

O 2: Focussed session: Theory and computation of electronic structure: new frontiers I (jointly with HL, DS)

Time: Monday 11:15–13:00

Location: TRE Phy

Topical Talk

O 2.1 Mon 11:15 TRE Phy
Range separation: success, doubts and perspectives — ●ANDREAS SAVIN — CNRS and UPMC Univ Paris 6, Laboratoire de Chimie Theorique, F-75252 Paris, France

The difficulty of finding simple approximations for density functionals can be alleviated by passing some of the exchange and correlation description to a wave function. A way to produce such hybrids is to consider that for short-range inter-electronic separations exchange and correlation effects are transferable and thus able to be captured by simple models.

Range-separated hybrids can be applied to different levels of density functional approximation (LDA, GGA, ...) and wave function approximation (single determinant, second order perturbation theory, RPA, coupled cluster, ...).

The methods do not bring significant improvement in most fields of application where density functional approximations have been successful. However, they improve accuracy when usual approximations fail, such as van der Waals interactions [1], or where self-interaction becomes an important issue. The computational effort is smaller than for the corresponding wave function method, mainly because smaller basis sets can be used.

Finally, some unexplored path / open questions will be discussed, such as the choice of the interaction operator, improving the density functional approximation, or the role of mixed "short-range/long-range terms".

[1] W. Zhu, et al, J. Chem. Phys., 132, 244108 (2010).

O 2.2 Mon 11:45 TRE Phy
Van der Waals interactions in semiconductor solids — ●GUOXU ZHANG, ALEXANDRE TKATCHENKO, JOACHIM PAIER, HEIKO APPEL, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der MPG, Berlin, Germany

The binding in semiconductor solids arises mainly from the covalent hybridization of atomic orbitals. Hence, it is typically assumed that van der Waals (vdW) interactions play a minor role for their cohesion. In order to probe this conventional wisdom we develop a method to calculate accurate long-range vdW coefficients for ions and atoms in crystals. We first assess the validity of the Clausius-Mossotti relation between the polarizability and dielectric function for bulk semiconductors by comparing periodic TDDFT calculations to direct extrapolation of the frequency-dependent TDDFT polarizability for finite clusters. We find a good agreement between these two approaches for computing vdW $C_6(V)$ coefficients for a broad variation in the unit cell volume V for diamond, Si, and Ge crystals. When using TDDFT@HSE with the Nanoquanta kernel, the volume-dependent dielectric constant of Si and Ge is in excellent agreement with experimental data. The crystal-field screening reduces the vdW coefficients by a factor of two compared to corresponding free-atom and effective hybridized $C_6[n(r)]$ values [1]. The use of accurate $C_6(V)$ coefficients in the PBE+vdW method [1] improves cohesive properties of Si and Ge in comparison to experimental data. [1] A. Tkatchenko and M. Scheffler, Phys. Rev. Lett., 102, 073005 (2009).

O 2.3 Mon 12:00 TRE Phy
Van der Waals interactions in complex materials: Beyond the pairwise approximation — ●ALEXANDRE TKATCHENKO¹, ROBERT A. DiSTASIO JR.², ROBERTO CAR², and MATTHIAS SCHEFFLER¹ — ¹Fritz-Haber-Institut der MPG, Berlin, Germany — ²Princeton University, NJ, USA

Despite the well-known fact that van der Waals (vdW) interactions are many-body in nature and the polarizability is a non-local function, popular vdW-DF [1] and DFT+vdW [2] methods are based on (semi)-local approximations for the polarizability and only model the pairwise part of vdW interactions. Here we show how to go beyond the pairwise (semi)-local approximation to vdW interactions by coupling the recently developed TS scheme [2] with the Fluctuating-Coupled-Dipole Model (CFDM) [3]. The TS scheme provides parameter-free input atomic polarizability distributions and the CFDM allows to model both polarizing and depolarizing local fields, and captures the many-body nature of vdW interactions. Results are presented for small and medium-size molecules, as well as solids. We find that the many-body

screening plays a major role in modifying the polarizability of large systems. Our results for vdW coefficients in semiconductor clusters and solids are in excellent agreement with TDDFT calculations. [1] M. Dion *et al.*, Phys. Rev. Lett., 92, 246401 (2004); [2] A. Tkatchenko and M. Scheffler, Phys. Rev. Lett., 102, 073005 (2009); [3] M. W. Cole *et al.*, Mol. Simul. 35, 849 (2009).

