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

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and Psi-k

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# 1 Editorial

In this issue we have three reports on Psi-k/CECAM meetings, two job announcements, and a number of abstracts of newly submitted or recently published papers.

The scientific highlight of this issue is by John F. Dobson and Timothy Gould (Griffith University, Nathan, Australia) on "Calculation of Dispersion Energies".

For details on this Psi-k Newsletter please check the table of content.

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**

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## 2 Psi-k Activities

### ”Towards Atomistic Materials Design”

#### 2.1 Reports on Workshops/Meetings/Schools supported by Psi-k

##### 2.1.1 Report on Psi-k/CECAM/CCP9 Biennial Graduate School in Electronic-Structure Methods

Oxford

10th-16th July 2011

Sponsors: CECAM, Psi-k, CCP9 (UK), ESF

Nicola Marzari (Oxford University)

Walter Temmerman (Daresbury Laboratory)

Jonathan Yates (Oxford University)

Web Page: <http://mml.materials.ox.ac.uk/Support/GraduateSchool2011>

**Summary** The Psi-k/CECAM/CCP9 Biennial Graduate School in Electronic-Structure Methods was held in Oxford from Sunday 10th July until Saturday 16th July 2011. This was a combined theory and hands-on school, with morning sessions dedicated to lectures introducing theory and application of electronic structure methods, and afternoon sessions providing hands-on experience with the relevant codes on a high-performance compute cluster provided by the Oxford Supercomputer Centre.

The first two days were dedicated to density functional theory within the planewave pseudopotential formalism and its implementation in the PWSCF program. Lectures were given by Stefano Baroni and Nicola Marzari, and the hand-on session run by Davide Ceresoli and Nicola Bonini. A poster session was held on the Tuesday evening which proved a well attended and much appreciated event. The following day was dedicated to linear scaling methods and was run by the developers of the ONETEP code; Peter Haynes, Arash Mostofi and Chris Skylaris. Thursday moved to LMTO taught by Martin Leuders, Leon Petit, Dzidka Szotek and Walter Temmerman. That evening the conference dinner was held at The Queen’s College with pre-dinner drinks in the Provost’s Garden courtesy of the current Provost, Paul Madden, and the dinner itself in the impressive 18th century Dining Hall. The final day of the school was dedicated to Quantum Monte Carlo with morning lectures by Richard Needs and an afternoon practical session on the Casino code run by Neil Drummond.

The School proved very popular and was significantly over-subscribed. We were able to find places for 38 students representing 13 different countries. The feedback was overwhelmingly positive, and many constructive suggestions were provided: typically students wanted us to add a particular topic - GW and Wannier functions were popular suggestions.

The school has run biennially for a number of years. From this year's experience we feel there is a clear need for this level of graduate training and we hope that there is support for such a school in 2013.

## Program

Monday 11th July

09:00-10:00 *Density-functional Theory* Stefano Baroni

10:00-11:00 *Density-functional Theory* Stefano Baroni

11:30-12:30 *Density-functional Practice* Nicola Marzari

14:00-17:30 *Quantum Espresso Hands-on 1* Davide Ceresoli, Nicola Bonini

Tuesday 12th July

09:00-10:00 *Density-functional Perturbation Theory* Stefano Baroni

10:00-11:00 *Time-dependent DFT* Stefano Baroni

11:30-12:30 *Density-functional Perturbation Theory* Nicola Bonini

14:00-17:30 *Quantum Espresso Hands-on 2* Nicola Bonini, Davide Ceresoli

Wednesday 13th July

09:00-09:40 *Introduction to Linear Scaling* Peter Haynes

09:40-10:20 *The Onetep code* Chris Skylaris

10:50-11:30 *Applications of Linear Scaling* Arash Mostofi

11:30-12:30 *Materials Modelling in Oxford* Jonathan Yates

14:00-17:30 *Onetep Hands-on* P. Haynes, A. Mostofi, C. Skylaris

Thursday 14th July

09:00-10:00 *LMTO* Martin Lueders

10:00-11:00 *Wannier functions and Model Hamiltonians* Jonathan Yates

11:30-12:30 *LMTO 2* Leon Petit

14:00-17:30 *LMTO Hands-on* W. Temmerman, D. Szotek, M. Lueders, L. Petit

Friday 15th July

09:00-10:00 *Quantum Monte Carlo* Richard Needs

10:00-11:00 *QMC 2* Richard Needs

11:30-12:30 *The Casino Code* Richard Needs

### **Organisers and lecturers**

Stefano Baroni *SISSA Italy*  
Nicola Bonini *University of Oxford UK*  
Davide Ceresoli *University of Oxford UK*  
Neil Drummond *University of Lancaster UK*  
Peter Haynes *Imperial College London UK*  
Martin Leuders *Daresbury Laboratory UK*  
Nicola Marzari *University of Oxford UK*  
Arash Mostofi *Imperial College London UK*  
Richard Needs *University of Cambridge UK*  
Leon Petit *Daresbury Laboratory UK*  
Chris Skylaris *University of Southampton UK*  
Dzidka Szotek *Daresbury Laboratory UK*  
Walter Temmerman *Daresbury Laboratory UK*  
Jonathan Yates *University of Oxford UK*

### **Participants**

Philippe Aeberhard *University of Oxford UK*  
Merid Legesse Belayneh *University College Cork Ireland*  
Raffaello Bianco *Universita Degli Studi di Trieste Italy*  
Frederic Blanc *University of Cambridge UK*  
Pietro Bonfa *Universita degli Studi di Pavia Italy*  
Peter Bryrne *University of Durham UK*  
Pascal Bugnion *University of Cambridge UK*  
Thomas Cathart *Trinity College Dublin Ireland*  
Shin Liang Chin *University of Cambridge UK*  
Nguyen Huu Chuong *Universite Libre de Bruxelles Belgium*  
Riza Dervisoglu *University of Cambridge UK*  
Marco di Gennaro *Universite de Liege Belgium*  
Domenico di Sante *University of L'Aquila Italy*  
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Natalie Tillack *University of Oxford UK*  
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## 2.2 Report on Psi-k Workshop on KKR and Related Greens Function Methods

Halle, Germany

July 8-10, 2011

Psi-k Network,

Max Planck Institute of Microstructure Physics and  
Martin Luther University Halle-Wittenberg

Arthur Ernst, Wolfram Hergert, Ingrid Mertig

[http://slab.physik.uni-halle.de/kkr\\_workshop](http://slab.physik.uni-halle.de/kkr_workshop)

Scientific Report

The importance of ab initio electronic structure simulations based on Density Functional Theory is well-established in materials science, new approaches and theories are being continuously implemented to study novel problems and materials. The Korringa-Kohn-Rostoker (KKR) method is known to be a highly versatile tool to investigate, e.g., relativistic effects and electron correlations, magnetic and chemical interactions, spectroscopic properties, as well as electric transport in solids ranging from bulk to nanoparticles. This versatility of the KKR method mainly stems from the Greens function formalism it employs.

Back to several decades, leading groups of the KKR method have organized annual or biannual meetings with the aim to exchange experiences in developing computer codes and to discuss scientific achievements and further progress that can be accessed in terms of this methodology. As those groups are mostly located in Europe, Psi-k naturally provided a background to host and support these meetings during the past decade. It was the very purpose of this workshop to continue this tradition and, thus, to keep the KKR method in the forefront of ab initio based computational materials science.

The workshop was intended to continue a regular series of meetings of the KKR research community organized under support of Psi-k (Munich 2004, Bristol 2006, Canterbury 2008, Budapest 2009). A particular feature of the current workshop was that not only the KKR community was presented but as well groups working with other Green function related methods. 73 participant from seven European countries joined the workshop.

Related to recent advances achieved and novel challenges met by the KKR method, the workshop was focused to developments and applications of relativistic electron theory and phenomena driven by spin-orbit interaction:

- The calculation of magnetic anisotropies and magnetic interactions of relativistic origin such as the Dzyaloshinskii-Moriya interaction.

- Advances in understanding the spin and the anomalous Hall effect in terms of Boltzmann's transport equation or of the Kubo formalism.
- Developments with respect to topological phases to consider phenomena like the intrinsic spin and the intrinsic anomalous Hall effect as well as orbital polarization.
- Ab initio vs. multiscale approaches to spin-dynamics to study finite temperature metallic magnetism from simple metals to heterogeneous systems of technological interest.
- Magnetism on the atomic scale: clusters and nanoparticles of different shape deposited on surfaces, beating the superparamagnetic limit for high density magnetic recording.
- Functional materials for spintronics: oxides, half-metals, multi- and nanoferroics.
- Excitations (magnons and phonons) based on the dynamic linear response theory. The latter formalism is particularly well implementable with the KKR method. (viii) Ab initio description of magnon and phonon assisted inelastic transport phenomena.
- First principles description of strongly correlated materials within the multiple-scattering theory.

Beyond the above topics, other research fields commonly accessed by Green function methods (e.g., to alloy theory) were presented during the workshop. In addition, a session was devoted to discuss computational methods and problems with emphasis to recent developments of full-potential KKR method and related Green function methods. Each presentation of the workshop was followed by intensive discussions among the participants of the workshop. The general scientific atmosphere of the discussions and the workshop in general was open and creative.

## Programme

Friday, 8th of July			
Time		Speaker	Title
12:30-13:25			<i>Coming together, Refreshments</i>
13:25-13:30			<i>Opening remarks</i>
<i>Magnetism</i>			
13:30-14:00	I1	J. Staunton	Competing magnetic interactions in transition metal and rare earth materials from ab-initio electronic structure electronic structure theory
14:00-14:30	I2	L. Udvardi	Finding a non-collinear magnetic groundstate
14:30-15:00	I3	B. Ujfalussy	Exchange interactions on alloy surfaces
15:00-15:30	I4	V. Drchal	Effective magnetic Hamiltonians
15:30-15:50			<i>Coffee break</i>
<i>Superconductivity, Magnons</i>			
15:50-16:20	I5	H. Gross	Ab-initio approach to superconductivity
16:20-16:50	I6	P. Buczek	Magnon-electron scattering in nanoscale transport
16:50-17:20	I7	L. Sandratskii	Interface electronic complexes and Landau damping of magnons in ultrathin magnets
17:20-17:30			<i>Coffee Break</i>
<i>Nanostructures, Surfaces</i>			
17:30-18:00	I8	P. Zahn	Transport properties of nanostructured thermoelectric materials
18:00-18:30	I9	V. Stepanyuk	Quantum confinement of electrons in atomic-scale nanostructures
18:30-18:45	C1	O. Brovko	Confined bulk-states as a long-range sensor for impurities and a transfer channel for quantum information
18:45-19:00			<i>Break</i>
19:00-21:00			Postersession / <i>Refreshments</i>

Saturday, 9th of July			
Time		Speaker	Title
<i>Rashba effect</i>			
08:30-09:00	I10	L. Szunyogh	Generalized Bychkov-Rashba Hamiltonians
09:00-09:30	I11	J. Braun	Actual trends in ARPES: Correlation, disorder and Rashba physics
09:30-09:45	C2	F. Freimuth	Spin-orbit mediated torque in Rashba systems
09:45-10:00	C3	O. Siper	Induced magnetic moments make MAE calculation fun or nightmare
10:00-10:30	<i>Coffee break</i>		
<i>Anisotropies, topological insulators</i>			
10:30-11:00	I12	H. Ebert	Fully relativistic calculations of the magnetic shape anisotropy and of the Gilbert damping parameter
11:00-11:30	I13	I. Turek	Tunneling anisotropic magnetoresistance in Fe/GaAs/Ag(001)
11:30-12:00	I14	J. Henk	Properties of the undoped and magnetically doped 3D topological insulator Bi <sub>2</sub> Te <sub>3</sub>
12:00-12:15	C4	M. Garcia Vergniory	Ab initio study of the surface properties of a new ternary compound topological insulator
12:15-12:30	C5	H. Zhang	Electrically tunable quantum anomalous Hall effect in 5d transition-metal adatoms on graphene
12:30-13:30	<i>Lunch break</i>		
<i>Spin Hall effect, spin relaxation</i>			
13:30-14:00	I15	M. Gradhand	The Berry curvature and the spin Hall effect calculated with the KKR
14:00-14:30	I16	D. Ködderitzsch	Spin and anomalous Hall effect in transition-metal alloys
14:30-15:00	I17	P. Mavropoulos	Spin relaxation due to impurity scattering in non-magnetic metallic systems
15:00-15:30	I18	D. Fedorov	Elliott-Yafet spin relaxation mechanism within the KKR method
15:30-16:00	<i>Coffee break</i>		
<i>Excitations</i>			
16:00-16:30	I19	Y. Mokrousov	Recent advances in ab initio theory of transverse scattering-independent transport
16:30-17:00	I20	B. Gyorffy	The Berry phase of Dirac electrons and spin-orbit coupling
17:00-17:30	I21	S. Lounis	Dynamical magnetic excitations of nanostructures
17:30-18:00	I22	Chr. Heiliger	Spin transfer torques in magnetic tunnel junctions
19:30-23:00	<i>Conference dinner</i>		

Sunday, 10th of July			
Time		Speaker	Title
<i>Methods</i>			
08:30-09:00	I23	L. Vitos	The EMTO method: Implementation and demonstration
09:00-09:30	I24	R. Zeller	Projection potentials, Loyd's formula and angular momentum convergence of total energies in full-potential KKR
09:30-10:00	I25	H. Akai	Total energy calculation within EXX+RPA
10:00-10:30	I26	R. Hammerling	The non-relativistic full potential single site problem
10:30-10:50	<i>Coffee break</i>		
<i>Order - Disorder - Electronic Structure</i>			
10:50-11:20	I27	M. Ogura	First-principles calculation of structural transformation
11:20-11:50	I28	J. Kudrnovsky	Quaternary Heusler alloys (Ni, Cu) <sub>2</sub> MnSn: Electronic, magnetic, and transport properties
11:50-12:20	I29	C. Etz	Ab initio study of strongly correlated materials
12:20-12:35	C6	A. Marmodoro	A multi-sublattice extension of the non-local coherent potential approximation
12:35-12:50	C7	S. Mankovsky	Spin spirals in ordered and disordered solids
12:50-13:00			<i>Closing remarks</i>
13:00-14:00	<i>Lunch</i>		

