Ψ_k Newsletter

AB INITIO (FROM ELECTRONIC STRUCTURE) CALCULATION OF COMPLEX PROCESSES IN MATERIALS

Number 114 December 2012

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Contents

1 Editorial

This newsletter is started with an obituary of Professor Balázs László Györffy (University of Bristol, U.K.), written by Professor Robert Evans, FRS, for the University of Bristol. From its very beginning, Balazs was one of the most prominent figures of Psi-k. A memorial article, celebrating Balazs's physics and life, will be published in the February 2013 Psi-k Newsletter.

In what follows we have four reports on the recent schools/workshops, two announcements of QMC events in Apuan Alps, and a number of abstracts of newly submitted or recently published papers.

The scientific highlight article of this issue is by Robert A. DiStasio Jr.(Princeton), Vivekanand V. Gobre (Berlin), and Alexandre Tkatchenko (Berlin) on "Many-Body van der Waals Interactions in Biology, Chemistry, and Physics".

For further details please check the table of content of this newsletter.

The *Uniform Resource Locator* (URL) for the Psi-k webpage is:

http://www.psi-k.org.uk/

Please submit all material for the next newsletters to the email address below.

The email address for contacting us and for submitting contributions to the Psi-k newsletters is

	function
psik-coord@stfc.ac.uk	**messages to the coordinators, editor & newsletter**

As it is the last newsletter of this calendar year, we would like to wish everybody

A VERY MERRY CHRISTMAS AND A HAPPY NEW YEAR 2013!

Z (Dzidka) Szotek, Martin Lüders, Leon Petit and Walter Temmerman
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2 General News

2.1 Death of Professor Balázs László Györffy

It is with great sadness that we inform you that Professor Balázs Györffy died on October 25, 2012. He was one of the most prominent figures among the Psi-k family. Balázs was the first chairman of the UK CCP9 programme (Collaborative Computational Programme No 9, on "Computational Studies of the Electronic Structure of Solids"), from 1980 until 1998. It was the CCP9 that gave rise to the European-wide programme, namely the Psi-k Network. The first funding came from the European Human Capital and Mobility programme in 1993. Over the years a number of topical subnetworks were formed within Psi-k, funded from the European TMR and RTN programmes and also the ESF. Balázs was always very active and passionate about Psi-k and instigated intense collaborations among its members. He firmly believed that young scientists should be broadly educated and encouraged this within Psi-k and indeed world-wide. Balázs was a very accomplished and enthusiastic scientist and to celebrate his physics and very broad interests in the field we plan to publish a memorial article dedicated to him in the February 2013 issue of the Psi-k Newsletter. There we shall have a compilation of contributions from Balázs's collaborators, friends and colleagues from within Psi-k and outside, reminiscing on his science and his enthusiasm for life.

Below, we present a formal obituary of Balázs written by Professor Robert Evans, FRS, H.O. Wills Professor of Physics, H.H. Wills Physics Laboratory, University of Bristol, U.K., prepared on November 14, 2012, for the University of Bristol, in which he pays tribute to an outstanding scientist and valued colleague, best described as a force of nature.

Balázs L. Györffy
1938-2012

Balázs was born in Eger, Hungary. In 1956 realising that as a 'class enemy' he would be barred from higher education, Balázs left on a train bound for Vienna. When this was stopped by

Russian soldiers he and his mates jumped off, ran through marshland, bribed a guard with watches and broke through the iron curtain into Austria. Landing up in the U.S. Balázs entered Yale University where he studied Electrical Engineering and Physics, obtaining a BS in 1961. His entry into Yale was facilitated by the fact that he was a swimmer of Olympic standard. He continued in Yale completing his PhD on the theory of pressure effects on the output of gas lasers in 1966. His PhD advisor was Willis E. Lamb Jr., Nobel Laureate in Physics. Balázs came to the U.K. in the same year and held postdoctoral research appointments in UCL, Queen Mary College London and Sheffield University before joining the Physics Department of the University of Bristol, as a lecturer, in August 1970. His presence was felt from day one. This tall, athletic, handsomely moustached, charming, and argumentative man brought new energy and ideas. By 1972 he was setting a new research agenda. Balázs was promoted to Reader in 1980 and to Professor in 1987. Balázs retired, rather the University ceased to pay his salary, in 2003. As Emeritus Professor his scientific productivity continued unabated. He published three papers in 2012 and was collaborating with several colleagues on new pieces of work until the final days of his illness.

Balázs Györffy was a theoretical physicist working across a broad area of solid state physics. Perhaps as a consequence of his training with Willis Lamb, Balázs always attempted to bring fundamental, first-principles approaches to the difficult problems he tackled. His goal, and it was an ambitious one, was to develop methodologies that would allow one to determine the electronic structure and the related physical properties of metals starting from knowledge of only the atomic numbers of the constituent atoms and the crystal lattice type. The quantum mechanics of the electrons, solved using intelligent approximations, should then yield all relevant physics. Of course this is a tall order; a typical crystal has 10^{24} electrons interacting with each other and with the atomic nuclei. Balázs was probably the first to coin the term electron 'glue' to describe the role of electrons in determining the structure and properties of metallic materials. He is perhaps best recognized for his seminal contributions to the theory of metallic alloys (mixtures of two or more atomic components) where he developed a powerful and tractable approach for calculating the electronic structure that continues to be a key tool for materials scientists. In the early 1970s, together with G.Gaspari, a visitor to Bristol, Balázs developed what was arguably the first successful quantitative theory for the strength of the electron-phonon coupling interaction - a quantity crucial in determining the temperature of the transition to the superconducting state in metals. His fascination in how superconductivity occurs continued throughout his career and on occasions he worked closely with experimentalists in Bristol and elsewhere to elucidate the properties of particular superconducting materials. Understanding the nature of the transition from the paramagnetic to the ferromagnetic state in metals such as iron and nickel was another research topic which intrigued Balázs. Unlike insulating magnets where the electrons responsible for magnetism are localized on atoms, in metals these are itinerant. The challenge is to construct a theory that treats all the electronic (spin and orbital) degrees of freedom on equal footing. This was achieved by Györffy and co-workers in the mid 1980s in a successful approach that allowed them to calculate the ferromagnetic transition (Curie) temperatures for transition metals. These are merely a few of the topics Balázs pursued. Throughout his career he published more than 260 scientific articles.

The significance of his contributions was recognized by international awards that include: Elected

External Member of the Hungarian Academy of Sciences 1995, Gordon Bell Prize of the Association of Computing Machinery (U.S.) 1998 and Hume-Rothery Award of the Minerals, Metals and Materials Society (U.S.) 2001.Balázs was frequently a visting professor. His ability to enthuse young researchers, and to re-invigorate some of the more senior ones, led to many invitations for extended stays. These included the University of Wuerzburg, Technical University of Vienna, Brookhaven National Laboratory, Oak Ridge National Laboratory, Institut Laue-Langevin Grenoble, Max-Planck Institute for Microstructure Physics Halle and the Central Research Institute for Physics Budapest. Balázs was a charismatic lecturer who took no prisoners. Those students who survived a Györffy undergraduate course often went onto great things. His talents were best reserved for final year undergraduates where his enormous enthusiasm and deep knowledge of theoretical physics were much appreciated. It was in postgraduate teaching where Balázs showed exceptional commitment. He was a fierce advocate for postgraduates continuing their formal education beyond BSc. Influenced by his experiences in the U.S. and certain European institutions, he argued passionately (and at a very early stage) that U.K. science students require courses that provide formal underpinning of their chosen discipline, more advanced than what is taught at undergraduate level. He delivered a renowned and very demanding course on 'Quantum Many-Body Theory', over a period of many years, to postgrads, postdocs and members of staff. Indeed some attended several times without mastering any of the subtleties. When Access Grid videoconferencing became available Balázs pioneered its use, broadcasting his course to several UK and European institutions.

Balázs was more than a leader in his discipline; he was an inspirational, generous and entertaining colleague. He possessed incredible energy and passion for everything that he engaged in - not only his research and scholarship. His interests were wide. However, politics was a particular passion. He was an active member of the Cotham and Redland Branch of the Labour Party and regularly made clear his views. Physicists will recall fondly the heated discussions in the tea-room. Balázs would urge the assembled academics, and any one else who happened to be near, to get off their backsides, be more active in getting rid of the Tories and vote for the person or party he is supporting. Those of us, from various departments across the University, who enjoyed lunch in the Hawthorns with Balázs will miss his stories, his knowledge of European history, his good humour, his hatred of pomposity, his distaste for administration as well as his forceful analysis of any current political situation. As an enthusiastic member of the University Arts Lectures Committee, Balázs brought a scientific perspective and with it a string of new ideas. He provided scientific advice to Michael Frayn for his famous play 'Copenhagen' that describes events in the history of quantum physics and advice on Hungary and Hungarians to Philip Ball for 'The Sun and Moon Corrupted', an intriguing novel about an eastern European communist physicist. In the 1990s Balázs used his connections with Budapest to initiate a student Exchange Fellowship scheme between Bristol and Eotvos Universities. This scheme now includes an exchange programme for mathematics teachers.

Balázs was a member of Bristol Central Swimming Club and of Gloucester Masters. In 2009 he held the European Masters record for the 200 metres freestyle (age group 70-74). I recall how upset he was when a young East German 'stole' his record. Balázs continued swimming in competitions until well into 2012 when his illness made this impossible.

There are many anecdotes about Balázs and all are true. Several involve his forgetting to take or mislaying his (U.S.) passport but somehow managing to talk his way back into the U.K. Sometimes this entailed a telephone call from the Border authorities to the Registrar, usually in the early hours of the morning, seeking confirmation that a certain Professor Györffy was indeed employed by the University of Bristol. On one occasion in the 1970s Balázs was driving from Bristol to a conference in Manchester with a Hungarian colleague. Happily talking physics and singing songs from the old days they were unaware of the motorway exit to that fine city. It was only when another passenger woke up and noticed they were about to enter Scotland that they realized that had gone slightly too far.

Many of us who knew Balázs imagined that a person with such spirit and such physical presence would be immortal- as is a force of nature. Sadly we were mistaken.

3 Psi-k Activities

”Towards Atomistic Materials Design”

3.1 Reports on the Workshops supported by Psi-k

3.1.1 Report on Berlin Workshop

Report on Workshop “Density Functional Theory and Beyond with Numeric Atom-Centered Orbitals 2012”

Berlin, Germany

August 28-31, 2012

Fritz Haber Institute of the Max Planck Society
Ψ_k Network
CECAM: SCM node, MM1P.de node, and CECAM (HQ)
Molecular Simulations from First Principles – MS1P e.V.

Volker Blum, Mariana Rossi, Matthias Scheffler

http://th.fhi-berlin.mpg.de/th/Meetings/FHI-aims_2012/index.php

Report

From August 28-31, 2012, we convened a workshop on electronic structure theory based on localized orbital basis sets, specifically numeric atom-centered basis functions, in Berlin, Germany. In electronic structure theory, these methods enjoy great and increasing popularity in a wide range of frameworks today (to name but a few examples: The Siesta code, the DMol^3 code, the FPLO code, the Conquest code, the ONETEP code, the FHI-aims code, and many others, as well as the traditional Gaussian-type orbital codes of quantum chemistry). A core focus of our workshop were scientific developments centered around the Fritz Haber *ab initio* molecular simulations (FHI-aims) code that originated in Berlin a few years ago. The workshop thus doubled as the “FHI-aims Developers’ and Users’ Meeting” 2012. Similar to an earlier event in 2010, it was our express intent to include participants from a wider background and related projects, a goal that was reflected in the mix of accepted participants.

We were able to accommodate a maximum of sixty participants at our workshop. In fact, the demand was higher, but a limit was imposed by the computer facilities at our disposal. The core program consisted of eighteen invited lectures, a poster session with 22 contributions, and three so-called “Hands-On discussion” sessions held in the afternoons. Especially the Hands-On discussions are a signature feature of our workshop format. Instead of following a traditional talk/discussion format, these afternoon sessions brought participants together in small or large groups to discuss particular topics of interest, with computers on-site if needed. Some topics were suggested by the organizers, but a key goal was to let participants determine their own topics interests, including the possibility to cover entirely different (related) areas. Each afternoon also offered one specific topic that was formally prepared as a computer tutorial for interested participants. Our experiences with this discussion format are excellent: The participants stayed on topic in motivated discussion groups throughout the conference site. We were fortunate to have the logistical support of the CECAM "SCM" node in Berlin, which helped us with a computer room, a seminar room, a comfortable coffee and posters session space with tables and an outside patio, giving us enough room to form individual discussion sessions in close proximity to one another. In addition, a large lecture theatre nearby provided the setting for the formal invited talks.

Overall, we encountered a lively group of participants that embraced the discussion and talk opportunities throughout the meeting with even more enthusiasm than the organizers could have hoped for. Details are given in the following sections.

The program was split into four morning sessions with invited talks, one evening poster session, and three afternoon "Hands-On Discussion" sessions with computers on site, including three separate tutorial topics that had been prepared with considerable effort by external speakers.

In order to allow the participants to arrive on the day of the event, the first-day program consisted of two talks: First, a welcome and overview of recent electronic structure developments realized in the FHI-aims code ("State of FHI-aims"; Volker Blum, Berlin), and second, a presentation on arguably one of the most-wanted features in current electronic structure theory: Hartree-Fock and screened Hartree-Fock like exchange for hybrid functionals in Bloch-periodic systems (solids, surfaces, nanowires etc.; Sergey Levchenko, Berlin). The afternoon program featured a presentation on the computation of phonons in solids (Jörg Meyer, Munich), followed by the afternoon Hands-On Session and evening poster session (see below).

Over the following days, the program covered a broad range of current topics in electronic structure theory:

- Scalable linear algebra (Bruno Lang, Wuppertal)
- Molecular transport (Paula Havu, Espoo; Alexej Bagrets, Karlsruhe)
- Excited-state formalisms beyond traditional G_0W_0 approaches (Xinguo Ren, Fabio Caruso, Berlin)
- Molecular dynamics based statistical mechanics from first principles (Christian Carbogno, Santa Barbara; Mariana Rossi, Berlin; Davide Branduardi, Frankfurt; Karsten Reuter, Munich)
- Structure prediction (Scott Woodley, London)
- New functionals for more accurate first-principles descriptions of molecules and materials (Noa Marom, Austin; Igor Ying Zhang, Berlin; Eduardo Fabiano, Lecce; Ken Jordan, Pittsburgh; Alexandre Tkatchenko, Berlin)

Thus, a significant set of the current developments in electronic structure theory was addressed, in parts based on the FHI-aims frameworks, but also by participants with a significant background in other localized basis set methods (Bagrets, Ying Zhang, Fabiano, Jordan). The set of scientific topics included the specific area of expertise for each participant, but was broad enough to ensure that no one was an "expert for everything". The underlying common bracket, localized basis sets as the method, ensured a common language. We also benefitted significantly from the mix of some senior researchers in the field and many Ph.D. students and postdoctoral researcher with a direct, active interest in the topics.

The afternoon "Hands-On Discussions" each offered either a prepared tutorial on a specific topic with computers, or the participation in one of several on-site scientific discussion groups with a common interest. The tutorials were prepared by invited experts on three different topics: Phonon calculations in the "phonopy" framework and heat transport in solids (Jörg Meyer, Munich; Christian Carbogno, Santa Barbara); molecular transport calculations in the "aitranss" framework developed in Karlsruhe (Alexej Bagrets, Karlsruhe); and free energy calculations in the "plumed" framework (Davide Branduardi, Frankfurt; Luca Ghiringhelli, Berlin). In addition, the afternoon discussion topics ranged from simple technical topics to basic frontiers of our field: "New to FHI-aims", scalability with system size and computational hardware, frameworks for embedding of quantum-mechanically treated regions into external environments, pseudoization methods, molecular transport, molecular vibrations, technical aspects of phonon calculations, van der Waals interactions, "DFT beyond LDA and GGA", molecular dynamics, and strategies to achieve faster self-consistency. From the vantage point of the organizers, these discussions displayed a remarkable degree of self-organization, self-motivation and scientific quality on the part of the participants. What helped greatly was the mix of experts present on each topic (some acting as informal discussion leaders) and participants with an active need. If there is one regret of the organizers, it is not having been able to attend each of the parallel discussion sessions simultaneously.

The same spirit of active participation and discussion was displayed at the formal poster session, with 22 presented abstracts by participants, covering molecular science, problems in solid state physics, algorithmic problems and technical implementations alike. The posters remained on display for the entire duration of the workshop.

In summary, we are excited to have received perhaps the best reward that the organizers of a conference could wish for: A field of motivated participants that enthusiastically embraced all aspects of the program, with significant contributions from each one. Since the meeting was partially centered around the electronic structure framework FHI-aims, an immediate impact is the connection between scientists and developers from different locations and the resulting activity in the code itself. This, over time, will lead to numerous scientific opportunities in electronic structure applications, covering all the aspects mentioned above: High-level approaches, molecular dynamics, transport, statistical mechanics from first principles, and much more. Time will tell which and how many of the numerous threads begun at the meeting will mature: More robust frameworks for "external embedding" of quantum mechanical regions into surrounding fields, more accurate high-level electronic structure methods that are affordable for real (large) materials and molecular simulations, path integral formalisms to incorporate nuclear quantum effects into spectroscopy of hydrogen bonded systems, new approaches to van der Waals interactions, and many more.

Program

Tuesday, August 28, 2012		
10:00 – 11:00	Registration	
11:00 – 11:15	Introductory Remarks	
11:15 – 11:50	Volker Blum	*State of FHI-aims*
11:50 – 12:25	Sergey Levchenko	*Hartree-Fock and hybrid functionals, periodic: Implementation and application to defects in doped MgO*
12:30 – 14:00	Lunch	
14:00 – 14:35	Jörg Meyer	*Phonons, FHI-aims, and the phonopy framework*
14:35 – 18:00	Jörg Meyer	*Tutorial: FHI-aims, phonopy, and heat transport*
	Christian Carbogno	and (in parallel)
	Participants	*Hands-On Discussion*
18:30 – 20:00	Dinner	
20:00 – 22:00	Poster Session	

Wednesday, August 29, 2012		
09:00 – 09:35	Bruno Lang	*Eigenvalue solvers – The ELPA Project and Beyond*
09:35 – 10:10	Paula Havu	*Graphane on* SiO_2*, transport in FHI-aims*
10:10 – 10:45	Alexej Bagrets	*Electron transport through molecular junctions and FHI-aims*
10:45 – 11:15	Coffee Break	
11:15 – 11:50	Xinguo Ren	*Beyond RPA and GW: renormalizated second-order perturbation theory for ground-state and excited-state calculations*
11:50 – 12:25	Fabio Caruso	*Self-consistent GW in FHI-aims*
12:30 – 14:00	Lunch	
14:00 – 16:00	Alexej Bagrets	*Tutorial: The aitranss transport framework*
		and (in parallel)
	Participants	*Hands-On Discussion*
16:00 – open end	Conference Outing and Dinner	

Thursday, August 30, 2012		
09:00 – 09:35	Christian Carbogno	*Heat transport from first principles in FHI-aims*
09:35 – 10:10	Mariana Rossi	*Ab initio molecular dynamics for biomolecular spectroscopy*
10:10 – 10:45	Davide Branduardi	*The PLUMED plug-in and free energy methods in electronic-structure-based molecular dynamics*
10:45 – 11:15	Coffee Break	
11:15 – 11:50	Karsten Reuter	*FHI-aims becomes embedded: QM/Me and water splitting*
11:50 – 12:25	Scott Woodley	*Structure prediction and solid solutions with evolutionary algorithms*
12:30 – 14:00	Lunch	
14:00 – 18:00	Davide Branduardi	*Tutorial: PLUMED and FHI-aims*
	Luca Ghiringhelli	and (in parallel)
	Participants	*Hands-On Discussion*
18:30 – 20:00	Dinner	
Friday, August 31, 2012		
09:00 – 09:35	Noa Marom	*Keeping Supercomputers Busy – Configuration Space Exploration and GW Calculations*
09:35 – 10:10	Igor Ying Zhang	*Development of the XYG3-type doubly-hybrid functionals*
10:10 – 10:45	Eduardo Fabiano	*Non-empirical semilocal functionals for improved performance in quantum chemistry and materials science*
10:45 – 11:15	Coffee Break	
11:15 – 11:50	Kenneth Jordan	*Exploring Intermolecular Correlation with SAPT, vdW-Corrected DFT, and Diffusion Monte Carlo Methods*
11:50 – 12:25	Alexandre Tkatchenko	*Van der Waals Interactions in Molecules, Solids, and Interfaces*
12:25 – 12:30	Closing remarks	
12:30	Lunch and end of workshop	

