package (VASP) to extract the figures necessary to quantify T_1: First, we obtain the equilibrium positions of the ions and the electronic charge density by a proper relaxation of the system. Next, we investigate on the local phonon modes of the color center within the harmonic approximation using the small displacement method. We extract the phononic density of states and bandstructure by diagonalizing the dynamical matrix using the phononpy package. Then, we model the electronic wavefunctions by calculating maximally localized Wannier functions with Wannier90 and building the orbitals according to the C_{3V} symmetry of the defect. Finally, we plug the simulated figures into our model and end up with three different types of first order processes for spin-phonon interaction in analogy with electron-photon interaction:

- An excitation of a spin is accompanied by the absorption of a phonon with the matching frequency of the spin transition.
- A deexcitation of a spin due to induced emission of a phonon.
- A temperature independent contribution where a spin relaxes spontaneously and a phonon is emitted.

To simulate the measured temperature dependence of T_1, an ensemble of spins decaying and getting reexcited due to coupling to the phonon bath has to be considered: Taking all these processes into account, the measured curves are quantitatively well described and we can clearly distinguish two regions of spin lattice relaxations in the system, depending on temperature: At temperatures above the spin transition energy ($k_B T > \hbar\omega_s$) the coupling to the thermal phonons is dominating the relaxation process while at temperatures below the spin transition the thermal phonons are frozen out and the only decay channel left is given by the temperature independent spontaneous emission of a phonon. A comparison with recent experimental data is presented.
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References

Keywords: NV *center, electron phonon interaction, spin lattice relaxation, spin dynamics*

Ab initio calculations of mechanical properties of reduced activation steels

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Abstract

Reduced activation ferritic/martensitic steels (RAFM) based on the Fe-Cr binary are structural materials with potential application in Generation IV fission and fusion reactors. To gain knowledge about the mechanical properties of these materials, we examine the main composition of three RAFM steels, CLAM/CLF-1, F82H, and EUROFER97, based on the quinery FeCrWVMn solid solution in bcc phase. Using first-principles density-functional theory, our starting point is an assessment of the lattice parameter, single-crystal elastic constants, and polycrystalline moduli of bcc ferromagnetic α-Fe and $Fe_{91}Cr_9$, which Cr content is close to that of the considered RAFM steels. We present a detailed analysis of the calculated alloying effects of W, V, and Mn on the mechanical properties of $Fe_{91}Cr_9$, as well as that arising from small variations in the Cr amount. As part of the analysis, we investigate ternary $Fe_{91-c}Cr_9M_c$ solid solutions, M=W, V, or Mn, in a larger compositional range c than typical for the RAFM compositions and decompose the total alloying effect of a solute into electronic and volumetric contributions. A linear superposition of the alloying effect of a solute on the properties of $Fe_{91}Cr_9$ is found to approximate those of the quinery RAFM steel closely. The effect of the alloying elements on the intrinsic ductility is evaluated in the framework of Rice's phenomenological theory on the basis of computed surface and unstable stacking fault energies and compared to empirical relationships employing elastic parameters, and close agreement between both approaches is found.

Keywords: *reduced activation ferritic/martensitic steels; elastic properties; ductility*

Structural transformations in two-dimensional transition-metal dichalcogenide MoS_2 under electron beam: insights from first-principles calculations

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Abstract

Recently a phase transition from the hexagonal 1H to trigonal distorted 1T'-phase in two-dimensional (2D) MoS_2 has been induced by electron irradiation [1]. Using density functional theory calculations, we study the energetics of these stable and metastable phases when electric charge, mechanical strain and vacancies are present. Based on the results of our calculations, we propose an explanation for this phenomenon which is likely promoted by charge redistribution in the monolayer combined with vacancy formation due to electron beam and associated mechanical strain in the sample. Considering variations of the total energy difference between both phases the described mechanism can be extended to other transition-metal dichalcogenides.

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Keywords: *phase transition, electron irradiation, first principle calculations, charge redistribution*

Improving DFT for Transition Metal Alloys: The V/DM-17 Test Set

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Abstract

The role of Density Functional Theory[1] (DFT) in solid-state physics is undergoing a fundamental shift from a descriptive to predictive technique, with undertakings like the Materials Project[2] and NoMaD[3] leading the charge. These high-throughput calculations databases leverage hundreds of thousands of simulations to rapidly explore a parameter space, e.g., to predict new chemistries for battery materials, superalloys, or photovoltaics. However, unlike the field of computational chemistry, only limited development and application of test sets has occurred in solid-state physics when evaluating new (or existing) functionals. This lack of validation is especially troubling in the field of transition metal alloys, where many of the underlying approximations and assumptions made in popular functionals (e.g., GGA-PBE) break down. The natural disconnect of length-scales and temperatures between simulation and experiment results in difficult questions when the two disagree[4]. In response, we are developing the V-DM/17 test set, designed to evaluate the performance implementations of DFT for periodic transition metal solids. Our test set evaluates 26 elements and 80 alloys across three physical observables: lattice constants, elastic coefficients, and formation enthalpies. We stress the fundamental importance of valuing formation enthalpies over lattice constants, as the only density functional we know is the energy functional, whereas equilibrium volumes and forces result from variational minimizations of these properties with respect to the energy. By application of the V/DM-17 test set, we aim to better characterize the performance of existing functionals on transition metals, and to offer a new tool to rigorously evaluate the performance of new functionals in the future.

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Keywords: *Transition Metals, Validation and Verification, High-Throughput, Test Set*

Effects of the Hubbard U on density functional-based predictions of $BiFeO_3$ properties

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Abstract

Bismuth ferrite (BFO) has been at the heart of the renaissance in multiferroic materials in recent years [1]. As one of only a handful of materials to combine magnetism and ferroelectricity in a single phase at room temperature, BFO is widely studied for both its technological promise, and the novel physics that underlie its rare properties. Examples of applications using BFO range from spintronics and non-volatile memory to photovoltaics [2]. First principles calculations based on density functional theory (DFT) have played an important role in the study of BFO, for example elucidating the mechanism behind the so-called bulk photovoltaic effect [3]. Standard DFT methods, however, fail to accurately capture the localisation of the Fe d orbitals in BFO, contributing to large errors in predicted band gaps. Here we demonstrate the importance of going beyond standard DFT in the context of BFO, via a systematic investigation of the DFT+U method. In addition, we identify an important limit to this approach, finding that a U value chosen to match the experimental band gap would result in the inversion of the t2g/eg ordering of the Fe d bands expected from crystal field theory. More generally, we find a strong dependence of the band character and curvature on the value of U employed, leading to widely varying predictions of the charge carrier effective masses in BFO.

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Keywords: *DFT+U, bismuth ferrite, multiferroics, effective mass*

Generalized stacking fault energy of C-alloyed γ-Fe: A study at paramagnetic state

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Abstract

We perform a first-principles calculation based on the exact muffin-tin orbitals (EMTO) method to investigate the generalized stacking fault energy (GSFE) of paramagnetic γ-Fe and Fe-C systems. The accuracy of the EMTO method is assessed using the case of nonmagnetic Fe for which additional full-potential calculations are carried out. The presence of spin polarization in the paramagnetic state lowers the energy barriers around the unstable planar faults but enlarges the energy of the intrinsic stacking fault (ISF). On the other hand, carbon is found to enhance the whole GSFE curve. The effect of C on the unstable staking fault (USF), ISF and unstable twinning fault (UTW) energies at the room-temperature volume is approximately 84, 106 and 148 mJ/m^2 per weight percent of C, respectively. Considering the correlation between various plastic deformation modes and the GSFE, we conclude that C addition can significantly alter the mechanical response of γ-Fe.

Keywords: *C-alloyed γ-Fe, GSFE, Paramagnetism, First-principles theory.*

Electrochemical dehydrogenation of glycerol and metanol on Au(111) with DFT

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Abstract

Glycerol, a byproduct from biodiesel production, is an abundant source of building blocks for more high-value chemicals. We investigate, with density functional theory, electrocatalytic dehydrogenation of glycerol to form H_2 and CO for e.g. hydrocarbon synthesis or fuel applications. As a smaller and related alcohol, methanol can be seen as a less complex model of glycerol, which is why its dehydrogenation was also studied.

Density functional calculations were performed using VASP, with optB86b-vdW as exchange-correlation functional. The functional was selected on basis of experimental agreement of key properties of the system in a previous study[1]. The Au(111) surface was modeled as a 4-layer $p(3 \times 3)$ supercell, separated by 20 of vacuum. The electrochemical modeling of potential dependence described by Nørskov et al.[2] was used. It was found that the dehydrogenation of methanol starts with the extraction of a C-bonded H atom, with an energy of 0.66 eV is the potential determining step. It may be noted that when formaldehyde is formed, it is energetically favorable to desorb.

For glycerol dehydrogenation, the potential determining step is found at a later stage. The potential determining step of the most favorable route is the formation of CHO-CO-CHO, which requires 0.5 V, while the second most favorable route requires 0.62 V. All of the intermediates in these routes bind to the surface, but for a few of them, the binding energy close to zero.

Cyclic voltammetry experiments of glycerol in 0.1 M $HClO_4$ on a gold electrode, with graphite as counter electrode and Ag/AgCl as reference electrode, were carried out for validation. The measurements indicate a small, but detectable, oxidation current in agreement with the theoretical data.

The results give insight to the reaction mechanism of glycerol and methanol dehydrogenation on gold. As outlook, the method allows screening for metals or alloys with lower onset potential and possibly higher activity.

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Keywords: *electrochemistry, glycerol, methanol, gold*

A DFT Study on the Reaction between Thiourea and $^{\bullet}$OH

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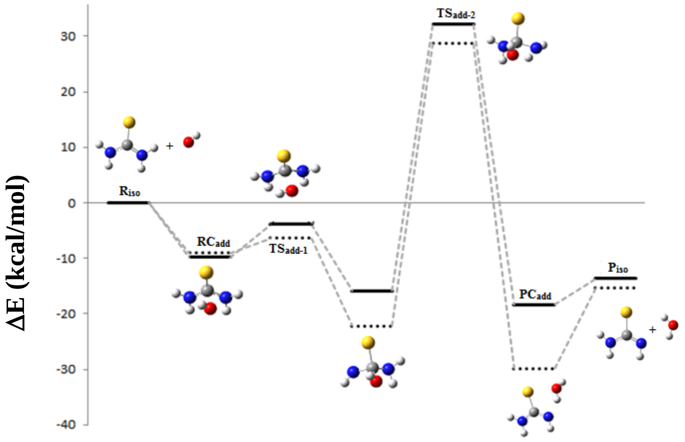
Thiourea (TU) is known to possess various biological and electrochemical properties [1–3]. There have been extensive experimental investigations on the reactions of TUs with various radical species [4 and ref. therein] in relation to their biological and electrochemical reactions; however, few theoretical investigations have been reported [5]. The objectives of this study were to determine the geometric, energetic and electronic properties related to the species in the TU + $^{\bullet}$OH reaction from a theoretical perspective. The study selected the $^{\bullet}$OH because TU is known as a specific scavenger of $^{\bullet}$OH [6]. The DFT/ωB97X–D, DFT/BHHLYP and DFT/M06–2X approaches were utilised for the investigation in conjunction with the 6-311++G(3df,2p) basis set. The investigation was carried out in *vacuum* and aqueous media, in order to simulate the conditions in biological systems. Furthermore, the geometric and electronic properties of the species involved were assessed using the AIM analysis scheme. Analysis of the geometries of the transition state in the direct H–atom abstraction mechanism and in the second step for the elimination of the water molecule in the $^{\bullet}$OH addition mechanism suggests that N–H bond breaking and O–H bond formation occur simultaneously. The results of the study indicate that the barrier of the reaction is media dependent; it is higher in aqueous solution than *in vacuo*, indicating that the reaction is faster *in vacuo* than in aqueous medium. The direct H–atom abstraction mechanism is kinetically favoured with respect to $^{\bullet}$OH addition mechanism in both media, suggesting that the TU + $^{\bullet}$OH reaction most likely proceeds through direct H–atom abstraction mechanism. The rate constant of the value ~7.50 x 10^9 dm^3.mol^{-1}.s^{-1} obtained in water solution is in good agreement with the experimentally determined value of 8.5 x 10^9 dm^3.mol^{-1}.s^{-1} [4]. The spin density distribution on the thiyl radical is delocalised through the S-C-N region for the results.



Energy profile for the $^{\bullet}$OH addition reaction mechanism for the “TU + $^{\bullet}$OH” reaction

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Keywords: Radical scavenging, Hydrogen transfer mechanism, Spin density, Density functional theory (DFT)

Importance of Madelung potential for magnetism of alloys: FePt studied via CPA and via supercells

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Abstract

When dealing with substitutional alloys, it is necessary to simulate the random occupation of sites. One can use supercells to include as many different local configurations as possible. Or one can use a mean field approach to simulate the disorder by a suitably chosen auxiliary effective medium. The mean field approach such as the single site coherent potential approximation (CPA) is computationally convenient. However, the long-range Madelung contribution, which is non-zero even for completely random alloys, cannot be included within the standard CPA.

To assess the effect of the Madelung potential on magnetism of alloys we performed a set of ab-initio calculations for disordered FePt, employing both the CPA and the supercell approach. The fluctuations of the local environment were thus either neglected (CPA) or included (supercells). The supercells were constructed within the concept of special quasirandom structures (SQS) containing $N = 4$, 8, 16, and 32 atoms per unit cell. We used two computational methods, namely, the FLAPW method as implemented in the WIEN2K code and the fully relativistic full-potential multiple scattering KKR-Green function method as implemented in the SPRKKR code.

Even for the largest SQS we explored, there remains a small but distinct difference between the magnetic moments obtained when using the supercells and when using the CPA. By analyzing the dependence of local charges and magnetic moments on the chemical composition of the nearest neighborhood of Fe and Pt atoms, we are able to trace this difference to the neglect of the Madelung potential in the standard CPA.

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Keywords: *disorder, magnetism, local environment effects, Madelung potential*

Performance of SIE and Dispersion in DFT Calculations Involving Ionic Liquids

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Abstract

Modern computer simulations for the design of potential green solvents of the future, involving the room temperature ionic liquids (ILs), heavily rely on density functional theory (DFT) [1,2]. Methods based on DFT are known to be affected by some intrinsic errors as dispersion; basis set superposition error (BSSE) and self-interaction error (SIE). In particular, dispersion terms modify the interaction energy between ions and the optimized geometries and the SIE strongly affects the charge transfer between cation and anion. Those charges are known to have a strong effect on the modelled structural and dynamic properties of ILs.

As it was previously pointed out [3], the errors related to DFT (as BSSE, dispersion or SIE) strongly affect calculations involving ionic liquids. Here, we have estimated the influence of the SIE and the dispersion in calculations of a set of ILs. The set is formed by the combination of [EMIm] and [MMIm] cations with four anions ($AlCl_4$, Cl, $N(CN)_2$ and SCN). The suitability of a set of DFT functionals for geometry optimization and description of charge density have been analyzed by comparing with calculations at MP2 and CCSD(T) levels [4].

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Keywords: *Ionic liquids, Self-interaction error, Dispersion energy*

Investigating metal dimer sites in ZSM-5 zeolites with electronic structure calculations and micro-kinetic modelling

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Abstract

Partial oxidation of methane to methanol is a difficult but desirable reaction. It has been realized in metal-exchanged zeolites with a high selectivity (>90 %) [1], where especcially copper-exchanged ZSM-5 has shown promising results, but it has also been realized for zeolites ion-exchanged with nickel, cobalt, and iron [4, 5, 6]. The active site in Cu-ZSM-5 is still under debate, but one promising candidate is a $[\text{Cu-O-Cu}]^{2+}$ motif identified by UV-vis assignment and electronic structure calculations [2, 3]. A remaining question is whether this motif is generic and also relevant for other metals, especially the ones that are known experimentally. Here [7] we use a cluster model and DFT with the DMol3 software, and micro-kinetic modelling with a straightforward reaction mechanism, to investigate whether the $[\text{Cu-O-Cu}]^{2+}$ motif is a relevant candidate for active site also when Cu is exchanged with Ni, Co, Fe, Ag, or Au. The results show that activation of the Ag and Au motif is endothermic and therefore unlikely, and trends in activity, both transient and steady-state, clearly show that for Ni, Co, or Fe, close-to-infinate reaction times or above-zeolite-disintegration reaction temperatures are needed for measurable methane conversion. This indicates that the same dimer motif can be excluded as an active site candidate for Ni, Co, Fe, Ag, and Au.

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Keywords: *methane-to-methanol, ZSM-5, micro-kinetic modelling.*

Shannon entropy and correlation energy for electrons in atoms

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Abstract

In this work, we compute the Shannon entropy defined in terms of the one particle electron density ρ for some neutral and charged atomic systems. As shown recently by Nagy [1], the knowledge of Shannon entropy density, namely $-\rho \log \rho$, is sufficient to know any physical observable for a Coulomb system. This definition of quantum entropy is here used to measure the entanglement of electrons due to Coulomb correlation. In particular, we compare different calculations performed with highly correlated methods (quantum Monte Carlo) with the Hartree-Fock independent particle model. All systems are considered in the ground state so we use the basic result of density functional theory that the electronic density brings all information about the N-particle wavefunction. We limit our test examples to a set of atoms in a spherically symmetric ground state including also fractional nuclear charges. We analyze the behaviour of Shannon entropy up to the limit of extremely weak binding where the ionization potential goes to zero.

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Keywords: *Electron density, Shannon entropy, Correlation.*

Quantifying the Accuracy of Molecular Excited State Emission Calculated with TDDFT

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Abstract

Molecular structure and electronic structure are, of course, intrinsically linked. This connection is particularly important, and often particularly opaque, when considering the excited states of molecules. The effect of structural change on electronic structure (and on excited states in particular) is one of the more readily observable molecular properties, with the colour of a molecule directly correlating with its excited state properties. In our research, we are particularly interested in the fundamental origin of the colour characteristics of molecules, both in absorption and emission. We apply electronic structure theory to enable us to understand the origin of the colour of a particular molecule.

The natural choice of electronic structure method for the investigation of excitation energies and more general excited state properties of molecules is time-dependent density-functional theory (TDDFT), which often provides a suitable balance between computational cost and accuracy. The success (or otherwise) of TDDFT in describing the *absorption* of molecules is well-established for many common exchange–correlation functionals, with notable successes for valence excitations and broadly publicised difficulties in describing charge-transfer and Rydberg states, or states associated with a wavefunction instability.

The *emission* energies and other emission properties of molecules (i.e., those calculated at the geometry minimum of an excited state potential energy surface) using TDDFT are less widely studied, and certainly are less widely benchmarked. Our research seeks to redress this, by considering in much greater detail the excited state structures of molecules and the connection to observed emission energies, and any associated issues in the accuracy of the description of the excited states as we move away from the ground state geometry minimum.

As part of our investigation, we calculate the geometry minima of a range of excited states (e.g., S_1, S_2,. . . , and T_1, T_2,. . .), across a broad range of organic molecules, and investigate the predicted emission energies at these structures. The influence of exchange–correlation functional, basis set, and treatment of the excitation process are all considered. Results are compared to resolution of the identity second order approximate coupled cluster (RI-CC2) data, and other wavefunction method results where possible.

Results suggest that the problems observed for absorption can be exacerbated as we move away from the ground state geometry minimum, and that consequently there can be significant problems in our ability to describe emission processes.

Keywords: *Excited states, TDDFT, Emission energies, Benchmarking.*

The geometrical and optical investigations of PEDOT and its selenium and tellurium derivatives from the density functional theory perspective

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Abstract

Poly(3,4-ethylenedioxythiophene), or PEDOT, is one of the most attractive conductive polymer used for flexible electronics. We present density functional theory based calculations of EDOT oligomers and isoelectronic selenium and tellurium derivatives (EDOS and EDOTe) to address the geometrical and optical properties of these systems. Both neutral oligomers and radical cations of the PEDOT, PEDOS and PEDOTe were studied for oligomer length effect, the twisting between monomer units, the polaron formation, and the optical properties. We used four different functionals (B3LYP, CAM-B3LYP, LC-ωPBE, and ωB97XD) to present the complete picture of the studied oligomers. Our computations indicate ωB97XD functional as the most preferable for the further studies of the systems. The poster presents bond length alternation, twisting between dihedral angles, Mulliken spin densities, and molecular orbitals analyses together with the absorption spectra of the studied oligomers.