### List of Participants

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42	Lounis	Samir	Forschungszentrum Jülich, Peter-Grünberg-Institut
43	Madjarova	Galia	University of Sofia
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53	Rühl	Andreas	Justus-Liebig-Universität Gießen
54	Sandratskii	Leonid	Max-Planck-Institut für Mikrostrukturphysik
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60	Tao	Kun	Max-Planck-Institut für Mikrostrukturphysik
61	Tauber	Katarina	Martin-Luther-Universität Halle-Wittenberg
62	Turek	Ilja	Czech Academy of Sciences, Institute of Physics
63	Udvardi	Laszlo	Budapest University of Technology and Economics
64	Ujfalussy	Balazs	HAS, Research Institute for Solid State Physics
65	Vitos	Levente	Royal Institute of Technology Stockholm
66	Wimmer	Sebastian	Ludwig-Maximilians-Universität München
67	Winter	Hermann	Karlsruher Institut für Technologie
68	Yavorsky	Bogdan	Martin-Luther-Universität Halle-Wittenberg
69	Zahn	Peter	Martin-Luther-Universität Halle-Wittenberg
70	Zeller	Rudolf	Forschungszentrum Jülich, IAS-3
71	Zhang	Hongbin	Forschungszentrum Jülich, Institute for Advanced Simulation
72	Zimmermann	Bernd	Forschungszentrum Jülich, Peter-Grünberg-Institut
73	Zubizarreta	Xabier	Donostia International Physics Center

## 2.2.1 Report on the Psi-k/CECAM Event on Self-Interaction Correction: State of the Art and New Directions

September 18, 2011 (evening) to September 21, 2011

Ramada Jarvis Hotel, Chester, UK



### Organisers:

Martin Lueders, Leon Petit and Zdzislawa (Dzidka) Szotek (STFC Daresbury Laboratory, UK)

### Local administration:

Wendy Cotterill and Shirley Miller (STFC Daresbury Laboratory, UK)

### Sponsored by

ESF/Charity Psi-k Network and CECAM Node at STFC Daresbury Laboratory (UK)

### Webpage

http:

[//www.cse.scitech.ac.uk/cecam\\_at\\_daresbury/self-interaction\\_correction.shtml](http://www.cse.scitech.ac.uk/cecam_at_daresbury/self-interaction_correction.shtml)

### Scientific report

This Psi-k/CECAM event on "Self-Interaction Correction: state of the art and new directions" took place on the thirtieth anniversary of John Perdew and Alex Zunger's seminal paper on correcting self-interaction error inherent in local density approximation to density functional theory [Phys. Rev. B23, 5048 (1981)]. This paper had initiated a variety of new implementations, generalizations, and extensions of the proposed self-interaction correction (SIC) approach, nominally giving rise to a new "field". It had also led to a plethora of applications in different fields of physics and chemistry. Over the years, it had become apparent that different "varieties" of SIC had been developed nearly independently of each other, in particular in the field of quantum chemistry and solid state physics, with the experiences/advances gained in one field barely

noticed in the other areas. Thus the paramount goal of this event was to bring together, for the first time, all the groups that had applied and worked on self-interaction correction, in order to discuss and assess the state of the art of all the different flavours of SIC, share the experiences and identify the most important and burning issues, unsolved problems, and perhaps find a common direction for future developments.

The meeting took place in a beautiful city of Chester, the capital of the Cheshire county, U.K. The city is unique in its rich history, and comfortably ranks alongside the cities of London, York, Bath and Edinburgh. Chester was founded by the Romans over 2000 years ago, and much of the Roman influence remains and Chester City Walls are the most complete in Britain. The venue of the meeting, the Ramada Chester Hotel, is situated 2 miles away from the centre of the city, in a quiet, green area. It provided nice and enjoyable atmosphere for the lectures and lively discussions.

The event attracted over 40 participants from all over the world, with 11 from the U. K., the country of the organizers of the meeting, seven from the USA, six from Germany, three each from Denmark and Iceland, two from France, Italy, Ireland, Japan, and Switzerland, and one from Brazil and Sweden. It was organized around 20 invited talks of 45 minutes (see the list below), a poster session to allow participants to present and discuss their contributed papers, and a two-hours long, concluding and summarizing, round table discussion.

### **Invited Speakers**

Hisazumi Akai (Osaka University, Japan)

Björn Baumeier (MPI Mainz, Germany)

Klaus Capelle (Sao Paulo, Brazil)

Aron Cohen (Cambridge, UK)

Olle Eriksson (Uppsala University, Sweden)

Alessio Filippetti (Cagliari, Italy)

Nikitas Gidopoulos (STFC RAL, U.K.)

Peter Küepfel (Faculty of Science, VR-II, Univ. of Iceland)

Stephan Kuemmel (University of Bayreuth, Germany)

Nicola Marzari (University of Oxford, UK)

Mark R. Pederson (NRL, USA)

John P. Perdew (Tulane University, USA)

Adrienn Ruzsinszky (Tulane University, USA)

Stefano Sanvito (Trinity College Dublin, Ireland)

Thomas C. Schulthess (ETH Zurich, Switzerland)

Julie B. Staunton (Warwick University, UK)

Eric Suraud (University of Toulouse, France)

Axel Svane (Aarhus University, Denmark)

Takao Tsuneda (Yamanshi University, Japan)

Alex Zunger (Colorado University Boulder, USA)

## Moderator of Round Table Discussion:

George Malcolm Stocks (ORNL, USA)

## Poster Session Presentations: Chair: Antonios Gonis (LLNL)

Markus Daene (Oak Ridge)

"Computationally Simple, Analytic, Closed Form Solution of the Self-Interaction Problem in Kohn-Sham Density Functional Theory"

Guntram Fischer (Halle)

"Magnetic Properties of Polar ZnO Surfaces: Application of SIC"

Hildur Guðmundsdóttir (Reykjavik)

"Self-interaction correction within the PAW formalism: implementation and applications"

Dirk Hofmann (Bayreuth)

"Self-interaction correction in the time-dependent Kohn-Sham scheme"

Simon Klüpfel (Reykjavik)

"More complex than expected: The Self-interaction corrected ground state of atoms and molecules"

Martin Lueders (Daresbury)

"Flavours of SIC"

Keld Lundgaard (Lyngby)

"Exchange correlation functionals including non-local correlation and error estimation"

The meeting was officially opened on Monday morning by Walter Temmerman, representing both the Psi-k ESF/Charity and the Daresbury node of CECAM, the institutions sponsoring the event. The opening invited talk of the meeting was by John Perdew, presenting his thoughts on SIC after 30 years. He discussed the dramatic successes and failures of the original Perdew and Zunger (PZ) SIC formulation. He also proposed two variants of PZ-SIC thus providing useful foundation for the rest of the meeting. Alex Zunger followed with his invited talk, addressing issues of the violation of the linear behaviour of the total energy on occupation number by approximate DFT approaches and discussed a simple, self-interaction-free, fix that restores the linearity. Mark Pederson presented a retrospective on computational challenges for wide-spread use of self-interaction corrections, discussing the physical significance of localized and canonical orbitals in applications of SIC to molecules and solids and the impact of full-scale implementation in application-oriented fields. Nicola Marzari discussed electronic structure challenges, some of which stem from the remnants of self-interaction, for trying to reach qualitative and quantitative

accuracy and ability to perform quantum simulations under realistic conditions. He suggested possible solutions for these challenges based on constrained DFT, extended Hubbard functionals, or on imposing a generalization of Koopmans' theorem. Klaus Capelle started from reviewing connections between DFT and model Hamiltonians, highlighting the many possible benefits that arise from using insights from DFT to study model Hamiltonians, and ideas arising from model Hamiltonians to improve functionals for DFT. He considered orbital-dependent functionals, the PZ-SIC, and compared results from six different levels of approximate implementation, ranging from simple post-LDA strategies to a full OEP, to available exact results. Stephan Kuemmel discussed the Kohn-Sham approach to the SIC using one global multiplicative potential and studied the effects of orbital localization and the physical reliability of the thus obtained eigenvalues of organic semiconductor molecules. Peter Kluepfel presented results of self-consistent calculations of PZ-SIC applied to GGA and LDA functionals for atoms, molecules and solids. The use was made of an efficient method to minimize the energy with respect to the orbitals, involving explicit unitary optimization. Olle Eriksson gave the last invited talk of Monday, briefly outlining the Lundin-Eriksson approach to SIC, then full-potential LMTO implementation of PZ-SIC and recent developments of DMFT.

The poster session was very lively and enjoyed by all the participants. A few minutes long oral introductions of the posters by their presenters were found very helpful in organizing one's viewing preferences. A special highlight of the evening was a cake presented to John Perdew and Alex Zunger (see the photos below), with the first page of their seminal SIC paper imprinted on the icing on the top of the cake. Since the CECAM Council had decided to fund the SIC meeting not as a regular workshop, but as a celebration event, we came to conclusion that a cake, would be a fitting tribute to the celebration. The cake was cut by Alex, with John's assistance, and as seen in the photograph below, both seem to have enjoyed the experience and, hopefully, the cake as well. The cake was large enough, so everybody could eat a piece of it, and the lucky ones could even get a taste of an equation or similar.



Axel Svane gave the first talk of the Tuesday morning presenting results of many applications to  $4f$  and  $5f$  electron solids, based on the PZ-SIC implementation within the LMTO-ASA band structure method, discussing localization/delocalization phenomena and valency. Thomas Schulthess presented early results from the PZ-SIC implementation in the full-potential LAPW code and discussed the importance of spherical vs. non-spherical issues in comparison with importance of the choice of the starting Wannier functions and energy minimization. Björn Baumeier started the sequence of talks related to the so-called pseudo-SIC approach for crystalline systems. Allesio Filippetti continued in the similar spirit, however concentrating on the applications to strongly correlated systems, outlining also the variational pseudo-SIC approach. Then Hisazumi Akai presented some results from the pseudo-SIC implementation in the KKR method, using the energy dependent functions, instead of projections on a fixed set of atomic functions. He also talked about EXX+RPA approach. Julie Staunton gave the last talk of the second day and described a combined approach of DLM with the so-called local SIC implementation in the KKR formalism. She presented results of its application to finite temperature magnetism in heavy rare earth and transition metal oxides (TMO), showing the existence of a well defined gap in the paramagnetic state of TMOs.

The late afternoon was spent on a few hours walk around the historic sights of the beautiful city of Chester. The day was finished with a "conference" dinner in The Ship Inn, overlooking the river Dee. It was a nice and pleasant event.

The first talk of the last day of the meeting was given by Adrienn Ruzsinszky on the non-empirical fully-nonlocal functionals for correlation, compatible with SI-free exact exchange. Her talk was followed by Eric Suraund's on time-dependent self-interaction free DFT. Takao Tsuneda talked about regional SIC of long-range corrected DFT. Aron Cohen discussed many electron self-interaction problem and the connection between self-interaction and strong correlation. Stefano Sanvito discussed the impact of self-interaction error on electronic transport across nanodevices based on an atomic/pseudo-SIC approach. The last talk of the meeting was by Nikitas Gidopoulos who discussed self-interaction free potentials from constrained density functional approximations.

The meeting was concluded with a two-hours long round table discussion well introduced and skillfully moderated by George Malcolm Stocks. The discussions were lively and useful, tackled many important issues of SIC implementations, importance of complex orbitals, minimization and transformation matrix optimizations, etc. There was also talk about establishing a SIC Club or a formal framework for validation and verification of SIC results obtained with different implementations. A follow-up meeting in a couple of years or so was also contemplated. All in all, it was a very interesting meeting, praised by many and assessed as very beneficial by all the participants.

Finally, the local administration of the meeting, the venue, food and all the services provided by the Ramada staff were very highly appreciated.

## Programme

### Sunday 18th September 2011

17:00 - 20:00 Arrival and Registration

### Monday 19th September 2011

08:45 Walter Temmerman (Daresbury): CECAM Daresbury Node Director  
and Vice-chair of Psi-k  
Opening Remarks

Chair: Thomas Schulthess (Zurich)

09:00 John Perdew (Tulane)  
"Rethinking the Perdew-Zunger Self-Interaction Correction,  
after 30 Years"

09:45 Alex Zunger (Colorado)  
"Predicting localization, delocalization and polaron behaviour  
in insulators via restoration of the proper energy vs.  
occupation (linear) dependence to DFT"

10:30 Coffee/Tea

11:00 M Pederson (Washington DC)  
"Computational Challenges for Wide-Spread Use of Self-  
Interaction-Corrections:A retrospective"

11:45 Nicola Marzari (Lausanne)  
"Nothing works! Electronic-structure challenges in modelling  
materials for energy applications" ("Three perspectives on  
self-interaction - long-range charge transfer, short-range  
hybridization, and photoemission levels")

12:30 Lunch

Chair: John Perdew (Tulane)

14:00 Klaus Capelle (Sao Paulo)  
"Model Hamiltonians: A Theoretical Laboratory for DFT"

14:45 Stephan Kuemmel (Bayreuth)

"Kohn-Sham Self-interaction correction - a route to physically meaningful orbitals"

15:30 Coffee/Tea

16:00 Peter Klüpfel, Simon Klüpfel, Hildur Guðmundsdóttir and Hannes Jónsson (Reykjavik)

"Perdew-Zunger SIC and other orbital density dependent functionals"

16:45 Olle Eriksson (Uppsala)

"Recent attempts of self-interaction"

18:30 Food and Posters: Chair: Antonios Gonis (LLNL)

**Tuesday 20th September 2011**

Chair: Olle Eriksson (Uppsala)

09:00 A Svane (Aarhus)

"Self-interaction corrections of solids in the LMTO formalism"

09:45 Thomas Schulthess (Zurich)

"Non-spherical self-interaction corrections implemented within the all-electron LAPW method"

10:30 Coffee/Tea

11:00 Bjoern Baumeier (Mainz)

"Self-interaction corrected pseudopotentials for crystalline systems"