List of participants

	Name	**Institution**	**Participant type**
1	Sadiq Abdul	Kaduna State University	Participant
2	Alberto Ambrosetti	Fritz Haber Institute	Participant
3	Balint Aradi	University of Bremen	Participant
4	Ido Azuri	Weizmann Institute of Science	Participant
5	Kurt Baarman	Aalto University School of Science	Participant
6	Alexej Bagrets	Karlsruher Institut für Technologie (KIT)	Speaker
7	Carsten Baldauf	Fritz Haber Institute	Participant
8	David Bende	MPI Chemische Physik fester Stoffe	Participant
9	Daniel Berger	TU München	Participant
10	Saswata Bhattacharya	Fritz Haber Institute	Participant
11	Robert Biele	European Theoretical Spectroscopy Facility (ETSF)	Participant
12	Björn Bieniek	Fritz Haber Institute	Participant
13	Volker Blum	Fritz Haber Institute	Speaker
14	Davide Branduardi	Max Planck Institute for Biophysics	Speaker
15	Christian Carbogno	University of California at Santa Barbara	Speaker

16	Fabio Caruso	Fritz Haber Institute	Speaker
17	Wael Chibani	Fritz Haber Institute	Participant
18	Jun-Hyung Cho	Hanyang University	Participant
19	Eduardo Fabiano	Nanoscience Institute of CNR	Speaker
20	Matthew Farrow	University College London	Participant
21	Luca Ghiringhelli	Fritz Haber Institute	Speaker
22	Hamidreza Hajiyani	ICAMS	Participant
23	Christopher Handley	Ruhr Universitat Bochum	Participant
24	Paula Havu	Research Associate at the Aalto University School of Science	Speaker
25	Ville Havu	Aalto University	Participant
26	Abdesalem Houari	University of Bejaia	Participant
27	Kenneth Jordan	University of Pittsburgh	Speaker
28	Yong-Hyun Kim	KAIST	Participant
29	Franz Knuth	Fritz Haber Institute	Participant
30	Peter Kratzer	University Duisburg-Essen	Participant
31	Bruno Lang	University of Wuppertal	Speaker
33	Florian Lazarevic	Fritz Haber Institute	Participant
33	Sergey Levchenko	Fritz Haber Institute	Speaker
34	Wenjin Li	CAS-MPG Partner Institute for Computational Biology	Participant
35	Xinzheng Li	Peking University	Participant
36	Andrew Logsdail	University College London	Participant
37	Luis Mancera	Universität Ulm	Participant
38	Noa Marom	The University of Texas at Austin	Speaker
39	Jörg Meyer	TU München	Speaker
40	Lydia Nemec	Fritz Haber Institute	Participant
41	Alim Ormeci	Max Planck Institute for Chem. Phys. of Solids	Participant
42	Diana Otalvaro	University of Twente	Participant
43	Zachary Pozun	University of Pittsburgh	Participant
44	Anthony Reilly	Fritz Haber Institute	Participant
45	Xinguo Ren	Fritz Haber Institute	Speaker
46	Karsten Reuter	TU München	Speaker
47	Patrick Rinke	Fritz Haber Institute	Participant
48	Mariana Rossi	Fritz Haber Institute	Speaker
49	Matthias Scheffler	Fritz Haber Institute	Participant
50	Franziska Schubert	Fritz Haber Institute	Participant
51	Jungho Shin	Korea Institute of Science and Technology	Participant
52	Alexey Sokol	University College London	Participant
53	Christian Spickermann	Atotech Deutschland GmbH	Participant
54	Alexandre Tkatchenko	Fritz Haber Institute	Speaker
55	Frank von Horsten	Atotech Deutschland GmbH	Participant
56	Vamsee Voora	University of Pittsburgh	Participant
57	Michael Walz	Karlsruher Institut für Technologie (KIT)	Participant
58	Chenchen Wang	University of Connecticut	Participant
59	Scott Woodley	University College London	Speaker
60	Jae Won Yang	Pohang University of Science and Technology	Participant
61	Ted Yu	University of California, Los Angeles	Participant
62	Igor Ying Zhang	Fritz Haber Institute	Speaker

3.1.2 Report on Workshop “Hybrid Excitations in Nano-Materials”

Place: Dipartimento di Fisica, Università di Modena e Reggio Emilia, Via Campi 213/A, 41125 Modena, Italy

Date: December 18-20, 2011

Sponsors:
Fondazione Cassa di Risparmio di Modena, IT;
Psi-K;
Center S3 CNR Institute of Nanoscience (CNR-NANO-S3), Modena, IT;
Dept. Physics, UNIMORE Modena, IT.

Organizers:
Guido Goldoni (UNIMORE, IT)
Rosa Di Felice (CNR-NANO-S3, IT);
Fabrice Valleé (CNRS Lyone, FR);
Danny Porath (Hebrew Univ. Jerusalem, IL).

Web Page: http://www.hyex2011.nano.cnr.it

Report

Hybrid nano-objects formed by two or more materials with very different electronic properties (metals, semiconductors, molecules) are emerging as the most promising and versatile nanosystems. Sensing, molecular electronics, photo-catalysis, photovoltaics, nano-medicine are fields where the peculiar properties of specific hybrid nano-systems, making advantage of the different, yet coupled optical properties of the different segments, may trigger revolutionary developments. Hybrid-nanomaterials are still little exploited though, and their development presents important fundamental challenges and necessitates convergence of different cutting-edge experimental and theoretical methods. From the synthesis and experimental side, the production of hybrid nanoobjects requie development of new strategies for the assembly of materials with different chemical, structural and symmetry properties. Their characterization and property measurements often requires the simultaneous use of different imaging and spectroscopy techniques, and the interpretation of the data may call for unconventional approaches mixing, for instance molecular and solid-state physics methods. Finally, from the theoretical viewpoint it is necessary to apply methods that allow the accurate description of components of different nature and their interaction. In other words, the investigation of hybrid nano-objects, which mix excitations with very different length and energy scales, also requires the development and application of hybrid methods for their investigation possibly unconventional multiscale approaches from the

computational point of view. The workshop brought together scientists active in the production and spectroscopy of hybrid nano-objects and theoretical/computational physicists. The invited speakers and participants discussed new investigation strategies based on merging different approaches. Fundamental challenges and future directions were identified. Topics:
1. Synthesis of hybrid nanoparticles;
2. Functionalization/coating of inorganic nanoparticles/surfaces with organic materials;
3. Plasmonics;
4. Optical characterization of hybrid nanoobjects;
5. Energy transfer and charge transfer at hybrid interfaces;
6. Ab-initio simulations and semi-empirical modeling;
7. Development of innovative predictive theoretical approaches for optical properties of hybrid materials at the Nano scale.

The workshop was successful from several viewpoints:

- It effectively brought together different communities with diverse expertise and multidisciplinary background (physics, chemistry, engineering);
- It created an informal atmosphere that enabled unbiased discussions;
- It brought into play early stage researchers, who animatedly participated not only in the oral/poster program but also in the discussions;
- It created new contacts between scientists;
- There was a very high scientific quality of the presentations;
- The participants were quite satisfied of all the aspects of the conference, including the science, the organization and the venue.

Workshop summary.

Here we sketch a brief overview. The details of the conference are contained in the attached program and the topics of each talk can be read enclosed abstracts.

The program consisted of 8 sessions spanning one full day and two half days. It started on Sunday, December 18, 2011, at 2pm and ended on Tuesday, December 20, 2011, at 1pm. Each half-day included a complimentary coffee break. The reception dinner on December 18, 2011, was offered to all the participants, as well as lunch on December 19, 2011. The local organizers also offered dinner to the invited speakers on December 19, 2011. The administrative staff at CNR-NANO-S3 Modena was extremely helpful in organizing the infrastructure and all social events, as well as in handling the administration in collaboration with the host Department of Physics of the University of Modena and Reggio Emilia.

We had invited talks of 45 minutes and short talks of 20 minutes selected from the submitted abstracts. The abstracts were collected through the conference webpage and screened by Guido

Goldoni and Rosa Di Felice, with the help of the other organizers.

The first session (December 18, 2011, afternoon) was fully devoted to experimental studies. It comprised one invited talk (Amit Sitt from the group of Uri Banin, Hebrew University of Jerusalem, Israel) and two short talks. The topics of this session ranged from fabrication of nanosystems to spectroscopy and the role of defects.

The second session (December 18, 2011, afternoon) was devoted to theoretical studies, ranging from modeling approaches to ab initio investigations. It comprised two invited talks (Benedetta Mennucci from Italy and Nacho Climente-Plasencia from Spain) and two short talks. In particular, Benedetta Mennucci emphasized the predictive power of hybrid methodologies to describe hybrid organic/inorganic systems.

The third session (December 19, 2011, morning) was devoted to theoretical studies, also including ab initio and modeling approaches. It comprised one invited talk (Ryan Artuso, representing Garnett Bryant who had a last-minute cancellation because of health problems) and two short talks.

The fourth session (December 19, 2011, morning) included both experimental and theoretical work. It comprised one experimental invited talk (Natalia Del Fatti from France) and two short talks (one experimental and one theoretical). Natalia Del Fatti talked about optical measurements of single nano-objects, which will be the ultimate instrument to identify the correlation between size and optics of nanoparticles.

The fifth session (December 19, 2011, afternoon) was devoted to experimental studies. It comprised one invited talk and two short talk. In his invited talk, Liberato Manna from the Italia Institute of Technology related on the production of nanoparticles (including hybrid nanoparticles) with diverse shapes and the relation between shape, size and optics.

The sixth session (December 19, 2011, afternoon) included one invited talk and one short talk. The invited speaker Yuri Khalavka represented the work of Carsten Soennichesens group (Mainz, Germany) on the fabrication of hyperbranched structures.

The seventh session (December 20, 2011, morning) was opened by Ulrich Hohenester (University of Graz, Austria) who talked about a computational toolbox based on finite-element simulations for the investigation of the optical properties of nanoparticles with a broad range of sizes and compositions. This invited talk was followed by two theoretical short talks.

The final eighth session (December 20, 2011, morning) comprised one theoretical invited talk (Andrea Ferretti from CNR-NANO-S3 Modena) and two short talks (one on experiments and one on theory).

The discussions were lively during the sessions and during the breaks. The organizers were stimulated to propose similar events in the future, to assess the progress deriving from ideas developed during this workshop.

The workshop venue was the Department of Physics of the University of Modena and Reggio Emilia, where a conference room was available free of charge.

Conference Program

Sunday, December 18	
Session I	
14:00-14:30	Opening (Guido Goldoni, Rosa Di Felice)
14:30-15:15	Invited: **Amit Sitt** *A core issue: The effects of core dimensionality in nano seeded rods on optical behavior and energy transfer*
15:15-15:35	**Clementine Symonds** *Spatial coherence induced by plasmon/exciton strong coupling*
15:35-15:55	**Tersilla Virgili** *Role of surface defects in the photophysics of a layer by layer assembled hybrid film*
15:55-16:25	*Coffee Break*
Session II	
16:25-16:45	**Luca Bergamini** *Plasmonic properties of metallic nanoparticles coated by dielectric shells*
16:45-17:05	**Carlo Andrea Rozzi** *Photo-induced charge-separation in light-harvesting supramolecular systems. A TDDFT perspective*
17:05-17:50	Invited: **Benedetta Mennucci** *Surface enhanced fluorescence: An hybrid quantum mechanical/continuum model*
17:50-18:35	Invited: **Juan Ignacio Climente Plasencia** *Excitons in semiconductor nanocrystals with polarized environment*
18:35-19:00	Discussion
20:30	*Reception dinner at Restaurant "Vecchia Pirri", Via Prampolini 8, Modena*
Monday, December 19	
Session I	
9:00-9:45	Invited: **Ryan Artuso** *Hybrid quantum dot-metal nanoparticle systems: connecting the dots*
9:45-10:05	**Fabio Della Sala** *Electrostatic Field Driven Alignment of Organic Oligomers on ZnO Surfaces*

10:05-10:25	**Arrigo Calzolari** *Ab-initio study of hybrid interfaces* *for photovoltaic applications*
10:25-10:55	*Coffee Break*
Session II	
10:55-11:15	**Sergio D'Addato** *Metal and metal-oxide core-shell nanoparticles:* *A detailed study on assembling,* *structure and morphology*
11:15-11:35	**Alessandro Mattoni** *Large scale atomistic investigation of* *polymer-metaloxide hybrid interfaces*
11:35-12:20	Invited: **Natalia Del Fatti** *Optical response and ultrafast spectroscopy of* *metal-based hybrid nanoparticles*
12:20-12:50	Discussion
13:00 - 14:30	*Lunch at University Cafeteria*
Session III	
14:30-15:15	**Liberato Manna** *Synthesis and assembly of complex nanocrystal structures*
15:15-15:35	**Gabriele Rainó** *Structural and Optical Properties of a Hybrid* *Nanocomposite Combining Dyes and Ag* *Nanoparticles in a Block Copolymer Micelle*
15:35-15:55	**Claudio Fontanesi** *Ag Nanoparticles (chemi)Adsorbed on Thiophene* *thin films grafted on Glassy Carbon*
15:55-17:25	*Coffee Break and Poster Session*
Session IV	
17:25-17:45	**Markus Schuster** *Manipulation of the distance between gold nanoparticles* *and a gold film by applied potentials*
17:45-18:30	Invited: **Yuriy Khalavka** *Synthesis of linear and hyperbrached* *metal-semiconductor hybrid nanoparticles*
18:30-19:00	Discussion

Tuesday, December 20	
Session I	
9:00-9:45	**Ulrich Hohenester** *Simulation of a particle plasmons with the MNPBEM toolbox*
9:45-10:05	**Sebastien Kawka** *Energy transfer in weakly coupled hybrid nanostructures*
10:05-10:25	**Simone Borlenghi** *Spin transport and magnetization dynamics in heterogeneous nanostructures: A multiscale approach*
10:25-10:55	*Coffee Break*
Session II	
10:55-11:15	**Valerio Voliani** *Multifunctionalized Gold Nanoparticles for Smart Intracellular Delivery by non-linear Excitation*
11:15-11:35	**Malte Strozyk** *One-Sided Growth of Large Plasmonic Gold Domains on CdS Quantum Rods observed on the single particle level*
11:35-12:20	Invited: **Andrea Ferretti** *Hybrid functionals and GW corrections to quantum transport calculations*
12:20-13:10	Final discussion and closing

List of Participants

Artuso Ryan (Invited)
Bergamini Luca
Bertoni Andrea
Bertoni Giovanni
Borlenghi Simone
Calzolari Arrigo
Climente Plasencia Juan Ignacio (Invited)
Cocchi Caterina
Coppedè Nicola
Corni Stefano
D'Addato Sergio
Del Fatti Natalia (Invited)
Della Sala Fabio
Di Felice Rosa (Organizer)
Ferretti Andrea (Invited)
Fontanesi Claudio
Goldoni Guido (Organizer)
Grillo Vincenzo
Hauber Anna
Hohenester Ulrich (Invited)
Kawka Sebastien
Khalavka Yuriy (Invited)
Manna Liberato (Invited)
Mattoni Alessando
Mennucci Benedetta (Invited)
Molinari Elisa
NifosìRiccardo
Pasini Mariacecilia
Petrova Jasmina
Pipolo Silvio
Rainò Gabriele
Rozzi Carlo Andrea

Ruini Alice Sai
Kiran Rajendran
Schuster Markus
Schwemer Alexander
Segarra Orti Carlos
Sitt Amit (Invited)
Strozyk Malte
Symonds Clementine
Vallée Fabrice (Organizer)
Virgili Tersilla
Voliani Valerio

3.1.3 Report on Summer School "Bandstructure meets Many Body Theory"

Vienna

September 18-22, 2012

Ψ_k, CECAM, SFB-ViCoM

G. Kresse and K. Held

http://www.cecam.org/workshop-0-834.html

Aim of the school A particular challenge of computational materials science is the calculation of materials in the presence of strong electronic correlations and exchange. In this case, the local density approximation (LDA) or generalized gradient approximation to the exchange correlation potential often yields unreliable results. In recent years we have seen tremendous progress in this field: The aim of the Summer School has been to educate the next generation of scientists in both, bandstructure and many body theory. To this end, there have been lectures in the morning and tutorials in the afternoon.

Scope of the school The first day of the summer school was devoted to density functional theory: E.K.U. Gross gave an introduction to DFT and, in a second lecture, explained time-dependent-DFT, emphasizing the importance of functionals. This was supplemented in the afternoon by a tutorial on DFT by P. Blaha, in which also related approaches such as DFT+U and hybrid functionals were tested for SrVO3.

On the second day, A. Toschi gave an introduction to quantum field theory, from Feynman diagrams to Green functions. The quantum Monte Carlo (QMC) method for solving lattice models such as the Hubbard model was introduced by R.T. Scalettar, who also guided the students in the afternoon's tutorial on QMC. G. Sangiovanni briefly explained additional aspects relevant for continuous-time quantum Monte Carlo approaches, employed e.g. for solving the dynamical mean field theory (DMFT) equations.

On the third day, R. Godby explained the GW approximation and the differences to DFT. The students did their own GW calculations in the afternoon, in a tutorial organized by G. Kresse and M. Marsmann. M. Head-Gordon introduced state-of-the-art quantum chemistry approaches from configuration interaction to coupled cluster.

On the fourth day, D. Vollhardt introduced DMFT and presented results of DFT and DFT+DMFT calculations. In a tutorial, J. Kunes guided the students on how to arrive from a DFT calculation at maximally localized Wannier orbitals. These are needed for a subsequent DMFT calculation, which the student's did for SrVO3 in the second tutorial of the day under the supervision of G. Sangiovanni.

On the fifth day, S. Biermann explained in her lecture the GW+DMFT approach and how to calculate frequency dependent screened interactions. The second lecture was given by R. Noack, who introduced the density matrix renormalization group approach (DMRG). In the subsequent tutorial the students ran their own DMRG calculations.

The school received a very postive feedback from the students who enjoyed the combination of lectures and tutorials, as well as the pedagogical presentations given by world leading scientists in the field.

Programme

Day 1 - September, 18th 2012

09:00 to 09:10	Karsten Held	Welcome
09:10 to 10:30	E.K.U. Gross	Density functional theory (DFT)
11:00 to 12:30	E.K.U. Gross	Time-dependent DFT
13:30 to 17:30	Peter Blaha	Tutorial DFT

Day 2 - September, 19th 2012

09:00 to 10:30	Alessandro Toschi	Quantum Field Theory
11:00 to 12:30	Richard T. Scalettar	Quantum Monte Carlo (QMC)
12:30 to 13:00	Giorgio Sangiovanni	Continuous-time Quantum Monte Carlo
14:30 to 17:30	Richard T. Scalettar	Tutorial Quantum Monte Carlo

Day 3 - September, 20th 2012

09:00 to 10:30	Martin Head-Gordon	Quantum Chemistry
11:00 to 12:30	Rex Godby	GW Approach
13:30 to 17:30	Georg Kresse	Tutorial GW

Day 4 - September, 21st 2012

09:00 to 10:30	Dieter Vollhardt	Dynamical Mean Field Theory (DMFT)
11:00 to 13:15	Jan Kunes	Tutorial Wannier Function Projection
14:15 to 18:00	Giorgio Sangiovanni	Tutorial DMFT

Day 5 - September, 22nd 2012

09:00 to 10:15	Silke Biermann	GW+DMFT
10:15 to 11:30	Reinhard Noack	Density Matrix Renormalization Group (DMRG)
12:00 to 14:00	Reinhard Noack	Tutorial DMRG

List of participants and lecturers

Elias ASSMANN	Silke BIERMANN	Lars BJAALIE
Peter BLAHA	Larisa CHIZHOVA	Andras DEAK
Krzysztof Pawel DYMKOWSKI	Marcus EKHOLM	Gregor FELDBAUER
Qingguo FENG	Anna GALLER	Martin GANAHL
Nirmal GANGULI	Faruk GELES	Rex GODBY
Luke GORDON	E.K.U. GROSS	Martin HEAD-GORDON

Marcel HIECKEL
Marc HÖPPNER
Viktor IVÁDY
Kunes JAN
Alamgir KABIR
Ferenc KARSAI
David KOLLER
Natalia KUROVA
DEBBICHI LAMJED
Stefan LEBERNEGG
Bora LEE
Quifeng LIANG
Jakob LISS
Brajesh Kumar MANI
Martijn MARSMAN
Reinhard NOACK
Martin NUSS
Chris OLSON
Ongun OZCELIK
Tomasz PABISIAK
Nicolaus PARRAGH
Xihong PENG
Andrei Valentin PLAMADA
Stefano PRADA
Kalpataru PRADHAN
Maciej PYLAK
Arthur RIEFER
Malte RÖSNER
Baisheng SA
Burkhard SACHS
Antia SÁNCHEZ BOTANA,
Giorgio SANGIOVANNI
Richard T. SCALETTAR
Malte SCHÜLER
Vijay SINGH
Jadwiga Ludmila SLAWINSKA
David TOMPSETT
Alessandro TOSCHI
Dieter VOLLHARDT
Markus WALLERBERGER
Aljoscha WILHELM
Philipp WISSGOTT
Sun YAN
Zhicheng ZHONG

3.1.4 Report on CECAM Conference

”Energy from the Sun: Computational Chemists and Physicists Take up the Challenge”

Chia Laguna, Sardinia, Italy

September 10-14 2012

Sponsors: CECAM, Psi-K, Department of Energy, Scuola Normale Superiore, Scuola Internazionale Superiore di Studi Avanzati (SISSA), Società Chimica Italiana, Istituto Officina dei Materiali - CNR, Sardegna Ricerche, Istituto Italiano di Tecnologia (IIT), DELL, HP.