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Keywords: *PEDOT, poly(3,4-ethylenedioxythiophene), selenium, tellurium, absorption spectra, polaron*

A Reliability Parameter for FDET Calculations

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Abstract

In the presence of an environment, excitation energies, properties and sometimes even reactivity of the target molecule may change drastically. Thus, including environmental effects into quantum chemical calculations either by implicit or explicit models is necessary for an adequate description of these systems. Frozen-Density Embedding Theory (FDET)[1, 2] provides a formal framework in which the whole system is described by means of two independent quantities: the embedded wavefunction (interacting or not) and the density associated with the environment. The FDET approach can conveniently be combined with pertubative wavefunction methods, e.g. the Algebraic Diagrammatic Construction (ADC) scheme for the polarization propagator[3] giving rise to FDE-ADC[4]. The current implementation of FDE-ADC uses the Linearized FDET formalism[5], which in comparison to FDET, is significantly less expensive computationally and more importantly leads to self-consistency between the energy and embedding potential preserving simultaneously the orthogonality of the embedded wave functions for each electronic state. We present a system-independent reliability parameter for FDE-ADC calculations which is computed at the beginning of each embedding calculation.

30 molecular model systems were studied using supermolecular FDE-ADC(2) and compared against their ADC(2) reference of the full system. The molecular test systems were chosen to investigate molecule - environment interactions of varying strength from dispersion interaction up to multiple hydrogen bonds. The mean absolute error of the excitation energies for each system shows linear correlation with the reliability parameter calculated with the densities $\rho_A^{ref}(\mathbf{r})$ and $\rho_B(\mathbf{r})$ used to construct the embedding potential. The initial results show that the reliability parameter is a promising tool to estimate the accuary of the embedding calculation from the start and to identify problematic results.

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Keywords: *Frozen-Density Embedding, ADC(2), WF-in-DFT, benchmark*

Spatial and temporal non-locality in approximate exchange-correlation kernels for TDDFT

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Abstract

In recent years linear response time-dependent density-functional theory (TDDFT) [1, 2] has become increasingly popular for the calculations of excited state properties of both finite and extended systems, since it combines a good accuracy with a low computational cost. The quality of the results obtained within this approach crucially depends on the approximations employed for the so-called exchange-correlation kernel (f_{xc}). The most widely used is the adiabatic LDA (ALDA), where the resulting f_{xc} is local in space and in time. While the ALDA has been often very successful, it has also exhibited serious shortcomings, notably in describing long-range charge transfer excitations, and bond breaking in molecules. When tackling these problems, spatial and temporal non-locality are two desirable properties of an approximate f_{xc}, as it was shown in Ref. [3].

In this work we give an overview of some recently derived kernels which are either non-local in space, or non-local in time (that is frequency dependent). We begin by presenting an adiabatic kernel, named ASCE [4], which has been derived from the strictly-correlated electrons functional [5], and we discuss its formal properties, from the compliance to some constraints of exact many-body theories, to its non-local features in space, which are promising to describe molecular dissociation.
We further show [6], for a model system of two electrons on a quantum ring in a regime of strong electron-electron interaction, that the ASCE kernel and its correction, so-called AZPE, coincide with the leading terms of the expansion for the exact kernel of this system, hinting at the fact that for strongly correlated systems a spatially non-local, but adiabatic f_{xc} can still perform well. Finally we address the issue of the frequency dependence, showing preliminary results for an f_{xc} derived from many-body perturbation theory, beyond the well-known exact exchange kernel. This approximation, when employed within the adiabatic-connection fluctuation-dissipation theorem (ACFDT) framework, should yield an improved description of bond-breaking in two electrons systems.

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Keywords: *TDDFT, exchange-correlation kernel, strictly-correlated electrons, molecular dissociation.*

Presentation in memory of Annick Leray-Goursot : 1945 – 2017

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Annick Leray-Goursot was born in Froges/France, June 1945 and grew up in the Nice area (French Riviera). She married Paul Goursot, a polymer chemist, and had two children, Sandrine and Joël. She studied chemistry in Marseilles/France, ending with a PhD/doctorat es sciences physiques in 1972, under the supervision of Professor Bodot. She entered CNRS in 1967 as attachée de recherches, and became successively 'chargée de recherches' (1975), and 'director of researches' in 1994. She made a post-doc in Montreal/Canada working with Professor Fliszar. Her scientific achievement will be presented during DFT2017. She passed away end of march 2017.

Annick's interests were always turned to theory. At first, she investigated organic chemistry phenomena, and, later, coordination chemistry, and solid-state chemistry and catalysis. After her post-doctoral stay in Montreal, she worked for 10 years in the Ecole Nationale Supérieure de Chimie de Mulhouse, in Professors Faure and Fouassier Laboratory, and then moved to the Ecole Nationale Supérieure de Chimie de Montpellier, in Professor Geneste's Laboratory.

During her period in Mulhouse, she started collaborations with Claude Daul, Jacques Weber and Henry Chermette, applying the multiple scattering MS-Xalpha (also called Xalpha scattered wave) method introduced by Slater and Johnson in the 1970s, to study the electronic structure of metallic complexes, and their physical and chemical properties. Her dynamism did bring the writing of highly cited papers (e.g. Refs. [1]; [2]; [3]; [4]; [5] ; [6]). She has been at the origin of the biennial meeting of X-alpha practitioners, started in 1984 in San Miniato, Italy, which became subsequently the well-known International Conferences on the Applications of Density Functional Theory in Chemistry and Physics. The third edition was successfully organised by Annick and Henry Chermette in Arles (France) in 1988. She also organised the 6th edition in Paris, 1995, and participated actively in the 11th one, in Geneva (2005, Jacques Weber, chairman).

When she moved to Montpellier, her interests turned to catalytic properties studied by DFT calculations—zeolites and metallic clusters—and development of DFT-LCAO codes. She was among the first theoreticians to calculate spectra (EPR, IR, NMR, etc.) of cations and guest molecules in various sites of zeolite cages (e.g. Refs. [7]; [8]; [9]; [10]; [11]; [12] ; [13]). She was several times invited professor at the Universities of Fribourg and Geneva in the late 1980s and 1990s.

She participated efficiently in the promotion of DFT calculations with local density approximation (LDA), and later gradient-corrected approximations (GGA) (at that time incorrectly called non-local functionals) for the exchange and correlation functionals. She also collaborated actively in the development of the deMon code, leading or participating in initiatives to implement molecular symmetry into the code, to build a module for atomic multiplets, and to incorporate Born–Oppenheimer molecular dynamics in association with the Tight-Binding approach as well as the usual DFT methods. Since the early days of deMon, Annick has supplied a steady stream of real experimental challenges in various areas of catalysis and, with her great ability to work with others in the deMon 'family', she was instrumental so as to ensure that deMon is kept up to date and relevant. Undoubtedly, the contribution of Annick Goursot to DFT itself and to its wide dissemination within the community of chemists is significant and Annick deserves both our high consideration and deep gratitude.

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Presentation in memory of Walter Kohn: 1923 – 2016

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Walter Kohn is, of course, extremely important for our field because he brought it into existence. He was born in Vienna on March 9, 1923 and he passed away on April 19, 2016 in Santa Barbara, California. In an obituary for him some parts of his fascinating life were summarized [1]. He was born in a Jewish family and thus was sent to Great Britain with one of the last children's rescue mission. Later he was sent to Canada in 1940. He started his scientific career in Toronto finishing with a master degree there. Then he moved to Harvard (with Julian Schwinger as adviser) where he received his PhD in theoretical physics in 1948. He was active at many places, such as in Pennsylvania, Michigan, Washington (Seattle), Paris, Imperial College (London) and the ETH (Zürich). In 1960 he became professor at the University of California, San Diego. In 1979 Walter Kohn became the founding director of the Institute for Theoretical Physics at the University of California, Santa Barbara, where he was director till 1984.

Let us focus on his scientific contributions for our community. We need a quantum mechanical treatment to describe the electronic structure of a system and solve a many-particle Schrödinger equation, a task that is intractable for realistic large systems. An alternative route to the direct solution of Schrödinger's equation is shifting the focus from the wave-function based theory to the fundamental observable of the problem, namely the electron density. His early work with Luttinger led him 1964 to establish the famous Hohenberg-Kohn theorem [2]. A year later he and Lu Sham proposed a scheme to make DFT calculations feasible, now called Kohn-Sham (KS) equations [2]. These two papers were the main reason for the Nobel Prize in Chemistry, which he (together with John Pople) was awarded in 1998 for his pioneering scientific contributions. He has received many awards (as summarized in [1]).

Walter Kohn was often the keynote speaker at the many DFT biennial meetings, which took place in Paris (1995), Vienna (1997), Rome (1999), Madrid (2001), Brussels (2003), Geneva (2005), Amsterdam (2007), Lyon (2009), Athens (2011), Durham (2013), and Debrecen (2015). The last one he attended was in Athens, where he - illustrating his interdisciplinary nature - gave a talk on "Nearsightedness of electronic matter".

Undoubtedly, the contribution of Walter Kohn to DFT itself and to its wide dissemination within the community of researchers in chemistry, physics and material science is enormous and thus Walter deserves both our high appreciation and deep gratitude.

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Exact Constraints for Creating Density Functionals, and Thoughts of Robert G. Parr

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Abstract

Several of the most successful approximate density functionals have been created and are being improved by implementing exact constraints that originate from the definition of either the original Hohenberg-Kohn functional or its constrained-search generalization.

These constraints include those that arise from consideration of both homogeneous densities and inhomogeneous finite densities whose coordinates are uniformly or non-uniformly scaled, and from use of the adiabatic connection, fractional electron number, and the ionization energy theorem.

First, the philosophy behind the derivations of the constraints shall be presented. Then ideas for deriving new constraints shall be given.

The lecture shall begin and end with thoughts and memories of Walter Kohn and Robert Parr.

The Four-Way Correspondence of Density-Functional Theory

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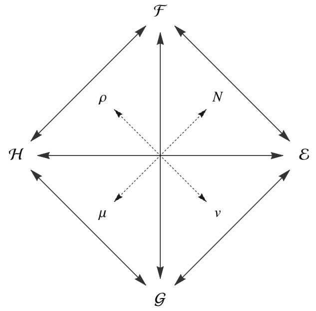
Abstract

Density-functional theory (DFT) is conveniently formulated in the language of convex analysis. From the observation that the ground-state energy $E(v)$ is concave and continuous in the external potential v, Lieb [1] observed that it can be represented in terms of a unique universal density functional $F(\rho)$, convex and lower semi-continuous in the density ρ:

$$E(v) = \inf_{\rho} \left(F(\rho) + (v|\rho) \right), \quad F(\rho) = \sup_{v} \left(E(v) - (v|\rho) \right).$$

The energy E and density functional F are said to be conjugate functions, depending on the conjugate variables v and ρ, respectively. The density functional defined in this manner is equivalent to Levy's constrained-search functional when formulated in terms of ensembles [2]. Here, we generalize Lieb's theory to situations where the energy depends on more than one variable, covering the following special cases: (1) *grand-canonical DFT*, where the energy $\mathcal{G}(v, \mu)$ depends also on the chemical potential μ, conjugate to the particle number N; (2) *current-DFT*, where the energy $\mathcal{E}(v, \mathbf{A})$ depends also on the vector potential $\mathbf{A}$, conjugate to the paramagnetic current density $\mathbf{j}_{\mathrm{p}}$, and (3) *adiabatic-connection DFT*, where the energy $\mathfrak{E}(v, \lambda)$ depends also on the two-electron interaction strength λ, conjugate to the two-electron expectation value ω. We show how such systems can be treated by a generalization of conjugation to bivariate functions, within the framework of the *four-way correspondence* of convex analysis [3]. Whereas standard DFT sets up a correspondence between two functions E and F, the four-way correspondence sets up a correspondence between four functions: the concave bivariate ground-state energy, the convex bivariate universal density functional, and two semi-universal saddle functions [4]. The four-way correspondence is illustrated below for grand-canonical DFT, where the system is described in terms of the conjugate variables v (external potential) and ρ (electron density) and the conjugate variable μ (chemical potential) and N (particle number).



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Keywords: *Density-functional theory, Legendre–Fenchel transform, convex conjugation, four-way correspondence, grand-canonical ensembles, current density functional theory, adiabatic connection.*

Direct extraction of excitation energies from ensemble density-functional theory

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Abstract

A very specific ensemble of ground and excited states is shown to yield an exact formula for any excitation energy as a simple correction to the energy difference between orbitals of the KohnSham ground state. This alternative scheme avoids either the need to calculate many unoccupied levels as in time-dependent density functional theory (TDDFT) or the need for many self-consistent ensemble calculations. The symmetry-eigenstate Hartree-exchange (SEHX) approximation yields results comparable to standard TDDFT for atoms. With this formalism, SEHX yields approximate double-excitations, which are missed by adiabatic TDDFT (to appear, Phys Rev Lett.)

See http://dft.ps.uci.edu

Keywords: *ensemble, DFT, excitations, double-excitations, TDDFT, atoms, Hooke's atom*

The Exact Density Functional

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Abstract

In 1964 Hohenberg and Kohn [1] developed density functional theory (DFT) by proving the existence of the exact functional, $F[\rho]$. However, recent development of improved approximations to this functional has not been able to provide chemical accuracy in all cases, especially in strongly correlated systems. It is now time to explore all aspects of the exact functional.

By explicitly carrying out the Levy constrained search [2] in simple model systems such as two electrons in one-dimension, we will illustrate many features of the exact functional. $F[\rho]$ not only exists, it is something that can be calculated, visualized and in some cases even 3d-printed [3]. The same technology that we develop for the constrained search optimisation of the wavefunction can also be applied to a mixture of states in ensemble DFT [4]. Overall, we hope that the exact density functional can guide the development of the next generation of improved approximations.

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Keywords: *Fundamental Theory, Constrained Search, Adiabatic Connection, Ensemble DFT.*

New Approaches to Memory-Dependent Functionals in Time-Dependent Density Functional Theory

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Abstract

Time-Dependent Density Functional Theory (TDDFT) [1,2] is increasingly being used in the non-perturbative regime, for dynamics in strong external fields, being driven out of its ground-state by nuclear motion, or when the system is prepared in a state other than the ground-state, for examples. It is this regime where, arguably, TDDFT is particularly useful, given the dearth of alternative methods. However, recent work on model systems have revealed large non-adiabatic features in the exact time-dependent exchange-correlation functional, that are missing in the commonly used approximations. Beginning with an exact expression for the time-dependent exchange-correlation potential in terms of kinetic and interaction components [3,4], we derive and test orbital-dependent functionals [5] that include both history-dependence and initial-state dependence to some extent.

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Keywords: *TDDFT, non-adiabatic, non-perturbative dynamics*

Triplet Emission Processes in Platinum Complexes

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Abstract

The emission properties of molecules are of particular current interest, due to the plethora of applications of luminescent molecules in creating efficient light-producing materials. As we seek to develop materials that emit more vibrant light of tuned colour for increasingly specific applications, the demands that we place on new materials are constantly increasing. Common examples include the development of new OLEDs for next-generation screen technology, or bioimaging devices able to probe the molecular environment of cells.

Of particular interest for such applications are triplet emitters, due to the typically high intensity emission processes that occur. Triplet excited states are made accessible via spin-orbit coupling from initial excitation to singlet excited states; therefore, many of the most promising of such molecules are based around heavy, 3rd row transition metal elements such as platinum.

The experimental design of new such luminescent molecules is often a time-consuming and expensive process, requiring significant iteration due to the complex relationship between the electronic structure of a molecule, and its molecular structure. There is significant scope for electronic structure theory to impact on our understanding of these emission processes and their relation to molecular structure, enabling the design of increasingly tuned molecules via a furthered understanding of the underlying photophysical processes that are occurring.

Application of electronic structure theory to such problems relies on our ability to employ an efficient electronic structure method, and obtain results of consistent accuracy across a range of molecules, and a range of different excited states within them. Fully modelling emission requires us to accurately compute the structures and relative energies of the low-lying excited state surface minima, together with how 'allowed' the emission process is, and the energy difference between the ground and excited state all at the different excited state structures.

A natural starting point is to use time-dependent DFT, with a Coulomb-attenuated exchange–correlation functional known to perform well in the description of absorption processes. For representative platinum complexes, the excited state structures of low-lying triplet excited states are calculated, and their energies and properties considered. Excited state structures and properties are computed using the SCF, TDDFT and TDDFT within the Tamm–Dancoff approximation approaches to treating the excited states. Results are compared with resolution of the identity approximate second order coupled cluster (RI-CC2), and coupled cluster with single and double excitations (CCSD) response calculations at the DFT geometries. Spin-orbit coupling is considered at various levels within the calculations to determine the impact on energies and intensities.

The experimentally observed emission properties are contrasted with the results from our electronic structure calculations, and the complexities in understanding the emission processes that are occurring are discussed.

The significant value of TDDFT within the Tamm–Dancoff approximation is highlighted, demonstrating the usefulness of electronic structure theory in addressing emission processes. Deficiencies of the various approaches are also discussed, highlighting aspects of functional design that need improving, and the care that needs taking in connecting theoretical and experimental results.

Keywords: *TDDFT, Luminescence, Triplet Emission, Excited States, Transition Metal Complexes*

Single and Double Hybridization Schemes in Density-Functional Theory

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Abstract

At the beginning of the nineties, the introduction of hybrid density functionals [1] through the mixing of exact-like exchange (EXX) with density-functional approximations (DFA) has opened new perspectives regarding the modeling of chemical applications. With respect to semilocal approximations, the single hybridization scheme provides a robust, fast and cross approach to estimate various ground- and excited-state properties of molecular systems, even if some problematic cases belonging to thermochemical or weak-interaction applications persist [2]. A reliable alternative to model such a difficult case consists in transforming the single into the double hybridization scheme by introducing a nonlocal correlation component via the second-order perturbation theory (PT2) [3]. The resulting double-hybrid class of approximation is nowadays the state-of-the-art to reach the chemical accuracy for molecular systems. We present here our last advances in term of double-hybrid density functionals with a special emphasis on the quadratic-integrand double hybrid (QIDH) parameter-free schemes (PBE-QIDH [4] and SOS1-PBE-QIDH [5]) developed under the framework of the adiabatic connection model. Their performance improvement with respect to their parent semilocal (PBE) and single hybridized (PBE0) density functionals will be illustrated through several challenging chemical applications dealing with covalent and weak interactions.

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Keywords: *double-hybrid density functionals, quadratic-integrand double hybrid model, covalent interactions, weak interactions*

Benchmark and Applications Studies of Double-Hybrid Density Functionals Based on the Adiabatic Connection Model

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Abstract

We present some advances and investigations related with a set of modern double-hybrid density functionals, mostly PBE-QIDH and SOS1-PBE-QIDH parameter-free expressions developed under the framework of the adiabatic connection model, such as: (i) their application to structural parameters of medium-sized organic molecules [1] or to challenging energy reaction datasets [2]; (ii) the merging with a pair of dispersion corrections, namely the pairwise additive D3(BJ) and the non-local correlation functional VV10, leading to the corresponding dispersion-corrected models [3]; (iii) the orbital-dependence of the models, feeding all their energy terms with different sets of orbitals obtained previously from self-consistent DFT calculations using several exchange-correlation functionals (e.g. PBE or PBE0) [4], or direclty optimizing the orbitals for the perturbative-like term [5]. Overall, these models behave robustly in all cases, overperforming the accuracy obtained by corresponding hybrid models at a moderately higher computational cost.