11:45 Alessio Filippetti (Cagliari)

"A variational approach to the study of strong-correlated oxides based on the self-interaction removal from local

density functional"

12:30 Lunch

Chair: Nicola Marzari (Lausanne)

14:00 Hisazumi Akai (Osaka)

"A pseudo-SIC implementation in the KKR code and applications"

14:45 Julie Staunton (Warwick)

"Magnetic and electronic structure at finite temperatures described ab-initio: disordered local moments and the self-interaction correction"

16:00 Walk around Chester + Dinner of the Event

### **Wednesday 21st September 2011**

Chair: Mark Pederson (Washington DC)

09:00 Adrienn Ruzsinszky (Tulane)

"Nonempirical Fully-Nonlocal Density Functional for Correlation, Compatible with Self-Interaction Free Exact Exchange"

09:45 Eric Suraud (Toulouse)

"The Self Interaction Correction revisited"

10:30 Coffee/Tea

11:00 Takao Tsuneda (Yamanashi)

"Regional self-interaction corrections of long-range corrected DFT"

11:45 Aron Cohen (Cambridge)

"Connection between self interaction and strong correlation"

12:30 Lunch

Chair: George Malcolm Stocks (Oak Ridge)

14:00 Stefano Sanvito (Dublin)

"The self-interaction error in electronic transport across nanodevices"

14:45 Nikitas Gidopoulos (Didcot)

"Constraining density functional approximations to yield self-interaction free potentials"

15:30 Coffee/Tea + Round Table Discussion:

George Malcolm Stocks (ORNL) - Moderator

17:30 Closing Workshop

## **Participants**

Prof Hisazumi Akai, Osaka University, Japan

Dr Bjoern Baumeier, Max Planck Institute for Polymer Research, Mainz, Germany

Dr Michael Brooks, STFC Daresbury Laboratory, UK

Prof Klaus Capelle, UFABC, Brazil

Prof Henry Chermett,e Univ. LYON 1, France

Dr Aron Cohen, University of Cambridge, UK

Dr Markus Daene, Oak Ridge National Laboratory, USA

Prof Olle Eriksson, Uppsala University, Sweden

Dr Arthur Ernst, MPI Halle, Germany

Dr Andrea Ferretti, CNR Istituto Nanoscienze, Modena, Italy

Dr Alessio Filippetti, CNR-IOM & University of Cagliari, Italy

Mr Guntram Fischer, Martin-Luther Universitt Halle, Germany

Mr Matthias Geilhufe, Martin-Luther Universitt Halle, Germany

Dr Nikitas Gidopoulos, ISIS, STFC Rutherford Appleton Laboratory, UK

Ms Hildur Guðmundsdóttir, Science Institute, University of Iceland

Prof Balazs Gyorffy, University of Bristol, UK

Mr Dirk Hofmann, University of Bayreuth, Germany

Ms Nina Kearsy, Imperial College London, UK

Dr Peter Klüpfel, Science Institute, University of Iceland

Mr Simon Klüpfel, Science Institute, University of Iceland

Prof Stephan Kuemmel, University of Bayreuth, Germany

Dr Martin Lueders, STFC Daresbury Laboratory, UK

Mr Keld Lundgaard, Technical University of Denmark

Prof Nicola Marzari, Theory and Simulations of Materials, EPFL,Switzerland

Dr Mark Pederson, Naval Research Laboratory, Washington DC, USA

Dr Chaitanya Das Pemmaraju, Trinity College Dublin, Ireland

Prof John P. Perdew, Tulane University, USA

Dr Leon Petit, STFC Daresbury Laboratory, UK  
Ms Effat Rashed, University of Bristol, UK  
Dr Adrienn Ruzsinszky, Tulane University, USA  
Prof Stefano Sanvito, Trinity College Dublin, Ireland  
Prof Thomas Schulthess, ETH Zurich, Switzerland  
Prof Julie Staunton, University of Warwick, UK  
Dr George Malcolm Stocks, Oak Ridge National Laboratory, USA  
Prof Axel Svane, Aarhus University, Denmark  
Prof Zdzislawa (Dzidka) Szotek, STFC Daresbury Laboratory, UK  
Prof Walter Temmerman, STFC Daresbury Laboratory, UK  
Dr Stanko Tomić, University of Salford, UK  
Prof Takao Tsuneda, University of Yamanashi, Japan  
Mr Jess Wellendorff, Technical University of Denmark  
Prof Alex Zunger, Colorado University Boulder, USA

### 3 General Job Announcements

#### **Postdoc Position: First-Principles Simulations and Modeling of Phonon Linewidths in Thermoelectric Materials at Oak Ridge National Laboratory, USA**

##### **Project description:**

The goal of this project is to gain knowledge about phonon linewidths (inverse of lifetimes), and their systematic dependence on temperature, composition, or the underlying electronic structure, to predict their impact on thermoelectric efficiency [1,2,3,4,5]. The project involves collaboration between leading experimentalists, ab-initio theorists, and computer scientists at ORNL. The research will involve performing detailed calculations of phonon energies and linewidths (using first-principles as well as force-field methods), and benchmarking against experimental measurements. The tasks will include writing software to fit experimental data with parameterized models, and perform numerical optimization of phonon lifetimes. The software will be implemented on the high-performance computers at ORNL (including hybrid architecture based on General Purpose Graphical Processing Unit) to optimize our phonon dynamics models, and directly fit the experimental datasets. The convolution of phonon simulations with the response function of neutron scattering spectrometers at the Spallation Neutron Source will produce realistic simulated datasets, directly comparable with experiments. The outcome of this research will enable benchmarking microscopic theories of thermal conductivity, and develop more efficient thermoelectric materials. This research will leverage the world-class computing and neutron scattering resources of ORNL.

##### **Qualifications:**

Candidates with a recent Ph.D. in Physics, Materials Science, Chemistry, or related fields will be considered. Expertise with first-principles simulations (density functional theory), and in particular phonon simulations (with linear response or direct method), is a requirement for this position. Experience with molecular dynamics simulations, anharmonicity calculations, many-body techniques, and numerical optimization will be helpful. Good programming skills with modern computer languages (C++, Python) will be a strong advantage. Strong written and oral communication skills and the desire to work in a team environment on scientifically challenging problems are required. The successful candidate will conduct research at Oak Ridge National Laboratory, and will make use of computing facilities at ORNL. Applicants cannot have received their Ph.D. more than five years prior to the date of application and must complete all degree requirements before starting their

appointment.

### **How to Apply:**

Please contact Dr. Olivier Delaire ([delaireoa@ornl.gov](mailto:delaireoa@ornl.gov)) for further information about the position and the application process.

### References:

1. O. Delaire, K. Marty , M. B. Stone, P. R. C. Kent, M. S. Lucas, D. L. Abernathy, D. Mandrus, B. C. Sales, Proc. Natl. Acad. Sci. USA 108, 4725 (2011).
2. B. C. Sales, O. Delaire, M. A. McGuire, and A. F. May, Phys. Rev. B **83**, 125209 (2011).
3. O. Delaire et al., Nature Materials, doi:10.1038/nmat3035 (2011).
4. O. Delaire, A. F. May, M. A. McGuire, W. D. Porter, M. S. Lucas, M. B. Stone, D. L. Abernathy, and G. J. Snyder, Phys. Rev. B 80, 184302 (2009).
5. O. Delaire, M.S. Lucas, J.A. Muoz, M. Kresch, and B. Fultz, Phys. Rev. Lett. 101, 105504 (2008).

Additional information and application instructions can be found on:

[https://www3.ornl.gov/ORNL\\_TOppS/Posting/Details/188](https://www3.ornl.gov/ORNL_TOppS/Posting/Details/188)

(Position Reference Code: ORNL11-123-NSSD)

## Postdoctoral Position

### Universidad de Oviedo, Oviedo, Spain

Radiation damage is known to lead to materials failure and thus is of critical importance to the lifetime and safety within nuclear reactors. Its detrimental effects can be prevented by appropriate advanced nanomaterials tailoring, inherent to which are composition and structure modelling. Due to the multi-scale nature of the problem, experts in the fields of materials simulation via ab initio, molecular dynamics and continuum modelling are building up ever-growing teams to contribute to the characterization and improvement of such highly demanding materials. It is in this context where a **THREE-YEAR POSTDOCTORAL RESEARCH FELLOW APPOINTMENT AT THE UNIVERSIDAD DE OVIEDO (SPAIN)** for a talented and motivated individual is offered. Expected starting date: From October the 15th, 2011 (could also start at a later convened date).

The Universidad de Oviedo was established in 1608. It is a public institution, with more than 1500 researchers and 250 research groups, devoted to higher education teaching and research that fosters the social, economic and cultural development of the local community through the generation and diffusion of knowledge. Today, it has become the main research centre of the Principado de Asturias, a Spanish autonomous region with a population of over one million inhabitants located in the north-west of Spain. Nanotechnology related research is very active at UNIOVI, with more than 100 researchers and the cooperation in the recently created Research Center on Nanomaterials and Nanotechnology (CINN). Both fabrication, characterization and modelling areas are present, the latter through the scientific and technological modelling computing cluster and the new supercomputing center which is being established this year.

The appointed researcher will work in a young but enthusiastic environment, based in Oviedo. The researchers involved in this particular work package participate in several HPC (High Performance Computing) initiatives through the RES (Spanish Supercomputing Network) and HPC Europe. Close collaboration with the University of Burgos, IMDEA-Materials (Madrid) and the Nuclear Fusion Institute (DENIM, Madrid) is envisaged. Permanent collaborations with international institutions, as Los Alamos National Laboratory (USA), Lawrence Livermore National Laboratory (LLNL), Georgia Tech Lorraine University (Metz, France), University of Tartu (Estonia), University of Uppsala (Sweden), or Paul Scherrer Institute (PSI, Switzerland), have been established.

#### **Lines of research:**

1. Multiscale modelling of advanced nano-structured materials for engineering applications under extreme environments.

2. Advanced materials in next generation fission nuclear reactors and the new inertial confinement and magnetic fusion initiatives. ESFRI - HiPER EU project and DEMO international collaboration.
3. Integration in the very attractive scientific developments of ever-growing international research community involved in fusion materials technology.

The research activity will concern atomistic mechanisms and materials properties at interfaces of interest. The Post Doctoral fellow will help develop atomistic scale interfacial models relevant to our multiscale modelling program by means of ab initio calculations using commercially widespread packages, such as Wien2k and VASP, already available within our group. Other first principles simulation packages (Abinit, SIESTA, QuantumESPRESSO,...) could possibly be used at some stage to perform specific computations. Previous experience with density-functional calculations based on plane waves and pseudopotentials is requested. Experience in ab initio simulations on surfaces and a basic knowledge on the foundations of density functional theory are highly recommended. Expertise in installation and running of computer codes in parallel environments is required. The applicant should be able to work with Linux, have at least a basic scripting knowledge, as well as be acquainted with Fortran and C programming languages. Expert handling of visualization tools is a plus. Since the results obtained from the first principle calculations will be used as an input for molecular dynamics and lattice kinetic Monte Carlo codes in order to analyse defect evolution at experimentally relevant time frames, familiarity in the use of such techniques would be advantageous. The Post Doctoral fellow will be working in a highly collaborative environment in close synergy with experimentalists from other institutions. Therefore, research performed at large facilities, such as an X-ray synchrotron or neutron sources, will be highly appreciated. Both theoretical and experimental background in fields related to nuclear materials science would also be of great interest. Finally, the applicant should be able to fluently communicate in English. Spanish basic knowledge would be helpful.

The interested candidates should submit (in PDF-format) their (1) curriculum vitae, (2) publication list, and (3) one reprint of representative previous research. The interested candidate should also express his/her motivation in a covering letter, including the prospected date of availability, and arrange confidential letters of recommendation to be sent to the address below. Only complete applications will be processed. The selection process will continue until a suitable candidate occupies this opening.

**Contact:** Prof. Roberto Iglesias Pastrana  
Department of Physics  
Faculty of Science  
University of Oviedo  
roberto@uniovi.es

## 4 Abstracts

### Symmetry reduction in multiband Hamiltonians for semiconductor quantum dots: the role of interfaces and higher energy bands

Stanko Tomić

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Nenad Vukmirović

*Scientific Computing Laboratory, Institute of Physics Belgrade,  
University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia*

#### Abstract

The role of interfaces and higher bands on the electronic structure of embedded semiconductor quantum dots (QDs) was investigated. The term in the multiband  $\mathbf{k}\cdot\mathbf{p}$  Hamiltonian that captures the effect of interface band mixing was derived starting from the microscopic theory. It was shown, analytically and numerically, that, with such a term included, the right symmetry of the QD system can be captured. It leads to splitting of otherwise degenerate energy levels of the order of several meV. The inclusion of additional higher bands beyond the ones from the standard eight-band model also leads to the reduction of symmetry from an artificially high one to the true atomistic symmetry of the system, however their quantitative effect is weaker. These results prove that the multiband  $\mathbf{k}\cdot\mathbf{p}$  Hamiltonians are fully capable of describing the correct symmetry of a QD.

(Published as: Highlight in Journal of Applied Physics **110**, 053710 (2011) )

Contact person: Stanko Tomić (s.tomic@salford.ac.uk)

# Modeling of the Cubic and Antiferrodistortive Phases of SrTiO<sub>3</sub> with Screened Hybrid Density Functional Theory

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## Abstract

We have calculated the properties of SrTiO<sub>3</sub> (STO) using a wide array of density functionals ranging from standard semi-local functionals to modern range-separated hybrids, combined with several basis sets of varying size and quality. We show how these combinations' predictive ability varies significantly, for both STO's cubic and antiferrodistortive (AFD) phases, with the greatest variation in functional and basis set efficacy seen in modeling the AFD phase. The screened hybrid functionals we utilized predict the structural properties of both phases in very good agreement with experiment, especially if used with large (but still computationally tractable) basis sets. The most accurate results presented in this study, namely those from HSE06/modified-def2-TZVP, stand as one of the most accurate modeling of STO to date when compared to the literature; these results agree well with experimental structural and electronic properties as well as providing insight into the band structure alteration during the phase transition.