Organizers: Wanda Andreoni, Vincenzo Barone, Stefano Fabris, Giulia Galli, Alessandro Mattoni

Webpage: http://www.cecam.org/workshop-820.html

This conference brought together communities of computational chemists, physicists, and materials scientists that are addressing the problem of solar energy conversion from different angles.

The introductory seminar was given by Walter Kohn, Nobel laureate for chemistry, eminent theoretical physicist and in particular creator of density-functional-theory, regular consultant for National Renewable Energy Laboratory (NREL), Golden, Colorado, and one of the leading voices worldwide supporting the use of solar and wind energy and the fight against global warming. The Conference benefitted from Walter Kohns active participation during all the sessions.

Both application to specific materials problems were covered and the critical discussion of current theoretical methods, namely both their power and limitations. Leading experimentalists were invited as key speakers in each of the thematic sessions of the conference: i) Inorganic photovoltaic materials, ii) Solar fuels, iii) Hybrid photovoltaic materials, iv) Organic solar cells, and v) Dye sensitized solar cells. In addition, the program also included a Forum (two sessions) devoted to the application of current methods to the calculation of excited electronic states.

The speakers presented several examples in which modeling and simulations gave suggestions for ways to improve the performances of materials (e.g. by increasing carrier mobility via chemical functionalization or by band-gap engineering via defect chemistry in semiconductors) as well as for reducing the costs (e.g. by substituting of expensive elements such as Ru with some that are Earth abundant). Several presentations addressed tstructural stability and degradation issues, in solid state systems (e.g. amorphous silicon films and heterogeneous junctions in organic solar cells), in solution (e.g. inorganic Co and Ru catalysts for water oxidation), or at complex interfaces (e.g. molecular dyes on semiconductor surfaces). Progress was reported in the calculations of proton and electron transfers in complex molecular materials for electrodes. The forum on calculations of excited states, optical properties and electron dynamics, fostered communication between the two communities there present, physicists and chemists, who traditionally approach the same problems using different methods. Concerning the optical properties of the dyes, the role of the solvent was stressed, and in particular the performances of different solvent models (implicit vs. explicit) were compared. High-throughput screening was recognized as a promising approach to discover new candidates for renewable energy materials, also via novel distributed approaches.

All in all, the conference clearly demonstrated the ongoing effort and the involvement from computational chemists, physicists, and materials scientists to optimize the efficiency of harvesting sunlight, converting it to electrical power or fuels and store it. Meeting these challenges requires substantial progress in the fundamental understanding of the physical and chemical properties and processes that control the energy conversion between light, electricity, and chemical fuels.

This conference marked a step forward in this direction. Gathering representatives from the different communities was crucial and also allowing for open exchange between experimentalists and theoreticians.

The workshop was attended by more than 90 participants, it comprised of eight thematic sessions and one poster session. The thematic sessions were: General overview; Inorganic; Forum on excited states calculations; Solar fuels; Hybrids; Organic; Electron dynamics; Dye sensitized solar cells. These sessions consisted in one or more key-invited talks from experimentalists, setting the state-of-the art in the synthesis and characterization of the materials and of the control of their functions. Most of the oral presentations addressed the field from the point of view of numerical modeling and simulations Contributed presentations from young researchers were introduced in the program together with the invited ones. The poster presentation consisted of about 40 posters and was very lively.

Programme

Day 1 - September, 10th 2012
14:30 to 14:45 - Registration
14:45 to 15:00 - Welcome
Introduction
15:00 to 16:00 - Walter Kohn, Prospects for a World Powered Predominately by Solar and Wind Energy
16:00 to 16:30 - Coffee Break
Overview
17:20 to 18:10 - Jeffrey C. Grossman, New Materials for Solar Capture and Storage
18:10 to 18:30 - Discussion

Day 2 - September, 11th 2012

Inorganic I
09:00 to 09:50 - Martha Lux-Steiner , Thin Film Photovoltaics and Nanotechnology: R&D Challenges

09:50 to 10:20 - Petr Khomyakov, Efficiency Limitations in a-Si:H Photovoltaics: New Insights from Large-Scale Atomistic Simulations
10:20 to 10:40 - Discussion
10:40 to 11:00 - Coffee Break

Inorganic II
11:00 to 11:40 - Clas Persson, Exploring Cu-Based Photovoltaic Materials Using Atomistic DFT Modeling
11:40 to 12:00 - Martijn A. Zwijnenburg, Excited State Behaviour of Inorganic Nanoparticles
12:00 to 12:40 - Stefano Ossicini, Silicon and Germanium Nanostructures for Photovoltaic Applications
12:40 to 13:00 - Discussion
13:00 to 15:00 - Lunch Break

Forum on Excited States Calculations I
15:00 to 15:40 - Eberhard K.U. Gross, Dynamics of Excitons: An Ab-Initio Perspective
15:40 to 16:20 - Adamo Carlo, Accurate Prediction of Optical Properties using DFT
16:20 to 16:40 - Discussion
16:40 to 17:00 - Coffee Break
17:00 to 17:40 - Steven G. Louie, Theory and Computation of Excited-State Properties for Solar Energy Applications
17:40 to 18:00 - Alfonso Pedone, Excited State Properties of Solar Energy Conversion Devices Based on Dye-Doped Silica Nano-Structures
18:00 to 18:20 - Ismaila Dabo, Accurate Optical-Properties of Organic Photovoltaics from Koopmans Functionals
18:40 to 19:00 - Discussion
20:00 to 23:00 - Poster Session and Buffet-Dinner

Day 3 - September, 12th 2012

Solar Fuels I &II

09:30 to 10:10 - Karsten Wedel Jacobsen, New Cubic Perovskite Materials for Single- and Two-Photon Water Splitting
10:10 to 10:30 - Dario Rocca, Ab Initio Modeling and Optimization of Solar Energy Materials Using Newly Developed Many-Body Perturbation Theory Approaches
10:30 to 10:50 - Discussion
10:50 to 11:10 - Coffee Break
11:10 to 12:00 - Sharon Hammes-Schiffer, Proton-Coupled Electron Transfer in Catalysis and Energy Conversion
12:00 to 12:20 - Leonardo Guidoni, Structure and Reactivity of a Cobalt-Based Catalyst for Water Oxidation

12:20 to 12:50 - Simone Piccinin Ab-Initio Modeling of Ru-Based Homogeneous Catalysts for Water Oxidation
12:50 to 13:10 - Discussion
13:10 to 15:00 - Lunch Break

Hybrids

15:00 to 15:50 - Maria Antonietta Loi, Organic-Inorganic Hybrids: Towards a New Class of Solution Processable Solar Cells
15:50 to 16:10 - Alessandro Mattoni, Modeling Self-Assembled Interlayers for Efficient Photoconversion at Polymer/Metaloxide Interfaces
16:10 to 16:30 - Arrigo Calzolari, Ab Initio Study of ZnO-based Interfaces for Photovoltaic Applications: from Hybrid to Fully Inorganic Heterostructures
16:30 to 16:50 - Discussion
16:50 to 17:10 - Coffee Break

Solar Fuels III

17:10 to 17:30 - Francesco Buda, Mechanism of Directional Charge Separation in Bacterial Reaction Centers
17:30 to 17:50 - Moyses Araujo, Solar Fuel from Pydirinium-Mediated CO2 Reduction on a Pt-Electrode Surface: Mechanistic Insight from Ab Initio Theory
17:50 to 18:10 - Discussion

Organic I

18:10 to 18:30 - Daniele Fazzi, Hot Dissociation in Organic Solar Cells: A Combined Theoretical and Experimental Investigation
18:30 to 18:50 - Marco Bernardi, Novel Tunable, Polymer-Free Excitonic Solar Cells from Ab-Initio Design
18:50 to 19:10 - Discussion
20:00 to 23:00 - Social Dinner

Day 4 - September, 13th 2012

Organic II

09:00 to 09:50 - Niyazi Serdar Sariciftci, Organic-Inorganic Nanostructures for Solar Energy Conversion
09:50 to 10:30 - Aln Aspuru-Guzik, Finding Renewable Energy Materials Using One Screensaver at a Time: Combinatorial Quantum Chemistry for Organic Photovoltaics
10:30 to 10:50 - Discussion
10:50 to 11:10 - Coffee Break

Electron Dynamics

11:10 to 12:00 - Martin P. Head-Gordon, Modeling Solar Energy Capture and Conversion: Case Studies of Singlet Fission and Electrocatalysis
12:00 to 12:20 - Natalia Martsinovich, Modelling Electron Transfer in Dye-Sensitised Solar Cells
12:20 to 12:40 - Carlo Andrea Rozzi, Light Harvesting and Photoinduced Charge Separation: A Time-Resolved Perspective
12:40 to 13:00 - Discussion
13:00 to 15:00 - Lunch Break

Dye Sensitized Solar Cells I

15:00 to 15:40 - Filippo De Angelis, Modeling Dye-Sensitized Solar Cells from First Principles
15:40 to 16:00 - Koichi Yamashita, A Theoretical Study on Electron Injection and Recombination of Surface Complexes with TiO2
16:00 to 16:30 - Cristiana Di Valentin, Electrons and Holes in Photoexcited Anatase TiO2
16:30 to 16:50 - Discussion
16:50 to 17:10 - Coffee Break

Inorganic III

17:10 to 17:50 - Risto Nieminen, Chalcopyrites as Solar-Cell Materials: A New Look at the Atomic-Scale Defect Physics
17:50 to 18:10 - Stanko Tomic, Modeling of Semiconductor Quantum Dots for High Efficiency Solar Cells
18:10 to 18:30 - Ivana Savic, Large Scale Atomistic Simulations of Nanostructured Thermoelectric Materials
18:30 to 18:50 - Discussion

Day 5 - September, 14th 2012

Dye Sensitized Solar Cells II

09:00 to 09:50 - Michael Grtzel, Nanostructured Photosystems for the Generation of Electricity and Fuels from Sunlight
09:50 to 10:10 - Steven Konezny, Modeling of Dye-Sensitized Solar Cells Based on High-Potential Porphyrin Photoanodes
10:10 to 10:30 - Annapaola Migani, Understanding Photocatalytically Active Interfacial Excited States of TiO2/CH3OH
10:30 to 10:50 - Discussion
10:50 to 11:10 - Coffee Break

Forum on Excited States Calculations II

11:10 to 11:50 - Angel Rubio, Hybrid Organic Photovoltaics from a Time-Dependent Density Functional Perspective
11:50 to 12:30 - Stefano Baroni, Modeling the Color of Natural Dyes
12:30 to 12:50 - Ursula Rthlisberger, Rational Design of Porphyrin Sensitizers: Tuning Optical Properties and Adsorption Behavior on TiO2 Nanoparticles
12:50 to 13:10 Discussion
13:10 to 13:20 - Closing Word

List of participants

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ANDREONI Wanda -Swiss Federal Institute Institute of Lausanne (EPFL) Switzerland
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ASPURU-GUZIK Alan -Harvard University, Cambridge Cambridge USA
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TRANI Fabio -Swiss Federal Institute Institute of Lausanne (EPFL) Switzerland
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YAMASHITA Koichi -The University of of Tokyo
ZWIJNENBURG Martijn -A. University College College London
-

4 General Workshop/Conference Announcements

4.1 Workshop on Quantum Monte Carlo in the Apuan Alps VIII

QMC versus desity functional theory

Apuan Alps Centre for Physics @ TTI
Vallico Sotto, Tuscany, Italy

Sat 27th July - Sat 3rd August 2013

`www.vallico.net/tti/tti.html`

A4 POSTER:
`www.tcm.phy.cam.ac.uk/∼mdt26/posterc13.png`

Continuing the series of alternative and very informal meetings at this venue, the Cambridge University Theory of Condensed Matter group is organizing an eighth International Workshop to discuss the development and application of the continuum quantum Monte Carlo (QMC) method and related topics such as density functional theory (DFT) in condensed matter physics and quantum chemistry. The conference will take place in our 15th Century monastery in the mediaeval high mountain village of Vallico Sotto (in the Tuscan Apuan Alps near the beautiful Italian city of Lucca).

For many types of problem the accuracy of QMC is much better than that of the more widely-used DFT, and its scaling with number of atoms is much more favourable than that of high-level quantum chemistry. Unlike most other methods, it is also fully capable of exploiting the full power of the largest computers in the world (e.g. the Cambridge CASINO code has been shown to have almost perfect parallel scaling to over 100,000 CPU cores). All topics related to applications of QMC and/or theory and algorithm development will be welcome, though it is expected that broader topics in the general area will also be discussed.

This year's meeting also has a special theme, concentrating on the relationship between QMC and density functional theory. In particular, we hope to look towards obtaining a better understanding of the relative benefits of QMC/DFT in systems and situations where DFT often fails, such as in weakly-interacting systems, strongly-correlated materials, metal-insulator transitions, magnetic properties, and biological systems. Furthermore, it is intended to look into the better integration of DFT and QMC codes. In industrial applications, where users typically require ease-of-use and a graphical user interface, how can we move towards a situation where the user may do e.g. pre-screening of candidate structures with the faster DFT, then press a 'Make the Answer Better button' which feeds the relevant wave function files into a QMC programme and spits out reliably accurate energetics for the selected problems. It is also if interest to understand how to 'move the atoms' in QMC i.e. how to exploit the power of QMC in cheaper DFT and classical-force-field molecular dynamics calculations (in the context of ‘embedding methods’ or otherwise). Additionally we can look at how to use QMC to develop better exchange-correlation functionals for use in DFT. Given the special nature of the meeting, we therefore warmly encourage applications to attend from DFT people who may never have a run a QMC simulation in their lives but are nevertheless interested in the topic. Suggestions for alternative discussion topics and other proposals are welcome.

The normal format for events at the Apuan Alps Centre for Physics involves formal presentations being restricted to the mornings, with the afternoons left free for relaxed discussion and participation in activities. For the young and vigorous, we organize mountain walks, caving and other healthy outdoor exercise, whilst the unfit and elderly might enjoy artistic tours, city visits, and gentle country strolls, with all participants reuniting in the evening for relaxed Tuscan dinners in local restaurants. The monastery is a unique venue where the community spirit and magnificent location have inspired memorable meetings in the past.

This year’s workshop will involve up to 50 people, all accommodated on site and in the village. Many speakers will be specifically invited, but anyone who feels that they have something to contribute and who wishes to attend the event is most welcome to contact the organizer (Mike Towler: mdt26 at cam.ac.uk) for further details. There is no charge either for attendance at the conference or accommodation. A provisional programmme is available at the above website.

FURTHER DETAILS/PHOTOGRAPHS/MATERIAL FROM PREVIOUS WORKSHOPS ACCESSIBLE ON TTI WEB PAGE - CLICK THE ‘PUBLIC EVENTS’ LINK.

4.2 School on Quantum Monte Carlo and the CASINO program VIII

Apuan Alps Centre for Physics @ TTI
Vallico Sotto, Tuscany, Italy

Sun 4th - Sun 11th August 2013

`www.vallico.net/tti/tti.html`

A4 POSTER:
`www.tcm.phy.cam.ac.uk/~mdt26/poster.png`

The eighth international summer school in the series 'Quantum Monte Carlo and the CASINO program' will take place during August 2013 at the TTI monastery in the Tuscan Apuan Alps in Italy, organized and hosted by members (and ex-members) of Cambridge University physics department's Theory of Condensed Matter Group. The aim of the school is to give students a thorough introduction to quantum Monte Carlo as a method for performing high-quality calculations of the electronic structure of atoms, molecules, and materials. The course is designed for young quantum chemists or theoretical physicists who have no previous experience with this technique, though people at any stage of their career who are interested are welcome to take part.

The monastery is a unique venue where the community spirit and magnificent location have inspired memorable workshops in the past. It is a delightful 15th century building incorporating an ancient church, and is situated in the isolated but spectacular setting of the Tuscan mountain village of Vallico Sotto. The church is fully equipped with relevant presentation and computer technology, and all accommodation is on-site. As with all events at the Institute, formal lectures are restricted to the mornings, and participants are given the freedom and space to think and to contemplate and discuss the issues at hand. In addition to hands-on exercises, a programme of healthy recreational activities such as mountain walks will be organized in the afternoons, and it is hoped that by following this strict regime, together with breathing the clean air of the Apuan Alps and by preparing and sampling fine Tuscan cuisine, the participant will be able to return home mentally and physically refreshed as well as better informed.

Describing the complex behaviour of materials at the atomic level requires a sophisticated description of the correlated motion of the electrons. Quantum Monte Carlo (QMC) is an increasingly popular and explicitly many-body method with the unusual capability of yielding highly accurate results whilst also exhibiting a very favourable scaling of computational cost with system size, and essentially perfect parallel scaling up to (at least) hundreds of thousands of computer cores. Over the last twenty years, the Cambridge group have been researching QMC methods and we have created a powerful, general computer program - CASINO - to carry out the calculations. The school will focus both on the basic theory of QMC and on more advanced practical techniques, and will include a thorough introduction to the CASINO program. A background in density functional theory or similar - though not essential - is normally thought to be useful.

Quantum Monte Carlo and the scaling behaviour of CASINO on the fastest computers in the world were the subject of one of a recent Psi-k 'Scientific Highlight of the Month' review articles. See '*Petascale computing opens new vistas for quantum Monte Carlo*' by M.J.Gillan, M.D. Towler and D.Alfè, available for download here:

`www.tcm.phy.cam.ac.uk/∼mdt26/papers/petascale_psik.pdf`

Instructors at the school will include the main authors of the CASINO program, Dr. Mike Towler (Cambridge/UCL), Dr. Neil Drummond (Lancaster) and Dr. Pablo Lopez Rios (Cambridge).

Participants would normally need to book a flight to Pisa airport from where onward transportation will be arranged (though other destinations are possible). Details of previous schools - including photographs - are available under the PUBLIC EVENTS link on the TTI web site.

Those interested should email Mike Towler (mdt26 at cam.ac.uk) for registration and further details.

5 Abstracts

Bond breaking and bond formation: How electron correlation is captured in many-body perturbation theory and density-functional theory

Fabio Caruso[1], Daniel R. Rohr[2,1,3], Maria Hellgren[3,4], Xinguo Ren[1],
Patrick Rinke[1], Angel Rubio[5,1,4], and Matthias Scheffler[1]
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Abstract

For the paradigmatic case of H_2-dissociation we compare state-of-the-art many-body perturbation theory (MBPT) in the GW approximation and density-functional theory (DFT) in the exact-exchange plus random-phase approximation for the correlation energy (EX+cRPA). For an unbiased comparison and to prevent spurious starting point effects both approaches are iterated to full self- consistency (i.e. sc-RPA and sc-GW). The exchange-correlation diagrams in both approaches are topologically identical, but in sc-RPA they are evaluated with non-interacting and in sc-GW with interacting Green functions. This has a profound consequence for the dissociation region, where sc-RPA is superior to sc-GW. We argue that for a given diagrammatic expansion, the DFT framework outperforms the many-body framework when it comes to bond-breaking. We attribute this to the difference in the correlation energy rather than the treatment of the kinetic energy.