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Keywords: *Double-hybrid density functionals, weak interactions, orbital-dependence.*

Recent Progress on Local Hybrid Functionals

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Abstract

Local hybrid functionals with position-dependent exact-exchange admixture [1], or more generally hyper-GGA-type functionals based on the exact-exchange energy density as crucial ingredient, hold great promise to solve many of the shortcomings of the currently most widely used global hybrid functionals. The fact that local hybrids so far have not yet replaced/superseded global (or also range-separated) hybrids has been due to two major obstacles: a) the presence of a local mixing of different exchange-energy densities generates new two-electron integrals that cannot be solved analytically [2]. Until recently, this has rendered local hybrid calculations significantly more computationally demanding than with global hybrids. b) The gauge ambiguity of local mixing of exact and semi-local exchange energy densities creates fundamental problems [3]. In my lecture I will show that significant progress has recently been made on both of these fundamental issues: a) using a semi-numerical integration scheme, we have implemented an efficient Kohn-Sham SCF scheme [4] for local hybrids, a fast semi-numerical TDDFT code [5], as well as molecular gradients for local hybrids [6] into the Turbomole program package. In fact, in combination with an RI-J approximation for Coulomb integrals, the new TDDFT implementation is even faster for large systems than the previous analytical implementation, thus offering now the possibility to evaluate the performance of sophisticated hyper-GGA-type functionals for the excitation spectra of large molecules (with large basis sets) at no extra cost beyond standard global hybrids. Initial comparisons [7] show that local hybrids indeed offer the potential to simultaneously describe excellently very different types of excitations (core, singlet and triplet valence, as well as Rydberg). b) We have furthermore recently designed suitable calibration functions to tackle the gauge problem. This improves on weak interactions and dispersion-dominated properties [8] and allows the construction of improved local hybrids with GGA and meta-GGA ingredients. A procedure based on partial integrations has been developed to systematically construct semi-local calibration functions of increasing complexity [9].

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Keywords: *Local hybrid functionals, exchange-energy densities, semi-numerical implementation, TDDFT*

Hybrid Functionals in Auxiliary Density Function Theory

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Abstract

Over the last years auxiliary density functional theory (ADFT) has established itself as a computationally attractive alternative to Kohn-Sham density functional theory methods. Because ADFT is based on auxiliary densities the computationally efficient inclusion of orbital dependent functionals is not straightforward. In this work we describe a new variational density fitting approach that permits the efficient calculation of Fock exchange with three-center electron integrals only [1]. Our approach exploits the short range nature of Fock exchange by using localized molecular orbitals. It also takes advantage of the spherical averaging of the exchange hole as utilized in density functional theory.

Based on the variational fitting of Fock exchange the implementation of global [2] and range-separated [3] hybrid functionals into the ADFT branch of deMon2k [3] is presented. Benchmark calculations show the superior computational performance with respect to conventional four-center integral approaches without loss of accuracy.

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Keywords: *ADFT, Fock Exchange, Hybrid Functionals, Density Fitting, deMon2k*

The budget way to quasiparticle and exciton binding energies

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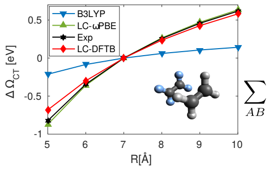
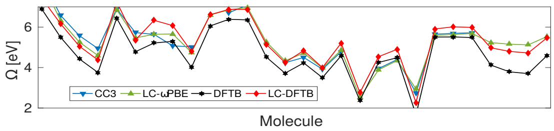
Abstract

In this contribution, we summarize recent advances in the development of the density functional based tight-binding method (DFTB) [1]. We first present a generalization of the method for the use with range-separated exchange correlation functionals (LC-DFTB) [2]. In contrast to the traditional DFTB scheme, the density matrix is used as basic variable in an expansion of the energy functional in generalized Kohn-Sham theory. The theory provides access to hybrid functionals in DFTB as a special case. Implementation issues and numerical aspects of the new scheme are also covered. We present results for quasiparticle gaps in organic molecules and discuss polaron formation in polymers [3]. We also present the recent time-dependent extension of LC-DFTB to treat electronic excited states, which overcomes the notorious problem of local functionals with charge-transfer excitations in very large systems with thousands of atoms [4, 5].



$$K_{ia\sigma,jb\tau} = \sum_{AB}\sum_{ll'}\left(q^{ia\sigma}_{Al}\Gamma^{\sigma\tau}_{Al,Bl'}q^{jb\tau}_{Bl'} - \delta_{\sigma\tau}q^{ij\sigma}_{Al}\gamma^{\mathrm{lr}}_{Al,Bl'}q^{ab\tau}_{Bl'}\right)$$



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Keywords: *DFTB, time-dependent DFT, quasiparticle energies*

Invertibility of the retarded response functions for initial mixed states: application to one-body reduced density matrix functional theory

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Abstract

The treatment of quantum mechanical systems at finite temperatures has become a hot topic. For computational efficiency, it is desirable to be able to use density-functional-like theories. Formal justification of these methods require an investigation to which extend the perturbation to observable mapping is invertible. Examples of particular mappings are the local potential to density, vector potential to current and non-local potential to one-matrix mappings. In the time-dependent linear response regime, this is identical to the characterisation of the kernel of the (linear) retarded response function. Recently, I have generalised the invertibility proof for Laplace transformable time-dependent potentials by Van Leeuwen [1] to general operators at zero temperature [2] and also finite temperatures [3]. In my presentation I will show how the kernel of the retarded response functions can be characterised for arbitrary operators. I will use the density operator and one-matrix operator as examples.

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Keywords: *time-dependent, response function, invertibility, v-representability, finite temperature, one-body reduced density matrix, Laplace transformable potentials.*

Optimized Effective Potential Method based on the Scaled–Opposite–Spin Second–Order Correlation

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The correlated optimized effective potential (OEP) method based on the spin resolved second-order correlation energy (SCS-MP2) is presented. The effect of scaling the same- and opposite- spin components is investigated in detail to determine optimal scaling coefficients for different properties in our new correlated OEP procedure. Special attention is dedicated in particular to the recently proposed scaled-opposite–spin OEP functional OEP2-SOS [1] which is the most advantageous from a computational point of view (*O(N^4)* scaling).

We find that for high accuracy, a careful (but costless), system dependent, selection of the scaling coefficient is required.[2]

The performance of the OEP2–SOS method is validated for benchmark atomic and molecular systems and we have found that all the OEP2-SOS results largely outperform those from second–order Görling–Levy perturbation being comparable with the most accurate OEP correlated approaches previously reported in the literature and can yield high accuracy for many properties like: correlation energies, HOMO-LUMO gaps, correlation potentials, correlated densities, and finally IPs [4], with almost CCSD(T) quality. [1-4]

The OEP2-SOS approach is thus an accurate and efficient DFT method to supplement exact-exchange with an *ab initio* correlation and, importantly, with a small additional computational cost *O(N^4)* [2].

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Keywords: OEP, correlation functional, *ab-initio* DFT

Accuracy of DFT self-consistent electron densities

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Abstract

The theorems at the core of density functional theory (DFT) state that the energy of a many-electron system in its ground state is fully defined by its electron density distribution. This connection is made via the exact functional for the energy, which minimizes at the exact density [1]. For years, DFT development focused on energies, implicitly assuming that functionals producing better energies become better approximations of the exact functional.

We have examined the other side of the coin — the energy-minimizing electron densities for atomic species, as produced by more than a hundred DFT functionals [2]. Self-consistent electron densities produced by these functionals were compared to the CCSD-full ones by means of three local descriptors: electron density (RHO), its gradient norm (GRD) and its Laplacian (LR); aug-cc-pωCV5Z basis was used for all calculations.

We have found that, reflecting theoretical advances, DFT functionals' densities became closer to the CCSD-full ones, until in the early 2000s this trend was reversed by flexible functionals with forms chosen to be suitable for empirical fitting.

Acknowledgements

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Keywords: *Electron density, Benchmark, DFT functionals accuracy, Empirical, Non-empirical*

DFT functional assessment from quasi-exact energies and densities at different correlation regimes

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Abstract

Density functional theory (DFT) is by far the most-employed computational method due to its excellent cost/accuracy ratio. The construction of density functionals approximations (DFA) has turned towards the disproportionate use of empirical parameters fitted to accurate computations or experimental data, gradually leading to very specific DFA that are very accurate for particular problems but lack universality and produce less accurate densities[1]. New theoretical models and calibration tools are needed to aid the design of new functionals.

In this work we use a model system that displays different correlation regimes where dynamic and static correlation are tunable[2, 3, 4]. The model is realistic as far as the electron correlation is concerned and it thus represents a suitable playground for DFA. Quasi-exact energies and densities of a large family of functionals are tested at different correlation regimes, showing that none of the tested functionals if both accurate for strongly and weakly correlated systems. Analytical results at the strong-correlated limit reveal incorrect asymptotic behavior of the correlation and exchange parts of many DFA. These results suggest new means to improve DFA, leading to less specific functionals.

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Keywords: *density functional theory, calibration, model systems, harmonium*

On the Structure Determination of $U_2@C_{79}$: $U_2C@C_{78}$ or $U_2C_3@C_{76}$? Insight from a DFT Study

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Abstract

In this talk the results of an extended first-principle study of the novel endohedral fullerene $U_2@C_{79}$ will be presented. For this systems the only available experimental information is its mass spectrum. In order to determine the structure and spin multiplicity of the ground state of this endohedral fullerene a three-fold problem was tackled. For this purpose the relevant isomers of neutral and anionic isolated fullerene cages, the uranium carbide clusters and the resulting actinide endohedral fullerenes have been studied. The auxiliary density functional theory (ADFT) approach as implemented in the deMon2k code [1] was employed. Results of the obtained ground state structures of the three system types will be presented and discussed, In particular, the origin of the structure changes from the empty fullerene cages to the actinide enedohedral fullerenes will be analyzed. Furthermore, the change of the spin multiplicity of the uranium carbide clusters by its embedding into the fullerene will be discussed.

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Keywords:*ADFT, Endohedral Fullerenes, deMon2k*

Time-dependent density-functional theory for strongly interacting electrons

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Abstract

We consider an analytically solvable model of two interacting electrons that allows for the calculation of the exact exchange-correlation kernel of time-dependent density functional theory. This kernel, as well as the corresponding density response function, is studied in the limit of large repulsive interactions between the electrons and we give analytical results for these quantities as an asymptotic expansion in powers of the square root of the interaction strength. We find that in the strong interaction limit the three leading terms in the expansion of the kernel act instantaneously while memory terms only appear in the next orders. We further derive an alternative expansion for the kernel in the strong interaction limit on the basis of the theory developed in [Phys. Chem. Chem. Phys. **18**, 21092 (2016)] using the formalism of strictly correlated electrons in the adiabatic approximation. We find that the first two leading terms in this series, corresponding to the strictly correlated limit and its zero-point vibration correction, coincide with the two leading terms of the exact expansion. We finally analyze the spatial non-locality of these terms and show when the adiabatic approximation breaks down. The ability to reproduce the exact kernel in the strong interaction limit indicates that the adiabatic strictly correlated electron formalism is useful for studying the density response and excitation properties of other systems with strong electronic interactions.

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Keywords: *Strongly, interacting, electrons*

Modeling the exact time-dependent exchange-correlation potential

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Abstract

Time-Dependent Density Functional Theory (TDDFT) has proven significantly successful in the linear response framework for the calculation of excitation spectra with a relatively good understanding of the approximations and limitations. For dynamics far from equilibrium, such as molecules in strong laser fields or time-resolved photoelectron spectra, one has to rely on real-time TDDFT with approximations that are mostly based on ground-state DFT, with poor knowledge of their reliability. In these non-perturbative regimes, the exact time-dependent exchange-correlation potential exhibits complex features such as peaks and steps that are missed by adiabatic approximations even using the exact ground-state functionals. An exact expression for the time-dependent exchange-correlation potential enables us to understand the origin of these features and highlights the importance of an appropriate choice of Kohn-Sham initial state. We explore a new route to developing approximations, based on this expression, and test these on a variety of dynamics of two-electron systems for which we can compare with the exact time-dependent exchange-correlation potential.

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Keywords: *Time-Dependent DFT, Kohn-Sham, nonadiabatic*

Ultrafast Charge and Spin Dynamics with TDDFT

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Abstract

Time dependent density functional theory (TDDFT) has recently[1] been applied to study ultrafast magnetization dynamics in periodic systems, as induced by strong laser pulses. Due to the femtosecond timescale, the non-classical behavior, and the non-linear response of the system, real-time TDDFT is the natural choice to study such dynamics. In this talk, I will discuss the progress made in addressing some of the outstanding problem in this field including 1) ultrafast demagnetization, 2) optimal control of such processes[2], 3) ultrafast magnetization as predicted for local moments in systems with complex magnetic sublattices, such as the Heusler compounds[3], 4) spin currents vs spin flips as demagnetization mechanisms, and 5) interface dynamics and spin-injection with relation to spintronic applications.

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Keywords: *TDDFT, Ultrafast, Demagnetization, Spin currents, Optimal Control*

A New Efficient Time Dependent Density Functional Algorithm for Large Systems: Theory, Implementation and Plasmonics Applications

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A new algorithm to solve the TDDFT equations in the space of the density fitting auxiliary basis set has been developed and implemented in ADF.[1] The TDDFT equations are recast to a non-homogeneous linear system, whose size is much smaller than in Casida formulation, allowing to calculate a wide portion of the absorption spectrum for large systems. The method extracts the spectrum from the imaginary part of the polarizability at any given photon energy, avoiding the bottleneck of Davidson diagonalization. The original idea which made the present scheme very efficient consists in the simplification of the double sum over occupied-virtual pairs in the definition of the dielectric susceptibility, which allows an easy calculation of such matrix as a linear combination of constant matrices with photon energy dependent coefficients. The method has been applied to very different systems in nature and size (from H_2 to $[Au_{309}]^-$)[2,3]. In all cases, the maximum deviations found for the excitation energies with respect to Casida approach are below 0.2 eV. The new algorithm has the merit to calculate the spectrum at whichever photon energy but also to allow a deep analysis of the results, in terms of Transition Contribution Maps,[4] plasmon scaling factor analysis[5], induced density analysis, and with a fragment projection analysis[6]. Circular Dichroism of large systems becomes also affordable.[7]

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Excited states for orbital-optimized second-order perturbation theory

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Abstract

Unrestricted Hartree-Fock (UHF) wave functions with spin contamination are usually poor zero-order approximations for second-order Moller-Plesset perturbation theory (MP2). Orbital-optimized second-order perturbation theory (OOMP2) tackle this problem by using approximate Brueckner orbitals. In OOMP2 the orbitals are optimized in the presence of the mean-field energy plus the second-order many-body correlation energy. Since in OOMP2 the energy is fully minimized with respect to orbital rotations, a Hellman-Feynman condition is fulfilled and first-order properties do not present discontinuities. This method improves the description of geometries, vibrational frequencies, and relative energies. Additionally, in OOMP2 the response function does not show spurious second order poles, making it suitable for linear-response excited state properties. In this contribution, we present an extension of OOMP2 and orbital-optimized double-hybrids (OODH) to excited states and we report test calculations for closed-shell systems and doublet radicals. The performance of method is compared with other second-order methods for excitation energies such as the approximate coupled-cluster singles and doubles model (CC2), configuration interaction with doubles corrections (CIS(D)), and the algebraic diagrammatic construction through second order (ADC(2)).

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An assessment of hybrid functionals for transport and excited-state properties of bulk semiconductors

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Abstract Hybrid functionals such as HSE[1] typically provides better accuracy than generalized-gradient (GGA) functionals for the structure, energetics, and band gaps of bulk semiconductors. They are therefore often used to model excited electronic properties. However, hybrid functionals can be less reliable for transition metals and metal-oxides. Here we examine the band curvature and position of higher lying bands of several semiconductors including half Heusler alloys both comparing with *GW* results and with experimental results such as the Seebeck coefficient. This comparison is made possible by a recently developed $\mathbf{k} \cdot \mathbf{p}$ -based interpolation scheme relying on velocity matrix elements[3] which provides rapid convergence of the Brillouin zone sampling[2]. The results highlight shortcomings of standard hybrid functionals for d-electron systems.

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Keywords: *Hybid functionals, GW, Seebeck coefficient, Brillouin zone interpolation,* $\mathbf{k} \cdot \mathbf{p}$ *method*

Rational Design of Single Molecule Magnets – Density Functional Perspective

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Abstract

In recent years, there has been a growing interest in the single molecule magnets (SMM) that display a bistable (up/down) magnetic spin state below certain critical temperature because of their potential applications. Obtaining SMMs working at room temperature is reduced to understanding Zero-Field-Splitting (ZFS) parameters that determines the magnetic anisotropy of isolated transition metal complex. In this work, computational study of the magnetic anisotropy in series of transition metal complexes, when changing the metal ion, or the ligands, in a controlled way will be presented. In order to achieve this goal, ligand field DFT method (LF-DFT) [1] is applied for the calculations of ZFS parameters and analysis of magnetic anisotropy. LF-DFT works by evaluating DFT energies of all the Slater determinants arising from a d^n configuration of the transition-metal ion in the environment of coordinating ligands using Kohn-Sham orbitals. This set of energies is then analysed within a LF model to obtain variationally energies and wavefunctions of the ground and excited states. In doing so, both dynamical correlation (via exchange-correlation energy) and non-dynamical correlation (via LF CI) are considered. Spin-orbit coupling constant was deduced from the LF analysis of the energy splitting of the spinors, obtained by the ZORA spin-orbit DFT calculations. Finally, ZFS parameters were obtained using an effective Hamiltonian from the lowest eigenvalues and corresponding eigenvectors from LF-DFT multiplet calculations. With this methodology, we accurately predict magnitude, sign of the ZFS parameters, orientation of the principal magnetic axes, and we can pin-point the excitations that control magnetic anisotropy. In this way, we rationalize the connection between the electronic structure, excited states and magnetic properties of transition-metal complexes. The present strategy will be illustrated by discussion of the magnetic anisotropy in trigonal-bipyramidal complexes of Ni(II) [2], scorpionate complexes [3], and octahedral complexes of Mn(IV) [4].

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Keywords: *Single Molecule Magnets, Zero-Field Splitting, Ligand Field Theory, Excited States, Spin-orbit Coupling*

Theory of non-collinear interactions beyond Heisenberg exchange; applications to bcc Fe

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Abstract

Although a formula for the exchange coupling, J_{ij}, in case of collinear arrangement has been known for a long time, due to the seminal work of Lichtenstein, Katsnelson, Antropov, Gubanov (LKAG) [1], even for relativistic [2] and correlated systems [3], a counterpart mapping onto a spin Hamiltonian for non-collinear arrangement is non-trivial. Similar to the LKAG derivation, a derivation was found in Ref. [4] for the pairwise

energy variation based on magnetic force theorem by allowing the presence of a non-collinear underlying spin configuration. The pairwise energy variation term, δE_{ij}^{two}, emerges for the case when two atomistic spins are infinitesimally rotated at two different sites *at the same time*. We show for a simple non-collinear configuration of the atomistic spins (in particular, where one spin is rotated by a finite angle in a ferromagnetic background) that δE_{ij}^{two} computed in terms of multiple scattering formalism cannot be fully mapped onto a bilinear Heisenberg spin model even in the lack of spin-orbit coupling. The non-Heisenberg terms induced by the spin-polarized host appear in leading orders in the expansion of the infinitesimal angle variations. However, an E_g-T_{2g} symmetry analysis based on the orbital decomposition of the exchange parameters in bcc Fe leads to the conclusion that the nearest neighbor exchange parameters related to the T_{2g} orbitals are *essentially* Heisenberg-like: they do not depend on the spin configuration, *and* can in this case be mapped onto a Heisenberg spin model even in extreme non-collinear cases. These findings strenghten the conclusions of Ref. [5] drawn within a collinear formalism.

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Thermochromism of Ferrocene

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Abstract

For the well known ferrocene molecule the hitherto undiscovered characteristic of thermochromism is reported[1]. Temperature-dependent (100 to 296 K) mono-crystal as well as solution UV-Vis spectroscopy reveals a clearly visible color change from orange to red. Since also no phase transition is observed in the crystals at different temperatures, the origin of this phenomenon seems to be a dynamic molecular structure effect. We present a theoretical study with the aim to explain the experimental findings. The UV-VIS spectra were simulated by sampling along MD trajectories generated by a new highly efficient tight-binding scheme (GFN-xTB[2]) and computing excitation energies and oscillator strengths with the fast and reliable simplified time-depended density functional theory (sTD-DFT[3]). Multiple lowest excited state potential energy surfaces along torsion, bending as well as stretching intramolecular coordinates were computed at the TD-PBE0 level of theory, providing together with the MD results a comprehensive picture of the phenomenon.