(Published in Physical Review B , vol. 84, issue 11, page 115122 )

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# Thermal conductivity of Si nanostructures containing defects: Methodology, isotope effects, and phonon trapping

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Faradayweg 4-6, 14195 Berlin, Germany*

## Abstract

A first-principles method to calculate the thermal conductivity in nanostructures that may contain defects or impurities is described in detail. The method mimics the so-called laser-flash technique to measure thermal conductivities. It starts with first-principles density-functional theory and involves the preparation of various regions of a supercell at slightly different temperatures. The temperature fluctuations are minimized without using a thermostat and, after averaging over random initial conditions, temperature changes as small as 5 K can be monitored (from 120 to 125 K). The changes to the phonon density of states and the specific heat induced by several atomic percent of impurities are discussed. The thermal conductivity of Si supercells is calculated as a function of the temperature and of the impurity content. For most impurities, the drop in thermal conductivity is unremarkable. However, there exist narrow ranges of impurity parameters (mass, bond strength, etc.) for which substantial drops in the thermal conductivity are predicted. These drops are isotope dependent and appear to be related to the vibrational lifetime of specific impurity-related modes.

(Phys. Rev. B **84**, 035317 (2011))

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# Structural Analysis of Silica-Supported Molybdena Based on X-ray Spectroscopy: Quantum Theory and Experiment

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J. P. Thielemann<sup>1</sup>, P. Kube<sup>1</sup>, L. J. Gregoriades<sup>3</sup>,  
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<sup>3</sup>*Humboldt-Universität zu Berlin,  
Unter den Linden 6, 10099 Berlin, Germany*

## Abstract

Oxygen core excitations in different molecular molybdena–silica models are evaluated using density-functional theory (DFT). These results can be compared with in situ X-ray absorption fine structure (NEXAFS) measurements near the O K-edge of molybdena model catalysts supported on SBA-15 silica, used for exploratory catalytic activity studies. The comparison allows an analysis of structural details of the molybdena species. The silica support is found to contribute to the NEXAFS spectrum in an energy range well above that of the molybdena units, allowing a clear separation between the corresponding contributions. Different types of oxygen species, O(1) in terminal M=O bonds, O(2) in interphase Mo–O–Si bridges and in Mo–O–Mo linkages, as well as O(2) in terminal Mo–O–H groups can be distinguished in the theoretical spectra of the molybdena species with molybdenum in tetrahedral (dioxo species), pentahedral (monooxo species), and octahedral coordination. The experimental NEXAFS spectra exhibit a pronounced double-peak structure in the O 1s to Mo 4–O 2p excitation range of 529–536 eV. Comparison with the present theoretical data gives clear indications that dioxo molybdena species with tetrahedral MoO<sub>4</sub> units can explain the experimental spectrum. This does not fully exclude species with other Mo coordination, like pentahedral. However, the latter are believed to exist in the present samples in much smaller amounts. The experimental NEXAFS spectrum for the supported molybdena species differs substantially from that for MoO<sub>3</sub> bulk material with octahedral MoO<sub>6</sub> units where the observed asymmetric peak structure is also reproduced by the calculations.

(J. Phys. Chem. C **115**, 15449 (2011).)

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# Impact of widely used approximations to the $G_0W_0$ method: An all-electron perspective

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Claudia Ambrosch-Draxl<sup>2</sup>, and Matthias Scheffler<sup>1</sup>

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<sup>2</sup>*Chair of Atomistic Modelling and Design of Materials,  
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## Abstract

Focussing on the fundamental band gaps in Si, diamond, BN, LiF, AlP, NaCl, CaSe, and GaAs, and the semicore  $d$ -state binding energies in ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, and GaN, we analyze the well-known discrepancies between the pseudopotential (PP) and all-electron (AE)  $G_0W_0$  results. Approximations underlying PP- $G_0W_0$ , *i.e.*, the frozen-core, the core-valence partitioning, and the use of pseudo-wavefunctions, are separately addressed. The largest differences, of the order of eV, appear in the exchange part of the self-energy and the exchange-correlation (xc) potential due to the core-valence partitioning. These differences cancel each other and, in doing so, make the final core-valence partitioning effect on the band gaps controllable when the semicore states are treated as valence states. This cancellation, however, is incomplete for semicore  $d$ -state binding energies, due to the strong interaction between these semicore states and the deeper core. The remaining error can be reduced by treating the outermost two shells as valence shell. However, reliably describing these many-body interactions at the  $G_0W_0$  level and providing benchmark results requires an all-electron approach.

(New J. Phys., submitted (2011).)

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# Electronic Structure of Dye-Sensitized TiO<sub>2</sub> Clusters from Many-Body Perturbation Theory

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## Abstract

The development of new types of solar cells is driven by the need for clean and sustainable energy. In this respect dye sensitized solar cells (DSC) are considered as a promising route for departing from the traditional solid state cells. The physical insight provided by computational modeling may help develop improved DSCs. To this end it is important to obtain an accurate description of the electronic structure, including the fundamental gaps and level alignment at the dye-TiO<sub>2</sub> interface. This requires a treatment beyond ground-state density functional theory (DFT). We present a many-body perturbation theory study, within the  $G_0W_0$  approximation, of two of the crystalline phases of dye-sensitized TiO<sub>2</sub> clusters, reported by Benedict and Coppens [J. Am. Chem. Soc. **132** (9), 2938 (2010)]. We obtain geometries in good agreement with experiment by using DFT with the Tkatchenko-Scheffler van der Waals correction. We demonstrate that even when DFT gives a good description of the valence spectrum and a qualitatively correct picture of the electronic structure of the dye-TiO<sub>2</sub> interface,  $G_0W_0$  calculations yield more valuable quantitative information regarding the fundamental gaps and level alignment. In addition, we systematically investigate the issues pertaining to  $G_0W_0$  calculations, namely: (i) convergence with respect to the number of basis functions, (ii) dependence on the mean field starting point, and (iii) the validity of the assumption that the DFT wave-function is a good approximation to the quasi-particle wave-function. We show how these issues are manifested for dye molecules and for dye-sensitized TiO<sub>2</sub> clusters.

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# Dispersion interactions with density-functional theory: Benchmarking semi-empirical and inter-atomic pair-wise corrected density functionals

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## Abstract

We present a comparative assessment of the accuracy of two different approaches for evaluating dispersion interactions: inter-atomic pair-wise corrections and semi-empirical meta-generalized-gradient-approximation (meta-GGA) based functionals. This is achieved by employing conventional (semi-)local and (screened-)hybrid functionals, as well as semi-empirical hybrid and non-hybrid meta-GGA functionals of the M06 family, with and without inter-atomic pair-wise Tkatchenko-Scheffler corrections. All those are tested against the benchmark S22 set of weakly bound systems, a representative larger molecular complex (dimer of NiPc molecules), and a representative dispersively bound solid (hexagonal boron nitride). For the S22 database, we also compare our results with those obtained from the pair-wise correction of Grimme (DFT-D3) and non-local Langreth-Lundqvist functionals (vdW-DF1 and vdW-DF2). We find that the semi-empirical kinetic-energy-density dependence introduced in the M06 functionals mimics the non-local correlation needed to describe dispersion. However, long-range contributions are still missing. Pair-wise inter-atomic corrections, applied to conventional semi-local or hybrid functionals, or to M06 functionals, provide for a satisfactory level of accuracy irrespectively of the underlying functional. Specifically, screened-hybrid functionals such as the Heyd-Scuseria-Ernzerhof (HSE) approach reduce self-interaction errors in systems possessing both localized and delocalized orbitals, and can be applied to both finite and extended systems. Therefore, they serve as a useful underlying functional for dispersion corrections.

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# Accurate and Efficient Method for Many-Body van der Waals Interactions

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## Abstract

An efficient method is developed for the microscopic description of the frequency-dependent polarizability of finite-gap molecules and solids. This is achieved by combining the TS-vdW method [Phys. Rev. Lett. **102**, 073005 (2009)] with the self-consistent screening equation of classical electrodynamics. This leads to a seamless description of polarization and depolarization for the polarizability tensor of molecules and solids. The screened long-range many-body van der Waals (vdW) energy is obtained from the solution of the Schrödinger equation for a system of coupled oscillators. We show that the screening and the many-body vdW energy play a significant role even for rather small molecules, becoming crucial for an accurate treatment of conformational energies for bio-molecules, and binding of molecular crystals. The computational cost of the developed theory is negligible compared to the underlying electronic structure calculation.

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# Hydrogen bonds and van der Waals forces in ice at ambient and high pressures

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## Abstract

The first principles approaches, density functional theory (DFT) and quantum Monte Carlo, have been used to examine the balance between van der Waals (vdW) forces and hydrogen (H) bonding in ambient and high pressure phases of ice. At higher pressure, the contribution to the lattice energy from vdW increases and that from H bonding decreases, leading vdW to have a substantial effect on the transition pressures between the crystalline ice phases. An important consequence, likely to be of relevance to molecular crystals in general, is that transition pressures obtained from DFT functionals which neglect vdW forces are greatly overestimated.

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# Large variation of vacancy formation energies in the surface of crystalline ice

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## Abstract

Resolving the atomic structure of the surface of ice particles within clouds, over the temperature range encountered in the atmosphere and relevant to understanding heterogeneous catalysis on ice, remains an experimental challenge. By using first-principles calculations, we show that the surface of crystalline ice exhibits a remarkable variance in vacancy formation energies, akin to an amorphous material. We find vacancy formation energies as low as 0.10.2eV, which leads to a higher than expected vacancy concentration. Because a vacancy's reactivity correlates with its formation energy, ice particles may be more reactive than previously thought. We also show that vacancies significantly reduce the formation energy of neighbouring vacancies, thus facilitating pitting and contributing to pre-melting and quasi-liquid layer formation. These surface properties arise from proton disorder and the relaxation of geometric constraints, which suggests that other frustrated materials may possess unusual surface characteristics.

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## 5 SCIENTIFIC HIGHLIGHT OF THE MONTH

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### Calculation of Dispersion Energies

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### 1 Introduction

”Dispersion forces” [1], [2] are generally understood in the solid-state physics community to be that part of the non-covalent van der Waals (vdW) interaction that cannot be attributed to any permanent electric mono- or multipoles. (In the chemistry community, the whole of the non-chemically-bonded interaction is often termed the ”van der Waals” (vdW) interaction, but in the physics community this term is usually reserved for the outer dispersion component as defined above. A useful categorization of the many components of the total force is given in [3] from a perturbation theory standpoint). The ubiquitous dispersion forces occur wherever polarizable electron clouds are present, and are typically weaker than ionic and covalent bonding forces, but are of longer range than the latter, decaying algebraically rather than exponentially with separation. They are important in protein interactions, in rare-gas chemistry and in soft condensed matter generally. They are especially important, for example, in the cohesion and self-assembly of graphenic nanostructures including nanotubes and planar graphene-based systems, which have attracted strong recent interest in the condensed matter community. Much work has been done on the vdW interaction in the two extremes of (i) small molecules (via high-level quantum chemical methods such as coupled cluster (CCSD(T)) [4] or Symmetry adapted Perturbation theory (SAPT) [3]) and (ii) well-separated macroscopic objects (via Lifshitz theory and its extensions, for example [5], [6], [2]). However the study of vdW interactions between solids and nanostructures down to intimate contact, where dispersion competes with other forces, is still an area of active research. The selective adhesion of graphene to various metal substrates is an example of a delicate phenomenon where vdW forces are important but where a successful fully quantitative theory seems still to be lacking. This paper will outline the development of simple and more complex theories to account

for these phenomena within the electromagnetically non-retarded regime, as defined in the following paragraph. The website [ <http://www.cecam.org/workshop-2-411.html> ] of a recent CECAM workshop will give the flavour of some relatively recent work in this area.

vdW forces are a special case of the more general electromagnetically retarded interaction between matter, an interaction that is properly treated by regarding both the matter and the electromagnetic field as dynamical quantum systems. When the distance  $D$  between the interacting bodies is sufficiently small, the light transit time  $\tau_{light} = D/c$  is small compared to the response time  $\tau_{matter}$  of the charges in the matter, and then we can neglect the retardation of the electromagnetic field. This is sometimes designated the "vdW regime", and here one can treat the electromagnetic field as a non-retarded scalar classical Coulomb field, that serves merely to induce correlations between the charge fluctuations within the interacting bodies. The emphasis is then focussed on the dynamics of the interacting matter - the electronic many-body problem. This is the approach that will mainly be pursued below.

It is worthwhile, however, to consider briefly the opposite limit where retardation is important, and here the dispersion-type forces are often termed Casimir forces [7]. In this "Casimir regime" the response of the matter is often treated approximately via a spatially local dielectric function  $\varepsilon(\omega)$  confined within sharp spatial boundaries representing the edges of the matter. The dispersion interaction is then often regarded as being due to the separation-dependence of the zero-point and/or thermal energy of the normal electromagnetic field modes. These modes are calculated from the classical Maxwell equations in the presence of chunks of matter characterized only by their macroscopic permittivity  $\varepsilon(\omega)$ . The two viewpoints are united by the very successful Lifshitz theory [5], [6], applied originally to the interaction between bulk samples with parallel planar faces, and quickly extended to other geometries in various approximate ways [1], [8], [9]. In recent years the Lifshitz type of approach has been applied, without approximation, to more general geometries such as spheres, cylinders, thin plates etc, but always with the caveat that the spatial scales must be long compared with the scale of the microscopic structure of the matter, so that only the long-wavelength response of the matter to e.m. fields is invoked [10], [11].

In fact the term "Casimir effect" has recently come to have a wider meaning, covering the dependence on geometry (shape, size or separation) of the total zero-point or thermal free energy of any kind of field in confined geometry. Apart from the electromagnetic Casimir forces described above, examples of this approach include (i) the effect of elastic wave fluctuations on the thermodynamics behavior of finite and/or curved elastic membranes (ii) the interaction between nuclei or nucleons in a Fermi sea of quarks, where the zero point kinetic energy of the free quark field carries the basic effect. Some flavor of the possibilities of this field-fluctuation approach can be obtained by visiting the website of a recent Kavli Institute for Theoretical Physics workshop entitled "Fluctuate 08": [ <http://www.kitp.ucsb.edu/directory/all/fluctuate08> ].