(Submitted to Phys. Rev. Lett. (October 23, 2012))
Contact person: Patrick Rinke (rinke@fhi-berlin.mpg.de)

Water adsorption at two unsolvated peptides with a protonated lysine residue: From self-solvation to solvation

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Abstract

We study the initial steps of the interaction of water molecules with two unsolvated peptides: Ac-Ala$_5$-LysH$^+$ and Ac-Ala$_8$-LysH$^+$. Each peptide has two primary candidate sites for water adsorption near the C-terminus: A protonated carboxyl group, and the protonated ammonium group of LysH$^+$, which is fully hydrogen bonded (self-solvated) in the absence of water. Earlier experimental studies have shown that H_2O adsorbs readily at Ac-Ala$_5$-LysH$^+$ (a non-helical peptide), but with a much lower propensity at Ac-Ala$_8$-LysH$^+$ (a helix) under the same conditions. The helical conformation of Ac-Ala$_8$-LysH$^+$ has been suggested as the origin of the different behaviour. We here use first-principles conformational searches (all-electron density functional theory based on a van der Waals corrected version of the PBE functional, PBE+vdW) to study the microsolvation of Ac-Ala$_5$-LysH$^+$ with one to five water molecules, and the monohydration of Ac-Ala$_8$-LysH$^+$. In both cases, the most favorable water adsorption sites break intramolecular hydrogen bonds associated with the ammonium group, in contrast to earlier suggestions in the literature. A simple thermodynamic model yields Gibbs free energies $\Delta G^0(T)$ and equilibrium constants in agreement with experiments. A qualitative change of the first adsorption site does not occur. For few water molecules, we do not consider carboxyl deprotonation or finite-temperature dynamics, but in a liquid solvent, both effects would be important. Exploratory ab initio molecular dynamics simulations illustrate the short-time effects of a droplet of 152 water molecules on the initial unsolvated conformation, including the deprotonation of the carboxyl group. The self-solvation of the ammonium group by intramolecular hydrogen bonds is lifted in favor of a solvation by water.

(Accepted to J. Phys. Chem. B (November 23, 2012))
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Electrodynamic response and stability of molecular crystals

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Abstract

We show that electrodynamic dipolar interactions, responsible for long-range fluctuations in matter, play a significant role in the stability of molecular crystals. Density functional theory calculations with van der Waals interactions determined from a semilocal "atom-in-a-molecule" model result in a large overestimation of the dielectric constants and sublimation enthalpies for polyacene crystals from naphthalene to pentacene, whereas an accurate treatment of non-local electrodynamic response leads to an agreement with the measured values for both quantities. Our findings suggest that collective response effects play a substantial role not only for optical excitations, but also for cohesive properties of non-covalently bound molecular crystals.

(Submitted to Phys. Rev. Lett. (November 07, 2012))

Contact person: Alexandre Tkatchenko (tkatchenko@fhi-berlin.mpg.de)

Interatomic methods for the dispersion energy derived from the adiabatic connection fluctuation-dissipation theorem

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Abstract

Interatomic pairwise methods are currently among the most popular and accurate ways to include dispersion energy in density functional theory (DFT) calculations. However, when applied to more than two atoms, these methods are still frequently perceived to be based on ad hoc assumptions, rather than a rigorous derivation from quantum mechanics. Starting from the adiabatic connection fluctuation-dissipation (ACFD) theorem, an exact expression for the electronic exchange-correlation energy, we demonstrate that the pairwise interatomic dispersion energy for an arbitrary collection of isotropic polarizable dipoles emerges from the second-order expansion of the ACFD formula. Moreover, for a system of quantum harmonic oscillators coupled through a dipole-dipole potential, we prove the equivalence between the full interaction energy obtained from the Hamiltonian diagonalization and the ACFD correlation energy in the random-phase approximation. This property makes the Hamiltonian diagonalization an efficient method for the calculation of the many-body dispersion energy. In addition, we show that the switching function used to damp the dispersion interaction at short distances arises from a short-range screened Coulomb potential, whose role is to account for the spatial spread of the individual atomic dipole moments. By using the ACFD formula we gain a deeper understanding of the approximations made in the interatomic pairwise approaches, providing a powerful formalism for further development of accurate and efficient methods for the calculation of the dispersion energy.

(Submitted to J. Chem. Phys. (October 31, 2012))

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Maximally-localized Wannier functions: theory and applications

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Abstract

The electronic ground state of a periodic system is usually described in terms of extended Bloch orbitals, but an alternative representation in terms of localized "Wannier functions" was introduced by Gregory Wannier in 1937. The connection between the Bloch and Wannier representations is realized by families of transformations in a continuous space of unitary matrices, carrying a large degree of arbitrariness. Since 1997, methods have been developed that allow one to iteratively transform the extended Bloch orbitals of a first-principles calculation into a unique set of maximally localized Wannier functions, accomplishing the solid-state equivalent of constructing localized molecular orbitals, or "Boys orbitals" as previously known from the chemistry literature. These developments are reviewed here, and a survey of the applications of these methods is presented. This latter includes a description of their use in analyzing the nature of chemical bonding, or as a local probe of phenomena related to electric polarization and orbital magnetization. Wannier interpolation schemes are also reviewed, by which quantities computed on a coarse reciprocal-space mesh can be used to interpolate onto much finer meshes at low cost, and applications in which Wannier functions are used as efficient basis functions are discussed. Finally the construction and use of Wannier functions outside the context of electronic-structure theory is presented, for cases that include phonon excitations, photonic crystals, and cold-atom optical lattices.

(Published as *Reviews of Modern Physics* **84**, 1419 (2012))

Bistability Loss as a Key Feature in Azobenzene (Non-)Switching on Metal Surfaces

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Abstract

Reversibly switching surface adsorbed functional molecules by external stimuli is a main ingredient for their possible application in future nanotechnological devices. Unfortunately, the presence of the surface introduces changes to the electronic structure of molecular switches that drastically alter or even inhibit isomerization mechanisms. Recent investigations have especially focused on a chemical design of molecular switches where strong coupling of the photochromic moiety to the surface is avoided. In this work we show that a mere focus on decoupling the stable states from the surface is not enough to successfully carry over the gasphase isomerization behaviour to the surface mounted system. We use dispersion-corrected density-functional theory to compute energy profiles of commonly studied isomerization mechanisms for the prototypical switch azobenzene adsorbed on a Ag(111) surface and analyze the electronic structure along the way. We find that surface adsorption strongly reduces the ground state barrier separating the two minima and at the same time destabilizes the metastable state, leading to an effective loss of bistability. These findings suggest that future chemical design of functional molecules must achieve a balanced interaction of all molecular geometries involved in the isomerization process with the surface and especially prevent overly strong stabilization of transition states. We propose electron-demanding coadsorbates as a strategy to reduce stabilization and regain the switching function.

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Evaluation of endohedral doping of hydrogenated Si fullerenes as a route to magnetic Si building blocks

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Abstract

Density-functional theory based global geometry optimization is used to scrutinize the possibility of endohedral doping of hydrogenated Si fullerenes as a route to Si nanostructures with high magnetic moments. In contrast to previous suggestions, our unbiased sampling finds the smallest $Si_{16}H_{16}$ endohedral cage generally too small to encapsulate $3d$ metal dopant atoms. For the next larger fullerene-like cage though, we identify perfectly symmetric $M@Si_{20}H_{20}$ (M=Co, Ti, V, Cr) cage structures as ground states. These structures conserve the high spin moment of the dopant atom and therewith underscore the potential of this Si nanoform for novel cluster-based materials with unique magnetic properties.

(Phys. Rev. B **86**, 045416 (2012))
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Plane-wave pseudopotential implementation of explicit integrators for time-dependent Kohn-Sham equations in large-scale simulations

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Abstract

Explicit integrators for real-time propagation of time-dependent Kohn-Sham equations are compared regarding their suitability for performing large-scale simulations. Four algorithms are implemented and assessed for both stability and accuracy within a plane-wave pseudopotential framework, employing the adiabatic approximation to the exchange-correlation functional. Simulation results for a single sodium atom and a sodium atom embedded in bulk magnesium oxide are discussed. While the first-order Euler scheme and the second-order finite-difference scheme are unstable, the fourth-order Runge-Kutta scheme is found to be conditionally stable and accurate within this framework. Excellent parallel scalability of the algorithm up to more than a thousand processors is demonstrated for a system containing hundreds of electrons, evidencing the suitability for large-scale simulations based on real-time propagation of time-dependent Kohn-Sham equations.

(Journal of Chemical Physics **137**, 22A546 (2012))

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Magnetic structure and ferroelectric activity in orthorhombic $YMnO_3$: relative roles of magnetic symmetry breaking and atomic displacements

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Abstract

We discuss relative roles played by the magnetic inversion symmetry breaking and the ferroelectric (FE) atomic displacements in the multiferroic state of $YMnO_3$. For these purposes we derive a realistic low-energy model, using results of first-principles electronic structure calculations and experimental parameters of the crystal structure below and above the FE transition. Then, we solve this model in the mean-field Hartree-Fock approximation. We argue that the multiferroic state in $YMnO_3$ has a magnetic origin, and the centrosymmetric $Pbnm$ structure is formally sufficient for explaining main details of the noncentrosymmetric magnetic ground state. The relativistic spin-orbit interaction lifts the degeneracy, caused by the frustration of isotropic exchange interactions in the **ab** plane, and stabilizes a twofold periodic noncollinear magnetic state, which is similar to the E-state apart from the spin canting. The noncentrosymmetric atomic displacements in the $P2_1nm$ phase reduce the spin canting, but do not change the symmetry of the magnetic state. The effect of the $P2_1nm$ distortion on the FE polarization $\Delta P_{\mathbf{a}}$, parallel to the orthorhombic **a** axis, is twofold: (i) it gives rise to ionic contributions, associated with the oxygen and yttrium sites; (ii) it affects the electronic polarization, mainly through the change of the spin canting. The relatively small value of $\Delta P_{\mathbf{a}}$, observed in the experiment, is caused by a partial cancelation of the electronic and ionic contributions, as well as different contributions in the ionic part, which takes place for the experimental $P2_1nm$ structure. The twofold periodic magnetic state competes with the fourfold periodic one and, even in the displaced $P2_1nm$ phase, these two states continue to coexist in a narrow energy range. Finally, we theoretically optimize the crystal structure. For these purposes we employ the LSDA+U approach and assume the collinear E-type antiferromagnetic alignment. Then, we use the obtained structural information again as the input for the construction and solution of the low-energy model. We have found that the agreement with the experimental data in this case is less satisfactory and $|\Delta P_{\mathbf{a}}|$ is largely overestimated. Although the magnetic structure can be formally tuned by varying the Coulomb repulsion U as a parameter, apparently LSDA+U fails to reproduce some fine details of the experimental structure, and the cancelation of different contributions in $\Delta P_{\mathbf{a}}$ does not occur.

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Spectral Properties of Correlated Materials: Local Vertex and Non-Local Two-Particle Correlations from Combined GW and Dynamical Mean Field Theory

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Abstract

We present a fully self-consistent combined GW and dynamical mean field (GW+DMFT) study of the extended two-dimensional Hubbard model. The inclusion of the local dynamical vertex stemming from the DMFT self-energy and polarization is shown to cure the known problems of self-consistent GW. We calculate momentum-resolved spectral functions, two-particle polarizations and electron loss spectra, as well as the effective dynamical interaction induced by non-local screening. The momentum-dependence introduced by GW into the extended DMFT description leads to a narrowing of the quasi-particle width and more pronounced Hubbard bands in the metallic regime as one approaches the charge-ordering transition. It further affects the shape of collective modes, giving rise to dispersive plasmon-like long-wavelength and stripe modes.

(arXiv:1205.5553, submitted to PRL)
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6 SCIENTIFIC HIGHLIGHT OF THE MONTH

Many-Body van der Waals Interactions in Biology, Chemistry, and Physics

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Abstract

This work presents increasing evidence that many-body van der Waals (vdW) dispersion interactions play a crucial role in the structure, stability, and function of a wide variety of systems in biology, chemistry, and physics. We start by deriving both pairwise and many-body interatomic methods for computing the dispersion energy by considering a system of coupled quantum harmonic oscillators (QHO) within the random-phase approximation (RPA). The resulting many-body dispersion (MBD) method contains two types of energetic contributions that arise from beyond-pairwise (non-additive) interactions and electrodynamic response screening. Applications are presented that address benchmark databases of intermolecular interactions, the stability of extended and globular conformations of alanine tetrapeptide, binding in the "buckyball catcher" supramolecular host–guest complex, and cohesion in oligoacene molecular crystals. We find that the beyond-pairwise vdW interactions and electrodynamic screening are shown to play a quantitative, and sometimes even qualitative, role in describing the properties considered herein. This highlight is concluded with a discussion of the challenges that remain in the future development of reliable (accurate and efficient) methods for treating many-body vdW interactions in complex materials.

1 Introduction

The relevance of van der Waals (vdW) interactions in the structure, stability, and function of molecules and materials can hardly be overemphasized [1–5]. Ubiquitous in nature, vdW interactions act at distances from just a few Ångström to several nanometers, with recent experiments suggesting that vdW forces can even be significantly longer-ranged [6, 7]. VdW interactions are largely responsible for the formation of the gas-phase benzene dimer at low temperatures, the stabilization required for the formation of molecular crystals, and the binding of molecules to proteins and DNA inside living cells. In addition, vdW interactions play a central role in the fields of supramolecular chemistry and nano-materials, in which non-covalent binding is essential for structure and functionality.

In order to enable rational predictions and design of molecular and condensed-matter materials, including interfaces between them, a reliable first-principles method is required that can describe vdW interactions both accurately and efficiently. However, an accurate description of vdW interactions is extremely challenging, since the vdW dispersion energy arises from the correlated motion of electrons and must be described by quantum mechanics. The rapid increase in computational power coupled with recent advances in the development of theoretical models for describing vdW interactions have allowed us to achieve so-called “chemical accuracy” for binding between small organic molecules. However, the lack of accurate and efficient methods for treating large and complex systems hinders truly quantitative predictions of the properties and functions of technologically and biologically relevant materials.

Many encouraging approaches have been proposed in recent years for approximately including long-range pairwise dispersion interactions in density-functional theory (DFT) [8–17]. Despite significant progress in the field of modeling vdW interactions, many questions still remain and further development is required before a universally applicable method emerges. For example, pairwise interatomic vdW methods are frequently employed to describe organic molecules adsorbed on inorganic surfaces [18–21], ignoring the relatively strong electrodynamic response screening present within bulk materials. On the other hand, the popular non-local vdW-DF functionals [22–24] utilize a homogeneous dielectric approximation for the polarizability, which is not expected to be accurate for molecules. Despite this fact, interaction energies between small organic molecules computed with such functionals turn out to be reasonably accurate. Understanding the physical reasons as to why these different approaches “yield good results” outside of their expected domain of applicability is important for the development of more robust approximations.

Interatomic pairwise dispersion approaches based on the standard C_6/R^6 summation formula were popularized by the DFT-D method of Grimme [10] and are now among the most widely used methods [9,12,13] for including the dispersion energy in DFT. Despite their simplicity, these pairwise models provide remarkable accuracy when applied to small molecular systems, especially when accurate dispersion coefficients (C_6) are employed for atoms in molecules [25,26]. Only recently have efforts been focused on going beyond the pairwise treatment of vdW contributions, for example, the importance of the non-additive three-body interatomic Axilrod-Teller-Muto term [27–29] was assessed, as well as the role of non-local screening in solids [30] and molecules adsorbed on surfaces [31]. Furthermore, an efficient and accurate interatomic many-body dispersion (MBD) approach has been recently proposed [32], which demonstrated that a many-body description of vdW interactions is essential for extended molecules and molecular solids, and the influence of many-body interactions can already become significant when considering the binding between relatively small organic molecules [32, 33].

In this highlight, we present a derivation of the pairwise and many-body interatomic dispersion energy for an arbitrary collection of isotropic polarizable dipoles from the adiabatic connection fluctuation-dissipation (ACFD) formula, which is an exact expression for the exchange-correlation energy. We distinguish and discuss two types of interatomic many-body contributions to the dispersion energy, which stem from beyond-pairwise non-additive interactions and self-consistent electrodynamic response screening. By using the ACFD formula we gain a deeper understanding of the approximations made in interatomic approaches, in particular the DFT+MBD method [32], providing a powerful formalism for further development of accurate and efficient methods for the calculation of the vdW dispersion energy.

Applications of the DFT+MBD method are presented for a variety of systems, including benchmark databases of intermolecular interactions, the stability of extended and globular conformations of alanine tetrapeptide, the binding in the "buckyball catcher" supramolecular host–guest complex, and the cohesive energy of several oligoacene molecular crystals. For all of these cases, the role of the beyond-pairwise non-additive vdW interactions and electrodynamic screening captured at the DFT+MBD level of theory is critically assessed and shown to contribute in a quantitative, and sometimes even qualitative, fashion. We conclude this highlight with a discussion of the challenges that remain in the future development of accurate and efficient methods for treating many-body vdW interactions in materials of increasing complexity.

As the modeling of vdW interactions is currently a very active field of research, it is impossible to cover all of the important developments in this highlight. For more information, we refer interested readers to the recent Ψ_k highlight by Dobson and Gould, which discusses several different approaches for computing dispersion interactions [34]; to the review by Klimes and Michaelides on dispersion methods within DFT [35]; and to the webpage for the recent vdW@CECAM workshop that brought together many of the key players in the development and application of vdW-inclusive first-principles methods [36].

2 Theory

The adiabatic connection fluctuation-dissipation (ACFD) theorem provides a general and exact expression for the exchange-correlation energy [37,38], thereby allowing for the calculation of the dispersion energy in a seamless and accurate fashion which naturally incorporates higher-order many-body effects. In this section, we explore the use of the ACFD theoretical framework as a basis for the understanding and future development of interatomic pairwise and many-body dispersion methods. Beginning with a brief derivation of the ACFD correlation energy within the random-phase approximation (RPA), we then consider the ACFD-RPA correlation energy for a system of quantum harmonic oscillators (QHO) interacting *via* the dipole-dipole potential. We derive the well-known C_6/R^6 interatomic pairwise summation formula from the second-order expansion of the ACFD-RPA correlation energy for an arbitrary collection of N QHOs, each of which is characterized by an isotropic frequency-dependent point dipole polarizability. We then extend our model to account for spatially distributed dipole polarizabilities and derive modified range-separated Coulomb and dipole–dipole interaction potentials that attenuate the short-range interactions. The self-consistent screening (SCS) method is introduced which allows us to obtain accurate screened atomic polarizabilities that are subsequently utilized as input for the MBD method to calculate the fully screened many-body dispersion energy. Finally, the coupling of the MBD method with standard DFT functionals (DFT+MBD method) is achieved by employing a range-separated Coulomb potential, and allows us to treat the full range of exchange and correlation effects.

2.1 The ACFD-RPA Correlation Energy Expression

For a system of nuclei and electrons, the ACFD theorem provides us with an exact expression for the exchange-correlation energy in terms of the density-density response function $\chi(\mathbf{r},\mathbf{r}',\mathrm{i}\omega)$ [37, 38], which measures the electronic response of the system at a point $\mathbf{r}$ due to a frequency-dependent electric field perturbation at a point $\mathbf{r}'$. Since the focus of this work is on dispersion, which is a quantum mechanical phenomena due to the instantaneous (dynamical) correlation between electrons, we write the ACFD formula for the correlation energy as (Hartree atomic units are assumed throughout):

$$E_c = -\frac{1}{2\pi}\int_0^\infty d\omega \int_0^1 d\lambda\, \mathbf{Tr}[(\chi_\lambda(\mathbf{r},\mathbf{r}',\mathrm{i}\omega) - \chi_0(\mathbf{r},\mathbf{r}',\mathrm{i}\omega))v(\mathbf{r},\mathbf{r}')]. \tag{1}$$

In this expression, $\chi_0(\mathbf{r},\mathbf{r}',\mathrm{i}\omega)$ is the bare or non-interacting particle response function, which can be computed given a set of single-particle orbitals $\{\phi_i\}$ with corresponding energies $\{\epsilon_i\}$ and occupation numbers $\{f_i\}$ [39, 40] as

$$\chi_0(\mathbf{r},\mathbf{r}',\mathrm{i}\omega) = \sum_{ij}(f_i - f_j)\frac{\phi_i^*(\mathbf{r})\phi_i(\mathbf{r}')\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r})}{\epsilon_i - \epsilon_j + \mathrm{i}\omega}, \tag{2}$$

and $\chi_\lambda(\mathbf{r},\mathbf{r}',\mathrm{i}\omega)$ is the interacting response function at Coulomb coupling strength λ, $v(\mathbf{r},\mathbf{r}') = |\mathbf{r}-\mathbf{r}'|^{-1}$ is the Coulomb potential, and $\mathbf{Tr}$ denotes the trace operator (or six-dimensional integration) over the spatial variables $\mathbf{r}$ and $\mathbf{r}'$. The interacting response function, χ_λ, is defined self-consistently *via* the Dyson-like screening equation, $\chi_\lambda = \chi_0 + \chi_0(\lambda v + f_\lambda^{xc})\chi_\lambda$, which contains $f_\lambda^{xc}(\mathbf{r},\mathbf{r}',\mathrm{i}\omega)$, the exchange-correlation kernel, which must be approximated in practice.