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Keywords: *TD-DFT, Ferrocene, Thermochromism, sTD-DFT, MD, GFN-xTB*

The Electronic Structure of CoPc from an Optimally Tuned Range-Separated Hybrid Functional

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Abstract

Transition metal phthalocyanines (TMPcs) are organic symmetric molecules hosting a metal atom at their center and which usually display a non-zero molecular spin. It has been recently shown, using a model Hamiltonian, that the electric current passing through a molecular spin dimer deposited in between two non-magnetic metal electrodes may be controlled via a voltage bias [1]. This would make possible the integration of molecular junctions in regular electronic devices. TMPcs in general and cobalt phthalocyanine (CoPc) in particular are good candidates for such applications. Since the valence electronic states of the molecule influence the shape of the current-voltage curves [1], it is important to accurately describe the molecular electronic structure both independently and in the presence of the metal leads or substrate. Optimally-tuned range-separated hybrid (OT-RSH) functionals have been show to provide reliable electronic structures of molecules and extended systems at a reasonable computational cost [2, 3, 4].

We analyse here the influence of the tunable parameters of an OT-RSH on the structural, electronic and magnetic properties of a single CoPc molecule. We tune the amount of exact exchange (α) and range-separation parameter (γ) such that the ionization energy theorem is fulfilled for both the highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO). We find an optimal value of $\alpha = 0.1$ and $\gamma = 0.146$ bohr^{-1} which provide a valence electronic structure which compares very well with experimental photo-electron spectroscopy (PES) data and GW calculations.

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Keywords: *Cobalt phthalocyanine, electronic structure, DFT, OT-RSH.*

Time-dependent density functional theory applied to calculation of electron current excited during atom ionization by intense two-color laser pulses

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Abstract

Great progress in computer technology has stimulated the development of mathematical models and numerical methods for simulation of various nonlinear phenomena occurring during the interaction of atoms and molecules with intense ultrashort laser pulses. The range of such phenomena includes ionization-induced phenomena arising in fields of moderate intensity (10^{14} - 10^{16} W/cm^2): above-threshold ionization [1], high-order harmonic generation [2], ultrashort attosecond pulse generation [3], generation of low-frequency (terahertz and mid-infrared) radiation [4, 6] and others.

Despite the fact that most of the atoms and molecules are essentially multi-electron quantum systems, the numerical studies of ionization-induced phenomena are traditionally based on the single active electron approximation. Within the framework of this approximation, electrons, with the exception of one, are "frozen" in their orbitals, while the field of the parent ion is described by a static potential well. Such models can have high accuracy under certain conditions, but in many problems single active electron aprroximation is inapplicable, since it does not describe a number of essentially multi-electron effects. Account of these effects can be made on the basis of time-dependent density functional theory (TDDFT), which is increasingly used in atomic physics and nonlinear optics. The basic equations for numerical simulation are the time-dependent Kohn-Sham equations, which take into account the interaction of electrons with the atomic nucleus, the external electric field of the laser pulse, and the electron-electron interaction [5].

This work is devoted to the *ab initio* TDDFT numerical simulation of ionization of noble gases by intense two-color laser pulses containing a strong field at the fundamental frequency and additional second harmonic field. The use of such pulses makes it possible to efficient excitation of low-frequency (with frequencies much lower than laser one) electron current density, responsible for the generation of terahertz and mid-infrared radiation [6]. We show that for argon and other atoms, already at moderate intensities $\sim 10^{15}$ W/cm^2, the amplitude and waveform of the low-frequency current density are strongly influenced by multi-electron effects associated with nonsequential multiple ionization. The ranges of the intensity and duration of the laser pulse are found in which the excitation of the low-frequency current density can be described in the framework of sequential-ionization model.

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Keywords: *Kohn-Sham equations, laser pulse, multielectron atom, ionization, terahertz and mid-IR radiation*

Modelling the π conjugation length in aromatic antenna: A simple predictive tool for the synthesis of functional material

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Abstract

The ability of photosynthetic centers to capture light and transform its energy into electronic potential is an extremely interesting feature of nature. The design of molecular systems of these capabilities would allow the design of synthetic photosystems for application in organic photovoltaics for example. Chromophores able to capture light and transfer it act as an antenna. One of the feature such antenna should have in order to be efficient is a high fluorescence quantum yield (Φ_F). An empirical model has been derived to relate the charge separation upon excitation to the fluorescence quantum yield of a chromophore [2, 1]. Having such a tool for the design of chromophore of desired luminescence properties would be a great advantage for synthetic chemists, allowing them to target the synthesis of new chromophores. In order to apply the proposed model for predicting Φ_F, a reliable quantum mechanical method to evaluate the magnitude of the charge separation is indispensable.

The failure of LR-TDDFT using conventional exchange-correlation functionals to describe charge-transfer excited states is well known [4], and some solutions have been presented, such as the design of range-separated functionals.

In Ref [1], we found that also the CAM-B3LYP exchange-correlation functional does not assure a proper description of the excited states in a series of terpyridil derivatives. This failure of CAM-B3LYP is somewhat unexpected and deserves a further investigation.

Range-separated functionals include some exact exchange in the long range, improving the description of charge separated states. CAM-B3LYP includes two parameters to control the amounts of Hartree Fock exchange included, namely the range-separation parameter ω, present in any range-separated functional, and the parameter controlling the long-range Hartree Fock exchange in the hybrid DFT part, β. Those two parameters have been screened with the idea to enhance the performance of the functional in the specific case of terpyridil derivatives.

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Keywords: *Charge transfer, aromatic antenna, fluorescence, range-separated functional*

Adsorption of oxygen onto aluminum — Performance of the density functionals: PBE, PBE0, M06, and M06-L

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Abstract

The study of the interactions between O_2(g) and metal surfaces is challenging for both experimental and theoretical methods because among other factors, these interactions proceed in short time scales and involve changes in the spin-state of O_2(g). In aluminum they are besides highly dynamical and the molecular and dissociative adsorption of O_2 at Al are considerably exergonic reactions that are accompanied by extensive surface reconstruction. In spite of the limitations of single determinant electronic structure calculation methods for describing the transition-state due to the spin transition in O_2 that occurs upon its molecular adsorption, DFT is an important tool to help to understand the reactions of O_2 with Al and valuable information about the products of molecular and dissociative adsorption of this molecule can be obtained. In this work we studied the reactions between O_2(g) and Al(111) using a series of DFT functionals – PBE, PBE0, M06 and M06-L; with and without classical force-field based corrections of the D3 type for accounting for van der Waals (vdW) interactions. In our models we used perfect and defective Al(111) surfaces and also surfaces with dopants of different types in different geometries. These systems constitute an interesting ground for testing the performance of different functionals and we found that their performance is highly dependent on the surface geometry. We obtained detailed information on the chemical bonding and geometries of the products of molecular and dissociative adsorption of O_2 and did an analysis of the performance of the functionals. For the molecular adsorption we found no significant differences in the performance of the hybrid functionals that incorporate Hartree-Fock exchange (HF-DFT) when compared to pure DFT, but the differences become very pronounced for dissociative adsorption, with the hybrids PBE0 and M06 predicting more exoergic adsorption than PBE and M06-L. Furthermore, PBE0 and M06 predicted trends in adsorption energies which are in line with the experimental knowledge of the effects of surface defects in adsorption energies. The predictions of the non-hybrids PBE and M06-L point in the opposite direction. The analysis of the contributions of the vdW forces to the adsorption energies reveals that the PBE and PBE0 functionals have similar difficulties in describing vdW interactions while the M06 functional can account for these interactions with an accuracy which is at least similar to that of the correction of the D3 type.

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Keywords: *Surfaces, adsorption, performance of functionals, PBE, PBE0, M06, M06-L*

Properties of the water to boron nitride interaction: from zero to two dimensions with benchmark accuracy

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Abstract

Molecular adsorption on surfaces plays an important part in catalysis, corrosion, desalination, and various other processes that are relevant to industry and in nature. There are many unanswered questions pertaining to adsorption on layered, low-dimensional materials in particular. The adsorption energy of water on boron nitride substrates, going from zero to 2-dimensional periodicity, is one that poses a practical challenge to experiments and to electronic structure methods. Indeed, one of the key challenges for DFT based methods has been the accurate inclusion of long-range correlation interactions. Unravelling the physics of molecular interactions on such low-dimensional substrates calls for an accurate and balanced treatment of polarizable electrostatics and dispersion interactions. Thanks to great progress in the development of codes and algorithms in recent years, such systems can now be studied with benchmark accuracy. Here, we present reference adsorption energies, static polarizabilities, and dynamic polarizabilities, for water on BN substrates of varying size and dimension. Adsorption energies are computed with coupled cluster theory, fixed-node quantum Monte Carlo, the random phase approximation, and second order Møller-Plesset theory. A number of widely used and recently developed exchange-correlation functionals are benchmarked.

The water adsorption energy on the BN substrates could be expected to grow monotonically with the size of the substrate due to increased dispersion interactions but interestingly, this is not the case here. This peculiar finding is explained using the static polarizabilities and molecular dispersion coefficients of the systems, as computed from time-dependent DFT and the many-body dispersion (MBD) method in DFT. Dynamic as well as static polarizabilities are found to be highly anisotropic in these systems. The MBD method in DFT is shown to capture this non-additive behaviour and also emerges as a particularly useful estimation of finite size effects for other expensive, many-body wavefunction based methods.

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Keywords: *many-body dispersion, anisotropy, accuracy, adsorption*

High-thoughput search for defects in SiC

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Abstract

Studying point defects in semiconductors to be used as qubits or photon emitters is a rapidly growing field. Examples of such suggested defects to be used as qubits are NV center in diamond and divacancies in SiC. However, one defect type can have many different non-equivalent configurations, *e.g.*, there are four different configurations that divacancies can form in 4H-SiC. Identifying and understanding both the defect type and the different configurations is a necessary step to realize these applications. A promising way to identify the defect is to combine experimental data and *ab initio* calculations for zero-phonon lines, zero-field splitting, and hyperfine coupling parameters. We are planning to do these calculations in a high-throughput manner and produce a database of zero-phonon lines for an array of different defects. In preparation of these calculations, we present a study of the convergence with respect to supercell size, k-point density, geometry, and exchange-correlation functional especially tested for divacancies in 4H-SiC in order to correctly identify the different configurations. Our findings for the zero-phonon line shows that a smaller supercell (96 atoms) with a higher k-point set gives sufficiently accurate results compared with a large supercell (2400 atoms) with Γ-point sampling only, but at a significantly lower computational cost. A good quantitative description of the absolute positions of the zero-phonon lines are achieved with hybrid functional calculations (HSE06). However, instead of using HSE06 for all steps of the calculations, the defect supercells can be relaxed using a semi-local functional, i.e., PBE or AM05. The result is only a minor loss in accuracy but a significant reduction of computational cost. Our results suggest that with a careful choice of methodology, useful data can be obtained at a computational cost feasible for high-throughput calculations of the large number of defect types and configurations available in SiC.

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Keywords: *SiC, point defects, high-throughput, zero-phonon lines*

Combining Density-functional Theory And Wave-function Methods: The RSλH + MP2 Scheme

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Abstract

Over the past two decades, Kohn-Sham [1] DFT (KS-DFT) has been a method of choice to study ground state properties of large system. KS-DFT is formally exact, but it involves a functional called the exchange-correlation functional. Nevertheless, the exact form of the exchange-correlation functional is still unknown, hence density functional approximations (DFAs) has been developed in order to improve the accuracy of KS-DFT. DFAs are able to describe properties that depend on short range exchange-correlation effects, molecular geometries and bond enthalpies for instance. However, there are still some problems to address to the current approximations However, there are still some problems to address to the current approximations:

The issue of self-interaction error (SIE): in one electron systems, the Hartree and exchange functional do not cancel each other exactly and of course. Another problem associated to the current DFAs is related to the fact correlation functional does not take into account the dispersion interactions. Perhaps, the most appealing approach to deal with the problem mentioned above consist in developing range separated double hybrid functionals, which mix exact exchange and non local correlation effects. These methods are able to deal with the SIE and to take into account the dispersion interactions.

In standard range separated hybrid methods[2], the short range part of the Coulomb interaction is usually handled by a functional of the density while the long range electron interaction is treated by wave-function theory. Herein, we propose to include a fraction wave-function theory in the short range part in order to improve the accuracy of short range properties.

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Keywords: **range separated, double hybrid, KS-DFT multi-determinental extension**

Quantum mechanics in metric space: distances between exchange-only correlations

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Abstract

The Density Functional Theory (DFT) transforms the problem of determining interacting many-body system properties into the solution of the Kohn-Sham (KS) equations, which only involve auxiliary non-interacting particles [1, 2, 3]. Practically, the KS approach relies on the possibility of devising approximate forms for the exchange-correlation energy as a functional of the particle density. D'Amico et al. [4] showed that using a suitable metric the Fock space can be stratified into concentric spheres where the distances between states can be geometrically interpreted. Following a similar approach we introduced a rigorous way to measure distances between exchange-only correlations of interacting many-electron systems. In particular we focused on the analysis of the x-hole function, a quantity at the core of the KS−DFT approach. We applied our metric on the isoelectronic Helium-like sequence for which the exact x-holes can be calculated, firstly the exact results were compared with an exact reference state identified by the atomic number Z. Secondly we performed an exact-to-approximated comparisons, by directly computing the distance between exact and approximated DFT x-holes. We considered popular functional as (i) the Local-Density Approximation (LDA) [5], (ii) the Generalized Gradient Approximation (GGA) [5] and (iii) the MetaGGA (MGGA) [6, 7]. We analyzed also physical trends moving along the rows of the periodic table, considering distances between x-holes of different systems calculated using the same approximation. The behavior of our metric follows from the sharp change of the corresponding atomic sizes. The curves also display characteristic minima at every start of double occupancy of p-shells of the atoms. We used our distances also for a direct comparison between different approximations, as meaningful example we calculated the distances between different approximations (again LDA, GGA and MGGA) applied to the same atom for the noble gas series. We noticed that the distances among the various approximations decrease substantially with increasing atomic number. Consistently, the GGA and MGGA result to be closer to each other that to the LDA. Our metric helped to define an error threshold to establish the parameter region for which LDA and GGA would be a good-enough cheaper substitute for MGGA. In summary, we showed that our distance can be used to analyze the performance of the exchange-only part of DFT approximations and also to capture fundamental physical features as the periodicity of atomic elements. We suggest that this metric can find useful applications in high-throughput materials design because it provides a geometrical intuitive picture (the onion structure) of the Fock Space and allows to establish practical error thresholds which are very helpful in exploring the relevant configurations of a large data sets.

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Keywords: *Density-functional theory, Electronic structure of ions and molecules, Quantum mechanics*

Thermal expansion in FeCrCoNiGa high-entropy alloy from theory and experiment

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Abstract

The recently developed high-entropy alloys have drawn significant attention and opened new exciting research areas with a high intrinsic degree of freedom for designing materials with exceptional properties [1-3]. Here, first-principle alloy theory and key experimental techniques are applied to determine the thermal expansion of FeCrCoNiGa high-entropy alloy. The magnetic transition, observed at 649 K, is accompanied by a significant increase of the thermal expansion coefficient. The phase stability is analyzed as a function of temperature via the calculated free energies accounting for the structural, magnetic, electronic, vibrational and configurational contributions. A mixture of the face-centered (fcc) and body-centered cubic (bcc) phases is predicted around room-temperature, in good agreement with experiment. By combining the measured and theoretically predicted temperature-dependent lattice parameters for the ferro- and paramagnetic states of the fcc and bcc phases, we reveal the structural and magnetic origin of the observed anomalous thermal expansion behavior. The present findings demonstrate that engineering the magnetic and structure transitions provides rich opportunities for designing and optimizing new high-entropy alloys with interesting thermophysics properties.

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Keywords: *High-entropy alloy; Magnetic transition; Duplex phase; Thermal expansion.*

Accurate Kohn-Sham Ionization Potentials from Scaled-Opposite-Spin Second-Order Optimized Effective Potential Methods

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Abstract

One important property of Kohn-Sham density functional theory is the exact equality of the energy of the highest occupied KS orbital (HOMO) with the negative ionization potential of the system

$$\varepsilon_H = -I_0 \, . \tag{1}$$

This exact feature is out of reach for standard density-dependent semilocal functionals. On the other hand, accurate results can be obtained using orbital-dependent functionals in the optimized effective potential (OEP) approach. In presentation we will discuss the performance of some advanced OEP methods, with special emphasis on the recently proposed scaled-opposite-spin OEP (OEP2-SOS) functional. Additionally, we will present the newly introduced OEP2-SOS(opt) method which allows to obtain results comparable with IP-EOM-CCSD ones. Moreover, we will also discuss the relevance of the so called HOMO condition for correlation in the accurate determination of the orbital energy.

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Keywords: *OEP method, ionization potential, HOMO condition, Spin Component Scaled*

Plastic deformation modes in lamellar TiAl alloys beyond the Schmid's law

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Abstract

The plastic properties of materials are decided by the operation of various deformation modes at atomic-level. Understanding the competition between dislocation slip and twinning is a critical step for optimizing materials with both high strength and ductility. Efficient design is however often hindered by the fact that the classical Schmid's law is found inoperative in intermetallics. Here we put forward a model based on first principles simulations for the selection of plastic deformation modes in γ-TiAl polysynthetic twinned alloys. The model is formulated in terms of intrinsic energy barriers associated with dislocation slip and twinning mechanisms and clearly demonstrates the fundamental role of generalized stacking fault energies (GSFEs) in choosing the active deformation modes with respect to loading orientation. Using the model, one can readily identify the atomic-level mechanisms behind the unique channelled flow phenomenon.

Keywords: *TiAl alloys, plastic deformation, the Schmid's law,*

A linear-scaling approximate DFT method for quantum mechanical molecular dynamics simulations of large systems

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Abstract

We present methodological developments of a computationally efficient approximation to density functional theory referred to as divide-and-conquer density-functional tight-binding (DC-DFTB) scheme [1]. The computational complexity of DC-DFTB electronic structure calculation is $O(N)$ by dividing the entire system into several subsystems. The evaluation of charge-charge interaction under periodic boundary conditions can be accelerated in combination with multipole- and interpolation-based algorithms. The numerical errors due to fragmentation and fast electrostatic calculation is fully controllable by appropriate settings of surrounding chemical environment region for each subsystem, order of multipole expansion, and grid size of interpolation. To enhance its applicability to system size of millions of atoms, the DC-DFTB method has been implemented into massively parallel program. Benchmark test showed that a single point energy and gradient of periodic water box consisting of 5,062,500 atoms was computed within two minutes using approximately 300,000 cores of the K computer. More details on theoretical aspects and scalability are discussed in the presentation.

We also introduce our recent applications of the DC-DFTB molecular dynamics simulations to proton transfer reactions in aqueous solutions [2–5]. The computational speed of the DC-DFTB allows to perform chemical reaction simulations of thousands of atoms routinely. The dynamical fluctuation of chemical bond formation and cleavage is described by means of automatic grid box. The calculated diffusion properties and free energy differences agree reasonably with experimental results, highlighting the reliability of the present approach.

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Keywords: Divide-and-conquer method, Density-functional tight-binding method, Linear-scaling computation, Massively parallel calculation, Chemical reaction simulation

Electrochemical Reduction of Carbon Dioxide in Sn-based Electrodes: A mechanistic study

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In a context where the high emissions of greenhouse gases are a well-known global problem, the possibility of using carbon dioxide as starting material in catalysis offers a quite interesting alternative of energy storage.[1] In such process, useful products can be obtained by varying electrode potentials, temperature and the electrocatalyst. Cu, Pb, Hg, Ni, Pt, Cd and Sn, for instance, are among the numerous catalysts and electrodes that have been recently tested for this purpose.[1,2] Particularly, Sn has the advantage of low cost and high activity in addition to the high overpotential for hydrogen evolution, an important parameter to assure the selectivity in the formate production.[3] In this work, we aim to understand the mechanism involved in CO_2 conversion into formic acid catalyzed by Sn-based electrodes in aqueous medium, by using the density functional theory framework.[4] Here, one fundamental scientific question is the possibility of having an tin oxide layer participating on the catalytic activity. Therefore, we have built different slab models starting from the bulk SnO and $Sn_6O_4(OH)_4$ compounds with focus on the formation of –OH groups at the water-oxide interfaces. The latter is suggested to play an important role in the interaction with CO_2 molecules. Our results indicate that indeed the insertion of CO_2 into the Sn-OH bond is thermodynamically favorable leading to the stabilization of carbonate structures, which is subsequently reduced to form the formic acid. The calculated redox potentials display fair agreement with the experimental findings supporting the proposed mechanism. An analysis of the electronic structure, correlating with the catalytic activity, has also been carried out to unveil the underlying physics of the catalysts providing the basis of the rational design of novel compounds with superior properties.