For the remainder of the present paper we will work in the electromagnetically non-retarded (non-Casimir) limit, which often means in practice that we can treat interacting systems at separations from about a micron down to full overlap of electronic clouds.

## 2 Simple models of the vdW interaction between small systems

It is worthwhile to consider first a very simple picture of the vdW interaction between two neutral spherical atoms at separation  $R \gg b$  where  $b$  is an atomic size. (For more detail see e.g. [12], [13], [14].) The Hartree field of a neutral spherical atom decays exponentially with distance, and so the Hartree energy cannot explain the algebraic decay of the vdW interaction.

### 2.1 Coupled-fluctuation picture

However the quantal zero-point motions of the electrons (or thermal motions where significant) can cause a temporary fluctuating dipole moment  $d_2$  to arise on atom #2. The nonretarded Coulomb interaction energy between this dipole, and another dipole of order  $\alpha_1 d_2 R^{-3}$  that it induces on atom #1, has a nonzero average value that can be estimated [12], [13] as

$$E = - \langle (\alpha_1 d_2 R^{-3}) (-R^{-3} d_2) \rangle \approx -C_6 R^{-6}, \quad C_6 = K \hbar \omega_0 \alpha_1 \alpha_2. \quad (1)$$

Here  $\alpha_1$  and  $\alpha_2$  are the dipolar polarizabilities of the atoms and  $\omega_0$  is a characteristic frequency (level spacing) of an atom. The coefficient  $C_6$  for this geometry has been obtained using a harmonic oscillator analogy to estimate  $\langle d_2^2 \rangle = K \alpha_2 \hbar \omega_0$  and this contains a dimensionless constant  $K$ , that is not easily specifiable from the above qualitative argument.

### 2.2 Model based on the static correlation hole: failure of LDA/GGA at large separations

The spontaneous dipole  $d_2$  invoked above would be implied *if* we had found an electron at a position  $\vec{r}'$  on one side of atom #2. The induced dipolar distortion on atom #1 then represents a very distant part of the correlation hole density  $n_2(\vec{r}, \vec{r}')|)$  [15] due to discovery of the electron at  $\vec{r}'$ . The shape of this hole is entirely determined by the shape of atom #1, and is thus quite unlike the long-ranged part of the xc hole present in a uniform electron gas of density  $n(\vec{r})$ . It is therefore unsurprising that the local density approximation (LDA) misses the long-ranged tail of the vdW interaction. In fact, the LDA and the GGAs can only obtain the vdW tail via the distortion of the density of each atom. This distortion is predicted by these theories to decay exponentially with separation of the two atoms, thus ruling out the correct algebraic decay of the energy. The situation with GGA is less clear when the densities of the interacting fragments overlap. If the principal attractive correlation energy contribution comes from electrons near the overlap

region, then treating this region as part of a weakly nonuniform gas might be reasonable. In keeping with this, various different GGAs can give qualitatively reasonable results for vdW systems such as rare-gas dimers. The results are neither consistent nor reliable, however [16], [17], [18], [19], though surprisingly good results *near the energy minimum* are obtained [20], [21] with Hartree-Fock exchange plus the Wilson-Levy functional. Some discussion is given in [12].

### 2.3 Model based on small distortions of the ground state density

Instead of considering the energy directly for two atoms separated by distance  $R$ , Feynman [22] and Allen and Tozer [23] considered the small separation-dependent changes  $\delta n(\vec{r}; R)$  in the groundstate density  $n(\vec{r})$  of each atom, caused by the Coulomb interaction  $V_{12}$  between atoms. The Coulomb field acting at the nucleus of each atom created by  $\delta n(\vec{r}; R)$  as source, leads to a force which was identified as the vdW force, in the distant limit. One can then obtain the correct result  $\vec{F} = -\nabla_R(-C_6R^{-6})$  in the widely-separated limit, in agreement with (1). Such a result emerges, for example, if  $\delta n(\vec{r}; R)$  is calculated from a many-electron wavefunction correct to *second* order in  $V_{12}$ , involving a double summation with two energy denominators. (The *first-order* wavefunction perturbation makes zero contribution to  $\delta n(\vec{r}; R)$ .) By contrast, looking at the total *energy* to second order in  $V_{12}$  one already obtains the dispersion interaction with only a single summation and one energy denominator, a substantially easier task of the same order as obtaining the *first-order* perturbed wavefunction. From here on we restrict attention to approaches based directly on the energy.

### 2.4 Coupled-plasmon model

Another simple way to obtain the  $R^{-6}$  interaction is to regard the coupled fluctuating dipoles invoked above as forming a coupled plasmon mode of the two systems [13]. One solves coupled equations for the time-dependent density distortions on the two systems, leading to two normal modes (in- and out-of-phase plasmons) of free vibration of the electrons. The  $R$  dependence of the sum of the zero-point plasmon energies  $\sum_i \hbar\omega_i/2$  gives an energy of form  $-C_6R^{-6}$ , in qualitative agreement with the coupled-fluctuation approach described above for the case of two small separated systems (see, e.g., [24], [1], [13]). A strength of the coupled-plasmon approach is that it is not perturbative, and is equally valid for large or small systems, even for metallic cases where zero energy denominators could render perturbation theory suspect. The coupled-plasmon theory is linked to the correlation-hole approach by the fluctuation-dissipation theorem to be discussed starting from Sect. 5 below.

## 2.5 Perturbation theory picture assuming no overlap

The factor  $R^{-6}$  in (1) can be understood as arising from *two* actions of the dipolar field, each proportional to  $R^{-3}$ , suggesting that this simplest approach relates to *second-order* perturbation theory in the inter-system Coulomb interaction. Indeed the application of standard 2nd order Rayleigh-Schrodinger perturbation theory, regarding the electrons of one system as distinguishable from those of the other and treating the inter-atom coulomb potential  $V$  as a perturbation, yields the formula

$$E_{AB}^{(2)} = -\frac{\hbar}{2\pi} \int_0^\infty du \int d\vec{r}_1 d\vec{r}_1' d\vec{r}_2 d\vec{r}_2' V(\vec{r}_1 - \vec{r}_2) \chi_A(\vec{r}_1, \vec{r}_1', iu) V(\vec{r}_2 - \vec{r}_1) \chi_B(\vec{r}_2, \vec{r}_2', iu) \quad (2)$$

where  $V$  is the bare electron-electron Coulomb potential and  $\chi_A(\vec{r}_1, \vec{r}_1', \omega) \exp(-i\omega t)$  is the linear electron number density response at position  $\vec{r}$  to an external potential perturbation of form  $\delta V(\vec{x}) = \delta(\vec{x} - \vec{r}') \exp(-i\omega t)$ : see (e.g.) [25], or [26].  $\chi_A$  is usually termed the electron density-density reponse of system A (or just the density response), and the expression (2) is sometimes known as the "(generalized) Casimir Polder formula". It is derived in a different fashion in Sect. 6.1 below.

By expanding the Coulomb potential in a multipole series around the centres of A and B, one obtains to lowest order a result of the form (1) with

$$C_6 = \frac{\hbar}{2\pi} \sum_{jklm=1}^3 \int_0^\infty A_{jk}^{(A)}(iu) t_{j\ell}(\hat{R}) t_{km}(\hat{R}) A_{\ell m}^{(B)}(iu) du, \quad t_{j\ell}(\hat{R}) = \hat{R}_j \hat{R}_\ell - 3\delta_{j\ell} \quad (3)$$

(See e.g. [12]). Here  $\vec{R}$  is the vector joining the centers of A and B,  $\hat{R} = \vec{R} / |\vec{R}|$  and

$$A_{j\ell}^{(A)} = \int x_j x'_\ell \chi_A(\vec{x}, \vec{x}', iu) d\vec{x} d\vec{x}'$$

is the dipolar polarizability tensor of species A.  $\vec{x}$  is the position of an electron relative to the center of A. For two isotropic systems  $A_{jk}^{(A)} = \delta_{jk} A^{(A)}$  and similarly for  $A_{jk}^{(B)}$ . This leads to the possibly more familiar expression

$$E^{(2)} = -C_6 R^{-6}, \quad C_6 = \frac{3\hbar}{\pi} \int_0^\infty A^{(A)}(iu) A^{(B)}(iu) du \quad (4)$$

Using (3) or (4) one reduces the calculation of the asymptotic vdW interaction between fragments to the calculation of the (imaginary) frequency-dependent dipolar polarizability  $A$  of each fragment. This is a surprisingly demanding task. It can be done accurately with high-level quantum chemical approaches, but even relatively sophisticated treatments like RPA or ALDA obtain accuracies only of order 10-20% for small atoms and molecules, where orbital self-interaction is an issue.

If the multipole expansion of the Coulomb potential in the Casimir-Polder formula (2) is taken to higher order, additional terms of form  $C_8 R^{-8}$ , and higher powers, are added to

the leading  $-C_6R^{-6}$  term. There are also mixed induction-dispersion terms in general. A good and very detailed enumeration of the possible terms is given in [3].

## 2.6 vdW and higher-order perturbation theory

For non-overlapping electronic systems one can go further within perturbation theory with respect to the inter-system Coulomb interactions  $V_{ij}$ . In third order one finds an interaction between three separated systems, which cannot be expressed as the pairwise sum of  $R^{-6}$  terms such as (1). At large separations for spherical systems the leading (dipolar) contribution to this third-order term has the Axilrod-Teller form  $E^{\text{vdW},(3)} \approx C_9R_{12}^{-3}R_{23}^{-3}R_{13}^{-3}$ , (see e.g. [27]) where  $C_9$  contains some angular dependence. There are also corrections to the pair interaction (2) from perturbation orders beyond 2 [3].

## 2.7 Perturbation theory including overlap: Symmetry Adapted Perturbation Theory

When the electron clouds of two systems 1 and 2 are allowed to overlap, the electrons in 1 and 2 can no longer be treated as indistinguishable, and Eq (2) is inapplicable. A perturbative approach in this case requires Symmetry Adapted Perturbation Theory (SAPT) [3]. In SAPT the antisymmetry of the many-electron wavefunction is imposed upon perturbation theory via a projection operator technique. This approach has been developed to a very high level of sophistication (including judicious use of Time Dependent Density Functional Theory to ease parts of the calculation) [28]. SAPT probably represents the current state of the art for the van der Waals interaction between pairs of molecules up to medium size. So far it seems not to be feasible for solids and large nanostructures, so it will not be considered further here.

# 3 The simplest models for vdW energetics of larger systems

## 3.1 Simple pairwise addition of $C_6R^{-6}$ for well-separated macroscopic bodies

The simplest approach to the vdW interaction between many-atom systems, including solids, is to add energy contributions of form  $-C_{6(ij)}R_{ij}^{-6}$  between each pair  $(i, j)$  of atoms. There is a large early literature of calculations of this kind for macroscopic solids with an empirical  $C_6$  value. Often one replaces sums over atoms by continuous integration using volume elements that may each contain many atoms. In this way one easily obtains analytic dependence on the separation  $D$  for macroscopic objects of each well-defined shape (thick slab, thin slab, sphere, cylinder etc). [1], [13], [8]. See also the right-hand column of Figure 1 below, for a few specific cases.

### 3.2 Pairwise addition with empirical short-range repulsion

If the interacting bodies can come into close contact, the attractive  $-C_6R^{-6}$  interaction must be attenuated (damped, saturated) at short range and replaced by a Pauli repulsion term. In empirical pairwise theories the short-ranged part is often of form  $+C_{12}R^{-12}$  (Lennard-Jones potential) or  $+B\exp(-CR)$ . Since the polarizability  $A$  (see (3)) of an atom in a molecule or solid is usually quite different from that of the isolated atom, all coefficients  $C_6$ ,  $C_{12}$  or  $B$  are often determined empirically. Two examples are the "universal graphitic potentials" [29], [30]. Such models have been used extensively to model interactions between carbon nanotubes, graphene sheets, bucky balls etc: see (e.g.) [31]. Similar terms are included in force fields (e.g. CHARMM) used for biochemical modelling.

### 3.3 Pairwise addition as a dispersion energy correction to LDA

Perhaps because of the availability of high-level quantum chemical methods, the simple pairwise approach seems to have been pursued much later for finite molecular systems than for other application areas. Wu and Yang [32] introduced a pair interaction of form  $\sum_{ij} f_d^{ij}(R_{ij})C_6^{(ij)}R_{ij}^{-6}$  to be added to the Local Density Functional (LDA) energy, which of course already contains the Pauli repulsion. The coefficients  $C_6$  were optimized by fitting a set of accurate molecular energies. They turned out to be surprisingly, though not perfectly, transferrable. This general approach is now often called "DFT+D" or DFT-D" and has been furthered by Grimme and others [33], [34]. In the last approach, transferability is improved by counting the number of effective bonds in which an atom participates, then using this to modify the atomic  $C_6$  coefficients. Another approach [35] starts from accurate quantum chemical data for the vdW  $C_6$  coefficients of free atom pairs. The vdW interaction is then modified to account for Pauli compression effects of nearby atoms on the atomic polarizabilities, using the effective volume of each atom in its molecular environment, according to a standard molecular space partitioning scheme.

## 4 Effects beyond pairwise additivity

As already indicated in Sect 2.5 above, perturbation theory naturally produces triplet and higher contributions to the dispersion energy, beyond pairwise interaction of atoms or spatial elements. For small weakly polarizable systems such as rare gas atoms, these terms are relatively small but can be significant, along with  $R^{-8}$  and higher terms, at shorter range as in rare gas crystals [36].

Stronger effects, not describable by a small number of triplet and higher perturbation terms, have been discovered in polarizable, highly anisotropic systems. Kim et al [37] studied chains of non-contacting polarizable SiO spheres in various geometric arrangements. They obtained the vdW interaction from the zero-point energy of coupled plasmons within a polarizable point-dipole model similar to that in [13] and found major

discrepancies compared with pair-summation. These discrepancies were not significantly improved by adding just triplet terms. Martyna et al. have applied a somewhat related model of coupled oscillators to solid xenon [38]. The multiple-coupled dipole approach has been popular in the past [13] and can be used [39] to derive the nonretarded Lifshitz interaction - see Sect 6.1 below.

