cecam Centre Européen de Calcul Atomique et Moléculaire	**Workshop Scientific Report** Please do not repeat the program (unless there were last-minute changes) or the initial description - we already have this material.
Title	Towards First-Principles Description of van der Waals Interactions in Complex Materials
Organizers	Alexandre Tkatchenko, Angel Rubio, Matthias Scheffler

Scope of the workshop (one-two paragraphs)

Van der Waals (vdW) interactions are ubiquitous in nature, playing a major role in defining the structure, stability, and function for a wide variety of molecules and materials.

Despite significant progress in the field of modeling vdW interactions during the last decade, many questions remain unanswered and much development needs to be done before a truly universally applicable (accurate and efficient) method emerges. Understanding the reasons of why different approaches ``work'' outside of their expected domain of applicability is important for the development of more robust approximations.

Within this context our CECAM Workshop ``Towards First-Principles Description of van der Waals Interactions in Complex Materials'' provided an opportunity to (i) bring the major players up to date in the most recent developments in the field, (ii) identify a set of (complex) systems -- beyond small molecules – that can be used to benchmark newly developed methods, (iii) discuss the implementation and validation of different vdW methods in electronic structure codes, and (iv) identify future major challenges in the area of modeling vdW interactions.

Main **outcomes** of key presentations (one page)

The workshop started with an introductory lecture by J. F. Dobson, who is an internationally renowned expert in the fundamental theory of vdW interactions. His lecture set the stage for the other talks and discussions during the workshop. He defined three types of non-additive contributions to vdW interactions (so called "A", "B", "C") that were frequently mentioned and vigorously discussed throughout the workshop.

The first session summarized current efforts in explicit wavefunction-based method for modeling vdW interactions, including coupled-cluster methods, quantum Monte Carlo (QMC), and going beyond the random phase approximation (RPA). Pavel Hobza presented a set of tests for benchmarking the accuracy of several approximations to coupled cluster, suggesting that there might exist an alternative method to the widely used CCSD(T) ``gold standard''.

David Sherrill discussed the efforts in his group to provide reliable benchmark data at complete basis set limit for a variety of molecular systems. Sandro Sorella presented an implementation of nuclear forces in QMC, showing evidence that short molecular dynamics simulations using QMC might become possible in the future.

The second session ``On the Fifth Rung of Jacob's Ladder'' concentrated on current developments in RPA methods and beyond. Georg Kresse showed an impressive implementation of wavefunction-based stochastic full configuration interaction method for solids. He presented first such calculations for simple solids, setting a new level of benchmark accuracy for first-principles solid state methods. The drawback is that these calculation are unaffordable for anything but the lightest of solids using only very small basis sets.

Furthermore, several improvements to the RPA have been suggested in the talks by Xinguo Ren (second-order renormalized perturbation theory), Julien Toulouse (range-separation between DFT and RPA), and Deyu Lu (the influence of different exchange-correlation kernels in the adiabatic connection formula).

The highlights in the session ``Interatomic Methods for vdW Interactions'' included the talk by Stefan Grimme, who presented a novel database of supramolecular systems, beyond the typical small molecules used for benchmarking purposes. His extrapolated experimental values for the binding energies of supramolecular dimers seem to agree well with recent QMC calculations of Dario Alfe et al. This finally opens up a possibility to study molecular systems that are of relevance to experiment in solvent phase.

Robert DiStasio talked about the recently developed many-body dispersion (MBD) method for computing interatomic vdW energies, that goes beyond the typical pairwise approximations that are used up to date for including vdW in DFT. It appears that many participants of the workshop considered necessary to move beyond the simple pairwise approximations, and the issue of many-body effects was frequently discussed during the workshop.

Several improvements of the vdW-DF functional were reported in the session ``Non-local Functionals for vdW Interactions''. Troy Van Voorhis introduced his proposed modification of the vdW-DF functional that improves the treatment of the long range and also the integration with semi-local functionals. Jiri Klimes and Angelos Michaelides highlighted the need to significantly improve the exchange functional used in the vdW-DF approach, and presented their empirical alternative. Angelos also mentioned several challenging systems for vdW-inclusive approaches, including different polymorphs of ice and organic/inorganic interfaces. This generated quite some interest in terms of benchmarking the different methods discussed during the workshop.