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Keywords: *"Density Functional Theory" "Computational Electrocatalysis" "Energy conversion" "CO_2 reduction"*

Study of the Keto-Enol Tautomerism in Acetylacetone, in Gas Phase and in Solvent

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Abstract

The keto-enol tautomerism constitutes a relevant process in organic and biological chemistry. For example, this reaction occurs in the DNA basis and can induce some mutation points. Hence, this isomerism has been, and is still, widely investigated. This process is a proton transfer which is influenced by many environmental factors as the solvent nature, the temperature and so on [1].

We studied this equilibrium involving acetylacetone (ACAC) molecule in vacuum [2] and in explicit water solvent. The role played by the water molecules on the reaction barrier and the origin of their catalytic effect were investigated. We used the density functional theory (DFT) through the VASP (Vienna Ab-initio Simulation Package) code [3, 4] and we applied the NEB (Nudged Elastic Band) method [5] to evaluate the activation energies. Besides, to understand the catalytic effect of the water molecules from the geometries of the activated complexes, we partitioned the different energy contributions in the solvent and in the ACAC molecules according to the QTAIM theory [6].

This study was done at 0 Kelvin. However, the temperature was proved, in literature, to have a strong influence on the activation barrier [7]. Therefore, it will be interesting to investigate this process by Metadynamics. This method accelerates the sampling of the free energy surface and allows to determine more rapidly, than a standard molecular dynamics, some rare events [8].

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Keywords: *DFT, NEB, QTAIM, Proton transfer*

The Becke Fuzzy Cells Integration Scheme for Exchange-Correlation in GPAW Density Functional Program

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Abstract

We implement the Becke Fuzzy Cells integration scheme [1, 2] in GPAW DFT code [3, 4] for the purposes of exchange-correlation and subsystem functional approach. Subsystem functional approach allows one to partition space into separate regions and use a different exchange-correlation functional in each region. When these regions are centered around the atomic nuclei a natural choice for the practical implementation of the space partitioning is the well-known fuzzy cells scheme first proposed by Becke [1]. In the Becke scheme space partitioning is governed by partition functions and instead of the original Becke partition function we use an alternative expression similar to Ref. [2], which is better suited for the computation of periodic systems because it scales only linearly as a function of atomic nuclei.

In general, the space partition functions change as a function of atomic coordinates, which means they will induce extra correction terms in forces and the stress tensor. These extra terms should be taken into account and we derive and implement these extra terms in GPAW using localized functions.

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Keywords: *GPAW, Becke Fuzzy Cells, Becke-ρ scheme, Subsystem Functional Approach*

Modification of Material Surface by plasma

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Abstract

Surface modification is an act for modifying the surface of materials by changing physical, chemical or biological characteristics different from ones previously. These modifications are usually made to solid materials. The modification can be done by different methods for altering characteristics of the surface such as roughness, hydrophilicity, surface charge, surface energy, biocompatibility and reactivity. It is possible either to improve wettability and therefore coating adhesion or to decrease wettability in order to provide an extra protection by surface treatment. The Improvement of material surface wettability can improve bonding properties; it can also enhance physical and mechanical properties of material composites. In this study, low-pressure plasma technique was carried out to modify the surface of material. The effects of different treatment parameters such as type of gas, percentage of gas and aging time on wettability were investigated. The treatment effect was evaluated by measuring contact angles of liquids and calculating the free surface energy. The effect of plasma treatment on morphology of surfaces was characterized using scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR).

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Keywords: *Plasma treatment, Contact angle, Surface energy, Wettability*

Density functional theory study of the formation energies of Cu-Au system

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Abstract

Based on our previous work [1, 2], the formation enthalpies of Cu-Au alloys are mainly affected by local lattice distortion (LLD), exchange-correlation functional (XC-QNA) [3, 4] and short-range order (SRO). This is due to the experimental formation enthalpies are reported for random Cu-Au alloys at high temperatures (about 200 K above the ordering temperature) [5, 6].

In our recent work, the LLD effect was considered in VASP calculations, QNA effect was considered in EMTO program, and SRO was obtained from the Ref. [7] which was calculated by LDA. Then the final formation enthalpies are -43.3, -53.4 and -30.7 meV/atom for $Cu_{0.75}Au_{0.25}$, $Cu_{0.5}Au_{0.5}$ and $Cu_{0.25}Au_{0.75}$, respectively. These theoretical results are surprisingly very close to the experimental values [5, 6]. Actually, the XC QNA effect turns out to be larger than the SRO effect and thus should be properly addressed when aiming for an accurate description of the formation enthalpies in Cu-Au system. In the present work, we consider the all effects (i.e., lattice relaxation, SRO effect and QNA) in GPAW program which accurately describe the properties of Cu-Au system.

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Keywords: *Cu-Au alloys, Formation enthalpies, Local lattice distortion, QNA exchange-correlation functional, Short-range order.*

Some Hydrated Molecular Complexes of 4-Cyanophenylboronic acid: Significance of Water in the Structure Stabilization by Theoretical Investigations

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Abstract

Objective: To study intermolecular interactions present in molecular complexes of boronic acids experimentally and computationally using DFT-D3 method.

Introduction: Crystal engineering is a study of intermolecular interactions exhibited by molecules in their crystal structure and utilized its understanding in design of new compounds with desired properties. Many experimental approaches have been made to study such interactions in complexes such as cocrystals, hydrates etc. But theoretical studies on such complexes are limited. To understand and evaluate such interactions, computational power and quantum mechanical approaches have been explored such as Monte Carlo method, quantum-chemical coupled cluster techniques etc. For modelling this type of system one difficulty is to correctly include vdW interactions. Here we use DFT-D3 method[2].

Methods: In our study[1], molecular complexes of 4-cyanophenylboronic acid(CyBA) with various aza donor coformers have been crystallized using slow solvent evaporation method. Crystal structure of complexes have been determined using single crystal X-ray diffraction technique. Nature of intermolecular interactions exhibited by CyBA with coformers are further studied using DFT-D3 method.

Outcomes: Single crystal analysis shows that though pure CyBA has anhydrate structure, it forms hydrates with various aza donor coformers. DFT simulations were performed, to rationalize the propensity of formation of hydrate structures and to evaluate the observed structural features with respect to the strength of the intermolecular interactions, for instance, hydrogen bonds. Interestingly binding energy simulations shows that water molecule form strong hydrogen bonds with CyBA as well as aza donors and play crucial role in structure stability. This study also highlights the CyBA as potential cocrystal former which has not been explored in crystal engineering field. Currently we are working on to explore other plausible forms of these complexes especially anhydrate forms using DFT-D3 methods.

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Keywords: *crystal engineering, boronic acid, DFT-D3, intermolecular interactions*

First helical Zn(II) complex based on N4-Schiff base: Experimental and theoretical approach

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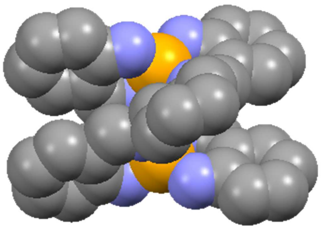
Abstract

The significant potential of Zn-sal(ph)en as building block in supramolecular chemistry and catalytic materials[1], is due to their high Lewis acid behavior, in which the Zinc metal center generally does not adopt its usual tetrahedral geometry, and expands its coordination sphere through axial binding site, affording usually a stable five-coordinated zinc (II)–salen complex, either dimers and oligomers through Zn-O intermolecular interactions, or monomers in which the zinc is coordinating at strong donor ligand (e.g. pyridine, DMSO). The geometry concerning the four coordinate Zinc (II) complex with a salen-type ligand is still less studied until now, and extremely rare characterization by X-ray crystallography are available. To the best of our knowledge, only two examples have been reported, which adopt an original helical complexes [2] based on salen ligand with pseudo-tetrahedral coordinate Zinc center.



Helical zinc(II)-4N complex

In this work, we report the synthesis and characterization approach for the first example of helical complex based on Shiff bases that bear N4 ligand. Unexpectedly, the N4-Helice is less stable than their analogue based on salen N2O2 ligand in the presence of water, leading to a demetalation process. The reaction mechanism for the degradation of Zn-4N-schiff base in aqueous conditions has been also investigated in detail by using DFT methods.

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Keywords: *N4-Schiff base, Zn(II), complex, DFT*

First-principles study of the semicoherent interface between TiC and Fe

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Abstract

Using ab initio calculations to study the semicoherent interface is usually difficult due to the very large size of supercell needed to model the interface [1, 2]. In the present work, we take the TiC/Fe semicoherent interface as an example to explore the way for estimating the interfacial disolocation structure and energetics. We demonstrate how one divide the semicoherent interface into small patches that fit ab initio calculations. An averaging method is developed to obtain the total interfacial energy for the semicoherent interface.

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Keywords: *Titanium carbide, Ferrite, Semicoherent interface, Ab initio, Interfacial energy*

The density-potential mapping in time-dependent density-functional theory

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In this talk we give an overview of the foundations of time-dependent density-functional theory (TDDFT)[1] and present recent developments in this research area and related open questions.
The structure of TDDFT is different from ground-state density functional theory as it is based on the time-dependent Schrödinger equation and represents an initial state problem rather than an eigenvalue problem; therefore different concepts, in particular initial state dependence and memory effects, play a role in the construction of approximate density functionals.
The basis of TDDFT is formed by a one-to-one correspondence between the time-dependent density and the time-dependent external potential, for a given initial state. Such a one-to-one dependence was first established by Runge and Gross [2] but recent mathematical work [3] shows that restrictions on the initial states, external potentials and two-body interactions must be rather severe for the proof to be rigorously valid. We will discuss the main ideas behind an alternative proof of the Runge-Gross theorem valid for a wider class of potentials as was presented in a recent review paper and Ph.D. thesis [4, 5]. We conclude by addressing remaining open issues and recent developments.

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Keywords: *Time-dependent density-functional theory, density-potential mapping*

Constructing exchange-correlation functionals using the strong-interaction limit and the correlation factor ansatz

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The adiabatic connection (AC) plays a central role in the construction of approximate exchange-correlation functionals. It relates the exchange-correlation hole to ground-state wave functions that depend on the coupling constant λ, which scales the electron-electron repulsion. Only λ values between 0 and 1 are relevant for the exchange-correlation energy of Kohn-Sham theory, however, large λ values are still useful for the construction of interpolations for the AC. In particular, we focus on the strong-interaction ($\lambda \to \infty$) limit and develop approximations [1,2,3] to the exchange-correlation hole in this limit. Starting from the electron density $\rho(\mathbf{r}+\mathbf{u})$ as a function of the reference point $\mathbf{r}$ and the electron-electron separation $\mathbf{u}$, exchange-correlation factors $f_{XC}(\mathbf{r},\mathbf{r}+\mathbf{u})$ are constructed that convert $\rho(\mathbf{r}+\mathbf{u})$ into the exchange-correlation hole $\rho_{XC}(\mathbf{r},\mathbf{r}+\mathbf{u})$ of the strong-interaction (SI) limit, i.e. $\rho_{XC}{}^{SI}(\mathbf{r},\mathbf{r}+\mathbf{u})= f_{XC}(\mathbf{r},\mathbf{r}+\mathbf{u})\, \rho(\mathbf{r}+\mathbf{u})$. The resulting exchange-correlation energy per particle of the SI limit is then used to construct [2,3] various AC interpolations and hybrid schemes. The exact exchange energy per particle and the exchange-correlation energy per particle of the SI limit are connected through interpolation functions whose construction is discussed in detail. Among other things, we show how static correlation is accounted for in the interpolation schemes.

Another route to obtain improved approximations to the exchange-correlation energy [4,5] is the factorization approach where $\rho_{XC}(\mathbf{r},\mathbf{r}+\mathbf{u})$ is written as $\rho_{XC}(\mathbf{r},\mathbf{r}+\mathbf{u})= f_C(\mathbf{r},\mathbf{r}+\mathbf{u})\, \rho_X(\mathbf{r},\mathbf{r}+\mathbf{u})$. The correlation factor $f_C(\mathbf{r},\mathbf{r}+\mathbf{u})$ turns the exchange hole $\rho_X(\mathbf{r},\mathbf{r}+\mathbf{u})$ into the exchange-correlation hole. An advantage of this approach is that, unlike global hybrids, it can recover exact exchange. Using exact constraints, we develop representations for $f_C(\mathbf{r},\mathbf{r}+\mathbf{u})$ that yield accurate approximations to the exchange-correlation energy. We show how strong correlation can be incorporated into the correlation factor model and also how self-correlation corrections can be devised.

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Keywords: *exchange-correlation energy, strong interaction limit, correlation factor ansatz.*

Quasi non-uniform approximation, flexible exchange-correlation functional for alloys and compounds

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Abstract

In this project we develop a semilocal exchange-correlation functional for the investigation of the properties of alloys and compounds. The starting point is the generalised gradient approximation (GGA) for the exchange-correlation potential giving a proper description of many important solids. The second building block is the subsystem functional approach (SFA) originating from the nearsightedness principle and incorporating inhomogeneous electron density effects through system partitioning. Here we use the SFA concept within the atomic sites of an alloy to extend the capability of GGA level functionals. Based on an element-specific optimisation of the GGA functional, the concept of semiempirical quasi-non-uniform gradient-level approximation (QNA) is introduced. The strength of the QNA scheme is demonstrated by comparing QNA lattice constants, bulk moduli, and formation energies of several transition-metal alloys and compounds with other theoretical results and with available experimental data. The QNA was first implemented using muffin-tin orbitals scope. Recently we have started the implementation of the QNA using plane wave basis. The very promising preliminary results of this plane wave project are also reviewed.

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Keywords: *Semilocal exchange-correlation, subsystem functionals, formation energy, lattice constant*

Electronic and topological properties of MXenes: a first-principles study

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Abstract

MXenes are a recently discovered large family of two-dimensional (2D) early transition metal carbides that have shown great potential for a host of applications ranging from electrodes in supercapacitors and batteries to sensors to reinforcements in polymers[1,2]. Here, based on first-principles calculations, their electronic, magnetic and topological properties are systematically studied. First, we predict that Cr2C MXene is a ferromagnetic half metal[3]. When it is covered by F, OH, H, or Cl groups, it becomes an antiferromagnetic insulator, with the size of the band-gap dependending on the type of functional groups. We further point out that the localization of Cr d electrons induced by the surface functionalization is responsible for the ferromagnetic-antiferromagnetic and metal to insulator transitions. Second, we report the quantum spin hall (QSH) effects in Mo2MC2O2 (M=Zr, Ti, or Hf) MXenes[4]. A tight-binding model based on the d_(z^2), d_xy and d_(x^2-y^2) orbital basis in a triangular lattice is also constructed to describe the QSH states in Mo2MC2O2. It shows that the atomic spin−orbit coupling (SOC) strength of M totally contributes to the topological gap at the Γ point, a useful feature advantageous over the usual cases where the topological gap is much smaller than the atomic SOC strength based on the classic Kane−Mele or Bernevig−Hughes−Zhang model. Consequently, Mo2MC2O2 show sizable gaps from 0.1 to 0.2 eV with different M atoms, sufficiently large for realizing room-temperature QSH effects. These results extend the potential applications of MXenes into spintronics and electronics.

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Keywords: *two-dimensional transition metal carbides (MXense), ferromagnetic half metal, quantum spin hall effects*

Superconducting order parameter in layered systems

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Abstract

In this talk we show the solution of the fully relativistic spin-polarized Kohn-Sham Bogoliubov de Gennes equations [1] for multilayers within multiple scattering theory. In this formalism the Green function and consequently various physical quantities can be calculated easily. Particularly interesting is the so called anomalous charge, as it can be related to the order parameter. Result will be presented for the NbAu, NbFe and NbAuFe overlayer systems. We find a linear decay of the order parameter in the non-magnetic case, however, we find that the spin splitting of the electron states in the ferromagnet leads to spatial modulation of the proximity induced pair amplitudes due to Cooper pairs with a finite center of mass momentum showing oscillatory behaviour, similarly to the FFLO state. More interestingly, in case of the NbAuFe system we also show that the existence of spin-polarized quantum well states can lead to such oscillations of the order parameter in the normal metal.

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Keywords: *Superconductivity, Multilayers, Fully relativistic, Spin-polarized, Bogliubov-deGennes equation*

Applications of Density Functional Theory on Design of Advanced Titanium Alloys

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Abstract

Titanium alloys possess attractive properties such as high specific strength, good damage tolerance, and excellent corrosion resistance such that they find wide applications in aerospace, marine, and biomedical areas. In recent years, first-principles methods based on density functional theory (DFT) are increasingly employed to understand the physics and to predict the mechanical properties of titanium alloys, which facilitates the rational design of advanced titanium alloys. However, due to the compositional and structural complexity of the titanium alloys, the DFT investigations of the mechanical properties are not straightforward. In this presentation, I'll present some examples to show the applications of DFT on the elastic modulus [1, 2], creep resistance [3, 4], ω-precipitation strengthening and embrittlement of titanium alloys [5].

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Keywords: *Density Functional Theory, Advanced Titanium Alloys, Mechanical Properties.*

Density Functional for Computing the Strong Nondynamic Correlation

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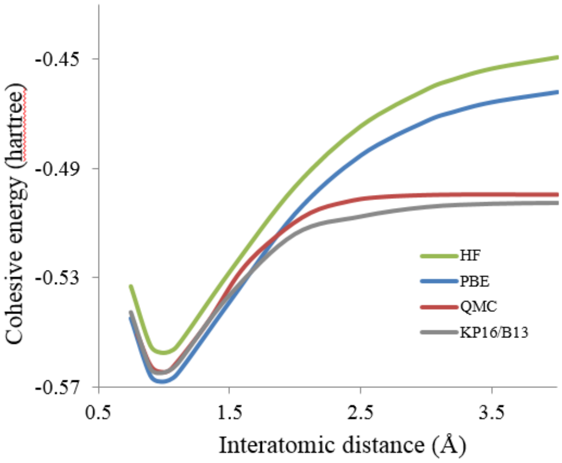
Abstract

We have recently developed a model functional for the nondynamic correlation based on single-determinant Kohn-Sham density functional theory [1]. It combines the potential correlation in the Becke'13 method [2] with a new model for kinetic correlation via adiabatic connection based on physical arguments and exact conditions for both the weak and strong correlations. The result is a single-term functional for nondynamic correlation of all strength, from weak to extremely strong. It is named as KP16/B13 (Kong-Proynov'16/Becke'13). KP16/B13 contains only three empirical parameters. It is also the first model of its kind implemented with self-consistent field. Benchmark results show that the model recovers the majority of the left-right strong correlation upon bond dissociation and performs well for near equilibrium properties such as the binding energy, reaction barrier, ionization potential, etc. It also describes well a linear chain of H atoms with many strongly correlated electrons, demonstrating the feasibility of DFT for strongly correlated materials [3]. A phase diagram for the transition between the metallic, Mott and regular insulator for the H-chain system can also be drawn using a density functional based index for the atomic population of effectively localized electrons [4]. Our work adds to the hope for efficient computation of systems with multireference in nature.



Cohesive energy curves of H_{70} chain.

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Keywords: *strong correlation, nondynamic correlation, density functional, DFT algorithm*

Automatic generation of pseudopotentials by an all-electron methods

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Abstract

All-electron (AE) DFT methods have been developed to the point of producing results essentially independent of implementation and method[1], and produce accurate evaluations of the predictions of available DFT functionals. Their complexity, however, inhibits their use for very large unit cells and large scale phenomena such as phonons. Pseudopotential methods, on the other hand, also produce excellent predictions of materials properties, are extensible to larger material systems and provide easier evaluation of, for example, phonon spectra. However, they depend on pseudopotentials constructed for each material. PAW pseudopotentials are derived from a construction of a wave-function which is similar to the all-electron treatment of the interstitial region of AE methods. In this talk I describe a tie between AE methods and PAWs which can allow the automatic production of a PAW pseudopotential from a self-consistent AE calculation which can then be used to provide, for example, phonon spectra consistent with, and directly comparable to, the AE total energy calculation.