O 2.4 Mon 12:15 TRE Phy
The random phase approximation and beyond: an assessment for molecular binding energies and reaction barrier heights — ●XINGUO REN¹, JOACHIM PAIER², PATRICK RINKE¹, ANDREAS GRÜNEIS³, GEORG KRESSE³, GUSTAVO E. SCUSERIA⁴, and MATTHIAS SCHEFFLER¹ — ¹Fritz Haber Institute (Berlin) — ²Humboldt University (Berlin) — ³University of Vienna (Vienna) — ⁴Rice University (Houston)

The random phase approximation (RPA) for the correlation energy has become a promising approach for describing electronic systems in various bonding situations. Recent efforts have focused mainly on correcting the general tendency of RPA to underestimate bond strengths e.g. by adding corrections from second-order screened exchange (SOSEX) [1,2] or single excitations (SE) [3]. In this work, we systematically assess the influence of SOSEX, SE and their combinations on the atomization energies of the G2-I molecular set, as well as the chemical reaction barrier heights of the HTBH38/04 and NHTBH38/04 benchmark sets [4]. We find that RPA+SOSEX+SE applied as a perturbation to the PBE exchange-correlation functional gives the most balanced description. However, for reaction barrier heights RPA based on PBE turns out to be better and is surprisingly accurate. The underlying mechanism governing the performance of RPA and its variants in different circumstances will be analysed. [1] A. Grüneis *et al.*, J. Chem. Phys. 131, 154115 (2009). [2] J. Paier *et al.* J. Chem. Phys. 132, 094103 (2010). [3] X. Ren *et al.*, arXiv:cond-mat/1011.2724. [4] Y. Zhao *et al.* J. Phys. Chem. A 109, 2012 (2005)

O 2.5 Mon 12:30 TRE Phy
Au_N clusters (N=1-6) supported on MgO(100) surfaces: the effect of exact exchange and dispersion interactions on adhesion energies. — ●LAURO OLIVER PAZ-BORBÓN¹, GIOVANNI BARCARO², ALESSANDRO FORTUNELLI², SERGEY LEVCHENKO¹, and MATTHIAS SCHEFFLER¹ — ¹Fritz Haber Institut der Max Planck Gesellschaft, Berlin. — ²Istituto per i Processi Chimico-Fisici del Consiglio Nazionale delle Ricerche, Pisa.

Understanding the interaction between a metal nanoparticle and an oxide surface is a prerequisite for further development of nanocatalysts displaying tailor-made properties. In this work, we study the interaction of an Au adatom and Au_N clusters (N=2-6) supported on pristine and defected MgO(100) surfaces, using a DFT all-electron full-potential approach [1], under a hierarchy of exchange-correlation (XC) functional approximations: ranging from the generalized gradient approximation (PBE and RPBE) to hybrid functionals (PBE0, HSE06) and exact exchange (EX) plus correlation in the random phase approximation (EX-cRPA/cRPA+). Our results for the Au adatom at the oxygen site show that, by reducing the *self-interaction error* (SIE) through the inclusion of EX, smaller adhesion energies values are found when compared to those calculated using hybrid and semi-local functionals; concurrently, the diffusion energy barrier increases. Dispersion interactions [2] are found to play a crucial role in determining the energetics of Au_N clusters. [1] Blum, V. *et al.*, *Computer Physics Communications* 2009, 2175, 180. [2] Tkatchenko, A., Scheffler, M., *Phys. Rev. Lett.* 2009, 102, 073005.

O 2.6 Mon 12:45 TRE Phy
One dimensional model systems in time-dependent density functional theory — ●NICOLE HELBIG¹, JOHANNA I. FUKS¹, ILYA V. TOKATLY^{1,2}, and ANGEL RUBIO^{1,3} — ¹ETSF Scientific Development Centre and Universidad del País Vasco, San Sebastián, Spain — ²IKERBASQUE, Basque Foundation for Science, Bilbao, Spain — ³Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

We present a local density approximation (LDA) for one-dimensional (1D) systems interacting via the soft-Coulomb interaction based on quantum Monte-Carlo calculations. Results for the ground-state en-

ergies and ionization potentials of finite 1D systems show excellent agreement with exact calculations, obtained by exploiting the mapping of an N -electron system in d dimensions, onto a single electron in $N \times d$ dimensions properly symmetrized by the Young diagrams. We conclude that 1D LDA is of the same quality as its three-dimensional (3D) counterpart, and we infer conclusions about 3D LDA. The linear and non-linear time-dependent responses of 1D model systems using LDA, exact exchange, and the exact solution are investigated and show

very good agreement in both cases, except for the well known problem of missing double excitations. Consequently, the 3D LDA is expected to be of good quality beyond linear response. We employ the 1D LDA and exact exchange functionals to investigate the description of Rabi oscillations in time-dependent density functional theory and show that adiabatic approximations to the exchange-correlation potential lead to detuned Rabi oscillations.