Other formalisms have yielded equally large discrepancies for semiconducting linear hydrogen chains [40], [41]. The beyond-pairwise effects can be understood in terms of the screening of the coulomb interaction that couples fluctuations on two atoms, due to polarization of the electron clouds on other atoms. The non-additive effects are strong when the systems are very anisotropic (e.g. chains or thin films) and highly polarizable. An extreme case of a polarizable system is a metal, especially in low dimensions (wires, sheets, graphene) where internal coulomb screening is less effective. For such cases it has been shown [42], [43], [44] that one can even obtain an exponent  $p$  in the asymptotic vdW power law  $E \approx -CD^{-p}$  that differs from that predicted by  $\sum C_6 R^{-6}$  theories. (See Figure 1 below).

## 5 The adiabatic connection - fluctuation dissipation (ACFD) approach to groundstate correlation energy

While coupled point polarizable dipole models are sensible and exhibit the required non-pairwise-additive vdW behavior, in general one needs a more general approach that allows for overlap and a detailed description of metals. This leads one to seek more fundamental approaches. The electronic Diffusion Monte Carlo (DMC) approach has been applied to a few simple nanostructures [45] [46], but it is very hard to ensure convergence of DMC in such systems, because of the need for a very big sample cell in order to capture long-ranged vdW correlations. In what follows we therefore concentrate mainly on approaches to the electronic correlation energy based on the Adiabatic Connection Formula and the Fluctuation Dissipation Theorem (ACFD approach) of which the simplest example is the (direct) Random Phase Approximation (dRPA) correlation energy to be described in the next Section.

The vdW energy is part of the electronic correlation energy in the groundstate of the total many-electron system. An exact formal expression for this groundstate correlation energy is the ACFD formula

$$E_c = -\frac{1}{2} \int_0^\infty du \int_0^1 d\lambda \int_0^\infty \frac{\hbar}{\pi} du \int d\vec{r} d\vec{r}' V(\vec{r}, \vec{r}') (\chi_\lambda(\vec{r}, \vec{r}', iu) - \chi_0(\vec{r}, \vec{r}', iu)) . \quad (5)$$

Here we have defined a "λ-system" in which the bare inter-electron coulomb interaction  $V(\vec{r}, \vec{r}') \equiv e^2 |\vec{r} - \vec{r}'|^{-1}$  has been replaced by  $\lambda V(\vec{r}, \vec{r}')$  while a λ-dependent static external potential is applied in order to keep the groundstate density constant at the true ( $\lambda = 1$ ) value while λ is varied.  $\chi_\lambda$  is the electronic density response of the λ-system, defined in general such that the linearized density perturbation of the λ-system under an external

potential  $\delta V^{ext}(\vec{r}) \exp(-i\omega t)$  is

$$\delta n(\vec{r}, t) = \exp(-i\omega t) \int \chi_\lambda(\vec{r}, \vec{r}', \omega) \delta V^{ext}(\vec{r}') d\vec{r}' .$$

In (5) the integration over imaginary frequency  $u$  implements the Fluctuation–Dissipation theorem [47], [48], [14]: as such it constructs the correlated groundstate pair density  $n_{2\lambda}(\vec{r}, \vec{r}')$  using the density response as input. The expression (5) is thus of the form of an electrostatic energy, except for the  $\lambda$  integration, which implements the Adiabatic Connection formula [49], [15]. The  $\lambda$  integration is based on the Feynman-Hellman theorem, and physically it re-introduces the zero-point *kinetic* energy of correlation, otherwise missed in an electrostatic energy type of integral. A particularly clear explanation of the Adiabatic Connection is given in Gunnarsson and Lundqvist [15] starting from their Eq (28), with their "g" representing our "λ". A complete pedagogic derivation of (5) in the present context, including a first principles derivation of the appropriate version of the FD theorem, is given in [14].

Expressions based on (5) can be obtained for the exchange-correlation energy

$$E_{xc} = -\frac{1}{2} \int_0^\infty du \int_0^1 d\lambda \left[ \int_0^\infty \frac{\hbar}{\pi} du \chi_\lambda(\vec{r}, \vec{r}', iu) + n(\vec{r})\delta(\vec{r} - \vec{r}') \right]$$

and the exact exchange energy

$$E_x = -\frac{1}{2} \int_0^\infty du \int_0^1 d\lambda \left[ \int_0^\infty \frac{\hbar}{\pi} du \chi_0(\vec{r}, \vec{r}', iu) + n(\vec{r})\delta(\vec{r} - \vec{r}') \right]$$

The latter reproduces the "DFT exact exchange", namely the Hartree-Fock expression for the exchange energy, but with Kohn-Sham orbitals in place of Hartree-Fock orbitals. An explicit constructive proof of this statement is given in [14].

## 6 The (direct) RPA for the correlation energy

Eq (5) is a purely formal expression giving the correlation energy in terms of the response function  $\chi$ , and it is not immediately clear how sophisticated an approximation to  $\chi$  is required in order to obtain useful accuracy in  $E_c$ . In fact it turns out that no explicit correlation physics is needed in  $\chi_\lambda$  in order to obtain a non-zero correlation energy from (5). Indeed a very simple time-dependent Hartree approximation for  $\chi_\lambda$ , namely

$$\chi_\lambda^{dRPA} = \chi_0 + \chi_0 \lambda V \chi_\lambda^{dRPA}, \quad (6)$$

produces the well-known Random Phase approximation for the correlation energy, first introduced long ago for the special case of the homogeneous electron gas. The correlation energy includes the mutual energy of coupled fluctuations of the density about the groundstate, fluctuations whose average value in the groundstate is zero so that they cannot contribute any extra energy in the static Hartree approximation. However when an explicit

density disturbance (with non-zero ensemble average) is introduced by a time-dependent external field, this can interact with disturbances elsewhere even at the (time-dependent) Hartree level. The Fluctuation Dissipation Theorem relates such interactions in the non-equilibrium driven system to the interactions between spontaneous fluctuations around the non-driven groundstate.

For the dRPA case the  $\lambda$  integration in (5) can be carried out analytically using the following formal operator identity in  $(\vec{r}, \vec{r}')$  space:  $\partial_\lambda \ln(1 - \lambda\chi_0 V) = (1 - \lambda\chi_0 V)^{-1} \chi_0 V = \chi_\lambda^{dRPA} V$  in which products are to be interpreted as spatial convolutions:

$$E_c^{dRPA} = -\frac{1}{2} \int_0^\infty \frac{\hbar}{\pi} du \int d\vec{r} [\ln(1 - V\chi_0) + (V\chi_0)]_{\vec{r}\vec{r}} \quad (7)$$

$$= -\frac{\hbar}{2\pi} \int_0^\infty du \text{Tr} [\ln(1 - V\chi_0) + (V\chi_0)] \quad (8)$$

$$= -\frac{\hbar}{2\pi} \int_0^\infty du \text{Tr} [\ln(1 - V^{1/2}\chi_0 V^{1/2}) + (V^{1/2}\chi_0 V^{1/2})] \quad (9)$$

where the properties of the trace operation have been used in the last line to introduce a hermitian operator  $V^{1/2}\chi_0 V^{1/2}$  which is convenient especially when diagonalization methods are used to evaluate the correlation energy.

While the dRPA correlation energy was calculated for the homogeneous electron gas many decades ago (see e.g. [50]), its practical evaluation in more complex systems including periodic systems is often numerically costly, and has only been carried out quite recently [51], [52], [53], [54], [55], [56], [57], [58], [59]. When used as a post-functional starting from PBE orbitals, it has proved to give a very good description of the lattice constants and elastic constants of many crystals [58] including most of the van der Waals bound rare gas crystals [60] (except He where self-interaction issues are arguably dominant - see the next Section). Atomization energies in the dRPA are good but slightly worse than those from a groundstate PBE calculation, which again may be related to self-interaction issues. Some methods have also been given to increase the numerical efficiency of dRPA and exact exchange calculations in solids [57].

For finite molecular systems the correlation energy in the dRPA and the related RPax (see below) have been implemented in an efficient way, via methods and codes originally designed for molecular time-dependent Hartree-Fock calculations (see [55] and references therein) . On the formal side Furche [55] proved that

$$E_c^{dRPA} = \frac{\hbar}{2} \sum_n (\Omega_n - \Omega_n^D)$$

where  $\Omega_n$  is an eigenfrequency of the RPA equation (6) and  $\Omega_n^D$  is the same quantity to linear order in the Coulomb coupling strength  $\lambda$ . In fact the notion of using the separation-dependent part of the sum of zero point energies  $\hbar\Omega/2$  of collective modes to obtain vdW energies is quite an old one ([1], [13]). For the macroscopic collective-mode-only models used in these old calculations one can show that this is correct (see e.g. [61]), but the Furche result is more general. For some discussion of the sum of zero

point energies see also Sec. 5 of [61] where it is pointed out that the asymptotic vdW interaction of undoped graphene planes is dominated by single-particle-type modes so that the older collective mode zero-point energy model is not sufficient.

Within formal perturbation theory, the dRPA is represented in Feynman energy diagrams by a sum of rings of open bubbles (where each open bubble represents  $\chi_0$ ). The dRPA and many other variants of the RPA idea can also be expressed as doubles ring diagrams in the Coupled Cluster approach.

### 6.1 Lifshitz-like vdW energy formula for non-overlapping systems, and its relation to RPA

The Lifshitz theory [5], [6] was the mainstay of macroscopic vdW calculations for many years. One can use a modified form of the ACFD to derive a slight generalization of the macroscopic Lifshitz formula [62] that renders it suitable for noncontacting nanosystems as well as the thick parallel slabs for which it was originally intended.

Consider 2 separated systems "1" and "2" separated by a variable distance  $D$  and with Coulomb interaction split into inter- and intra system interactions

$$V_{11} + V_{22} + \mu(U_{12} + U_{21}) \equiv V_{11} + V_{22} + \mu V_{12}$$

We assume no overlap so the systems lie in separated regions " $S_1$ " and " $S_2$ " of space. Then  $U_{12}(\vec{r}_1, \vec{r}_2) = e^2 |\vec{r}_1 - \vec{r}_2|^{-1}$  when both  $\vec{r}_1 \in S_1$  and  $\vec{r}_2 \in S_2$  but  $U_{12}$  is zero otherwise. Similarly for  $U_{21}$  while  $V_{11}, V_{22}$  only connect points inside the same system, Then  $V_{12} \equiv U_{12} + U_{21} = 0$  if  $\vec{r}_1$  and  $\vec{r}_2$  lie in the same subsystem.

We start from two systems with no intersystem interaction ( $\mu = 0$ ), but with full Coulomb interactions inside each subsystem. The energy in this situation is the same as for  $D \rightarrow \infty$ . That is

$$E(D \rightarrow \infty) = E(D, \mu = 0)$$

Then the  $D$ -dependent part of the energy is

$$\begin{aligned} E^{cross} &\equiv E(D, \mu = 1) - E(D \rightarrow \infty) = E(D, \mu = 1) - E(D, \mu = 0) \\ &= \int_0^1 \frac{dE(D, \mu)}{d\mu} d\mu = \frac{1}{2} \int \rho(D, \mu, r, \vec{r}') V_{12}(\vec{r}, \vec{r}') d\vec{r} d\vec{r}' \end{aligned}$$

where  $\rho(D, \mu, r, \vec{r}')$  is the electronic pair distribution for slabs at distance  $D$  and interaction  $V_{11} + V_{22} + \mu V_{12}$ : the Feynman-Hellmann theorem was used in the last step.

By the Fluctuation Dissipation theorem this is related to the density response function

$$\frac{dE(D, \mu)}{d\mu} = \frac{1}{2} \int \left[ -\frac{\hbar}{\pi} \int_0^\infty \chi(D, \mu, \vec{r}, \vec{r}', \omega = iu) du - n_0(\vec{r}) \delta(\vec{r} - \vec{r}') + n_0(\vec{r}) n_0(\vec{r}') \right] V_{12}(\vec{r}, \vec{r}') d\vec{r} d\vec{r}'$$

where  $\chi$  is the density-density response of the fully interacting system. The direct Hartree cross energy (the last term) is not part of the vdW energy, and so will be ignored (see also [63]). The self-term with the delta function gives zero when folded with  $V_{12}$ . Thus

the cross energy is entirely due to correlation (because the in-principle-included exchange part is zero in this non-overlapped regime) and is given by

$$\begin{aligned} E^{cross}(D) &= -\frac{\hbar}{2\pi} \int_0^\infty du \int_0^1 d\mu \int_0^\infty \chi(D, \mu, \vec{r}, \vec{r}', \omega = iu) V_{12}(\vec{r}, \vec{r}') d\vec{r} d\vec{r}' \\ &= -\frac{\hbar}{2\pi} \int_0^\infty du \int_0^1 d\mu \int_0^\infty (\chi_{12}(D, \mu, \vec{r}, \vec{r}', \omega = iu) V_{12}(\vec{r}, \vec{r}') + [1 \leftrightarrow 2]) d\vec{r} d\vec{r}' \end{aligned}$$

where  $\chi_{12}$  (unlike  $\chi_{012}$ ) is NOT zero because of the coulomb interaction between the slabs. We now make the RPA assumption for the interaction between the slabs. This is the essential Lifshitz approximation - see the ring diagrams in [6]. Then  $\chi_{21} = \delta n_2 / \delta V_1$  can be found from the linear mean field equations in the presence of time dependent external potentials  $\delta V_1, \delta V_2$  acting separately on the two systems. This gives

$$\chi_{21} = (1 - \mu^2 \chi_{22} V_{21} \chi_{11} V_{12})^{-1} \mu \chi_{22} V_{21} \chi_{11}$$

and similarly for  $\chi_{12}$ . Then the vdW interaction is

$$\begin{aligned} E^{cross}(D) &= -\frac{\hbar}{2\pi} \int_0^\infty du \int_0^1 d\mu \int_0^\infty \chi_{12}(D, \mu, \vec{r}, \vec{r}', \omega = iu) V_{12}(\vec{r}, \vec{r}') d\vec{r} d\vec{r}' + \{12 \rightarrow 21\} \\ &= -\frac{\hbar}{2\pi} \int_0^\infty du \int d\vec{r} \int_0^1 d\mu \frac{d}{d\mu} \ln (1 - \mu^2 \chi_{11} V_{12} \chi_{22} V_{21})_{\vec{r}\vec{r}'} \\ &= \frac{\hbar}{2\pi} \int_0^\infty du Tr \ln (1 - \chi_{11} V_{12} \chi_{22} V_{21}) \end{aligned} \quad (10)$$

where in general the "ln" is an operator log over the  $(\vec{r}, \vec{r}')$  space. Also,  $\chi_{11}$  and  $\chi_{22}$  are for  $D \rightarrow \infty$  - i.e. for the isolated subsystems but with full-strength e-e-interactions within each subsystem. Using the operator identity  $Tr \ln \hat{O} = \ln Det \hat{O}$  one can see that (10) is related to the interaction in the general Casimir scattering theory, Eq (5.16) of [10].