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Keywords: *PAW, pseudopotential, all-electron*

Semi-Local Functionals with Non-vanishing Asymptotic Potentials: Beyond the AK13

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Abstract

In recent literature, a scheme has emerged for addressing certain nonlocal exchange features with semilocal functionals. The key feature in these functionals is a non-vanishing system-dependent asymptotic potential, i.e., a potential with a limiting value far outside a finite system that approaches a constant proportional to the square root of the highest occupied eigenvalue of the system. Existing realizations of this scheme, the Becke-Johnson model potential with various modifications, and the non-empirical semilocal GGA exchange functional AK13 [1] have been shown to reproduce features in the potential not seen in commonly used semilocal functionals. The result is a qualitative improvement of the orbital description and band structure which give, e.g., polarizabilities, optical properties, band gaps, and atomic and molecular properties closer to those of exact exchange (and, thus, experimental values) [2]. For example, the Kohn-Sham band gap is greatly expanded similarly as in calculations using exact exchange. However, functionals with non-vanishing asymptotic potentials bring a new set of challenges that have to be overcome before they can be adopted as general-purpose methods [3, 4, 5]. This talk discusses the AK13 construction idea, some of its relevant challenges, and outlines recent efforts towards new exchange-correlation functionals based on, and extending, the AK13 construction idea. The aim is to address issues seen with the quantitative accuracy, the description of energetics, and other issues found with the original formulation.

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Keywords: *exchange energy, semilocal, functional, ak13*

Which is the best exchange-correlation functional for describing atomic and molecular clusters?

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Abstract

Clusters represent the intermediate stage between microscopic atoms/molecules and macroscopic condensed matters. It is fundamentally important to reveal the evolution of cluster structures and electronic properties as function of cluster size. Atomic clusters are usually glued by the metallic or covalent bonding, whereas non-covalent interactions play determinant role in the structures molecular clusters. High-level CCSD(T) calculations are certainly reliable to provide accurate description for bonding of all these clusters but are limited in very small sizes. Aided by CCSD(T) and MP2 benchmark calculations as well as experimental photoelectron spectra, we have done systematic studies about the performance of various exchange-correlation functionals on atomic and molecular clusters, including boron clusters [1], copper and silver clusters, silicon clusters, water clusters [2], methane-water complex clusters [3], and protonated water clusters [4].

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Keywords: *cluster, benchmark calculation, exchange-correlation functional*

Alloying-Driven Phase Stability in Group-VB Transition Metals Under Compression

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Recently, measurements on vanadium raise some doubts about the conventional view of bonding that leads to high-symmetry crystal structures in the transitional metals. Namely, a low-symmetry rhombohedral phase (rh) was discovered around 60-70 GPa in synchrotron x-rays diffraction measurements [1]. It has been proposed that the intra-band Fermi surface (FS) nesting is responsible for this peculiar behavior [2]. The change in phase stability of group-VB (V, Nb, and Ta) transition metals due to pressure and alloying is explored by first-principles electronic-structure theory [2-4]. It is shown that under compression stabilization or destabilization of the ground-state body-centered-cubic (bcc) phase of the metal is mainly dictated by the band-structure energy that correlates well with the position of the Kohn anomaly in the transverse acoustic phonon mode [2,3]. The predicted position of the Kohn anomaly in V, Nb, and Ta is found to be in a good agreement with data from the inelastic x-ray or neutron-scattering measurements [4]. In the case of alloying the change in phase stability is defined by the interplay between the band-structure and Madelung energies. Alloying with a neighboring element to the left in the Periodic Table destabilizes the bcc phase while alloying with the neighbor to the right conversely stabilizes the bcc phase. When V is alloyed with neighbors of a higher (4*d*- or 5*d*-) transition series, both Madelung and band-structure energies stabilize the bcc phase. The opposite effect (destabilization) happens when Nb or Ta is alloyed with members of the 3*d*-transition series.

Even though the existence of the intra-band FS nesting in V is widely acknowledged, it has repeatedly been argued that elevated temperatures would remove the destabilization of the bcc phase and thus preventing the bcc → rh transformation. However, our investigation of V and V-Cr alloys at high temperatures and pressures [5] show that the pressure-induced mechanical instability of bcc V, which results in formation of the rh phase at room temperatures, will prevail significant heating and compression. Furthermore, alloying with Cr decreases the temperature at which stabilization of the bcc phase occurs at elevated pressure. The possibility of bcc → rh transformation in Nb under compression, when alloyed with Zr, is also discussed [6].

This work was performed under the auspices of the U.S. DOE by LLNL under contract No. DE-AC52-07NA27344.

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Keywords: *Phase transformation, high pressures, elevated temperatures, transition metals, alloys.*

Phase stability, elasticity, and phonons for plutonium from electronic-structure theory

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Abstract

We apply electronic-structure theory to compute phase stability, elasticity, and phonons for plutonium. The model accurately predicts this very broad range of properties for plutonium because the character of the 5f electrons is very well captured by itinerant (band like) states that are perturbed by spin and orbital interactions. The computed total energy is obviously quite accurate because otherwise phase stability, elastic constants, and lattice dynamics could not be computed realistically. This work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344.

Keywords: *Plutonium, electronic structure, density-functional theory*

Ab initio **calculation of spin lattice relaxation of** NV^- **centers in diamond**

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Abstract

The negatively charged nitrogen vacancy center NV^- is a very important colour center in diamond[1] with applications in magnetometry[2, 3], biolabelling[4], nano-sensing[5, 6] and it is a promising candidate for a solid state quantum bit[7]. Since the spin of the system is the carrier of information, a proper understanding of spin relaxation is of utmost importance. At low temperatures around the spin transition energy of this system $k_BT \approx \hbar\omega_s$ spin lattice relaxation times T_1 of up to 8h are measured by our experimentalists using a cavity QED protocol. These very low relaxation rates of the NV^- spins ask for a theoretical explanation.
We investigate on the fundamental mechanism of spin phonon coupling in this system in order to calculate the spin lattice relaxation time T_1 and its temperature dependence. Starting from the dipolar spin-spin interaction between two electrons, we couple the spins of the electron to the movements of the ions and end up with an effective spin-phonon interaction potential $V_{\mathrm{s-ph}}$ [8]. Taking this time dependent potential as a perturbation of the system leads to Fermi's golden rule for transition rates which allows to calculate the spin lattice relaxation time T_1. We simulate the color center with the Vienna *Ab Initio* Simulation Package (VASP) [9, 10] to extract the figures necessary to quantify T_1: First, we obtain the equilibrium positions of the ions and the electronic charge density by a proper relaxation of the system. Next, we investigate on the local phonon modes of the color center within the harmonic approximation using the small displacement method. We extract the phononic density of states and bandstructure by diagonalizing the dynamical matrix using the phononpy package[11]. Then, we model the electronic wavefunctions by calculating maximally localized Wannier functions with Wannier90[12] and building the orbitals according to the C_{3V} symmetry of the defect. Finally, we plug the simulated figures into our model and end up with three different types of first order processes for spin-phonon interaction in analogy with electron-photon interaction:

- An excitation of a spin is accompanied by the absorption of a phonon with the matching frequency of the spin transition.
- A deexcitation of a spin due to induced emission of a phonon.
- A temperature independent contribution where a spin relaxes spontaneously and a phonon is emitted.

To simulate the measured temperature dependence of T_1, an ensemble of spins decaying and getting reexcited due to coupling to the phonon bath has to be considered: Taking all these processes into account, the measured curves are quantitatively well described and we can clearly distinguish two regions of spin lattice relaxations in the system, depending on temperature: At temperatures above the spin transition energy ($k_BT > \hbar\omega_s$) the coupling to the thermal phonons is dominating the relaxation process while at temperatures below the spin transition the thermal phonons are frozen out and the only decay channel left is given by the temperature independent spontaneous emission of a phonon. A comparison with recent experimental data is presented.
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Keywords: NV *center, electron phonon interaction, spin lattice relaxation, spin dynamics*

Properties of electron density in weak binding conditions

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Abstract

When electrons are bounded by a weak external potential, the electronic density becomes smaller and smaller. In this regime, electron correlation becomes increasingly important. We analyze in details few relatively simple systems for which analytical or accurate numerical calculation can be performed. In particular we consider model atoms in which electrons are confined by a positive fractional charge [2, 4, 5, 6] or by a harmonic potential [1, 3]. In the first case we study the limit of the critical nuclear charge at which spontaneous ionization occurs and in the second case the limit of the so-called Wigner regime.

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Keywords: *Electron density, model atoms, weak trapping limit.*

The insight into the Dzyaloshinskii-Moriya interaction through first-principles study of chiral magnetic structures

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Abstract

The purpose of the work is to gain deeper insight into microscopic formation of the Dzyaloshinckii-Moriya interaction (DMI). The work aims at the development of the physical picture able to address apparently contradicting conclusions of recent studies concerning the location of the DMI energy in the real and reciprocal spaces as well as the relation between values of the atomic moments and the DMI strength. The main tool of our study is the first-principles calculations of the energies of the spiral magnetic states with opposite chiralities. We suggest a new method of the calculation of the spiral structures with account for the spin-orbit coupling (SOC). It is based on the application of the generalized Bloch theorem and generalized Bloch functions and allows to reduce the consideration of arbitrary incommensurate spiral to small chemical unit cell. For comparison, the supercell calculation with full account for the SOC is performed. The concrete calculations are performed for the Co/Pt bilayer. We consider the distribution of the DMI energy in both real and reciprocal spaces and the dependence of the DMI on the number of electrons. The results of the calculations reveal a number of energy compensations in the formation of the DMI. Thus the partial atomic contributions as functions of the spiral wave vector $\mathbf{q}$ are nonmonotonic and have strongly varying slopes. However, in the total DMI energy these atom-related features compensate each other resulting in a smooth $\mathbf{q}$-dependence. The reason for the peculiar form of the partial DMI contributions is $\mathbf{q}$-dependent difference in the charge distribution between $\mathbf{q}$ and $-\mathbf{q}$ spirals. Therefore the real-space distribution of the DMI energy between atomic spheres is not bearing deep physical insight into the microscopic nature of the DMI. The physical process of the DMI formation is connected with the difference in the hybridization of the Co and Pt states for $\mathbf{q}$ and $-\mathbf{q}$ spirals under the influence of the SOC and broken spatial inversion. It depends sensitively on details of the electronic structure. The calculations with constraints on the values of the Co and Pt atomic moments show that there is no direct relation between these atomic quantities and the DMI strength since the details of the electronic structure crucial for the DMI are not reflected in these integral characteristics. The application of the new method to the calculation of the magnon energies in systems with DMI is briefly addressed.

Keywords: *Dzyaloshinskii-Morya Interaction, spin-orbit coupling, chirality, relativistic spiral structures, anticrossings*

The power series representation of the Pauli kinetic energy functional, shell structure and the Sturm-Liouville problem

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Abstract

An approximate expression for the Pauli kinetic energy functional T_p is advanced in terms of the Liu-Parr expansion which involves a power series of the one-electron density. [1, 2] We use this explicit funtional for T_p to compute the value of the non-interacting kinetic energy functional T_s of 34 atoms, from Li to Kr (and their positive and negative mono-ions). In particular, we examine the effect of incorporating shell-inducing traits into this functionals. [3] This is done in the present case by carrying out a shell-by-shell mean-square optimization of the expansion coefficients. We explore the effect that the size of the expansion, given by the parameter n, has on the accuracy of the approximation for the non-interacting kinetic energy values. The results yield a mean absolute relative error $\Delta_{abs} = (1/N)\sum_{i=1}^{N}\Delta_i$ for 34 neutral atoms of 0.15, 0.08, 0.04, 0.03 and 0.01 for expansions with n=3, 4, 5, 6 and 7, respectively (where $\Delta_i = 100|T_s^{app}(i) - T_s^{HF}(i)|/T_s^{HF}(i)$). These results are the most accurate ones obtained to date for the representation of the non-interacting kinetic energy functional. Finally, we examine the relationship between shell structure and the Sturm-Liouville problem.

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Keywords: *Kinetic energy functional, Orbital-free molecular dynamics, Shell structure*

Axiomatically Derived Kinetic Energy Density Functionals

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Abstract

The main obstacle to implement the "pure" Hohenberg-Kohn density functional theory (HK-DFT) is the lack of accurate kinetic energy density functional (KEDF). This is why Kohn and Sham suggested an alternative scheme where the "orbitals" are reintroduced such that the kinetic energy is the kinetic energy of the introduced fictitious system. Recently, there has been a growing interest in developing KEDF for the original DFT. The subject is not; however, the existing KEDFs are far from being accurate. Most of the early proposed KEDF are based on special solvable models, e.g. constant potential with plane waves solution for Thomas-Fermi model or modified plane waves for von Weizsacker KEDF. That was followed by many extensions and further developments of "specific physical models" or using some abstract mathematical tools.

We revisited this from a different perspective [1]. Instead of starting from a specific physical model or using mathematical tools to improve KEDF, we started by asking what are the physically acceptable forms for KEDF. To answer this, an axiomatic approach is used to determine these physically acceptable KEDFs in D-dimension. In axiomatic approaches and in mathematical terms, a set of axioms are used in conjunction to derive equations, expressions, or theorems. The resulted expansion captures most of the known forms of one-point KEDFs. For $D=1$ case, the expansion coefficients are found statistically using the numerical solutions of a large number of potentials. An efficient spectral method is used with an accuracy of 10^{-12} for the exact noninteracting kinetic energy [2, 3].

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Keywords: *kinetic energy density, kinetic energy density functionals, orbital-free density functional theory.*

Ab initio investigation on high-entropy alloys

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Abstract

As compared to the conventional alloys, high-entropy alloys (HEAs) open a new path for developing and designing novel alloys. These multicomponent concentrated solid solutions have been found to possess interesting and tunable properties. Hence, HEAs offer potential applications in many fields. Many HEAs have been found to form single phase solid solutions within certain temperature range rather than complex structures with intermetallic compounds and multi-phases. The equiatomic CrMnFeCoNi alloy is often regarded as a model HEA. To achieve excellent structural materials, it is vital to optimize alloy components and their ratios. Using the exact muffin-tin orbitals (EMTO) method in combination with the coherent potential approximation (CPA), we systematically investigate the lattice stability, elastic properties, stacking fault energy of paramagnetic Al_xCrMnFeCoNi ($0 \leq x \leq 5$) high-entropy alloys considering the competing body-centered cubic (bcc) and face-centered cubic (fcc) crystal structures. The calculated lattice constants in both bcc and fcc phases strongly increase with increasing Al, in good agreement with experimental data. However, the predicted elastic parameters follow complex composition dependence. Upon Al addition, the crystal structure changes from fcc to bcc with a broad two-phase field region, agreeing well with the observations. Bain path calculations support that within the duplex region both phases are dynamically stable. The predicted stacking fault energies exhibit complicate concentration dependence.

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Keywords: *High-entropy alloys, Phase stability, elastic properties, Ab initio calculation*

Phase stability of CrCoNi ME alloys and CRSS for twinning nucleation in CrCoNi M-HE alloys

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Abstract

CrCoNi medium entropy(ME) alloy has drawn much attention due to its exceptional mechanical properties. However the phase stability at finite temperatures is still unclear. The EMTO-CPA method with magnetic spin fluctuation has been applied to calculate the ground state properties and free energies at temperatures from 100 $\sim$ 1200K. The critical temperature of phase transition from fcc to hcp is estimated and the contributions from magnetic and vibrational entropies to free energies are discussed. Using the improved twinning nucleation model based on the classic Peierls-Nabarro formalism, the critical resolved shear stress(CRSS)es of CrCoNi-based medium and high entropy(M-HE) alloys are predicted at cryogenic temperatures. The calculated results agree very well with the experimental results and the model used in this work could be useful for designing the new M-HE alloys.

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Keywords: *medium entropy(ME) alloy, high entropy(HE) alloy, phase stability, critical resolved shear stress(CRSS), twinning nucleation model*

Tuning the plasticity of Ni-Mo solid solution in Ni-based superalloys by ab initio calculations

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Abstract

The generalized stacking fault energies of face centered cubic Ni-Mo solid solutions are calculated using the exact muffin-tin orbital method in combination with coherent potential approximation at 0K and high temperature. The alloying of Mo in Ni is found to decrease the intrinsic stacking fault energy of the solid solution from 150 mJ/m^2 (pure Ni) to 50 mJ/m^2 (17.5 at. % Mo) almost linearly at 0K. At the same time, the unstable stacking fault energy (the unstable twin fault energy) of the Ni-based solid solution increases (decreases) in a small extent with increasing Mo concentration. Three different twinnability measures are adopted and all indicate a substantially enhanced twinning mechanism in Ni-Mo solid solutions with increasing concentration of Mo. The weaker Ni-Ni bonding at high Mo concentrations is considered to be the main mechanism behind the disclosed phenomena. Segregation of Mo to the fault plane is proved to have strong effect on the generalized stacking fault energy of Ni-based solid solution. Moreover, the generalized stacking fault energy of Ni-5.at%Mo decreases with increasing temperature and makes its twinnability increase as a result. However, temperature has few effect on the variation law in the generalized stacking fault energy of Ni-Mo with increasing concentration of Mo. The magnetic transformation at high temperature has enhanced contribution to the intrinsic stacking fault energy of Ni-Mo with increasing temperature, but has limit influence on the twinnability especially with higher Mo concentration. The results obtained in the present study shed light on the solid solution strengthening mechanism in γ matrix via the plasticity tuning by Mo, and establish theoretical foundation on the novel materials design of Ni-based single-crystal superalloys.

Keywords: *Superalloys, Solid solution, Stacking fault energy, Twinning, Ab initio calculations*

First-principles study of the structural and elastic properties of $\mathrm{Au}_x\mathrm{V}_{1-x}$ and $\mathrm{Au}_x\mathrm{Nb}_{1-x}$ alloys

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Abstract

Ab initio total energy calculations, based on the Exact Muffin-Tin Orbitals (EMTO) method in combination with the coherent potential approximation (CPA), are used to calculate the total energy of $\mathrm{Au}_x\mathrm{V}_{1-x}$ and $\mathrm{Au}_x\mathrm{Nb}_{1-x}$ random alloys along the Bain path that connects the body-centered cubic (bcc) and face-centered cubic (fcc) structures as a function of composition x ($0 \leq x \leq 1$). The equilibrium Wigner-Seitz radius and the elastic properties of both systems are determined as a function of composition. Our theoretical prediction in case of pure elements ($x = 0$ or $x = 1$) are in good agreement with the available experimental data. For the Au-V system, the equilibrium Wigner-Seitz radius increase as x increases, while for the Au-Nb system, the equilibrium Wigner-Seitz radius is almost constant. The bulk modulus B and C_{44} for both alloys exhibit nearly parabolic trend. On the other hand, the tetragonal shear elastic constant C' decreases as x increases and correlates reasonably well with the structural energy difference between fcc and bcc structures. Our results offer a consistent starting point for further theoretical and experimental studies of the elastic and micromechanical properties of Au-V and Au-Nb systems.

Keywords: *The Bain path, The Exact Muffin-Tin Orbitals (EMTO) method, Au-V alloys, Au-Nb alloys, Transition metals, Elastic properties, Structural properties.*

Existence of Topological Nontrivial Surface States in Strained Transition Metals: W, Ta, Mo, and Nb

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Abstract

We show that a series of transition metals, direct neighbors in the periodic table, with strained body-centered cubic lattice -W, Ta, Nb, and Mo - exhibit a very similar electronic structure and hosts surface states that are topologically protected by mirror symmetry and, thus, exhibits nonzero topological invariants. These findings, reported in Ref.[1], extend the class of topologically nontrivial systems by topological crystalline transition metals. The investigation is based on calculations of the electronic structures and of topological invariants. The signatures of a Dirac-type surface state in W(110), e. g., the linear dispersion and the spin texture, are verified. To further support our prediction, we investigate Ta(110) both theoretically and experimentally by spin- and angle-resolved inverse photoemission: compared with tungsten, however, the bands of tantalum are less occupied due to the lack of one electron and, as such, also topologically nontrivial surface states. As a consequence, an exceptional Dirac-cone-like surface state, observed below the Fermi level for W(110), appear above the Fermi level for Ta(110).