Within the ACFD formalism, the *adiabatic connection* between a reference non-interacting system (defined at $\lambda = 0$) and the fully interacting system (with $\lambda = 1$), yields the correlation energy of the system of interest, which contains the many-body dispersion energy as well as other electron correlation effects. This is most easily facilitated by neglecting the explicit dependence of f_λ^{xc} on the coupling constant, which allows for analytic integration over λ in the ACFD correlation energy expression in Eq. (1), and forms the basis for the most widely employed approximation for f_λ^{xc}, namely the random-phase approximation (RPA) [41, 42]. In what follows, we utilize the RPA, wherein $f_\lambda^{xc} = 0$, which has been shown to yield reliable results for a wide variety of molecules and extended systems [43–58]. In the RPA, the ACFD correlation energy expression can be written as a power series expansion in $\chi_0 v$, following elimination of χ_λ using the Dyson equation and analytical integration over λ (*c.f.* Eq. (1)) [59, 60]:

$$E_{c,\mathrm{RPA}} = -\frac{1}{2\pi}\int_0^\infty d\omega \sum_{n=2}^{\infty}\frac{1}{n}\mathbf{Tr}[(\chi_0(\mathbf{r},\mathbf{r}',\mathrm{i}\omega)v(\mathbf{r},\mathbf{r}'))^n]. \tag{3}$$

For a more detailed review of the RPA approach for computing the correlation energy, see Refs. [34, 58, 61] and references therein.

2.2 Derivation of the Long-Range Interatomic Pairwise Dispersion Energy

We now apply the ACFD-RPA approach to compute the correlation energy for a collection of interacting QHOs representing the atoms in a molecular system of interest. In doing so, we will first derive the standard C_6/R^6 interatomic pairwise summation formula for a system of two QHOs as the second-order expansion of the ACFD-RPA correlation energy within the dipole approximation. We will then demonstrate the validity of this formula for an arbitrary collection of N QHOs, providing a rigorous quantum mechanical derivation of the long-range interatomic pairwise summation formula for the dispersion energy.

In what follows, each atom p in a molecular system of interest will be mapped onto a single QHO characterized by a position vector $\mathbf{R_p} = \{x_p, y_p, z_p\}$ and a corresponding frequency-dependent dipole polarizability,

$$\alpha_p(\mathrm{i}\omega) = \frac{\alpha_p^0}{1 + (\omega/\omega_p)^2}, \tag{4}$$

which is completely determined by an isotropic static dipole polarizability, $\alpha_p^0 \equiv \alpha_p(0)$, and an effective (characteristic) excitation frequency, ω_p. To evaluate the ACFD-RPA correlation energy expression in Eq. (3), we first need the bare or non-interacting response function for the collection of QHOs, which is assembled as a direct sum over the individual QHO response functions, $\chi_0^p(\mathbf{r}, \mathbf{r'}, \mathrm{i}\omega)$, which take on the following matrix form for a QHO located at $\mathbf{R_p}$ and characterized by an isotropic point dipole polarizability [61]:

$$\chi_0^p(\mathbf{r}, \mathbf{r'}, \mathrm{i}\omega) = -\alpha_p(\mathrm{i}\omega) \nabla_{\mathbf{r}} \delta^3(\mathbf{r} - \mathbf{R_p}) \otimes \nabla_{\mathbf{r'}} \delta^3(\mathbf{r'} - \mathbf{R_p}), \tag{5}$$

where $\delta^3(\mathbf{r}-\mathbf{r'})$ is the three-dimensional Dirac delta function, and $\otimes$ is the tensor (outer) product. For the moment, we assume that the QHOs are separated by a sufficiently large distance, allowing us to use the bare dipole-dipole interaction potential to describe the interoscillator couplings, a condition that will be relaxed when the general case is considered in the next section. This dipole-dipole interaction potential between oscillators p and q is straightforwardly obtained from the bare Coulomb potential, $v_{pq} = |\mathbf{R_p} - \mathbf{R_q}|^{-1}$, *via*

$$\mathfrak{T}_{pq} = \begin{cases} \nabla_{\mathbf{R_p}} \otimes \nabla_{\mathbf{R_q}} v_{pq} & \text{if } p \neq q \\ 0 & \text{if } p = q \end{cases} \tag{6}$$

and is therefore a 3×3 second-rank tensor with components given by

$$\mathfrak{T}_{pq}^{ab} = -\frac{3R_aR_b - R_{pq}^2 \delta_{ab}}{R_{pq}^5}, \tag{7}$$

in which a and b represent the coordinates $\{x, y, z\}$ in the Cartesian reference frame, R_a and R_b are the respective components of the interoscillator distance R_{pq}, and δ_{ab} is the standard Kronecker delta function. With the individual QHO response functions and the dipole-dipole interaction tensor as defined above, we now consider the quantity $\chi_0 v$ in the ACFD-RPA correlation energy expression in Eq. (3), which can be represented in matrix form as the product AT. Here, A is a diagonal $3N \times 3N$ matrix with $-\alpha_p(\mathrm{i}\omega)$ values on the 3×3 diagonal atomic subblocks, representing the bare or non-interacting response function for the collection of N QHOs. The dipole-dipole interaction matrix T is a $3N \times 3N$ matrix comprised of the 3×3 blocks of the $\mathfrak{T}_{pq}$ tensor defined in Eqs. (6) and (7).

For a system composed of two QHOs separated by a distance $R = |\mathbf{R_p} - \mathbf{R_q}|$ along the z-axis and characterized by the isotropic point dipole polarizabilities $\alpha_p(\mathrm{i}\omega)$ and $\alpha_q(\mathrm{i}\omega)$, the AT matrix takes on the following form:

$$\chi_0 v \Leftrightarrow AT = \begin{pmatrix} 0 & 0 & 0 & -\frac{\alpha_p(\mathrm{i}\omega)}{R^3} & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{\alpha_p(\mathrm{i}\omega)}{R^3} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{2\alpha_p(\mathrm{i}\omega)}{R^3} \\ -\frac{\alpha_q(\mathrm{i}\omega)}{R^3} & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{\alpha_q(\mathrm{i}\omega)}{R^3} & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{2\alpha_q(\mathrm{i}\omega)}{R^3} & 0 & 0 & 0 \end{pmatrix} . \tag{8}$$

With the above matrix as input, the second-order ($n = 2$) term of the ACFD-RPA correlation energy expression in Eq. (3) yields

$$E^{(2)}_{c,\mathrm{RPA}} = -\frac{1}{2\pi} \int_0^\infty d\omega \, \alpha_p(\mathrm{i}\omega) \alpha_q(\mathrm{i}\omega) \mathbf{Tr}[(\mathfrak{T}_{pq})^2] = -\frac{C_6^{pq}}{R^6}, \tag{9}$$

where we have used the fact that $\mathbf{Tr}[(\mathfrak{T}_{pq})^2] = 6/R^6_{pq}$ and the Casimir-Polder integral

$$C_6^{pq} = \frac{3}{\pi} \int_0^\infty d\omega \, \alpha_p(\mathrm{i}\omega) \alpha_q(\mathrm{i}\omega) \tag{10}$$

to determine the C_6^{pq} dispersion coefficient from the corresponding pair of frequency-dependent dipole polarizabilities. The above equation is of course the familiar expression for the long-range dispersion interaction between two spherical atoms.

To demonstrate the validity of this formula for an arbitrary collection of N QHOs, one needs to consider the action of the spatial trace operator in Eq. (3) on the general $3N \times 3N$ AT matrix. As seen above, the second-order term in the ACFD-RPA correlation energy expansion requires the trace of the square of the AT matrix, for which the p-th diagonal element is simply the scalar product between the corresponding p-th column and p-th row of AT. As such, the overall trace corresponds to an accumulated sum of the diagonal elements contained in the smaller $(\mathfrak{T}_{pq})^2$ subblocks $\forall \, p, q$, each weighted by the product $\alpha_p(\mathrm{i}\omega)\alpha_q(\mathrm{i}\omega)$. Since $\mathbf{Tr}[(\mathfrak{T}_{pq})^2] = 6/R^6_{pq}$ for any subblock $\mathfrak{T}_{pq}$, regardless of the geometry of the oscillator assembly, the second-order expansion of Eq. (3) reduces to

$$E^{(2)}_{c,\mathrm{RPA}} = -\frac{1}{2} \sum_{pq} \frac{C_6^{pq}}{R^6_{pq}}, \tag{11}$$

following the repeated use of the Casimir-Polder identity in Eq. (10) to determine the set of interoscillator dispersion coefficients. The reader will notice that this expression is nothing more than the standard interatomic pairwise summation formula utilized by methods such as DFT-D to compute the dispersion energy corresponding to a collection of N atoms.

Although the second-order expansion of the ACFD-RPA correlation energy in Eq. (3) yields the familiar interatomic pairwise expression for the dispersion energy given by Eq. (11), the former equation is more general and provides us with a powerful formalism for the further development of highly accurate and efficient methods for computing the dispersion energy in molecular systems of interest. For one, the ACFD-RPA correlation energy expression allows for the explicit utilization of the tensor form of the frequency-dependent dipole polarizability, enabling a fully anisotropic treatment of the dispersion energy. In this regard, anisotropy in the polarizability has been found to play a non-negligible role in the accurate description of intermolecular dispersion interactions [62, 63]. In the next two sections, we extend our above treatment by considering QHOs characterized by spatially distributed (instead of point) dipole polarizabilities and describe a method for capturing the anisotropy in the frequency-dependent dipole polarizability based on the solution of the self-consistent Dyson-like screening equation of classical electrodynamics. Secondly, the use of the untruncated ACFD-RPA correlation energy expression allows for the explicit inclusion of the higher-order ($n > 2$) energetic contributions that arise naturally in the power series expansion of $\chi_0 v$. These terms include two distinct energetic contributions: the beyond-pairwise (non-additive) many-body interactions (to N^{th} order) and the higher-order electrodynamic response screening (to *infinite* order). The first example of the beyond-pairwise many-body interactions is captured in the third-order expansion of the ACFD-RPA correlation energy (for a system with $N \geq 3$), which is the so-called Axilrod-Teller-Muto triple-dipole term [64]. The higher-order response screening is most easily illustrated by considering a system composed of two QHOs p and q and expanding Eq. (3):

$$E_{c,\text{RPA}} = -\frac{1}{2\pi} \int_0^\infty d\omega \left(\frac{6\,\alpha_p(\mathrm{i}\omega)\alpha_q(\mathrm{i}\omega)}{R_{pq}^6} + \frac{9\,\alpha_p^2(\mathrm{i}\omega)\alpha_q^2(\mathrm{i}\omega)}{R_{pq}^{12}} + \dots \right), \tag{12}$$

in which the second-order term corresponds to the "standard" C_6/R^6 pairwise dispersion interaction and the higher-order terms (which only survive with even powers of n) correspond to the electrodynamic screening of the polarizability of atom p by the presence of atom q and vice versa. In section 2.5, we again extend our above treatment and describe a method that accurately and efficiently accounts for both beyond-pairwise non-additive many-body and higher-order electrodynamic response screening contributions to the dispersion energy for an arbitrary system of N QHOs.

2.3 Extension to Spatially Distributed Dipole Polarizabilities

Correlation energy calculations carried out using the ACFD-RPA formula typically employ the bare response function, χ_0, computed using the set of occupied and virtual (unoccupied) single-particle orbitals obtained from self-consistent Hartree-Fock, semi-local DFT, or hybrid DFT calculations *via* Eq. (2). When constructed in this fashion, χ_0 accounts for orbital product (overlap) effects between the single-particle occupied and virtual states and is therefore a relatively delocalized object. On the other hand, when χ_0 is completely localized, its real-space matrix representation is diagonal in form, reflecting the fact that orbital product (overlap) effects have been neglected in the bare response function—this was the case for the A matrix corresponding to the collection of QHOs considered in the previous section. In this limit of fluctuating point dipoles, the interaction between QHOs diverges when the interoscillator distances become relatively close.

In the previous section, we assumed that the QHOs were separated by a sufficiently large distance to allow us to describe the interactions between them using the bare dipole-dipole potential, a condition that will now be relaxed in order to consider the general case, in which QHOs can be separated by typical chemical bond distances. The most straightforward way to avoid the near-field divergence is to incorporate orbital product (overlap) effects for the set of QHOs through a modification of the interaction potential at short interoscillator distances. Therefore, instead of using the bare Coulomb potential to derive the dipole-dipole interaction tensor, we will utilize a modified Coulomb potential that (*i*) accounts for orbital product (overlap) effects at short interoscillator distances and (*ii*) becomes equivalent to the bare Coulomb potential in the long-range. This range-separated Coulomb potential can actually be rigorously derived from first principles by utilizing fundamental quantum mechanics, *i.e.*, the solutions of the Schrödinger equation for the QHO. In order to proceed, we first note that the ground state QHO wavefunction, $\psi_0^{\mathrm{QHO}}(\mathbf{r})$, is a spherical Gaussian function and hence the corresponding ground state QHO charge density is also a spherical Gaussian function by the Gaussian product theorem, *i.e.*,

$$n_0^{\mathrm{QHO}}(\mathbf{r}) = |\psi_0^{\mathrm{QHO}}(\mathbf{r})|^2 = \frac{\exp[-\mathrm{r}^2/2\sigma^2]}{\pi^{3/2}\sigma^3}, \tag{13}$$

in which σ represents the width or spread of the Gaussian. The corresponding Coulomb interaction between two spherical Gaussian charge distributions associated with oscillators p and q can then be derived as [65]

$$\overline{v}_{pq} = \frac{\mathrm{erf}[R_{pq}/\sigma_{pq}]}{R_{pq}}, \tag{14}$$

in which $\sigma_{pq} = \sqrt{\sigma_p^2 + \sigma_q^2}$, is an effective width obtained from the Gaussian widths of oscillators p and q, that essentially determines the correlation length of this interaction potential. Since the dipole polarizability relates the response of a dipole moment to an applied electric field, the σ parameters physically correspond to the spatial spread of the local dipole moment distribution centered on a given oscillator. In fact, these Gaussian widths are directly related to the polarizability in classical electrodynamics [66] and can be derived from the dipole self-energy (*i.e.*, the zero-distance limit of the dipole-dipole interaction potential derived below in Eq. (15)) as $\sigma_p = (\sqrt{2/\pi}\,\alpha_p/3)^{1/3}$.

From Eq. (14), it is clear that this modified Coulomb potential satisfies both of the aforementioned conditions, so we now proceed to derive the dipole-dipole interaction tensor between two QHOs p and q from this modified Coulomb potential, which takes on the following form after straightforward algebra (*c.f.*, Eqs. (6) and (14)):

$$\begin{aligned} \overline{\mathfrak{T}}_{pq}^{ab} &= \nabla_{\mathbf{R_p}} \otimes \nabla_{\mathbf{R_q}} \overline{v}_{pq} \\ &= -\frac{3R_aR_b - R_{pq}^2\delta_{ab}}{R_{pq}^5}\left(\mathrm{erf}[R_{pq}/\sigma_{pq}] - \frac{2}{\sqrt{\pi}}\frac{R_{pq}}{\sigma_{pq}}\exp[-(R_{pq}/\sigma_{pq})^2]\right) \\ &+ \frac{4}{\sqrt{\pi}}\frac{R_aR_b}{\sigma_{pq}^3R_{pq}^2}\exp[-(R_{pq}/\sigma_{pq})^2]. \end{aligned} \tag{15}$$

We note that the above expression describes a potential that (*i*) attenuates the interaction between oscillators at short distances in comparison to the bare dipole-dipole interaction potential, converging to a finite value even in the zero-distance limit, and (*ii*) becomes equivalent to the bare dipole-dipole interaction potential for large interoscillator distances. Hence, the use of this range-separated dipole-dipole interaction potential for an arbitrary collection of QHOs not only allows us to avoid the near-field divergence that plagues the short-range, but also provides us with the simultaneous ability to correctly describe the long-range dispersion energy.

2.4 Electrodynamic Response Screening and Polarizability Anisotropy

Neglecting retardation effects due to the finite speed of light, the long-range dispersion energy between two atoms *in vacuo* originates from the electrodynamic interaction of "atomic" dipolar fluctuations. However, when an atom is embedded in a condensed phase (or in a sufficiently large molecule), the corresponding dipolar fluctuations significantly differ from the free atom case, and in fact, this difference originates from *both* the local chemical environment surrounding the atom and the long-range electrodynamic interaction with the more distant fluctuating dipoles decaying *via* a $\sim 1/R^3$ power law. In other words, each atom located inside a molecule or material experiences a dynamic internal electric field created by both the local and non-local fluctuations associated with the surrounding atoms. Depending on the underlying topology of the chemical environment, this fluxional internal electric field can give rise to either polarization or depolarization effects, and is largely responsible for the anisotropy in the molecular polarizability tensor [67, 68]. Therefore, it is essential to include the environmental screening effects arising from both the short- and long-range in accurate first-principles calculations of the dispersion energy.

To address this issue, we again represent the N atoms in a given molecular system of interest as a collection of N QHOs, each of which is characterized by an isotropic frequency-dependent point dipole polarizability, the form of which is given in Eq. (4). Up to this point, we have yet to specify the parameters necessary to construct this polarizability for a given QHO, namely, an isotropic static dipole polarizability, α_p^0, and an effective excitation frequency, ω_p. From the discussion above, it is clear that we need to incorporate both short- and long-range environmental effects in our description of the QHO frequency-dependent polarizability in order to accurately capture the electrodynamic response screening and anisotropy effects. To account for the local chemical environment, we utilize the Tkatchenko-Scheffler (TS) prescription [25], in which $\alpha_p^0[\mathrm{n}(\mathbf{r})]$ and $\omega_p[\mathrm{n}(\mathbf{r})]$ are defined as functionals of the ground-state electron density, obtained from an initial self-consistent quantum mechanical calculation using either semi-local or hybrid DFT [69]—methods that can accurately treat electrostatics, induction, exchange-repulsion, and local hybridization effects, but lack the ability to describe long-range dispersion interactions [70]. Assuming that the system (whether it be an individual molecule, a collection of molecules, or even condensed matter), has a finite electronic gap and can therefore be divided into effective atomic fragments, the Hirshfeld, or stockholder [71], partitioning of the electron density is then utilized to account for the local chemical environment surrounding each atom. Since both parameters are referenced to highly accurate free-atom reference data, short-range quantum mechanical exchange-correlation effects are accounted for in these quantities by construction. In fact, the frequency-dependent polarizabilties defined in this manner yield C_6 coefficients that are accurate to 5.5% when compared to reference experimental values for an extensive database of atomic and (small) molecular dimers. Nevertheless, this parameterization of the frequency-dependent dipole polarizability clearly lacks the aforementioned long-range electrodynamic screening that extends beyond the range of the exponentially decaying atomic densities, and these effects must be accounted for self-consistently within this system of fluctuating oscillators.

To accurately capture the long-range electrodynamic response screening and anisotropy effects, we self-consistently solve the Dyson-like screening equation utilizing the range-separated dipole-

dipole interaction tensor derived above in Eq. (15), thereby improving upon our initial description of the bare response function corresponding to this collection of QHOs. To proceed forward, we recall that this initial bare response function, χ_0, was constructed as a direct sum over the individual oscillator response functions given in Eq. (5), *i.e.*, $\chi_0 = \chi_0^p \oplus \chi_0^q \oplus \ldots$, which now correspond to QHOs characterized by isotropic frequency-dependent dipole polarizabilities parameterized using the TS definitions for $\alpha_p^0[\mathrm{n}(\mathbf{r})]$ and $\omega_p[\mathrm{n}(\mathbf{r})]$ presented above. Therefore, the real-space matrix representation of χ_0 is diagonal and as a result, the corresponding self-consistent Dyson-like screening (SCS) equation is separable and can be recast as the following nonhomogeneous system of linear equations for a given frequency ω:

$$\overline{\alpha}_p(\mathrm{i}\omega) = \alpha_p(\mathrm{i}\omega) - \alpha_p(\mathrm{i}\omega) \sum_{q \neq p}^{N} \overline{\mathfrak{T}}_{pq} \overline{\alpha}_q(\mathrm{i}\omega) \qquad\qquad p = 1, 2, \ldots, N. \tag{16}$$

In Eq. (16), the complexity associated with integrating over spatial variables $\mathbf{r}$ and $\mathbf{r}'$ has been absorbed into $\overline{\mathfrak{T}}_{pq}$, the 3×3 block of the range-separated dipole-dipole interaction tensor in Eq. (15), which facilitates the use of overlapping spatially distributed frequency-dependent dipole polarizabilities by eliminating the issues associated with the near-field divergence. The set of $\overline{\alpha}_p(\mathrm{i}\omega)$ are the unknowns in the SCS equation and physically correspond to QHO dipole polarizabilities that account for both short-range (*via* the TS scheme) and long-range (*via* the solution of the SCS equation) electrodynamic response screening effects arising from the chemical environment. The solution of Eq. (16) with input polarizabilities computed at the TS level will be referred to as TS+SCS throughout the remainder of this work.