(10) is also valid within the dRPA. A more direct proof of (10) from the full RPA-adiabatic connection formalism, switching on all interactions together, can be constructed by diagrammatic means: a version for a specific case is given in ref. [62]. We will show presently that Eq (10) reduces to the non-retarded Lifshitz formula [5] for macroscopic slab systems. (See Eq (12) below). In general, because (10) is closely related to the Lifshitz approach, we expect that it will lead to the same asymptotic vdW power laws as Lifshitz in the electromagnetically nonretarded limit.

To obtain the nonretarded Lifshitz result we note that, from charge conservation and from insensitivity to a spatially uniform applied potential [64], the "direct" responses  $\bar{\chi}_{11}$  and  $\bar{\chi}_{22}$  can be written in terms of a (generally nonlocal) polarizability  $\alpha = (\varepsilon - 1) / 4\pi$ ,

$$\bar{\chi}_{11} = \sum_{\mu\nu=1}^3 \frac{\partial^2}{\partial r_\mu \partial r'_\nu} \alpha_{11\mu\nu}(\vec{r}, \vec{r}', \omega). \quad (11)$$

For insulators (and for 3D metals with a finite plasma frequency  $\omega_P(q \rightarrow 0)$ ),  $\alpha$  remains finite as both  $q \rightarrow 0$  and  $\omega \rightarrow 0$ . For two thick slabs of matter in vacuo with parallel surfaces separated by  $D$ , the standard non-retarded limit of the Lifshitz formula is

reproduced from (10) by approximating  $\alpha_{11}$  and  $\alpha_{22}$  via a macroscopic local dielectric functions  $\varepsilon_1, \varepsilon_2$ :

$$\alpha_{11\mu\nu} = \delta(\vec{r} - \vec{r}') \frac{\varepsilon_1(\omega) - 1}{4\pi} \theta(\vec{r}) \delta_{\mu\nu}$$

and similarly for  $\alpha_{22}$ . Here  $\theta$  restricts  $\vec{r}$  and  $\vec{r}'$  to lie within the slabs and  $\varepsilon(\omega)$  is a local spatially constant dielectric function of each slab. After some algebra for fields varying as  $\exp(i\vec{q}_{\parallel}\vec{r})$  parallel to the slab surfaces, we obtain  $\chi_{ii}$  from  $\bar{\chi}_{ii}$  via the screening relation  $\chi = \bar{\chi} + \bar{\chi}V\chi$ , and we then reduce (10) to

$$E^{cross} = \frac{\hbar}{32\pi^2 D^2} \int_0^\infty du \int_0^\infty dx x^2 \left( \frac{\varepsilon_1(iu) + 1}{\varepsilon_1(iu) - 1} \frac{\varepsilon_2(iu) + 1}{\varepsilon_2(iu) - 1} e^x - 1 \right)^{-1}, \quad x = 2q_{\parallel}D \quad (12)$$

which upon differentiation yields the nonretarded Lifshitz force result given in Eq 3.1 of [5].

An expansion of the logarithm in (10) to lowest order in  $V_{12}$  also reproduces the generalized Casimir Polder formula (2), so (10) can also be regarded as a generalization of (2). At the RPA level, higher terms in the expansion of the logarithm in (8) produce vdW interactions between three or more centres (Axilrod-Teller and higher terms) [65]. One might think the perturbative form (2) always becomes asymptotic to (10) at sufficiently large separation between two subsystems so that the perturbation  $V_{12}$  is "small". This is not in fact the case when the interacting systems have an infinitely large area as in sheets or slabs. The reason is that as  $D \rightarrow \infty$  the interaction is dominated by excitations with a small wavenumber  $q_{\parallel} = O(D^{-1}) \rightarrow 0$  parallel to the surface, and the coulomb interaction between such excitations goes as  $\exp(-q_{\parallel}D)q_{\parallel}^{-1}$  which is never small since  $q_{\parallel}D = O(1)$ . For thick parallel plates this can give a discrepancy of up to around 20% between the Lifshitz result (10) and the generalized Casimir-Polder formula (2), a point already noticed by Lifshitz [5]. A discussion of this discrepancy for other geometries is given in Sec. 4 of [61].

In (10) no approximation has yet been made for the internally-interacting responses  $\chi_{11}, \chi_{22}$  of the isolated fragments. If these are approximated with the dRPA then (10) gives a useful form of the dRPA correlation energy, suitable for nonoverlapping systems.

## 6.2 Unusual asymptotic vdW power laws from dRPA

The dRPA correlation energy can sometimes be evaluated analytically for widely-separated nanostructures ( $D \rightarrow \infty$ ) because then only the long-wavelength ( $q \approx D^{-1} \rightarrow 0$ ) limit of the response  $\chi_0$  is needed. This long-wavelength form can be taken as  $\chi_0(\vec{q}, \omega = iu) \approx -n_0q^2/mu^2$  for metals,  $-n_0q^2m^{-1}(u^2 + \omega_0^2)^{-1}$  for insulators and (see [66], [67], [63])  $\chi_0(q_{\parallel}, \omega = iu) = \frac{1}{4}\hbar^{-1}q_{\parallel}^2(u^2 + v_0^2q_{\parallel}^2)^{-1/2}$  for graphene. When these bare responses are applied to the dRPA for non-overlapping structures distant  $D$ , one can show [42], [43], [68], [69], [59], [70] that the asymptotic form of the vdW interaction is sometimes qualitatively different in dRPA from the predictions of pairwise additive theories where  $E = \sum_{ij} C_{6ij}R_{ij}^{-6}$ . In particular the exponent  $p$  in the form  $E^{vdW} = -CD^{-p}$  can be different as summarized in Fig. 1.

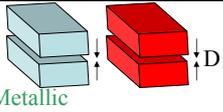
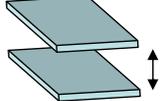
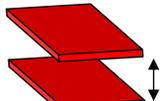
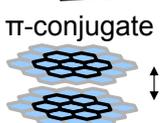
System	Present Theory [ref.]	Conv. Theory ( $\sum D^{-6}$ )
 Metallic	$E^{\text{vdW}} \propto D^{-2}$	$E^{\text{vdW}} \propto D^{-2}$
	$E^{\text{vdW}} \propto D^{-\frac{5}{2}}$	$E^{\text{vdW}} \propto D^{-4}$
	$E^{\text{vdW}} \propto D^{-4}$	$E^{\text{vdW}} \propto D^{-4}$
 $\pi$ -conjugate	$E^{\text{vdW}} \propto D^{-3}$	$E^{\text{vdW}} \propto D^{-4}$
	$E^{\text{vdW}} \propto D^{-2}(\log \frac{D}{D_0})^{-\frac{3}{2}}$	$E^{\text{vdW}} \propto D^{-5}$
	$E^{\text{vdW}} \propto D^{-5}$	$E^{\text{vdW}} \propto D^{-5}$

Figure 1: Asymptotic vdW energy formulae for thick and thin slabs, and for parallel wires, pictured in the left column. Red indicates an insulator, blue a conductor, purple a semimetal (graphene). Right column: Predicted energy from pairwise additive theories. Middle column: Predicted energy from RPA [43]. For further cases of unusual powers see Refs. [44], [69], [70].

This can occur when all of the following are satisfied: (i) each system is macroscopic in at least one dimension so that electron density fluctuations of arbitrarily long wavelength ( $q \rightarrow 0$ ) are possible; (ii) each system is small in at least one other space dimension, so that intra-system Coulomb screening of the charge fluctuations is incomplete; and (iii) the systems have a zero homo-lumo gap, as in 2D or 1D metals or graphene. The unusual power laws arise from the coupling of long-wavelength excitations that involve the coherent motions of electrons on many atoms, quite different from the pairwise physics. Significant differences in vdW interaction have also been predicted between metals and semiconductors in the non-asymptotic limit [71]. When condition (iii) is not satisfied but the gap is small, as in highly polarizable systems, then the asymptotic power exponent  $p$  in the form  $E^{vdW} = -CD^{-p}$  will not be anomalous, but nevertheless non-pairwise additivity makes the coefficient  $C$  differ strongly from the prediction of  $\sum C_6 R^{-6}$  theory. The unusual power exponents  $p$  predicted by dRPA (Fig. 1, second column) have been verified by electron Diffusion Monte Carlo calculations [46] for the case of parallel linear conductors. In the case of planar conductors these DMC calculations only partly confirmed the analytic dRPA result [68], but in this case there is a possibility that the simulation cell did not have a large enough area to capture the very long-wavelength fluctuations/correlations involved in the large- $D$  vdW interaction. For the case of graphite a full numerical dRPA calculation of the layer binding energy  $E(D)$  has recently been performed [59]. This calculation was able to confirm the presence of the predicted anomalous  $D^{-3}$  contribution at the largest  $D$  values ( $\approx 3\text{ nm}$ ) where the numerics were still feasible, but also showed that the  $D^{-3}$  contribution from the gapless electronic  $\pi_z \rightarrow \pi_z^*$  transitions was still essentially negligible at this separation, compared with the much larger vdW energy from the gapped transitions involving "majority" Bloch bands other than the  $\pi_z$  bands. A similar consideration applies to observation of the anomalous asymptotic  $-CD^{-2}(\ln D)^{-3/2}$  energy predicted [42], [43] for parallel metallic carbon nanotubes (though the unusual energy contribution may be more dominant for nanowires made of metallic atoms). Nevertheless at sufficiently large separation  $D$  the anomalous metallic term will dominate, and it will be interesting to see whether sensitive modern force detection techniques such as atomic Force Microscopy are able to measure these anomalous forces directly. In terms of general modelling of solids and nanostructures, however, the wrong magnitude of the vdW interaction at short to intermediate distances because of non-pairwise-additivity effects is probably more important than the power law at asymptotic separations.

## 7 Diseases of dRPA

Despite the good success of the dRPA for many solids, with inclusion of vdW effects as just described, this theory has some very serious shortcomings in general, and it is important to use it only in circumstances where these are not significant or where they can be easily corrected.

## 7.1 Over-correlation by dRPA

Firstly, the depth of the short-ranged part of the electronic correlation hole is seriously over-estimated in dRPA, resulting in overestimation of the magnitude of the absolute correlation energy. This was apparent already in early work on the homogeneous electron gas. Fortunately, one is most often interested in energy *differences*  $\Delta E_c = E_c(\{\vec{R}_j\}) - E_c(\{\vec{R}'_j\})$  between different arrangements of the same set of nuclei, with positions  $\vec{R}_j$  in one configuration and  $\vec{R}'_j$  in the other configuration. Here the incorrect short-ranged part of the hole is much less important as it is likely to be very similar in the two nuclear configurations and hence largely cancels in  $\Delta E_c$ , provided that the nuclei are not moved too close to one another. Indeed Perdew and co-workers [72] noted that dRPA tends to overestimate  $|E_c|$  per electron by a constant amount, so that "isoelectronic" energy differences (those with  $N_{electrons}$  held constant) are relatively well described. Since the short-ranged hole is described much better in LDA/GGA, Perdew and collaborators also proposed in the same paper a theory correcting the RPA correlation energy for short-ranged effects by using LDA data

$$E_c^{RPA+} = E_c^{dRPA} + \int (\varepsilon_c^{\text{hom}}(n(\vec{r})) - \varepsilon_c^{\text{hom,dRPA}}(n(\vec{r}))) n(\vec{r}) d\vec{r}.$$

Here  $\varepsilon_c(n)$  is the correlation energy per electron in the homogeneous electron gas of density  $n$ . More sophisticated versions termed "RPA+" based on gradient functionals were also derived [73]. Note that all of the successful dRPA calculations for solids by Harl et al., [58] were for isoelectronic energy differences.

A different approach to the short-ranged diseases of dRPA is that of *range separation*, originally introduced by Savin and Stoll for molecular problems [74], [75]. This involves splitting the bare Coulomb interaction into short ranged and long ranged parts, with different many-body treatments applied to the two parts - e.g. dRPA for the long ranged part and LDA for the short ranged part. This has been tried recently as a correction to the dRPA with some success [76], but the approach probably deserves wider application for RPA as it also lessens the computational load associated with reproduction of the coulomb cusp in the pair function

## 7.2 Spurious electron self-interaction and dRPA

In a one-electron system the bare density response  $\chi_0$  is the exact response, and the correlation energy should be zero. However the time-dependent Hartree equation (6) contains a non-zero self-interaction term, the second mean-field term on the right side, which corresponds in this case to an electron avoiding itself. As a result the dRPA contains an incorrect self-correlation energy for a one-electron system. Because of the  $r^{-1}$  dependence of the Coulomb energy, this can be a very serious error for orbitals that are highly localized (having small radius  $r$ ), as in the He atom for example. Partly as a result of this, dRPA starting from LDA or GGA orbitals gives an extremely bad account of the

binding energy curve of small dimers [77], [78]. Some improvement can be obtained by using starting orbitals and/or KS potential that incorporate groundstate self-interaction correction, since the corresponding effective potential includes the correct  $-e^2/r$  tail and reduces the polarizability of the outer orbitals compared with the incorrect high values obtained from the LDA potential. The problem of singles contributions, related to a non-self-consistent choice of starting orbitals, is also a significant issue [79].