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Keywords: *Semi-metal, surface states, topology*

FeO_2: a possible novel magnetic constituent of Earth's lower mantle

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Abstract

The recent discovery [1] of FeO_2, which can be an important ingredient of the Earths lower mantle and which in particular may serve as an extra source of oxygen and water at the Earths surface and atmosphere, opens new perspectives for geophysics and geochemistry, but this is also an extremely interesting material from physical point of view. We found that in contrast to naive expectations, its properties are very different from the well-known pyrite FeS_2. FeO_2 turned out to be metallic with Fe ions nearly 3+, while FeS_2 is an insulator with Fe ions having 2+ oxidation state. Moreover, while FeS_2 is diamagnetic, FeO_2 is magnetic, with nontrivial temperature dependence of the magnetic susceptibility[2]. Doping, which is most likely to occur in the Earth's mantle, makes FeO_2 much more magnetic. The fact that FeO_2 lies "in between" the usual dioxides and peroxides makes it also an extremely interesting material for physics and solid state chemistry.

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Keywords: *DFT, Iron oxides, high pressure*

First-principles studies of plutonium oxides and their surface interaction with gaseous molecules

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Abstract: Plutonium is very easy to react with oxygen in the environment to form surface oxides, such as PuO_2 and Pu_2O_3, due to its strong chemical activities. It is a crucial research goal in the plutonium community to fully understand the characteristics of these surface plutonium oxides by studying the competitive diversity in $5f$ orbitals, such as delocalization/localization, spin-orbit coupling, directionality and anisotropy in chemical bonding. We have carried out systemic first-principles calculations to study the plutonium oxides and their surface interaction with gaseous molecules. Our research progress, which can be summarized as follows: (1) The electronic structure, mechanical, and thermodynamic properties of the plutonium oxides have been studied by DFT+U theory. By comparing with the ground-state electronic structures of a series of actinide oxides, it is found that the covalent Pu-O, U-O, and Np-O bonds are all stronger than that of Th-O one, i.e., the ionicity in the Th-O bond is strongest in these difference actinide oxides. (2) The dielectric function and optical properties of PuO_2 and α-Pu_2O_3 have been calculated and compared with each other by using the linear-response theory in the framework of DFT+U. The results provide a useful optical criterion to distinguish different plutonium oxides. (3) We have obtained the DFT+U phonon dispersions of PuO_2 and α-Pu_2O_3. Prominently, our predicted phonon dispersion of PuO_2 was subsequently confirmed by inelastic X-ray scattering measurement from Lawrence Livermore National Laboratory and the Argonne National Laboratory. (4) We have studied the thermodynamic equilibrium and oxidation–reduction transformation between PuO_2 and α-Pu_2O_3. The obtained spontaneous reduction conditions of $PuO_2 \rightarrow \alpha$-Pu_2O_3 are in good agreement with the experiments. (5) The point defects and helium diffusion behavior in PuO_2 have been investigated from first principles. It is revealed that the most stable dissolved sites in PuO_2 are linked to the concentration of oxygen vacancies. Helium atoms tend to occupy the octahedral interstitial sites and oxygen vacancies in intrinsic and oxygen-vacancy pre-existing PuO_2 systems, respectively. (6) Our first-principles molecular dynamic simulations based on DFT+U+vdW approach show that it is difficult for H_2 to get close to the PuO_2 surface directly. However, H_2 can penetrate into the α-Pu_2O_3 layer and then reach the plutonium layer while still keeping its molecular state. This theoretical result supports the experimental observation that α-Pu_2O_3 can accelerate the hydrogenation of plutonium with respect to PuO_2. (7) PuO_2(111) has been found to be the most stable surface, while for PuO_2(001), there is a prominent surface reconstruction. (8) The interactions between H_2O molecules and plutonium oxide surfaces have been largely clarified by our most recent first-principles studies. (9) The temperature-dependent diffusion coefficients of oxygen defects in plutonium oxides have been theoretically predicted.

Adsorption, dissociation and diffusion of hydrogen on PuO_2 (110) surface: A DFT study

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Abstract
The adsorption, dissociation and diffusion of hydrogen on PuO_2 (110) surface have been investigated by density functional theory corrected for onsite Coulombic interactions (GGA+U). In order to find out the energetically more favorable adsorption site, optimum dissociation and diffusion path, adsorption energy of hydrogen on various sites, the dissociation and diffusion energy barrier are derived and compared. The results show that H_2 molecules are weakly adsorbed on PuO_2 (110) surface, while H atoms are strongly bonded at the top of O atom sites. One possible dissociation pathway of H_2 molecule is investigated using the climbing nudged-elastic-band (cNEB) approach. The calculated barriers show that the dissociation of H_2 molecule on PuO_2 (110) surface is kinetically the most favorable and can occur even below room temperature. We have identified two diffusion mechanisms, leading to migration of atomic H on the surface and diffusion from surface to subsurface. The results indicate that it is energetically more favorable for H atom to be on the surface. Hydrogen permeation through purity PuO_2 surface is mainly inhibited from hydrogen atom diffusion from surface to subsurface.

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Keywords: *PuO_2 (110) surface, Hydrogen, GGA+U, cNEB*

Structural and electronic properties of U_nO_m (n=1-3,m=1-3n) clusters: A theoretical study using screened hybrid density functional theory

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Abstract: The structural and electronic properties of small uranium oxide clusters U_nO_m (n=1-3, m=1-3n) are systematically studied within the screened hybrid density functional theory. It is found that the formation of U–O–U bondings and isolated U–O bonds are energetically more stable than U–U bondings. As a result, no uranium cores are observed. Through fragmentation studies, we find that the U_nO_m clusters with the m/n ratio between 2 and 2.5 are very stable, hinting that UO_{2+x} hyperoxides are energetically stable. Electronically, we find that the O-2p states always distribute in the deep energy range, and the U-5f states always distribute at the two sides of the Fermi level. The U-6d states mainly hybridize with the U-5f states in U-rich clusters, while hybridizing with O-2p states in O-rich clusters. Our work is the first one on the screened hybrid density functional theory level studying the atomic and electronic properties of the actinide oxide clusters.

Orbital-free density-functional theory models for radiation damage in Al

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Abstract

Traditionally radiation damage is modeled by classical molecular dynamics simulation [1] and the electronic effect are often neglected or treated implicitly. Current treatments to allow explicit incorporation of quantum mechanical electrons into atomistic models are restricted to small systems or model metals [2]. Here using large-scale orbital-free density-functional theory (OF DFT) [3] simulation of radiation damage in Al, we directly investigate the time evolution of charge density, the electronic damping effect, and the energy exchange between ions and electrons. At first, the formation and migration energies for various point defects are systematically calculated using OF DFT to validate this method as an accurate technique [4]. Furthermore, displacement threshold energies are determined along $\langle 100\rangle \rightarrow \langle 110\rangle \rightarrow \langle 111\rangle \rightarrow \langle 001\rangle$ directions. Two pockets of low threshold energy are found around $\langle 100\rangle$ and $\langle 110\rangle$, which is consistent with the experiment [5]. Finally, simulations of displacement cascades with primary knock-on atom energy up to 1 keV are performed using a supercell of 32000 atoms. Compared to the classical molecular dynamics simulations, the displacement spike from OF DFT simulation has a lower peak and shorter duration time, which is attributed to the electronic damping. The charge density profiles clearly display the existence of depleted zones, vacancy and interstitial clusters. And it is found that the energy exchanges between ions and electrons are mainly contributed by the kinetic energies.

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Keywords: *radiation damage, orbital-free density-functional theory, threshold energy, displacement cascade, electronic effects*

First principle molecular dynamics studies of warm dense matter

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Abstract

Thermodynamic properties of materials under warm dense conditions are of crucial importance in condensed matter physics, plasma physics, astrophysics, and inertial confinement fuions etc. Warm dense matters are characterized by strong ionic coupling and partially degenerated electronic states, and the relative experimental detections and theoretical modelings are still full of challenges. In the present work, we have demonstrated a self consistant method based on density functional theorey to investigate the thermodynamic properties of high energy density matters. Including: i) Wide range equation of state, and transprot coefficients for hydrogen and ite isotopes have been built and applied to hydrodynamic simulations in inertial confinement fusion; ii) The phase transition and Hugoniot of CH, NH, CO, NO materials under extreme condition are studied; iii) The physical properties of metals (Be and Fe) from expanded to highly compressed regime are discussed.

Keywords:*First principles; equation of states; transport properties*

First-principles Stopping Power in Warm Dense Matter

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Abstract

Recent experimental advances enabled the precise measurement of the stopping power of fusion products in warm dense matter. We assess the ability of real-time time-dependent density functional theory to reproduce these results. Our approach facilitates the prediction of the stopping power in future experiments from first principles and advances our empirical and phenomenological understanding of transport properties in this technologically challenging thermodynamic regime.

Keywords: *warm dense matter, stopping power, density functional theory, time-dependent density functional theory, coupled nuclear-electron dynamics*

Computational Insights into Reactivity of the Supported CrO_x/SiO_2 (Phillips) Catalyst Towards Ethylene

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Abstract

Since the discovery of the Phillips (CrO_x/SiO_2) catalyst activity in ethylene polymerization in early 1960s, many efforts have been made to establish a mechanism of this reaction and the structure of the active sites. Nevertheless, these issues remain unknown [1, 2].

In this work, based on DFT calculations and using cluster models of silica, we aim to unravel these mysteries by proposing a possible mechanism of ethylene polymerization over the Phillips catalyst. Geometry optimization of the models were performed using the PBE0 functional combined with the def2-SVP basis sets. Harmonic vibrational frequencies were calculated to confirm local minimum or transition state, and to compute thermodynamic quantities. To account for adequate description of energy of the system studied, further single point calculations were performed employing the PBE0-D3(BJ) method and the def2-TZVPP basis stets. The choice of this computational methodology was validated by test calculations.

Having calculated many potentially possible reaction pathways, including various oxidation states of Cr and geometries of the oxide precursors, we were finally able to conclude that hydroxylated Cr(III) oxide species should generate active sites the most efficiently [3, 4]. Such a structure was not postulated so far. Other mechanisms proposed in the literature were found to be kinetically less accessible. Additionally, surface defects might play a role in a transformation of the Cr(II) species to active Cr(III) sites. The former dominates at the surface of activated/reduced catalyst [1, 2, 5]. The results of our calculations are consistent with the experimental data [3].

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Keywords: *chromium, silica, modelling, Phillips catalyst, DFT, pathway, kinetics*

A DFT Study on the Preferred Hydrogen Atom Transfer Pathway for the Reaction between Diethylthiourea and •OH

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Abstract

Thiourea and its derivatives, such as diethylthiourea (DETU), are known to act as specific OH radical scavengers [1,2]. In this work, the hydrogen atom transfer mechanism for the DETU + •OH reaction has been investigated *in vacuo* and in water solution to elucidate the •OH scavenging ability by DETU. The two pathways through which the reaction could take place (i.e., the direct H atom transfer and the •OH addition) have been analysed and compared with available literature. The objectives of the work have been to elucidate the nature of the reaction species as well as to characterise them in respect to their energetic, geometric, electronic and kinetics properties. The study has been performed with the DFT/ωB97X–D, DFT/BHHLYP and the DFT/M06–2X methods, using the 6-311++G(3df,2p) basis set. Atom in Molecule scheme has also been utilised to analyse the geometric and electron features of the reaction species. The results of the study suggest that the direct H atom abstraction mechanism and the water elimination step in the •OH addition mechanism involve simultaneous N–H bond breaking and O–H bond formation. The direct H atom transfer pathway is kinetically preferred to the •OH addition reaction pathway, both *in vacuo* and in aqueous solution. The activation energy is dependent on the media; it is higher in water solution than *in vacuo*. The estimated rate constant for the direct H atom transfer mechanism [3], is similar among the methods and consistent with experimental findings [4]. The spin density on the thiyl radical is mainly delocalized through the S-C-N region; this result is also in agreement with experimental findings [4]. The N–H bond dissociation enthalpy value is better estimated using DFT/ωB97X–D and suggests that it is minimally influenced by the media. A comparison of the N–H bond dissociation enthalpy with the O–H bond dissociation enthalpy found in most phenol derivatives suggests that phenolic derivatives are better radical scavenger than thiourea derivatives

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Keywords: *Thiyl species, Spin density distribution, Reaction rate constant*

Transesterification mechanism in alkyl *hydrogeno*-phenylphosphinates

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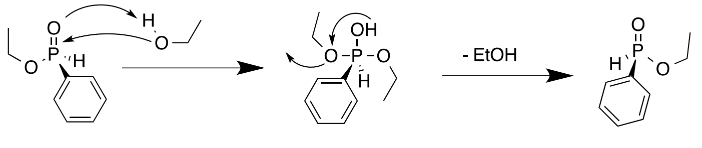
Abstract

The enantioselective synthesis of P-stereogenic alkylphenylphosphine oxides from chiral alkyl phenylphosphinates (APP) by Buono et *al.* have shown a clear dependency of the final enantiomeric excess upon the alkyl group beard by the APP. [1] It has then been postulated that the alcohol molecules freed during the synthesis are responsible for this dependency. The postulated mechanism would then consist in a transesterification of the APP with inversion of configuration.

Using DFT (SMD//M06-2X/6-31++G**), we determined the dominant mechanism out of 24 possible approaches between the reactants. It proceeds through a syn-addition of the alcohol on the P=O bond leading to a pentavalent phosphorus intermediate **2** in which both alkoxy groups occupy the apical positions. This intermediate can subsequently evolve backwards or forwards, leading, in this last case, to an inversion of the initial configuration of the APP. Additionally, the pentavalent intermediate can also undergo 15 pseudorotations [2] which have all been systematically investigated and have been shown to be competitive with the alkoxy elimination mechanism.



(R_p)-**1** **2** (S_p)-**1**

Finally, experimental kinetic studies were performed on ethyl phenylphosphinate using chiral HPLC that exhibited a 1st order reaction rate with a 135 kJ/mol transition standard Gibbs free energy. From the very good agreement with DFT simulations (136 kJ/mol), we conclude that the proposed transesterification mechanism is fully compatible with the experiment.

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Keywords: *phosphorus, phosphinate, phosphine oxide, nucleophilic substitution, kinetic, mechanism*

Design of Flexible Anodes for Lithium-Ion Batteries using vdW Heterostructures

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Abstract

The idea of forming van der Waals (vdW) heterostructures by integrating various two-dimensional materials breaks the limitation of the restricted properties of single material systems. The electronic structure modulation, stability, entire stress response and the Li adsorption properties of heterostructures by combining blue phosphorene (BlueP) and MS_2 (M = Nb, Ta) together were systematically investigated using first-principles calculations based on vdW corrected density functional theory. We revealed that BlueP/MS_2 vdW heterostructures possess good structural stability with negative formation energy, enhanced electrical conductivity, improved mechanical flexibility (ultimate strain >17%) and high-capacity (528.257 $mAhg^{-1}$ for BlueP/NbS_2). The results suggest that BlueP/NbS_2 and BlueP/TaS_2 heterostructures are ideal candidates used as promising flexible electrode for high recycling rate and portable lithium-ion batteries, which satisfy the requirement of next-generation flexible energy storage and conversion devices.

Moreover, an unexpected isotropic vdW heterostructure was theoretically proposed by assembling the two dimension crystals of anisotropic black phosphorene (BP) and transition metal carbide TiC_2 together. Good structural and mechanical stability, superior electrical conductivity, omnidirectional flexibility, and high Li storage capacity of the BP/TiC_2 vdW heterostructure were predicted based on the vdW corrected density functional theory. We have unraveled the physical origin of the good stability as well as the adsorption preference ranking of the lithiated heterostructure based on the three-step analysis of the stability of the Li adsorbed processes. Meanwhile, the BP/TiC_2 vdW heterostructure can be applied as the anode material for flexible Na-ion batteries due to the high Na storage capacity and strong Na binding. Compared with Na adsorption, the capacity is higher and the adsorption energy is more negative for Li adsorption. Our findings provide valuable insights into exploring a rich variety of vdW heterostructures for next-generation flexible energy storage devices.

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Keywords: *van der Waals heterostructures; two-dimensional materials; phosphorene; flexible anodes; lithium-ion batteries.*

Practical hints on the selection of functionals for optical band shapes simulations: BF_2-carrying compounds as test cases

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A reliable computational protocol for the simulations of electronic one- or two-photon absorption spectra of molecules in solution should be capable of reproducing positions, intensities and shapes of bands. During the last two decades, efficient computational approaches to predicting vibrationally-resolved optical spectra have been developed by various groups. In order to assure computational feasibility, it is a common practice to employ TD-DFT to simulate absorption/emission band shapes in the spectra of medium-sized molecules in solution. However, the accuracy of simulated spectra is strongly dependent on the choice of approximate exchange-correlation functional. The aim of the presentation is to assess the performances of functionals for predicting the vibrationally-resolved absorption spectra from a different viewpoint. It will be shown that the vibrational reorganization energy, a quantity closely related to the band shape through the normal mode frequencies and the displacements, can be successfully used for quantitative assessment of functionals. The results of simulations of vibrationally-resolved spectra will be presented for a large family of highly fluorescent BF_2-carrying compounds.

Photocatalytic power of graphitic carbon nitride from first-principles theory: band alignment, excitonic effects and dispersive interactions

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Abstract

Solar-based production of organic fuels (e.g. methanol) through the reduction of carbon dioxide (CO_2) had attracted great attention in the last decades. One of the challenges is to find Earth abundant materials that meet at the same time the properties of efficient sunlight absorption and suitable band edge potentials, facilitating photon-driven charge transfer reactions. In this work, we have employed quasi-particle theory and time-dependent density functional theory to achieve fundamental understanding of the electronic structure and optical properties of C_3N_4 in the graphitic structures (g-h-triazine and g-h-heptazine). The aim is to assess the photocatalytic power of these compounds and establish structure-properties relationships. The calculations have been carried out within the framework of semilocal and van der Waals (vdW) exchange-correlation functionals for DFT. The quasi-particle energies were calculated by the non-self-consistent GW approximation. Our results show that graphitic g-h-triazine displays the band edge potentials at suitable positions for direct CO_2 reduction to formic acid with a catalytic power of about 1 eV. These results provide the basis for further improvement of the materials properties for application as suitable photocatalyst. The optical properties is further investigated through Bethe-Salpeter equation and time dependent DFT with focus on the dimensionality dependence of excitonic effects.

Keywords: *solar energy conversion, photocatalysis, optical properties, DFT*

A non-empirical calculation of 2*p* core-electron excitation by Ligand-Field and Density Functional Theory (LFDFT)

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Abstract

Progress in the development of the Ligand-Field Density Functional Theory (LFDFT) program [1] will be presented. This theoretical method allows the calculation of multiplet energy levels, which belong to a multiple-open-shell electron configuration in compounds with metal transition or lanthanide or actinide ions. Special attention will be paid to the interpretation of experimental X-ray Absorption spectra in terms of multiplet structures. Methodological advents will be presented in relation with the non-empirical parameterization of the effective ligand-field Hamiltonian by means of DFT, [2] and calculation of the oscillator strengths (intensities) of the electronic transitions within the electric-dipole moment approximation. [3] Two examples for applications will be discussed, in the context of 2*p* core-electron excitation mechanisms. First in metal transition compounds, detailed theoretical modeling of the $2p^5 3d^{n+1}$ multiplets, with n = 0, 1, … and 9, will be performed. The influence of the multipet energy levels and oscillator strengths of the $3d^n \rightarrow 2p^5 3d^{n+1}$ transitions on to the spectral shape will be shown. Comparison with available experimental data will be realized, revealing *in fine* the advantages and limitations of the LFDFT program in terms of the predictive power and performance. Second, a project particularly dedicated to nuclear materials [4] will be presented. The theoretical model will be extended, because the challenging aspect of this project is the explicit treatment of a ligand-field problem with three non-equivalent electrons: $2p^5 5f^2 6d^1$. The measured spectra of uranium L_3-edge X-ray absorption of nuclear UO_2 fuel both in the fresh and in irradiated samples will be characterized. In the results, [5] the impact of the ligand-field splitting of the uranium 6*d* orbitals on the absorption edge will be discussed; and the weak contribution of the $5f^2$ electrons will be shown.

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Keywords: *LFDFT, ligand-field theory, multiple-open-shell electron configuration, multiplet structure*

Computational-chemistry modelling of surface reactions and CVD growth

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Abstract

Modelling of chemical processes at surfaces using computational-chemistry tools can elucidate the molecular mechanisms at the detailed atomistic level. Examples of such tools are quantum-chemical calculations, molecular dynamics simulations, thermodynamic equilibria deductions and kinetics computations. In this presentation examples of our ongoing theoretical studies on surface reactions are given, namely sensing of ammonia by ruthenium dioxide-based [1-2] chemical sensors [3-4], conversion of carbon dioxide to methanol by heterogeneous catalysis using metal/metal oxide nanoparticle catalysts [5], and surface reaction mechanisms during chemical vapor deposition [6-10].