The SCS equation can be solved in matrix form *via* inversion of the $3N \times 3N$ Hermitian $\overline{A}$ matrix, which contains the inverse of the atomic frequency-dependent dipole polarizability tensors, $\alpha_p^{-1}(\mathrm{i}\omega)$, along the diagonal 3×3 atomic subblocks, and the range-separated dipole-dipole coupling tensor, $\overline{\mathfrak{T}}_{pq}$, in each of the corresponding 3×3 non-diagonal subblocks. Inversion of $\overline{A}$ yields the fully screened polarizability matrix, $\overline{B}$, from which one can obtain the fully screened *molecular* polarizability tensor by internally contracting over all atomic subblocks, $\overline{\alpha} = \sum_{pq}^{N} \overline{B}_{pq}$ and the fully screened set of *atomic* polarizability tensors by partial internal contraction $\overline{\alpha}_p = \sum_{q}^{N} \overline{B}_{pq}$. From these screened atomic polarizability tensors, $\overline{\alpha}_p^0$ and $\overline{\omega}_p$ can be obtained for each atom as described in Ref. [32] and will be used to compute the full many-body dispersion energy in the next section.

2.5 The Many-Body Dispersion Energy: The DFT+MBD Method

To compute the full many-body dispersion (MBD) energy, we represent the N atoms in a given molecular system of interest as a collection of QHOs, each of which is now characterized by a screened static dipole polarizability, $\overline{\alpha}_p^0$, and screened excitation frequency, $\overline{\omega}_p$, computed at the TS+SCS level of theory. We then directly solve the Schrödinger equation for this set of fluctuating and interacting QHOs within the dipole approximation, with the corresponding Hamiltonian [72–76]:

$$H = -\frac{1}{2} \sum_{p=1}^{N} \nabla_{\boldsymbol{\mu}_p}^2 + \frac{1}{2} \sum_{p=1}^{N} \overline{\omega}_p^2 \mu_p^2 + \sum_{p>q}^{N} \overline{\omega}_p \overline{\omega}_q \sqrt{\overline{\alpha}_p^0 \overline{\alpha}_q^0} \boldsymbol{\mu}_p \widetilde{\mathfrak{T}}_{pq} \boldsymbol{\mu}_q, \tag{17}$$

in which $\boldsymbol{\mu}_p = \sqrt{m_p}\boldsymbol{\xi}_p$ is defined in terms of $\boldsymbol{\xi}_p$, the displacement of a given QHO p from its equilibrium position, and $m_p = (\overline{\alpha}_p^0 \overline{\omega}_p^2)^{-1}$. In Eq. (17), the first two terms correspond to the single-particle kinetic and potential energy, respectively. The last term in the Hamiltonian describes the coupling between QHOs *via* the dipole-dipole interaction tensor ($\widetilde{\mathfrak{T}}_{pq} = \nabla_{\mathbf{R}_p} \otimes \nabla_{\mathbf{R}_q} W(R_{pq})$, where $W(R_{pq})$ will be defined below).

For a system of coupled QHOs, we have in fact proven the equivalence [77] between the full interaction energy obtained from the diagonalization of the Hamiltonian in Eq. (17) and the ACFD-RPA correlation energy expression in Eq. (3). Therefore, the full ACFD-RPA correlation energy can be efficiently computed by diagonalizing the $3N \times 3N$ Hamiltonian matrix. Hence, the MBD energy is computed as the difference between the zero-point energies of the coupled (collective) and uncoupled (single-particle) QHO frequencies, *i.e.*,

$$E_{\text{MBD}} = \frac{1}{2}\sum_{p=1}^{3N} \sqrt{\lambda_p} - \frac{3}{2}\sum_{p=1}^{N} \overline{\omega}_p = E_{c,\text{RPA}}, \tag{18}$$

in which λ_p are the Hamiltonian matrix eigenvalues.

Although the MBD energy is part of the long-range correlation energy, the full correlation energy in general also includes other contributions. In order to construct an electronic structure method that treats the full range of exchange and correlation effects, we need to couple the MBD energy in Eq. (18) to an approximate semilocal DFT functional. Instead of utilizing an *ad hoc* damping function, as typically employed in interatomic pairwise approaches, the coupling of MBD to an underlying functional (DFT+MBD) is achieved via the following range-separated Coulomb potential [78,79], which suppresses the short-range interactions that are already captured at the DFT level,

$$W(R_{pq}) = \left(1 - \exp(-(R_{pq}/\overline{R}_{pq}^{\text{vdW}})^{\beta})\right)/R_{pq}, \tag{19}$$

where β is a range-separation parameter that controls how quickly $W(R_{pq})$ reaches the long-range $1/R_{pq}$ asymptote, and $\overline{R}_{pq}^{\text{vdW}} = \overline{R}_{p}^{\text{vdW}} + \overline{R}_{q}^{\text{vdW}}$ are the screened vdW radii as defined in Refs. [25,32].

The value of the single range-separation parameter, β, is obtained from global optimization of the total DFT+MBD energy on the S22 test set, a widely employed benchmark database of noncovalent intermolecular interactions [80,81]. For the PBE [82] and PBE0 [83,84] functionals, the optimized values of the β parameter were found as 2.56 and 2.53, respectively.

Finally, we remark that our choice of using the screened $\overline{\alpha}_p^0$ and $\overline{\omega}_p$ parameters as input in Eq. (17) is not unique. Other choices are certainly possible from the viewpoint of the ACFD formula and we will investigate such alternatives in more detail in future work. In addition, the coupling of the long-range MBD energy to a semilocal or hybrid DFT functional distinguishes the DFT+MBD method from the widely used RPA@DFT approaches [43–58] for computing the electron correlation energy. Furthermore, the MBD energy can be efficiently computed by diagonalizing the $3N \times 3N$ Hamiltonian matrix, enabling MBD calculations for thousands of atoms on a single processor.

3 Applications: The Role of Electrodynamic Response Screening

The simplest possible model for the polarizability of molecules and solids consists of a sum over effective hybridized polarizable atoms, as given by Eq. (4). This model can be very effective in reproducing accurately known isotropic molecular polarizabilities and isotropic C_6 coefficients. For example, the TS method uses a localized atom-based model and yields an accuracy of $\approx 14\%$ for the isotropic polarizabilities of more than 200 molecules [85] and 5.5% for the C_6 coefficients in 1225 cases [25]. However, one has to recognize that the polarizability measures the response of a dipole moment to an applied electric field. Since both the dipole moment and the electric field are vector quantities, the dipole polarizability is evidently anisotropic and should be described by a second-rank tensor. Hence, the rather simplified additive model fails to correctly capture the anisotropy in the molecular polarizability [2]. Within the framework of electronic structure calculations, the static polarizability can be computed as the second derivative of the total energy with respect to an applied electric field. An alternative, but equivalent formulation for computing the polarizability is based on the fact that the single-particle orbitals in a molecule are electrodynamically coupled. The solution of the coupling equations leads to the many-electron frequency-dependent polarizability of the full system.

The TS+SCS method introduced above in Eq. (16) is based on such an electrodynamic interaction model. Upon obtaining effective isotropic parameters for atoms in a molecule or a solid from the ground-state electron density, the non-local polarizability tensor is determined from the solution of a system of dipole–dipole coupling equations. The dipole–dipole coupling between atoms naturally introduces anisotropy in the molecular polarizability, even if we start with purely isotropic atomic polarizabilities. We now illustrate the importance of electrodynamic screening for three different cases: small and medium-size molecules, a linear chain of H_2 molecules, and silicon clusters of increasing size.

3.1 Small and Medium-Size Molecules

Table 1 shows the three components of the molecular static polarizability, α_{xx}, α_{yy}, and α_{zz}, along with the isotropic static polarizability, α_{iso}, for a database of 18 molecules [68]. The TS atomic partitioning of the polarizability integrated in different directions yields a mean absolute error of 13.2% for the isotropic molecular polarizability, and a much larger error of 76.3% for the fractional anisotropy (FA), defined as

$$\text{FA} = \sqrt{\frac{1}{2}\frac{(\alpha_{xx}-\alpha_{yy})^2+(\alpha_{xx}-\alpha_{zz})^2+(\alpha_{yy}-\alpha_{zz})^2}{\alpha_{xx}^2+\alpha_{yy}^2+\alpha_{zz}^2}}. \tag{20}$$

Upon including screening effects using the TS+SCS model [Eq. (16)], the isotropic polarizability is improved to 9.1%, and, more importantly, the accuracy of FA is improved by a factor of two to 33.5%. We suggest that a substantial part of the remaining error stems from the isotropic input into the SCS model. Using the full electron density anisotropy at the TS level requires a substantial extension of the TS+SCS model, which is work that is currently in progress. We note that for the calculation of the vdW energy, what matters is the integration of the polarizability over imaginary frequencies, $\alpha(\mathrm{i}\omega)$, hence the error in the static polarizability is ameliorated when computing the vdW energy.

Table 1: The isotropic polarizability α_{iso}, along with its three components α_{xx}, α_{yy}, and α_{zz} (in bohr^3) for a database of molecules with reference data taken from Ref. [68]. The MARE for the components corresponds to the error in the fractional anisotropy (see text). The results are reported for the TS method (with anisotropy computed from the Hirshfeld partitioning, where the $\mathbf{r}^3$ operator is partitioned as $(xx + yy + zz)\mathbf{r}$), and the TS+SCS method.

	Experiment				TS				TS+SCS			
molecule	α_{iso}	α_{xx}	α_{yy}	α_{zz}	α_{iso}	α_{xx}	α_{yy}	α_{zz}	α_{iso}	α_{xx}	α_{yy}	α_{zz}
H_2	5.33	4.86	4.86	6.28	4.61	4.57	4.63	4.63	3.98	3.15	3.15	5.64
N_2	11.88	9.79	9.79	16.06	12.59	12.02	12.02	13.73	11.24	8.79	8.79	16.14
O_2	10.80	8.17	8.17	15.86	10.03	10.02	10.02	10.06	9.86	7.61	7.61	14.36
CO	13.16	11.00	11.00	17.55	14.62	13.80	13.80	16.27	13.21	10.76	10.76	18.13
ethane	30.23	26.86	26.86	37.05	33.72	33.18	33.18	34.79	31.86	28.78	28.79	38.02
propane	43.05	38.74	38.74	51.69	49.04	47.68	48.88	50.55	46.66	39.75	42.79	57.43
cyclopentane	61.75	56.69	61.88	66.67	74.56	72.49	75.56	75.63	68.49	57.54	73.95	73.98
cyclohexane	74.23	63.30	79.70	79.70	90.59	88.36	91.70	91.70	83.27	67.91	90.96	90.96
dimethylether	35.36	29.63	33.34	43.05	39.24	38.53	39.47	39.70	37.82	32.11	32.70	48.66
P-dioxane	58.04	47.24	63.43	63.43	70.50	69.68	70.17	71.64	65.76	53.12	67.20	76.97
methanol	22.40	17.88	21.80	27.60	24.44	23.99	24.61	24.72	23.11	19.96	21.44	27.92
ethanol	34.28	30.37	33.61	38.87	39.71	38.73	39.15	41.23	37.64	32.33	37.28	43.29
formaldehyde	16.53	12.35	18.63	18.63	19.06	17.09	19.54	20.55	18.09	11.42	18.86	24.00
acetone	43.12	29.83	49.74	49.74	49.07	45.80	50.22	51.18	48.05	35.41	49.90	58.83
acetonitrile	30.23	25.98	25.98	38.74	32.51	31.17	31.17	35.19	32.82	23.62	23.62	51.22
$(CH_3)_3CCN$	64.72	60.94	60.94	72.27	79.13	78.16	78.16	81.07	77.09	70.65	70.65	89.98
methane	17.68	17.68	17.68	17.68	18.90	18.90	18.90	18.90	17.39	17.39	17.39	17.39
benzene	69.70	45.10	82.00	82.00	75.29	71.82	77.02	77.03	71.95	33.02	91.41	91.42
MARE	-	-			13.2%	76.3%			9.1%	33.5%		

For a pair of atoms or molecules A and B, the C_6^{AB} coefficient determines their long-range vdW interaction energy. One of the main achievements of the TS method consists of a parameter-free definition to determine the C_6^{AB} coefficients with an accuracy of 5.5% for a broad variety of small and medium-size molecules (1225 C_6^{AB} coefficients). The performance of the TS method is shown in Figure 1, where a remarkable correlation can be seen with reliable C_6^{AB} values computed from the experimental dipole-oscillator strength distributions (see Ref. [25] for a detailed analysis). The reason behind such a good performance is that SCS effects beyond semilocal hybridization largely average out when computing C_6 coefficients for small molecules. In fact, the TS+SCS method yields an accuracy of 6.3% for the aforementioned 1225 C_6 coefficients and its performance is also shown in Figure 1. We attribute the slight increase of the error with respect to TS as stemming from the approximation of the dipole moment distribution by a single isotropic QHO. The largest errors of TS+SCS are found for linear alkane chains, where the anisotropy along the chain is overestimated. Full tensor formulation of the input TS

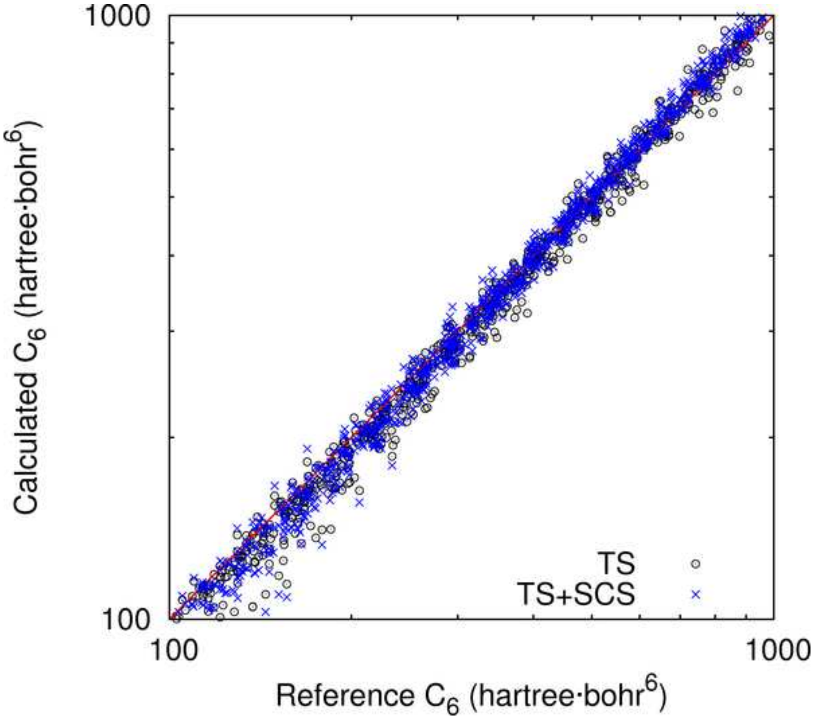

Figure 1: Isotropic C_6 coefficients for a database of 50 atoms and molecules (1225 data points) computed with TS and TS+SCS methods, compared with reliable DOSD values (see text).

polarizabilities is under way and preliminary results indicate that the molecular anisotropy is improved.

3.2 Linear Chain of H_2 Molecules

We further illustrate the importance of SCS effects with the example of the linear $(H_2)_3$ chain, consisting of three H_2 dimers with alternating bond lengths (2 bohr inside the dimer and 3 bohr between the dimers). An accurate calculation of the polarizability of such hydrogen dimer chains is considered to be a significant challenge for electronic structure theory [86]. We have calculated the reference frequency-dependent polarizability for $(H_2)_3$ using the linear-response coupled-cluster method (LR-CCSD) as implemented in the NWChem code [87, 88]. The LR-CCSD method is a state-of-the-art approach for computing static and frequency-dependent molecular polarizabilities, and it yields results that agree to ≈3% when compared to reliable experimental values. The results for the isotropic and anisotropic C_6 coefficients for this chain at the TS, TS+SCS, and LR-CCSD levels of theory are shown in Table 2. The TS method yields a vanishingly small anisotropy in the C_6 coefficient since it only accounts for the local environment. On the contrary, TS+SCS correctly captures the dipole alignment (polarization) along the $(H_2)_3$ chain, leading to a significant anisotropy that is in fair agreement with the reference LR-CCSD values. Also, the isotropic C_6 coefficient is noticeably improved when using the TS+SCS approach in comparison to TS.

Table 2: Anisotropic ($C_{6,\perp}$, $C_{6,||}$) and isotropic ($C_{6,\text{iso}}$) C_6 coefficients for the linear $(H_2)_3$ chain using the TS and TS+SCS methods. Reference linear-response coupled-cluster (LR-CCSD) results are also shown. All values in hartree·bohr^6.

	$C_{6,\perp}$	$C_{6,\|\|}$	$C_{6,\text{iso}}$
TS	166	161	165
TS+SCS	89	692	223
LR-CCSD	115	638	238

3.3 Silicon Clusters

We have shown that the TS+SCS method can rather effectively describe the anisotropy and polarization effects in molecules. We now illustrate that the TS+SCS approach can also accurately treat depolarization in clusters and solids with the example of hydrogen-saturated silicon clusters of increasing size. The cluster–cluster C_6 coefficients are shown in Figure 2. The reference values correspond to the TDLDA calculations of S. Botti *et al.* [89]. We measured the accuracy of TDLDA using the experimentally derived C_6 coefficient for the SiH_4 molecule [90] and the $C_6^{\text{Si-Si}}$ coefficient in the silicon bulk determined from the Clausius-Mossotti equation with the experimental dielectric function. For the SiH_4 molecule, TDLDA yields a 13% overestimation and this error is further reduced to 3% for the silicon bulk. Therefore, we deem the TDLDA C_6 coefficients as good references for the larger silicon clusters. For smaller clusters, the TS values are accurate and are in good agreement with experiment and TDLDA as expected. However, the error in the TS method increases progressively with the cluster size. For the largest $Si_{172}H_{120}$ cluster, the TS approach yields an overestimation of 27%. TS+SCS leads to an overall depolarization for the larger clusters, decreasing the error significantly in comparison to TDLDA. The depolarization effect is even larger for the Si bulk. The TS scheme yields an overestimation of 68% in the $C_6^{\text{Si-Si}}$ coefficient in comparison to the value derived from the experimental dielectric function, while the TS+SCS approach reduces the overestimation to just 8%.

4 Applications: Performance of the DFT+MBD Method

Having established the accuracy of the TS+SCS method for computing the vdW coefficients for a wide variety of systems from molecules to solids, we now assess the performance of the DFT+MBD method based on the TS+SCS input (see Section 2.5) for a broad variety of molecular systems. The cases studied herein include the binding energies of molecular dimers, conformational energetics of extended and globular alanine tetrapeptide, binding in the supramolecular host–guest buckyball catcher complex, as well as cohesion in molecular crystals composed of oligoacenes. The all-electron numeric atom-centered orbital code FHI-aims [91] was utilized for the DFT calculations discussed in this work.

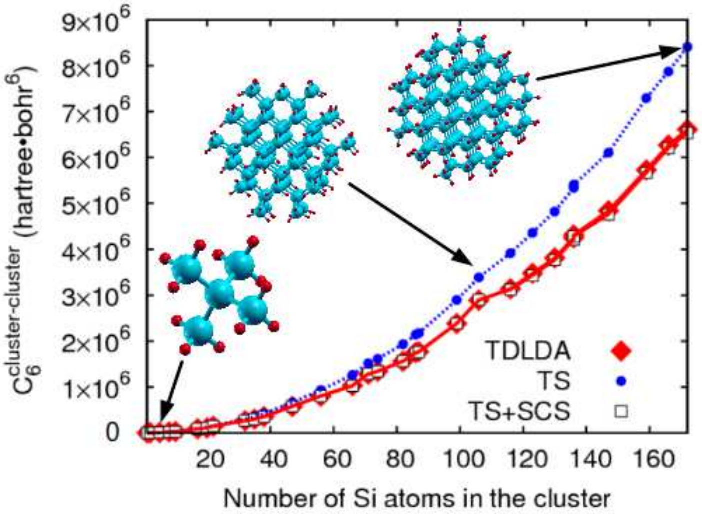

Figure 2: Cluster–cluster isotropic C_6 coefficients for hydrogen-terminated silicon clusters of increasing size. The TDLDA results are from Ref. [89].