The best-justified method to correct the self-interaction in dRPA is to go to higher members of the RPA class of theories. For example the "RPAx" energy comes from replacing (6) by the antisymmetrized Hartree Fock version of the mean field, and this entails the response of the 1-electron density matrix rather than just the density. This is implemented in a number of molecular packages, and it does improve the binding energy curves of small dimers where self interaction correction (SIC) is an issue [77], [76]. RPAx does have some problems and instabilities of its own, however, and is computationally demanding in solids.

Another systematic way to improve dRPA is to add, to the dRPA ring energy diagrams, a sum of higher terms in the form of the Second Order Screened Exchange (SOSEX) diagram [80]. This exactly cancels the one-electron self-correlation term in the dRPA. It also makes a significant further improvement to the already good dRPA results for the energetics of solids [80] and gives excellent lattice spacings. Unfortunately it adds significantly to the already large computational cost of dRPA energy calculations for solids.

Another possible improvement to dRPA is the use of the Inhomogeneous Singwi-Tosi-Land-Sjolander (ISTLS) correlation theory [81], [82], [83], which not only cures the one-electron self-interaction problem but may improve the "many-electron self interaction" properties discussed by Perdew and coworkers [84] and by Yang and coworkers [78], related to the need for a linear dependence on any fractional orbital occupation numbers. Of course ISTLS is also computationally very costly.

The success of the dRPA energetics for crystals with diffuse outer orbitals such as the  $\pi$ -clouds of graphene systems [59], or crystals of the larger rare-gas atoms [60], reflects the unimportance of orbital self-interaction for such diffuse orbitals. Significantly, the bonding of the He crystal with its tightly bound atomic orbitals was described much less well by dRPA than the higher rare-gas crystals [60].

## 8 Approximations to microscopic energy expressions for vdW energetics

A number of approaches have been proposed to obtain efficient vdW energy functionals by approximating microscopic energy expressions. Racpewicz and Ashcroft [27] and Andersson, Langreth and Lundqvist [85] postulated a nonlocal density based approximation for well-separated pairs of systems via indirect arguments. Dobson and Dinte [64] showed that this expression could be derived directly from the generalized Casimir Polder pertur-

bation theory (Eq (2) above) , via a local conserving density-based approximation to the density response  $\chi$ . More complex theories have recently been proposed with this type of approach as a starting point [86], [87].

It is also possible to approximate *non-perturbative* ACFD energy expressions using only the groundstate electron density  $n(\vec{r})$  as input. An early attempt in this direction was the functional of Dobson and Wang [88]. This approximated  $\chi_0$  by the double space gradient of a density-based approximation to the polarizability, followed by RPA screening without further approximation. This approach reproduced the RPA cohesion energy of a pair of metal slabs right down to contact with overlap of electron clouds. Unfortunately the functional is not very efficient numerically and needs explicit cutoffs to describe insulators, and so far it has not been pursued further.

### 8.1 vdW-DF

By far the best-known functional of the "approximated ACFD" type is the "vdW-DF" of Dion et al [89], [90], [91]. A complete self-contained derivation of this functional seems to be lacking in the literature, but an attempt will be made here to list some features of the reasoning. The starting point is the exact ACFD, Eq (5). From this starting point the vdW-DF provides a nonlocal correction  $E_c^{nl}$  to the LDA correlation energy of a nonuniform system. The method is not limited to the RPA, but it is approximate, and five distinct approximations/assumptions appear to have been made in obtaining it:

*Approximation (i)* The method notes that the quantity  $\varepsilon(\vec{r}, \vec{r}', \omega)$  defined in electrodynamics is equal to the screening function  $1 - \bar{\chi} * V$  for the special case of the uniform gas. Here  $\bar{\chi}$  denotes the "direct" response function relating the electron density to the total classical electrodynamic potential. The ACFD then assumes that plugging  $\varepsilon$  into the ACFD, instead of the exact  $\chi_\lambda = (1 - \bar{\chi}_\lambda * V)^{-1} \bar{\chi}_\lambda$ , results in the LDA correlation energy. The nonlocal correction to the LDA would then be given by

$$E_c^{nl} = \frac{1}{2} \int \frac{d\lambda}{\lambda} \int_0^\infty \frac{\hbar}{\pi} du Tr [(1 - \bar{\chi}_\lambda * \lambda V)^{-1} \bar{\chi}_\lambda V_\lambda - \varepsilon_\lambda^{-1} (\varepsilon_\lambda - 1)]$$

where the dependence on  $(\vec{r}, \vec{r}', \omega = iu)$  is suppressed for brevity, products are space convolutions and the Trace operation is  $Tr F = \int F(\vec{r}, \vec{r}) d\vec{r}$ . The subtracted term is not exactly the LDA, so this amounts to the first approximation.

*Approximation (ii)* The "full potential approximation", explicitly introduced in vdW-DF, assumes that the  $\lambda$  integration in the ACFD can be done analytically to give an operator logarithm:

$$E_c^{nl} = \frac{\hbar}{2\pi} \int_0^\infty du Tr \ln [\varepsilon^{-1} (1 - \bar{\chi}_\lambda * \lambda V)] \quad (13)$$

This is exactly true in the dRPA where  $\bar{\chi}_\lambda = \chi_0$  independent of  $\lambda$ , but it constitutes an approximation in other formalisms.

*Approximation (iii)* Since  $\bar{\chi} = \nabla(\varepsilon - 1)\nabla/4\pi$  exactly in general (see e.g. [64]), the nonlocal correlation energy correction (13) can be expressed in terms of  $\varepsilon$  alone. The logarithm

in (13) represents the solution of the time-dependent Hartree-coulomb screening problem. In vdW-DF, this screening problem is solved approximately by expanding the logarithm to second order in the quantity  $(\varepsilon^{-1} - 1)$ , termed "S" in [89], (but not exactly equal to the dynamic structure factor despite the similarity to a common notation). This gives

$$E_c^{nl} = \frac{\hbar}{4\pi} \int_0^\infty Tr \left( S^2 - \left( \frac{\vec{\nabla} S \cdot \vec{\nabla} V}{4\pi e^2} \right)^2 \right) du. \quad (14)$$

Here once again all products represent convolutions in position space.

*Approximation (iv)* Finally a modified plasmon pole type of approximation is made for  $S$  and substituted into (14), yielding after some algebra a functional of form

$$E_c^{nl} = \int n(\vec{r})n(\vec{r}') \phi(\vec{r}, n(\vec{r}), \nabla n(\vec{r}) : \vec{r}', n(\vec{r}'), \nabla n(\vec{r}')) d\vec{r}d\vec{r}' \quad (15)$$

where  $\phi \sim |\vec{r} - \vec{r}'|^{-6}$  as  $|\vec{r} - \vec{r}'| \rightarrow \infty$ . The dependence on gradients is built into the modification to the simple plasmon pole approximation, and the physics of this is based on many years of success by Langreth and co-workers with the development of gradient density functionals.

*Approximation (v)* In order to implement the functional in practice, it must be combined with a suitable approximation for the exchange energy  $E_x^0$ . Tests on a number of systems showed that neither LDA exchange nor exact DFT exchange produced results of useful accuracy. However it was found that the revPBE exchange functional was suitable, and some physical reasons were advanced for this choice. This is very crucial to the behavior of the functional for vdW-bound systems near to their equilibrium binding separation  $D_0$ .

## 8.2 Features of vdW-DF

The vdW-DF turns out to be a numerically efficient approach with some very good general features. It has the  $-\sum C_6 R^{-6}$  form at for well separated systems and hence never fails to produce a vdW interaction where required. A very strong feature is the natural saturation of the function  $\phi$  at short distances (see Eq (15) above), without the need for any empirical input, in contrast to more empirical pairwise summation approaches. vdW-DF gives sensible results for a wide range of van der Waals bonded systems from rare gas dimers to solids and surfaces, often giving good vdW energies but sometimes significantly over-estimating  $D_0$  [92], [93], [94]. Significant improvements have recently been made in its numerical implementation (e.g. [95], [96] and its speed is now quite competitive with more empirical pairwise-additive theories. Attention has also been focussed on improving the generalized plasmon pole approximation ("approximation (iv)" described above). Vydrov and van Voorhis [97], [98] took a frankly empirical approach and modified approximation (iv) so as to improve the predicted  $C_6$  for atom dimers. The original authors [99] also suggested improvements to aspects (iv) and (v). Overall the method is robust and continues to be used for a variety of systems [100].

There are however a number of further aspects (approximations (i)-(iii) listed above) that could probably be improved. For example, as a result of approximating the logarithm as in Approximation (iii) above, the theory ends up having a pairwise additive form, with  $\sum_{ij} C_{ij} R^{-6}$  behavior at large separations (compare Sect 4 above). This  $\sum_{ij} C_{ij} R^{-6}$  long-ranged behavior means that the asymptotic vdW interaction for metallic systems will have the same exponent as for insulators in any geometry, contrary to known properties of thin metal or graphene sheets or metallic wires: see Sect 6.2 above. While the unusual behavior of such low-dimensional zero-gap systems at large distances is interesting, the force there is small and this alone would not constitute a serious disadvantage of the theory for practical binding calculations [59]. However the same pairwise property means that one might need to be careful about this functional for polarizable, highly anisotropic systems even in the non-asymptotic region of electron cloud overlap (see for example [37], [71], [41]). One should probably not be surprised that the theory appears not give a satisfactory account of the selective binding of graphene to specific metal surfaces [94], for example.

### 8.3 New directions for ACFD-based vdW functionals

It is tempting to try to go beyond the dRPA by using the ACFD (Eq (5)) but replacing the time dependent Hartree equation (6) of dRPA by the exact equation of linear Time Dependent Density Functional Theory (TDDFT) [101]:

$$\chi_\lambda = \chi_0 + \chi_0 (\lambda V + f_{xc\lambda}) \chi_\lambda. \quad (16)$$

If the usual Adiabatic Local Density Approximation (ALDA) is used for the dynamic exchange-correlation kernel  $f_{xc}$ , the ACFD energy from (16) is typically not improved over dRPA, because the ACFD energy samples all frequencies, not just low frequencies for which the ALDA is suited. Instead of this dRPA+ALDA approach, an ACFD energy formalism has been tried, with use of an "energy optimized" local exchange correlation kernel  $f_{xc}$  designed to improve the short ranged hole properties, and fitted to the xc energy of the homogeneous gas [102], [103]. This approach improved the energy over RPA for jellium spheres [104] and in fact it did better than the RPA+ approach described above in Sec 7.1. Other than this it has received little testing. The xc kernel  $f_{xc}[n](\vec{r}, \vec{r}')$  used in these theories was local or semi-local in  $r$  and  $\vec{r}'$  and had a similarly local functional dependence on the groundstate density  $n(\vec{r}'')$ . However it has become clear that any beyond-dRPA theory of van der Waals interactions requires  $f_{xc}$  to have a highly nonlocal functional dependence on  $n(\vec{r}'')$ . A limited discussion of this is given in [14], and work is proceeding on a possible implementation of this idea.

Even the simplest of the full many-body theories, the dRPA, is very costly numerically. For example a recent implementation [59] of dRPA for the binding energy curve  $E(D)$  of graphite as a function of the layer spacing  $D$  using an efficient periodic code was near the limit of present numerical capabilities despite the small size (4 atoms) of the unit cell of graphite. This was partly because of the need to sample  $k$  space finely near the

Dirac points in the Brillouin zone - see e.g. [63]. dRPA-based modelling of technologically interesting graphenic nanostructures, such as graphene bound on various metals, would seem to be presently out of reach because large crystal unit cells are required. Pairwise additive theories including vdW-DF are not a priori reliable because of the highly anisotropic, highly polarizable nature of the systems involved. (see Sect 4). Thus a highly non-additive nonlocal but numerically efficient theory is required. One current approach to this problem is to keep a full solution of the time dependent Hartree screening problem (Eq (6)), corresponding to retention of the full logarithm in (8) or (13), without use of a second order expansion, thus avoiding restriction to pairwise additive physics. Instead one approximates the independent-electron response function  $\chi_0(\vec{r}, \vec{r}', iu)$ . A very recent development [105] is the use of the new Continuum Mechanics (CM) formalism of Tokatly, Vignale and co-workers [106], [107] to calculate  $\chi_0$ . CM is a hydrodynamic-style theory with the remarkable property that it gives the exact response  $\chi_0$  of one-electron and two electron systems at all frequencies, and for general many-electron systems at high frequencies. It satisfies the f-sum rule and various other exact constraints such as the Harmonic Potential Theorem [108]. Ref [105] develops this approach into a general-geometry non-pairwise theory that has good vdW properties both for insulators and for a simple metal test model. Work is proceeding on formal properties of the CM-based correlation theory, and on its numerical implementation for realistic geometries.

## 9 Summary

Macroscopic (Lifshitz) and few-atom (quantum chemical) approaches to dispersion forces have long been available. In recent years there has been much progress in the first-principles microscopic description of dispersion forces in solids and larger nanostructures, right down to microscopic contact separations. Modellers can now choose from a variety of computationally tractable semi-empirical pairwise-additive theories of these phenomena, as well as the pairwise additive vdW-DF theory. These are adequate for medium-accuracy calculations in the electromagnetically non-retarded limit, with the possible exception of systems that are simultaneously highly anisotropic and highly polarizable. An improvement for such cases can be obtained with models evaluating the zero point energy of self-consistent dynamical collective polarization modes, in arrays of localized polarizable dipoles. For a full description of such cases however, including a detailed account of low-dimensional, low-gap systems one probably needs the computationally expensive full many body approaches, which are now available in packages such as VASP and ABINIT. These start with the simplest direct Random Phase Approximation (dRPA). Recent additions such as RPax and dRPA+SOSEX can improve numbers but are even more costly. Currently these approaches are not feasible for large nanostructures in realistic, technologically interesting geometries. Work is continuing to remedy this situation.

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