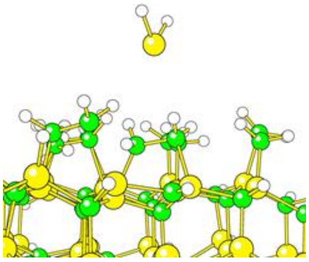

Figure 1. Modelling of an intermediate reaction step in the CVD growth process; a SiH_2 molecule interacting with a C_2H_4-captioned SiC surface.

In these studies the surface reactions have been modelled first using quantum-chemical first-principles computations, and then from these results the thermodynamic equilibrium distributions at the surfaces have been inferred and also the kinetic reaction rates and the concentrations as functions of time have been calculated. This procedure enables multi-scale models to be derived.

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Keywords: *DFT, surface reactions, chemical sensors, heterogeneous catalysis, CVD*

Interrogating the "B05" density functional for non-locality information.

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Abstract

In two papers[1, 2], Becke introduced Kohn-Sham density-functional approximations for static and dynamic correlation to be partnered with 100 percent exactly-computed exchange. Known as "B05", this was the first non-local correlation model designed to work with the full non-locality of exact (or Hartree-Fock) exchange. Non-locality issues, often referred to as the "delocalization" problem, have emerged as one of the most vexing problems in DFT today. Questions such as... how much exact exchange should be used in a hybrid functional, or... what value of the range parameter should be used in a long-range corrected functional, abound, and the answers are system dependent. The physics of non-locality is built into the B05 functional in a natural way and one wonders, therefore, if B05 might provide a mechanism to answer such questions. We are exploring a procedure, "B05min", to do this.

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Keywords: *B05, Exact-exchange, non-local*

Analytically inverted non-additive kinetic potential functional at small density overlaps

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In density-dependent embedding methods [1], non-additive kinetic potential plays an important role. This functional is a bi-functional depending on a pair of electron densities ρ_A and ρ_B. We report here the first time use of the numerical inversion procedure to generate reference non-additive kinetic potentials for weakly overlapping ρ_A and ρ_B. To obtain exact quantity of non-additive kinetic potential, analytically inverted procedure is proposed [2].

It is especially suited for small overlap cases and it is applicable only for a special case of ρ_A being a two-electron density. The procedure requires particular constraint on the choice of pair of electron densities to assure their admissibility as well as the smallness of the overlap between ρ_A and ρ_B. The constraint is applied over total density to provide the pair of electron densities. Mathematical challenge of this preparation and the accuracy of the pair electron densities will be presented in detail. All reported results are obtained using basis set free numerical solver of Kohn-Sham equation for diatomic systems [3].
The non-additive kinetic potential at small overlap is constructed for different systems of four electrons ($LiHe^+$, $BeHe^{2+}$, LiH and BeH^+). The exact potential was calculated for a chosen four electron system changing interatomic distance.

For all investigated systems , the non-additive kinetic potentials derived by means of the proposed analytical inversion method was compared to the potential obtained using the common approximations to the density functional of the kinetic energy.
We showed that exact potential is smooth in overlap region for all system and a system with different interatomic distances.

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Keywords: *non-additive kinetic potential, embedded density, analytical inversion*

On the transferability of a parametrized kinetic functional for orbital-free density functional theory calculations

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Abstract

Because of issues with accuracy and transferability of existing orbital-free (OF) density functionals, OF functional development remains an active research area. Due to numerical difficulties, all-electron self-consistent assessment of OF functionals is limited. Using the projector augmented wave method we compute OFDFT all-electron values [1] and we evaluate the performance of a parametrized OF functional for atoms and molecules. We combine the parametrized Thomas-Fermi-Weizsäcker (TF-W) kinetic model λ and γ for the fractions of Weizsäcker and TF functionals, respectively, with LDA for atoms [2]. We found that one-to-one relation between λ and γ values defines a region in parameter space that allows the atomic energies and eigenvalues to be approximated with a small average error with respect to the Kohn-Sham values. The optimum values is however different for every property and for every atom. Recently, these results have been combined to test parameter transferability from atoms to molecules and we expect will help for further systematic improvement of OF density functionals.

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Keywords: *Orbital-Free Density Functional Theory, Projector Augmented Wave method, Thomas-Fermi-Weizsäcker kinetic model*

Systems with disorder, interactions, and out of equilibrium: The exact independent-particle picture from density functional theory

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Abstract

The formalism of density-functional theory almost exclusively makes use of the concept of an auxiliary independent-particle system that reproduces exact quantities of the original interacting system. We use this construction to access the exact effective potential and effective bias of non-equilibrium systems with disorder and interactions. We propose that this effective potential non-ambiguously defines the screening of disorder due to interaction effects.
We find that interactions always smoothen the effective disordered landscape. The interactions do not, however, always lead to an increase of the current. Our construction leads to an interpretation of this behavior as a competition between the increased disorder screening and the reduced effective bias.
Our results put forward density-functional theory as a diagnostic tool to study disorder screening in a wide class of interacting disordered systems.

Keywords: *density-functional theory, disorder, interactions, quantum transport*

Development and application of theoretical models for the characterization of complex reactions.

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Abstract

The understanding of complex chemical reactions of value in organic chemistry and biology is a challenging research field, especially when the interaction with light is involved. Indeed, the understanding of elementary steps (which can involve ground and excited states species) ruling reaction's key-factors continues to challenge our understanding.

In this scenario, the theoretical modeling supported by suitable computations represents both an interpretative and, even more importantly, a predictive tool. Indeed, it is possible to partition the complex reaction in single steps such as excitation, rearrangement of the nuclear structure, electronic density reorganization and in case, de-activation.

The adoption of quantum mechanical methods based on Density Functional Theory (DFT) or on its Time-Dependent variant (TDDFT) provides a powerful tool to model these reaction's key factors.

In this presentation some case studies[1,2,3] will be introduced and it will be shown the importance of insights gained by the adoption of DFT and TDDFT methods for the modeling of ground and excited state reactions.

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Keywords: *DFT, TDDFT, excited state reactivity.*

The new GMTKN55 database: comprehensive and state of the art benchmarking of various density functional methods including newly developed robust "high-speed" approaches

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Abstract

A thorough benchmark study of various density functionals is presented with the new **GMTKN55**[1] database for energies of general main group thermochemistry, kinetics and noncovalent interactions. It is an extension and revision of the widely used GMTNK30 database[2] including newly developed sets and state of the art reference values. The general aim of the study is to work out which functionals are robust and generally well applicable to describe the energies of molecules. Moreover, the classification of density functionals according to Perdews' metaphoric picture of Jacob's Ladder will be discussed and compared with the density functional theory (DFT) poll.

Futhermore, a DFT based composite electronic structure approach is presented to efficiently compute structures *and* interaction energies of extended chemical systems with several hundreds of atoms. It is based on the well-known and numerically robust Becke97 generalized-gradient-approximation and the orbitals are expanded in stripped-down and re-optimized Ahlrichs-type valence-triple ζ atomic orbital (AO) Gaussian basis sets, which are available for many elements. In order to account for the important long-range London dispersion effects, our well-established atom-pairwise potentials are used. Together with the recently proposed three-fold corrected (3c) Hartree-Fock (HF-3c[3]) and global hybrid (PBEh-3c[4]) methods, the new composite scheme (termed **B97-3c**[5]) represents the next member in a hierarchy of "low-cost" electronic structure approaches. They are mainly free of BSSE and account for most interactions in a physically sound and asymptotically correct manner and can be efficiently applied to condensed phase problems. Their performance for the extensive GMTKN55 energy database is discussed as well as for a newly developed large benchmark set (**MOR**[6]) of metal-organic reactions.

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Keywords: *density functional theory, benchmark, GMTKN55, B97-3c, metal-organic reactions*

Semiclassical atom theory applied to solid-state physics

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Abstract

Using the semiclassical neutral atom theory [1], we have extended to fourth order the modified gradient expansion of the exchange energy of density functional theory. This expansion can be applied both to large atoms and solid-state problems. Moreover, we have showed that it can be employed to construct a simple and nonempirical generalized gradient approximation (GGA) exchange-correlation functional competitive with state-of-the-art GGAs for solids, but also reasonably accurate for large atoms and ordinary chemistry [2].
This functional has been named SG4 GGA (a.i. the semiclassical GGA at fourth order). We have also constructed a van der Waals functional for solids, by adding the rVV10 non-local correlation [3] to the SG4 GGA functional. The resulting functional can well describe various interactions in solids, including dispersion and Hydrogen bonding present in layered materials [4, 5] and molecular crystals [6].

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Keywords: *gradient expansion, GGA for solids*

Electronic Localization in Semiconductor Alloys

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Abstract

Mixing of semiconductors enables tuning of their optical properties, lattice parameters (epitaxial strain), and transport characteristics to the desired application. Alloying elements perturb the electronic structure of the host material that may introduce traps, which can detrimentally affect the performance of devices, which should be taken into account when selecting alloying elements. Objective of this work is to propose a quantitative approach to characterization of spatial localization for electronic eigenstates.

One of the main challenges in the interpretation of supercell electronic structure calculations is to recover the Bloch character of electronic eigenstates perturbed by the disorder. It is possible to overcome this challenge by analysis of plane waves, which is a popular choice for the basis set in *ab initio* calculations of solids [1, 2]. A spectrally-resolved wavefunction participation ratio calculated for individual eigenstates complements the analysis of a localization spectrum and measure of its extremity [3, 4].

These techniques are applied to a range of compound semiconductors including hybrid perovskites for solar cells, group-IV thermoelectric alloys, dilute bismides as a gain medium for telecommunication lasers. The analysis reveals perturbations of the host band structure and signatures of localization, which can be directly linked to optical/transport characteristics of the alloy, and compared with experimental data on broadening of the photoluminescence spectrum and charge carrier mobilities of semiconductor alloys.

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Keywords: *Semiconductor alloys, compositional disorder, spatial electron localization, inverse participation ratio, effective band structure*

Defect chemistry and size effects in $SrRuO_3$

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Abstract

The metal-insulator transition in strontium ruthenate ($SrRuO_3$) is an unsolved issue of great relevance.

Indeed, SrRuO3 is one of the oxide materials with the highest conductivity and it is widely used in applications such as electrodes of capacitors. In addition, it is ferromagnetic, it has low intrinsic disorder and its epitaxial growth is well understood. It is thus a good candidate for applications in spintronics where realizing a two-dimensional spin-polarized conducting system is a long-standing goal. Some investigations in the behavior of ultrathin SrRuO3, however, have revealed an insulating state for film thicknesses of fewer than three unit cells[1]. These findings are however not unanimous, and single-layer conductive SRO might be experimentally possible[2].

We investigate by means of DFT+U structural phenomena which could occur in the crystal deposition of $SrRuO_3$ and lead to an insulating state. In particular, we focus on the influence of single point defects and defect dipoles on the electronic structure of an $SrRuO_3$ thin film and we investigate changes in octahedral distortions and lattice tetragonality as a function of film thickness.

We find that confinement effects suppress the tilting of the tetrahedra and thus affect the structure of the resulting film, for thickness up to 4 unit cells. Moreover, the presence of defect is found to be linked to changes in the electronic structure and in the magnetic behavior of the film.

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Keywords: *Perovskites, point defects, DFT+U*

Challenges and solutions for the description of hybrid perovskites with first principles methods

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Abstract

The efficiency of organometal halide perovskites solar cells generated a push to find accurate first principles descriptions for this soft ionic material. In this talk, I will discuss two of the most urgent and technically demanding challenges. First, the precise ordering of the molecules and the inorganic ocatahedra in the perovskite at elevated temperatures are difficult to determine. Density functional theory calculations proposes ordering patterns[1], but they depend on the type of exchange-correlation functional used. We use the Random Phase Approximation (RPA) to evaluate various density functionals for the perovskites, specifically $MAPbI_3$. The evaluation is done by creating finite temperature ensembles (using finite temperature RPA Molecular Dynamics (MD)) for small supercells, and then evaluating the variance between the RPA and various approximate density functionals. Secondly, in order to obtain accurate absorption spectra it is necessary to take many body effects as well as spin orbit coupling into account. Relativistic Bethe-Salpeter Equation calculations (GW-BSE) bring the absorption spectrum into good agreement with experiments[2]. For $MAPbI_3$, a large range of exciton binding energies has been reported by various experiments. The question is whether the soft ionic framework can screen the excitons. By calculating the dielectric function including ionic contributions we show that polar phonons are unable to screen the exciton, but can couple to separate charges to form large polarons[2].

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Keywords: *ab-initio molecular dynamics, structure, hybrid perovskites, RPA*

Exact Exchange Plane-Wave-Pseudopotential Approach to Non-Jellium Slabs

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Abstract

In this contribution the exact exchange (EXX) potential v_x is examined for non-jellium-like slabs, for which one has a Bravais lattice in the x-y-directions, while the electrons are confined to a finite region in z-direction. It is first demonstrated analytically that the exact v_x of these systems behaves as $-1/z$ for z far outside the slab (similar to the case of jellium slabs). In the second part of the talk an EXX plane-wave-pseudopotential (PWPP) approach to slabs will be presented. As usual in the context of PWPP calculations, this scheme relies on a periodic repetition of the slab in z-direction, so that the width a of the vacuum between the slabs becomes a crucial parameter of the calculation. Relying on moderate a, it will then first be demonstrated that the Krieger-Li-Iafrate (KLI) approximation for v_x reproduces the full solution of the optimized effective potential equation for slabs rather accurately (using free-standing graphene as a prototype). In order to deal with large a, a method for combining the plane-wave representation of the Kohn-Sham (KS) states inside the slab and close to its surface with the analytical solutions of the KS equations far outside the slab will be introduced. This method allows to perform EXX PWPP calculations for rather wide vacua (in the KLI approximation), without a need to employ excessive energy cut-offs. On this basis it will be shown that there is an extended region, both far outside the surface of the slab and far from the middle of the vacuum, in which the numerical v_x behaves as $-1/z$. While the observation of a clean $-1/z$-behavior requires a to be quite large, it seems that a decoupling of the slabs is achieved for much more moderate a, in spite of the long-range EXX potential: both the valence band structure and the work function of graphene and different Si(111) slabs converge rather rapidly with a.

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Keywords: *exact exchange, optimized potential, slabs, plane-wave pseudopotential approach*

Spin and orbital currents in magnetic solids

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Abstract

The coherent treatment of spin and orbital currents provides the ultimate basis for a proper description of magnetic phenomena. In the first part of the talk a quantum-mechanical description of the magnetic shape anisotropy, that is usually ascribed to the classical magnetic dipole-dipole interaction, is presented [1]. This is achieved by including in the underlying Hamiltonian the Breit interaction, that can be seen as an electronic current-current interaction in addition to the conventional Coulomb interaction, within fully relativistic band structure calculations. The major sources of the magnetic anisotropy, spin-orbit coupling and the Breit interaction, are treated coherently this way. This seems to be especially important for layered systems for which often both sources contribute with opposite sign to the magnetic anisotropy energy.

The second part of the talk deals with the definition for the orbital magnetisation of magnetic solids. Recent work on this issue makes use of a Bloch representation of the electronic structure [2]. Results for the spin-orbit induced magnetisation of Fe, Co and Ni based on this approach were presented by various authors [3]. To avoid the approximations and limitations of these investigations we present a coherent relativistic definition for the total magnetisation that is derived from the interaction of the total electronic current density with an external magnetic vector potential. Representing the electronic structure in terms of the Green function using the KKR band structure method leads to two terms that can be related to the Van Vleck and Landau contributions of the magnetic susceptibility [4]. A decomposition of the total magnetisation may be obtained by subtracting the spin part, that can be unambiguously determined, from the total magnetisation. Another route is to make use of the Gordon decomposition of the total electronic current density leading in a natural way to a spin and orbital contribution. Numerical results for the elemental ferromagnets Fe, Co and Ni will be presented and discussed.

While most investigations on magnetic solids are in general based on conventional spin-density functional theory, the occurrence of an appreciable orbital contribution to the magnetisation raises the need to account for this within self-consistent calculations. In fact, an approach was worked out by Vignale and Rasolt [5] about thirty years ago that supplies the formal basis for such calculations. An implementation [6] of this current density functional theory (CDFT) is sketched and corresponding results for Fe, Co and Ni presented.

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Keywords: *Spin and orbital currents, orbital magnetism, solids, current density functional theory*

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Notes

Timetable

Monday, 21.8

15.00 - 23.00	Registration
15.30 - 17.00	Coffee and refreshments
19.00 - 22.00	Get together

legend

⌂	room (all talks in the same column)
🪑	session chair
C(n)	n contributed talks
S(n)	n short talks

Tuesday, 22.8.

	⌂*Oppsittu*	⌂*Rådstuggu*
8.30 - 8.40	Opening (Vitos)	
	🪑 *Vitos*	
8.40 - 9.20	Mattsson	
9.20 - 10.00	Röthlisberger	
10.00 - 10.30	Break	
	🪑 *Kaupp*	🪑 *Sancho-Garcia*
10.30 - 11.00	Toulouse	Hyldgaard
11.00 - 11.30	Yang	Tognetti
11.30 - 12.00	Elstner	De Proft
12.00 - 12.30	Witek	Hermansson
12.30 - 14.00	Lunch	
	🪑 *Mohn*	🪑 *Hermansson*
14.00 - 14.30	Aryasetiawan	Nakai
14.30 - 15.00	Chioncel	Saue
15.00 - 15.30	Richter	Teale
15.30 - 16.00	Break	
	🪑 *Wills*	🪑 *Kokko*
16.00 - 16.40	Perdew	
16.45 - 17.45	C(4)	C(4)
19.00 - 20.30	Dinner	
	⌂*Storstuga* 🪑 *Chermette, Daul*	
20.30 - 22.00	Poster A	

Wednesday, 23.8.

	⌂*Oppsittu*	⌂*Rådstuggu*
	🪑 *Nagy*	
8.00 - 8.40	Memorial	
	🪑 *Nagy*	
8.40 - 9.20	Levy	
9.20 - 10.00	Helgaker	
10.00 - 10.30	Break	
	🪑 *Yang*	🪑 *Nakai*
10.30 - 11.00	Burke	Brémond
11.00 - 11.30	Cohen	Sancho-Garcia
11.30 - 12.00	Maitra	Kaupp
12.00 - 12.30	Peach	Köster
12.30 - 14.00	Lunch	
	🪑 *Gori-Giorgi*	🪑 *Marques*
14.00 - 15.30	C(6)	C(6)
15.30 - 16.00	Break	
16.00 - 19.00	Excursion	
19.30 - 21.00	Conference dinner	
	⌂*Storstuga* 🪑 *Garcia de la Vega, Geerlings*	
21.00 - 22.30	Poster B	

Thursday, 24.8.

	⌂*Oppsittu*	⌂*Rådstuggu*
	🪑 *Burke*	
8.40 - 9.20	van Leeuwen	
9.20 - 10.00	Ernzerhof	
10.00 - 10.30	Break	
	🪑 *Sandratskii*	🪑 *Saue*
10.30 - 11.00	Kokko	Kong
11.00 - 11.30	Sun	Wills
11.30 - 12.00	Ujfalussy	Armiento
12.00 - 12.30	Hu	Zhao
12.30 - 14.00	Lunch	
	🪑 *Richter*	🪑 *Witek*
14.00 - 14.30	Landa	Amovilli
14.30 - 15.00	Söderlind	Sandratskii
15.00 - 15.30	Mohn	C(2)
15.30 - 16.00	Break	
	🪑 *Schwarz*	🪑 *Tozer*
16.00 - 18.00	S(12)	S(12)
19.00 - 20.30	Dinner	

Friday, 25.8.

	⌂*Oppsittu*	⌂*Rådstuggu*
	🪑 *Hyldgaard*	🪑 *Ujfalussy*
8.30 - 9.15	C(3)	C(3)
9.20 - 10.00	Engel	
10.00 - 10.30	Break	
	🪑 *Ujfalussy*	
10.30 - 10.35	Poster prizes	
10.35 - 11.15	Ebert	
11.15 - 11.20	Closing (Schwarz/ Vitos)	
11.20 - 13.20	Lunch	