4.1 Intermolecular Interactions: The S22 and S66 Databases

In order to assess the performance of the DFT+MBD method, we first study the S22 database of intermolecular interactions [80], a widely used benchmark database for which reliable binding energies have been calculated using high-level quantum chemical methods [80,81]. In particular, we use the recent basis-set extrapolated CCSD(T) binding energies calculated by Takatani *et al.* [81]. These binding energies are presumed to have an accuracy of ≈ 0.1 kcal/mol (1% relative error), and this level of accuracy is required for an unbiased assessment of approximate approaches for treating dispersion interactions.

Figure 3 shows the performance of the DFT+MBD method on the S22 database when used with the standard semilocal PBE [82] functional and the hybrid PBE0 [83,84] functional which includes 25% Hartree-Fock exchange. The inclusion of the many-body vdW energy leads to a remarkable improvement in accuracy compared to the PBE+TS-vdW method [25]. The largest improvement when using the MBD energy over the pairwise TS-vdW energy is observed for the methane dimer and the parallel-displaced benzene dimer. We note that the methane dimer is bound by only 0.53 kcal/mol at the CCSD(T) level of theory, and the MBD energy reduces the binding by 0.19 kcal/mol with respect to TS-vdW, explaining the large reduction in error seen in Figure 3. This reduction does not come mainly from the many-body dispersion energy, rather it is due to a more physical definition of the short-range interactions in the MBD method arising from a range-separated Coulomb potential [32]. Taking the second-order expansion of the MBD energy, which yields a strictly pairwise energy, leads to a change of only 0.05 kcal/mol [77] compared to the full MBD energy. This simple test illustrates that the main difference between PBE+TS-vdW and PBE+MBD for the methane dimer stems from the different way of treating the short-range dispersion interactions. In addition, the inclusion of Hartree-Fock exchange in the PBE0 functional allows for a better description of permanent electrostatic moments and static polarizabilities for molecules, and leads to improved binding energies when compared to the semilocal PBE functional. We note that there are two systems in the S22 database for

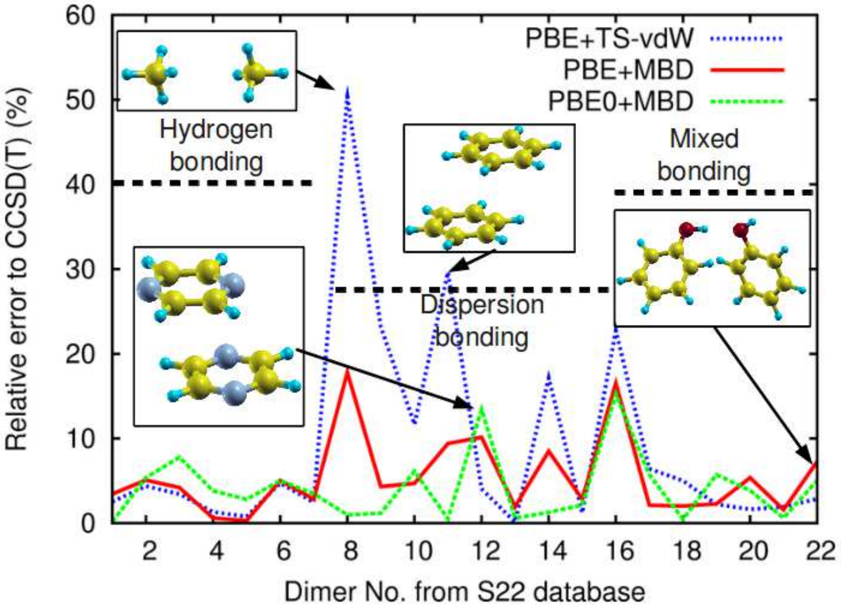

Figure 3: The performance of the PBE+TS-vdW method of Tkatchenko and Scheffler [25], PBE+MBD, and PBE0+MBD methods on the S22 database of intermolecular interactions. The error is reported to the basis-set converged CCSD(T) results of Takatani *et al.* [81].

which the relative PBE0+MBD error exceeds 10% when compared to the CCSD(T) binding energies: pyrazine dimer (system 12) and ethene–ethyne (system 16). We attribute this finding to the remaining inaccuracy in the anisotropy for the molecular polarizabilities computed with the TS+SCS method. This issue will be analyzed in more detail for the case of the buckyball catcher complex below.

To put the performance of the DFT+MBD method in the context of other currently available approaches, we show the mean absolute relative errors (MARE) on the S22 database for a variety of state-of-the-art methods in Table 3 and in Figure 4. The number of empirical parameters employed for the dispersion energy in every method is also enumerated in Table 3. Only the PBE0+MBD method [32] and the rPW86+cPBE+VV10 approach [24, 92] yield consistent performance with errors below 6% with respect to the CCSD(T) reference data for all interaction types. We note that the rPW86+cPBE+VV10 method uses two empirical parameters in the expression for the dispersion energy, while the PBE0+MBD method uses only a single range-separation parameter for the coupling of the long-range dispersion energy to the underlying DFT functional.

Recently, Hobza's group has significantly revised and extended the S22 database to include a broader variety of molecules and intermolecular interactions. The result of this effort is the so-called S66 database, composed of 66 molecular dimers [93]. The reference binding energies for the S66 database have been computed at the CCSD(T) level of theory employing medium-size basis sets, with an expected accuracy of ≈2-3% from the basis set limit. In order to cover non-equilibrium geometries, CCSD(T) binding energies have also been computed for 8 different intermolecular separations, ranging from a factor of 0.9 to 2.0 of the equilibrium distances. Therefore, the so-called S66x8 database contains binding energies for a total of 528 complexes

Table 3: Performance of different methods on the S22 database of intermolecular interactions, measured in terms of the mean absolute relative error (MARE, in %). The errors are measured with respect to the basis-set extrapolated CCSD(T) calculations of Takatani *et al.* [81]. The error is reported for hydrogen-bonded (H-B), dispersion-bonded (D-B), and mixed (M-B) systems. The number of empirical parameters used in every approach is shown in the "N. param." column. Results are shown for MP2, EX+cRPA, EX+cRPA+SE [57], vdW-DF1 and vdW-DF2 [23], rPW86+cPBE+VV10 [24,92], PBE0-D3 [28], PBE0+TS-vdW [25,26], and PBE0+MBD [32].

Method	H-B	D-B	M-B	Overall	N. param.
MP2	1.8	37.4	14.8	18.9	0
EX+cRPA	11.2	21.6	14.8	16.1	0
vdW-DF1	15.2	13.0	10.8	13.0	0
PBE0-D3(Grimme)	8.4	15.5	12.7	12.3	> 3
EX+cRPA+SE	5.9	11.6	5.4	7.8	0
vdW-DF2	5.3	6.8	10.8	7.6	1
PBE0+TS-vdW	3.4	12.0	6.0	7.3	2
rPW86+cPBE+VV10	6.1	2.6	4.8	4.4	2
PBE0+MBD	4.1	3.4	5.1	4.2	1

computed at the CCSD(T) level of theory. The performance of the PBE0+MBD approach on the S66 database is comparable to the S22 results presented above. For equilibrium geometries in the S66 database, the mean absolute error (MAE) and MARE of the PBE0+MBD method are 0.38 kcal/mol and 6.1%, respectively. When all 528 equilibrium and non-equilibrium complexes are taken into account, the calculated MAE and MARE are 0.37 kcal/mol and 8.5%, respectively. The increase in the MARE stems from the S66(0.9x) and S66(0.95x) complexes with shorter-than-equilibrium interaction distances. This is a well-known weakness of all dispersion-inclusive DFT methods, with errors increasing when considering shorter distances, since the dispersion energy contribution for such distances becomes very small.

We conclude that the MBD energy beyond the standard pairwise approximation is important even when studying the binding between rather small molecules. Empirical pairwise methods for the dispersion energy mimic some of the higher-order effects by adjusting sufficiently flexible damping functions, but this strategy is prone to fail for different molecular conformations and for more complex molecular geometries. We illustrate one such case in the next subsection.

4.2 Intramolecular Interactions: Conformational Energies of Alanine Tetrapeptide

The study of biomolecules in the gas phase corresponds to ideal "clean room" conditions, and recent progress in experimental gas-phase spectroscopy has yielded increasingly refined vibrational spectra for peptide secondary structures [94–96]. Joint experimental and *ab initio* theoretical studies can now successfully determine the geometries of small gas-phase peptides [97–99]. Polyalanine is a particularly good model system due to its high propensity to form helical structures [100], and its widespread use as a benchmark system for peptide stability in experiments

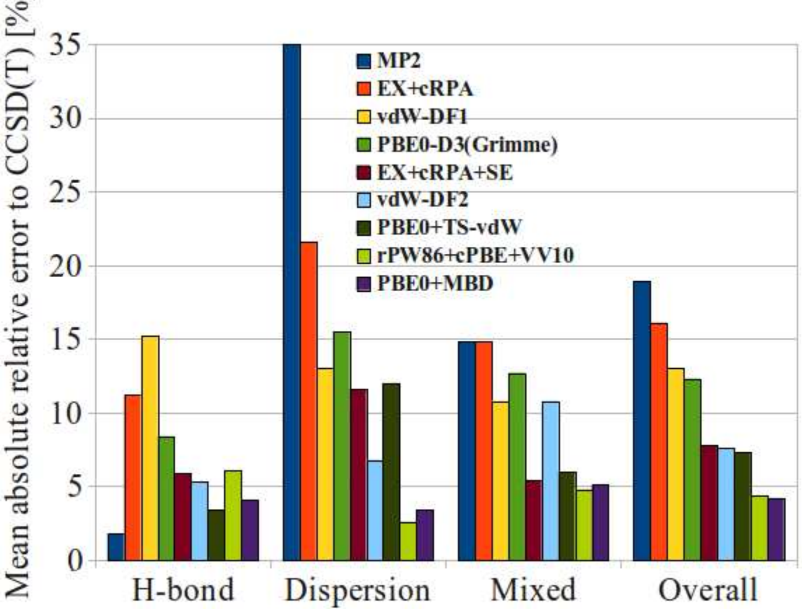

Figure 4: Performance of different methods on the S22 database of intermolecular interactions, measured in terms of the mean absolute relative error (MARE, in %). The errors are measured with respect to the basis-set extrapolated CCSD(T) calculations of Takatani *et al.* [81]. Results are shown for MP2, EX+cRPA, EX+cRPA+SE [57], vdW-DF1 and vdW-DF2 [23], rPW86+cPBE+VV10 [24, 92], PBE0-D3 [28], PBE0+TS-vdW [25, 26], and PBE0+MBD [32].

and theory.

Here we assess the accuracy of the PBE0+MBD method for 27 conformations of alanine tetrapeptide (Ace-Ala$_3$-NMe, for brevity called Ala$_4$ here), for which benchmark CCSD(T) conformational energies were computed in Ref. [101], based on converged MP2/CBS values from Refs. [102, 103]. The Ala$_4$ conformations range from a β-sheet-like fully extended structure to a globular ("folded") conformer. The wide variety of interactions present in peptides ranging from hydrogen bonds to dispersion and electrostatics makes an accurate prediction of the conformational hierarchy of these systems quite a daunting task for affordable electronic structure calculations. We illustrate the performance of PBE0+TS-vdW and PBE0+MBD for Ala$_4$ conformers in Figure 5. The PBE0+MBD method predicts a MAE of 0.29 kcal/mol with respect to the CCSD(T) reference, which is a significant reduction from 0.52 kcal/mol for PBE0+TS-vdW. We find that the main effect of the MBD energy over the pairwise TS-vdW approximation is to destabilize the extended conformations of Ala$_4$, bringing their energies in much better agreement with the reference CCSD(T) values.

4.3 Supramolecular Systems: The Buckyball Catcher

Supramolecular host–guest systems play an important role for a wide range of applications in chemistry and biology. The prediction of the stability of host–guest complexes represents a great challenge for first-principles calculations due to the interplay of a wide variety of covalent and non-covalent interactions in these systems. Here we assess the performance of the DFT+MBD

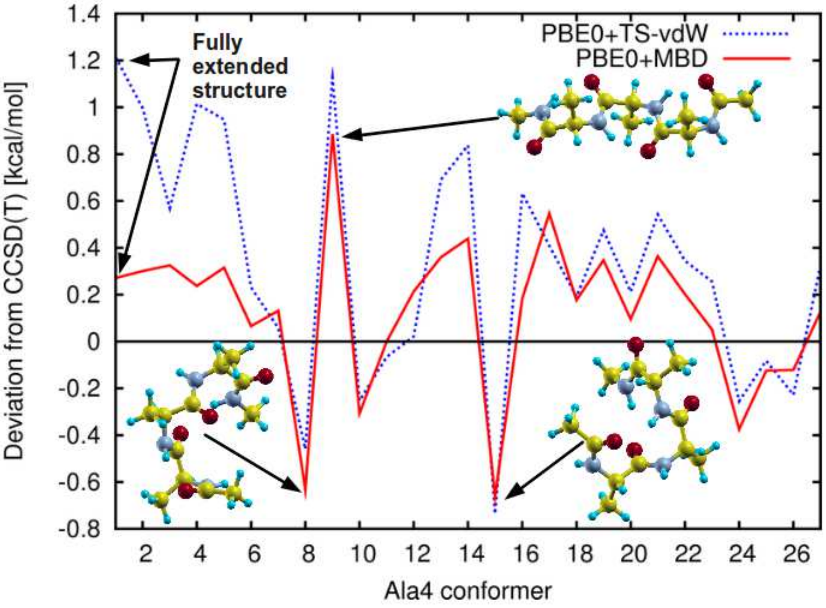

Figure 5: Performance of PBE0+TS-vdW and PBE0+MBD for the conformational energies of Ala_4. The reference CCSD(T) energies are taken from Ref. [101].

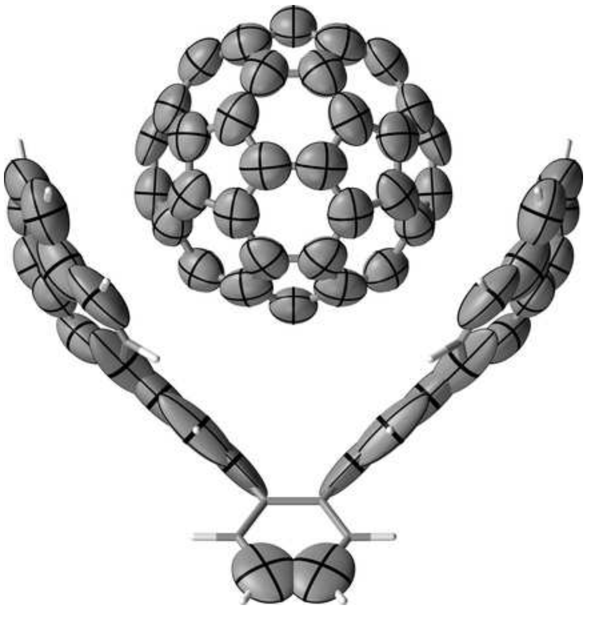

Figure 6: Illustration of the geometry and the anisotropy in the atomic TS+SCS polarizabilities of the C_{60}@$C_{60}H_{28}$ complex. The polarizability tensors are visualized as ellipsoids [104].

method on the binding of the so-called "buckyball catcher" complex, C_{60}@$C_{60}H_{28}$, shown in Figure 6. Since its synthesis [105], the buckyball catcher has become one of the most widely used benchmark systems for supramolecular chemistry. Recently a reliable binding energy of 26 ± 2 kcal/mol has been determined for the C_{60}@$C_{60}H_{28}$ complex from large-scale diffusion Monte Carlo (DMC) calculations [63]. This value is in excellent agreement with an extrapolated binding energy determined from the experimentally measured binding affinity [29].

All pairwise-corrected dispersion-inclusive DFT calculations significantly overestimate the stability of the buckyball catcher complex, anywhere from 9 to 17 kcal/mol [63]. The PBE+MBD method yields a binding energy of 36 kcal/mol, improving the binding by 7 kcal/mol compared to the PBE+TS-vdW method. The inclusion of exact exchange using the PBE0+MBD method leads to a negligible change in the binding energy. Therefore, the PBE0+MBD method overestimates the binding by at least 8 kcal/mol compared to the DMC and extrapolated experimental reference binding energies.

In order to understand the most likely origin of why the binding energy of C_{60}@$C_{60}H_{28}$ complex is overestimated by PBE0+MBD, we show the projected polarizability tensors of the full complex resulting from the TS+SCS calculation in Figure 6. One can clearly see that the polarizability distribution is highly anisotropic, with an increasing anisotropy close to the linker moiety that connects the two corannulene molecules of the catcher complex. While the approximation of isotropic C_6 coefficients used in DFT+MBD becomes sufficient as the distance between the atoms is increased, at shorter interatomic distances the anisotropy plays a non-negligible role [62]. At present, there is no efficient method that can accurately account for the fully anisotropic dispersion energy at close interatomic distances. This statement applies to the widely employed interatomic dispersion energy methods, as well as the non-local density functionals (e.g., different variants of the vdW-DF method [11]). Work is currently in progress to seamlessly include anisotropy in dispersion energy expressions [62,77]. The anisotropy in the atomic polarizabilities will change the vdW energy contribution in different directions. In the case of the C_{60}@$C_{60}H_{28}$ complex, the polarizability of the $C_{60}H_{28}$ molecule is highly anisotropic as shown in Figure 6. In the isotropic approximation, the dispersion energy between the C_{60} molecule and the corannulene moieties is therefore overestimated, because the polarization is artificially extended towards the C_{60} molecule. The fully anisotropic treatment of the dispersion energy is therefore likely to bring the binding energy closer to the DMC reference value.

4.4 Molecular Crystals

The understanding and prediction of the structure and stability of molecular crystals is of paramount importance for a variety of applications, including pharmaceuticals, non-linear optics, and hydrogen storage [106, 107]. The crystal structure prediction blind tests conducted by the Cambridge Crystallographic Data Centre have shown steady progress toward theoretical structure prediction for molecular crystals [108]. However, the insufficiency of DFT with pairwise dispersion corrections for the reliable predictions of molecular crystals is well documented, see e.g., Refs. [27,109–111].

To illustrate the role of MBD interactions in the stability of molecular crystals, we have studied a series of oligoacene crystals from naphthalene to pentacene. We have recently shown that reliable structures of oligoacene crystals (2% accuracy compared to low-temperature X-ray data) can be obtained with PBE+TS-vdW calculations, while MBD interactions play only a minor role in determining the geometry of these molecular crystals [112]. However, the MBD energy plays a more significant role for the lattice energies of oligoacene crystals. Table 4 shows lattice energies at 0 K for naphthalene (2 benzene rings), anthracene (3 rings), tetracene (4 rings), and pentacene (5 rings) calculated using the PBE+TS-vdW and PBE+MBD methods, as well as a range of measured sublimation enthalpies extrapolated to 0 K. We have only taken those experimental values that are recommended as reliable after critical revision by the authors of Ref. [113], thus avoiding anomalously small or large sublimation enthalpies. Both naphthalene and anthracene crystals have been rigorously studied, and their sublimation enthalpies are well known with a spread of 0.05 and 0.12 eV per molecule, respectively. There are fewer measurements available for tetracene and pentacene, and for the latter the three available experimental values deviate by 0.55 eV per molecule.

For naphthalene, anthracene, and tetracene, the PBE+MBD method decreases and improves the binding by about 0.1 eV (2.3 kcal/mol) per molecule when compared to PBE+TS-vdW. This is a notable improvement, especially if viewed in the context of intermolecular interactions for the S22 and S66 databases. We remind the reader that the errors of PBE+TS-vdW and PBE+MBD for molecular dimers in the S22/S66 databases are well below 0.5 kcal/mol. The much larger difference between the pairwise PBE+TS-vdW approach and the many-body PBE+MBD method for molecular crystals can be explained by the presence of significant electrodynamic screening effects in extended systems, that are virtually absent in small molecules. We refer the reader to Ref. [112] for a detailed analysis of the importance of electrodynamic screening in molecular crystals.

The remaining slight overestimation of lattice energies in Table 4 by PBE+MBD compared to the experimental range can be explained by the fact that the sublimation enthalpy is measured at finite temperatures, where the crystal unit cell undergoes thermal expansion. When using the experimental unit cell at 295 K for naphthalene, the PBE+MBD method yields a lattice energy that is increased by 50 meV per molecule, which places it essentially within the experimental range reported in Table 4. Finally, we studied the influence of exact exchange for oligoacene crystals, finding that the PBE0+MBD method leads to an almost negligible difference when compared to PBE+MBD; the lattice energy is decreased by only 10 meV/molecule when the PBE0+MBD functional is employed instead of PBE+MBD.