The role of vdW interactions for intermolecular interactions was analyzed in Session IV. Kwang Kim presented a series of challenging applications in nanotechnology that require accuracy beyond what is currently possible with approximate vdW-inclusive methods. Alston Misquitta and Alisa Krishtal discussed the need to go beyond simple pairwise methods for vdW interactions, and to include type B screening (defined by J. F. Dobson) due to long-range electrodynamic Coulomb interactions, which also leads to anisotropy of the molecular polarizability. VdW interactions are now known to play a crucial role for molecular liquids and solids. These two applications have been actively discussed by Roberto Car, Giulia Galli, Jose Soler and Noa Marom in Session VI. A consensus has been established that vdW interactions should be included for an accurate description of liquid water and ice. However, there are still many questions of how quantum nuclear effects interplay with vdW interactions, and much more future work is required to answer this question. Noa Marom clearly showed that many-body vdW interactions should be included in DFT in order to accurately treat polymorphism in molecular crystals.

The final session discussed the role of vdW interactions in Hybrid Inorganic/Organic Interfaces (HIOS). A variety of successful applications to HIOS have been presented. However, the main issue in this field is the scarcity of accurate experimental data, and the fact that few methods have been systematically benchmarked on well defined databases. The discussion was centered upon agreeing upon a set of benchmark systems that can be used to assess the performance of different vdW-inclusive methods.

Report on selected discussions (one page)
eg. Were there interesting hints for new research? for new developments? for collaborations?

Scientific discussions played a prominent role during this workshop. On average, every talk was followed by 10 minutes of active discussion. In addition, there was a dedicated 3-hour discussion session. Throughout the workshop, there was a consensus that the community needs to go beyond simple additive pairwise approximations to vdW interactions that are widely used today, addressing the different types of non-additivity discussed during the workshop. However, in order to make progress the typical small molecule databases cannot be considered as a benchmark. The truly non-additive many-particle nature of vdW interactions emerges for larger and more complicated systems such as supramolecular complexes, molecular crystals, solids, interfaces, etc. Several groups are now working to define benchmark sets of complex systems that can help us in assessing the performance of next-generation vdW-inclusive methods.

Several researchers expressed a view that the large number of available methods to calculate vdW interactions creates confusion in the community. The differences and similarities between different methods are not completely understood and the approximations employed in each method are frequently not clear. There was a suggestion to create a document that classifies the different methods in terms of the employed approximations. However, most participants disagreed with this suggestion, and expressed a view that the robustness and the performance of a method decides whether it will be broadly used by others. With so much activity happening in the field of modeling vdW interactions, at this point it is probably preliminary to summarize the wide variety of existing methods.

In terms of truly first-principles methods for modeling vdW interactions, quite some discussion was dedicated to how to go beyond the random phase approximation (RPA) for the correlation energy.

There are many proposals to do this, such as including single excitations based on DFT orbitals, designing exchange-correlation kernels, etc. Another issue consists of eliminating the self-correlation problem in RPA. The inclusion of screened exchange seems to alleviate this problem, but makes the calculations significantly more expensive. It is clear that much progress has been achieved in this field over the last few years, still this subject remains a challenging open issue.

Another open issue that was discussed is the influence of vdW interactions on properties other than the total energy. This includes, for example, electronic and vibrational properties. This aspect has not received much attention yet, and several participants expressed their interest in studying the role of vdW interactions on response properties.

To what extent were the **objectives** of the workshop achieved (strong points, weak points)? (one paragraph at least)

The proposed objectives of the workshop were achieved. Several new research directions have been identified, and it was useful to see the impressive progress achieved by several groups over the last couple of years. However, more needs to be done to continue the dialog between solid state and molecular communities. Although people are aware of the work in both communities, there is still a barrier to communication, partly due to the different language employed in different communities. The modeling of vdW interactions is certainly a very active field, and this workshop provided an opportunity to bring several communities together. In this aspect, the workshop was a success, as recognized by majority of the participants.

Do you have suggestions for new workshops/tutorials/conferences on the topic?

Since the modeling of vdW interactions is an important and very active field, it would be optimal to have another CECAM workshop in two years because the field is very dynamic and many advancements and new developments are already in sight.