Table 4: Lattice energies of oligoacene crystals including zero-point energy (PBE+TS-vdW and PBE+MBD calculations were carried out using optimized PBE+TS-vdW geometries). The range of experimental ("Exp.") "lattice energies" from Ref. [113] and extrapolated to 0 K. All values are in units of eV per molecule.

	PBE+TS-vdW	PBE+MBD	Exp.
naphthalene	-0.950	-0.862	-0.803 to -0.752
anthracene	-1.324	-1.206	-1.148 to -1.024
tetracene	-1.666	-1.587	-1.525 to -1.299
pentacene	-2.035	-2.018	-2.082 to -1.533

Our current work on a broad dataset of molecular crystals and their polymorphs [114,115] shows that beyond-pairwise many-body vdW interactions can be even more significant than found here for the oligoacene crystals.

5 Remaining Challenges

In this highlight we have described a recently developed method for the many-body vdW dispersion energy based on a system of quantum harmonic oscillators (QHO). The resulting DFT+MBD approach is parameter-free for the determination of the frequency-dependent polarizability, and uses a single range-separation parameter for the coupling between the long-range many-body vdW energy and a given DFT functional. We view the DFT+MBD model as a crucial first step in the development of a reliable (accurate and efficient) method for describing many-body vdW interactions in complex materials.

Currently, the DFT+MBD method essentially amounts to solving the ACFD-RPA correlation energy equation for a system of localized screened QHOs in the dipole (long-range) approximation. There are several important extensions that can be accomplished within the ACFD framework that would allow us to go beyond the DFT+MBD method:

1. **Improving the dipolar response.** The TS+SCS method defined in Eq. (16) yields the full non-local interacting response matrix as a function of atomic positions $\mathbf{r}$ and $\mathbf{r}'$. Currently, this information is not fully utilized in the DFT+MBD approach, since we use contracted isotropic TS+SCS atomic polarizabilities as input for the ACFD-RPA formula. In principle, the full response matrix can be used in the ACFD-RPA expression, however this requires a matching definition for the range-separated Coulomb potential. The interacting TS+SCS response matrix transforms the original atom-based representation to an eigenvector representation for the coupled modes of the system. The Coulomb interaction between the coupled modes needs to be extended from our current definition of range-separation that is based on atomic vdW radii.

2. **Going beyond the dipole approximation.** The QHO model possesses a response to infinite order in the multipole expansion. The current MBD method restricts the response to the dipole approximation, effectively allowing excitations only to the first excited state for every QHO due to the dipole selection rule. In principle, the full response function given by Eq. (2) can be computed for a system of QHOs up to an arbitrary energy cutoff for the excited states. This would allow us to treat multipole responses higher than dipole (quadrupole, octupole, etc.). The ACFD-RPA expression can still be utilized in this case, allowing us to compute dispersion interactions at shorter interatomic distances. It remains to be assessed whether or not this model will be useful, as a single QHO per atom might not be able to properly describe vdW interactions at shorter interatomic distances. However, in principle, our method can also be extended to represent every atom by several QHOs.

3. **Coupling between the long-range vdW energy and the DFT energy.** The DFT+MBD method couples the long-range vdW energy to the DFT energy by using a single range-separation parameter in the Coulomb potential. In order to improve this

empirical component of the DFT+MBD method, the DFT functional has to be derived in the presence of the long-range vdW energy. To date, we have not used the fact that different functionals yield different results for the electron density tails; this information can be useful for developing a functional in which the long-range vdW energy is seamlessly integrated with the semilocal exchange-correlation functional.

4. **Simultaneous description of localized and metallic states.** Successful non-empirical DFT functionals are based on the local-density approximation (LDA) and converge to the LDA in the homogeneous electron gas (HEG) limit. LDA is an exact functional for the HEG, hence it includes vdW interactions inside the HEG. Therefore, a seamless vdW functional should yield a vanishing correction for the HEG. This can easily be accomplished by letting the polarizability vanish for slowly-varying regions of the electron density, as done in the vdW-DF [22] and VV10 [92] approaches. However, real materials (transition metals, nanostructures, etc.) are more complex than the rather simplified HEG model. In such systems, vdW interactions between ions are significant and are *screened* by the itinerant metallic electrons [116]. State-of-the-art vdW functionals do not correctly describe this complex situation. However, the DFT+MBD method can be extended to systems with localized and metallic states by introducing both localized and delocalized oscillators for every atom. The challenge consists of defining the oscillator parameters directly from the electron density and its gradient.

5. **Interatomic forces, geometry optimization, and molecular dynamics.** Currently, the DFT+MBD method only yields the total energy for a specified geometry. In principle, geometry optimizations are possible by using the finite difference approximation for the interatomic forces. This is, however, computationally expensive especially in the case of molecular dynamics. Work is in progress to derive an analytic expression for the interatomic forces corresponding to the MBD energy. Such development would allow for the routine application of the DFT+MBD method in large-scale molecular dynamics simulations.

6 Conclusions

There is mounting evidence that many-body vdW interactions, beyond the standard pairwise approximation, play a crucial role in the structure, stability, and function of a wide variety of systems of importance in biology, chemistry, and physics. In this highlight, we have illustrated the importance of including many-body vdW interactions when describing small molecular dimers, conformational energies of peptides, binding in supramolecular systems, and cohesion in molecular crystals. We presented a derivation of both the pairwise and many-body interatomic vdW dispersion energy from the exact quantum-mechanical ACFD-RPA correlation energy expression. The ACFD formula provides us with a powerful framework for the understanding and future development of accurate and efficient electronic structure approaches.

The DFT+MBD method [32, 33] represents a first step towards the development of reliable methods for describing many-body vdW interactions in complex materials. In this work, we derived the MBD energy expression from the exact ACFD formula, discussed the approximations involved, and identified the remaining challenges that need to be addressed in future work. Over the next few years, we anticipate extensive development of new dispersion energy methods that will address the truly collective many-body nature of these ubiquitous quantum-mechanical forces.

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References

[1] V. A. Parsegian, *Van der Waals forces: A Handbook for Biologists, Chemists, Engineers and Physicists* (Cambridge University Press, 2005).

[2] A. J. Stone, *The Theory of Intermolecular Forces* (Oxford University Press, 1996).

[3] I. G. Kaplan, *Intermolecular Interactions: Physical Picture, Computational Methods and Model Potentials* (John Wiley and Sons, 2006).

[4] R. French *et al.*, Rev. Mod. Phys. **82**, 1887 (2010).

[5] B. Jeziorski, R. Moszynski and K. Szalewicz, Chem. Rev. **94**, 1887 (1994).

[6] P. Loskill, H. Hähl, T. Faidt, S. Grandthyll, F. Müller and K. Jacobs, Adv. Coll. Interf. Sci. **107**, 179182 (2012).

[7] P. Loskill, J. Puthoff, M. Wilkinson, K. Mecke, K. Jacobs and K. Autumn, J. R. Soc. Interface (2013), doi:10.1098/rsif.2012.0587.

[8] K. E. Riley, M. Pitonak, P. Jurecka and P. Hobza, Chem. Rev. **110**, 5023 (2010).

[9] F. O. Kannemann and A. D. Becke, J. Chem. Theory Comput. **6**, 1081 (2010).

[10] S. Grimme, Comput. Mol. Sci. **1**, 211 (2011).

[11] V. R. Cooper, L. Kong and D. C. Langreth, Physics Procedia **3**, 1417 (2010).

[12] S. Steinmann and C. Corminboeuf, J. Chem. Theory Comput. **7**, 3567 (2011).

[13] A. Tkatchenko, L. Romaner, O. T. Hofmann, E. Zojer, C. Ambrosch-Draxl and M. Scheffler, MRS Bull. **35**, 435 (2010).

[14] A. J. Misquitta, R. Podeszwa, B. Jeziorski and K. Szalewicz, J. Chem. Phys. **123**, 214103 (2005).

[15] O. A. von Lilienfeld, I. Tavernelli, U. Rothlisberger and D. Sebastiani, Phys. Rev. Lett. **93**, 153004 (2004).

[16] E. R. Johnson and A. D. Becke, J. Chem. Phys. **123**, 024101 (2005).

[17] P. L. Silvestrelli, Phys. Rev. Lett. **100**, 053002 (2008).

[18] G. Mercurio, E. R. McNellis, I. Martin, S. Hagen, F. Leyssner, S. Soubatch, J. Meyer, M. Wolf, P. Tegeder, F. S. Tautz and K. Reuter, Phys. Rev. Lett. **104**, 036102 (2010).

[19] N. Atodiresei, V. Caciuc, P. Lazic and S. Blügel, Phys. Rev. Lett. **102**, 136809 (2009).

[20] K. Tonigold and A. Gross, J. Chem. Phys. **132**, 224701 (2010).

[21] D. Stradi, S. Barja, C. Diaz, M. Garnica, B. Borca, J. J. Hinarejos, D. Sanchez-Portal, M. Alcami, A. Arnau, A. L. Vazquez de Parga, R. Miranda and F. Martin, Phys. Rev. Lett. **106**, 186102 (2011).

[22] M. Dion, H. Rydberg, E. Schroder, D. C. Langreth and B. I. Lundqvist, Phys. Rev. Lett. **92**, 246401 (2004).

[23] K. Lee, E. D. Murray, L. Kong, B. I. Lundqvist and D. C. Langreth, Phys. Rev. B **92**, 081101 (2010).

[24] O. A. Vydrov and T. Van Voorhis, J. Chem. Theory Comput. **8**, 1929 (2012).

[25] A. Tkatchenko and M. Scheffler, Phys. Rev. Lett. **102**, 073005 (2009).

[26] N. Marom, A. Tkatchenko, M. Rossi, V. V. Gobre, O. Hod, M. Scheffler and L. Kronik, J. Chem. Theory Comput. **7**, 3944 (2011).

[27] O. A. von Lilienfeld and A. Tkatchenko, J. Chem. Phys. **132**, 234109 (2010).

[28] S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys. **132**, 154104 (2010).

[29] S. Grimme, Chem. Eur. J **18**, 9955 (2012).

[30] G.-X. Zhang, A. Tkatchenko, J. Paier, H. Appel and M. Scheffler, Phys. Rev. Lett. **107**, 245501 (2011).

[31] V. G. Ruiz, W. Liu, E. Zojer, M. Scheffler and A. Tkatchenko, Phys. Rev. Lett. **108**, 146103 (2012).

[32] A. Tkatchenko, R. A. DiStasio, Jr., R. Car and M. Scheffler, Phys. Rev. Lett. **108**, 236402 (2012).

[33] R. A. DiStasio Jr., O. A. von Lilienfeld and A. Tkatchenko, Proc. Natl. Acad. Sci. USA **109**, 14791 (2012).

[34] J. F. Dobson and T. Gould, Calculation of Dispersion Energies, `http://www.psi-k.org/newsletters/News_107/Highlight_107.pdf`, 2011.

[35] J. Klimes and A. Michaelides, J. Chem. Phys. **137**, 120901 (2012).

[36] Towards First-Principles Description of van der Waals Interactions in Complex Materials, `http://www.cecam.org/workshop-791.html`, 2012.

[37] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

[38] D. C. Langreth and J. P. Perdew, Phys. Rev. B **15**, 2884 (1977).

[39] S. L. Adler, Phys. Rev. **126**, 413 (1962).

[40] N. Wiser, Phys. Rev. **129**, 62 (1963).

[41] D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953).

[42] M. Gell-Mann and K. A. Brueckner, Phys. Rev. **106**, 364 (1957).

[43] M. Fuchs and X. Gonze, Phys. Rev. B **65**, 235109 (2002).

[44] F. Furche and T. van Voorhis, J. Chem. Phys. **122**, 164106 (2005).

[45] F. Furche, J. Chem. Phys. **129**, 114105 (2008).

[46] G. E. Scuseria, T. M. Henderson and D. C. Sorensen, J. Chem. Phys. **129**, 231101 (2008).

[47] B. G. Janesko, T. M. Henderson and G. E. Scuseria, J. Chem. Phys. **130**, 081105 (2009).

[48] J. Toulouse, I. C. Gerber, G. Jansen, A. Savin and J. G. Ángyán, Phys. Rev. Lett. **102**, 096404 (2009).

[49] J. Harl and G. Kresse, Phys. Rev. B **77**, 045136 (2008).

[50] J. Harl and G. Kresse, Phys. Rev. Lett. **103**, 056401 (2009).

[51] D. Lu, Y. Li, D. Rocca and G. Galli, Phys. Rev. Lett. **102**, 206411 (2009).

[52] J. F. Dobson and J. Wang, Phys. Rev. Lett **82**, 2123 (1999).

[53] M. Rohlfing and T. Bredow, Phys. Rev. Lett **101**, 266106 (2008).

[54] X. Ren, P. Rinke and M. Scheffler, Phys. Rev. B **80**, 045402 (2009).

[55] L. Schimka, J. Harl, A. Stroppa, A. Grüneis, M. Marsman, F. Mittendorfer and G. Kresse, Nature Mater. **9**, 741 (2010).

[56] Y. Li, D. Lu, H.-V. Nguyen and G. Galli, J. Phys. Chem. A **114**, 1944 (2010).

[57] X. Ren, A. Tkatchenko, P. Rinke and M. Scheffler, Phys. Rev. Lett. **106**, 153003 (2011).

[58] X. Ren, P. Rinke, C. Joas and M. Scheffler, J Mater. Sci. **47**, 7447 (2012).

[59] D. Lu, H.-V. Nguyen and G. Galli, J. Chem. Phys. **133**, 154110 (2010).

[60] X. Ren, P. Rinke, V. Blum, J. Wieferink, A. Tkatchenko, A. Sanfilippo, K. Reuter and M. Scheffler, New. J. Phys **14**, 053020 (2012).

[61] J. F. Dobson, Quasi-local-density approximation for a van der Waals energy functional, in *Topics in Condensed Matter Physics*, edited by M. P. Das, p. 121, Nova (New York), 1994.

[62] A. Krishtal, K. Vannomeslaeghe, D. Geldof, C. V. Alsenoy and P. Geerlings, Phys. Rev. A **83**, 024501 (2011).

[63] A. Tkatchenko, D. Alfè and K. S. Kim, J. Chem. Theory Comput. **8**, 4317 (2012).

[64] B. M. Axilrod and E. Teller, J. Chem. Phys. **11**, 299 (1943).

[65] T. Helgaker, P. Jørgensen and J. Olsen, *Molecular Electronic Structure Theory* (Wiley, Chichester, 2000).

[66] A. Mayer, Phys. Rev. B **75**, 045407 (2007).

[67] D. W. Oxtoby and W. M. Gelbart, Mol. Phys. **29**, 1569 (1975).

[68] B. T. Thole, Chem. Phys. **59**, 341 (1981).

[69] R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford Science Publications, 1989).

[70] W. Koch and M. C. Holthausen, *A Chemist's Guide to Density Functional Theory* (Wiley-VCH, 2002).

[71] F. L. Hirshfeld, Theor. Chim. Acta **44**, 129 (1977).

[72] W. L. Bade, J. Chem. Phys. **27**, 1280 (1957).

[73] J. Cao and B. J. Berne, J. Chem. Phys. **97**, 8628 (1992).

[74] A. G. Donchev, J. Chem. Phys. **125**, 074713 (2006).

[75] M. W. Cole, D. Velegol, H.-Y. Kim and A. A. Lucas, Mol. Simul. **35**, 849 (2009).

[76] H. Berthoumieux and A. C. Maggs, Europhys. Lett. **91**, 56006 (2010).

[77] A. Tkatchenko, A. Ambrosetti and R. A. DiStasio, Jr., arXiv:1210.8343 (2012).

[78] T. W. Whitfield and G. J. Martyna, Chem. Phys. Lett. **424**, 409 (2006).

[79] A. Jones, A. Thompson, J. Crain, M. H. Müser and G. J. Martyna, Phys. Rev. B **79**, 144119 (2009).

[80] P. Jurecka, J. Sponer, J. Cerny and P. Hobza, Phys. Chem. Chem. Phys. **8**, 1985 (2006).

[81] T. Takatani, E. G. Hohenstein, M. Malagoli, M. S. Marshall and C. D. Sherrill, J. Chem. Phys. **132**, 144104 (2010).

[82] J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[83] J. P. Perdew, M. Ernzerhof and K. Burke, J. Chem. Phys. **105**, 9982 (1996).

[84] C. Adamo and V. Barone, J. Chem. Phys. **110**, 6158 (1999).

[85] V. V. Gobre *et al.*, in preparation.

[86] R.-F. Liu, J. G. Angyan and J. F. Dobson, J. Chem. Phys. **134**, 114106 (2011).

[87] J. R. Hammond, M. Valiev, W. A. de Jong and K. Kowalski, J. Phys. Chem. A **111**, 5492 (2007).

[88] J. R. Hammond, K. Kowalski and W. A. de Jong, J. Chem. Phys. **127**, 144105 (2007).

[89] S. Botti, A. Castro, X. Andrade, A. Rubio and M. A. L. Marques, Phys. Rev. B **78**, 035333 (2008).

[90] A. Kumar, M. Kumar and W. J. Meath, Chem. Phys. **286**, 227 (2003).

[91] V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter and M. Scheffler, Comp. Phys. Commun. **180**, 2175 (2009).

[92] O. A. Vydrov and T. Van Voorhis, J. Chem. Phys. **133**, 244103 (2010).

[93] J. Rezac, K. E. Riley and P. Hobza, J. Chem. Theory Comput. **7**, 2427 (2011).

[94] W. Chin, F. Piuzzi, I. Dimicoli and M. Mons, Phys. Chem. Chem. Phys. **8**, 1033 (2006).

[95] J. P. Simons, Mol. Phys. **107**, 2435 (2009).

[96] F. Bierau, P. Kupser, G. Meijer and G. von Helden, Phys. Rev. Lett. **105**, 133402 (2010).

[97] M. P. Gaigeot, Phys. Chem. Chem. Phys. **12**, 3336 (2010).

[98] J. A. Stearns, C. Seaiby, O. V. Boyarkin and T. R. Rizzo, Phys. Chem. Chem. Phys. **11**, 125 (2009).

[99] M. Rossi, V. Blum, P. Kupser, G. von Helden, F. Bierau, K. Pagel, G. Meijer and M. Scheffler, J. Phys. Chem. Lett. **1**, 3465 (2010).

[100] R. L. Baldwin, J. Mol. Biol. **371**, 283 (2007).

[101] A. Tkatchenko, M. Rossi, V. Blum, J. Ireta and M. Scheffler, Phys. Rev. Lett. **106**, 118102 (2011).

[102] R. A. DiStasio Jr., Y. Jung and M. Head-Gordon, J. Chem. Theory Comput. **1**, 862 (2005).

[103] R. A. DiStasio Jr., R. P. Steele, Y. M. Rhee, Y. Shao and M. Head-Gordon, J. Comp. Chem. **28**, 839 (2007).

[104] K. N. Trueblood, H.-B. Bürgi, H. Burzlaff, J. D. Dunitz, C. M. Gramaccioli, H. H. Schulz, U. Shmueli and S. C. Abrahams, Acta Crys. A **52**, 770 (1996).

[105] A. Sygula, F. R. Fronczek, R. Sygula, P. W. Rabideau and M. M. Olmstead, J. Am. Chem. Soc. **129**, 3842 (2007).

[106] J. Bernstein, *Polymorphism in Molecular Crystals* (Oxford University Press, USA (New York), 2002).

[107] S. L. Price, Phys. Chem. Chem. Phys. **10**, 1996 (2008).

[108] D. A. Bardwell *et al.*, Acta. Cryst. B **67**, 535 (2011).

[109] G. J. O. Beran and K. Nanda, J. Phys. Chem. Lett. **1**, 3480 (2010).

[110] S. Wen, K. Nanda, Y. Huang and G. Beran, Phys. Chem. Chem. Phys. **14**, 7578 (2012).

[111] K. Hongo, M. A. Watson, R. S. Sanchez-Carrera, T. Iitaka and A. Aspuru-Guzik, J. Phys. Chem. Lett. **1**, 1789 (2010).

[112] B. Schatschneider, J.-J. Liang, A. M. Reilly, N. Marom, G.-X. Zhang and A. Tkatchenko, arXiv:1211.1683.

[113] M. V. Roux, M. Temprado, J. S. Chickos and Y. Nagano, J. Phys. Chem. Ref. Data **37**, 1855 (2008).

[114] A. M. Reilly and A. Tkatchenko, in preparation.

[115] N. Marom, R. A. DiStasio, Jr., V. Atalla, S. Levchenko, J. R. Chelikowsky, L. Leiserowitz and A. Tkatchenko, arXiv:1210.5636.

[116] J. J. Rehr, E. Zaremba and W. Kohn, Phys. Rev. B **12**, 2062 (1975).