Ψ_k Scientific Highlight Of The Month

No. 122 April 2014

Success Stories of eminent research in ab-initio calculations

Ab-initio calculations based on density functional theory have been enormously successful. They allow the understanding of real materials and the design of new materials with improved properties and functionalities and can be applied to all condensed matter systems. The success is such that in certain fields new experimental activities are not meaningful without accompanying ab-initio calculations.

However, when one is asked to list the very important contributions of ab-intio calculations to materials science, or to the design of new materials with much improved functionalities, or with properties which are extremely important for applications etc., then one finds out, that this is a very difficult task. Exactly these aims are behind the present effort to collect success stories in our field. These are stories written for non-experts in our field, with the aim of demonstrating the success of ab-initio calculations and e.g. convincing funding agencies about the importance of the field.

Thus, please, read the following stories. We hope that you will enjoy them. In case that you know about another success story, worth to be written up, please let me know.

With best regards,

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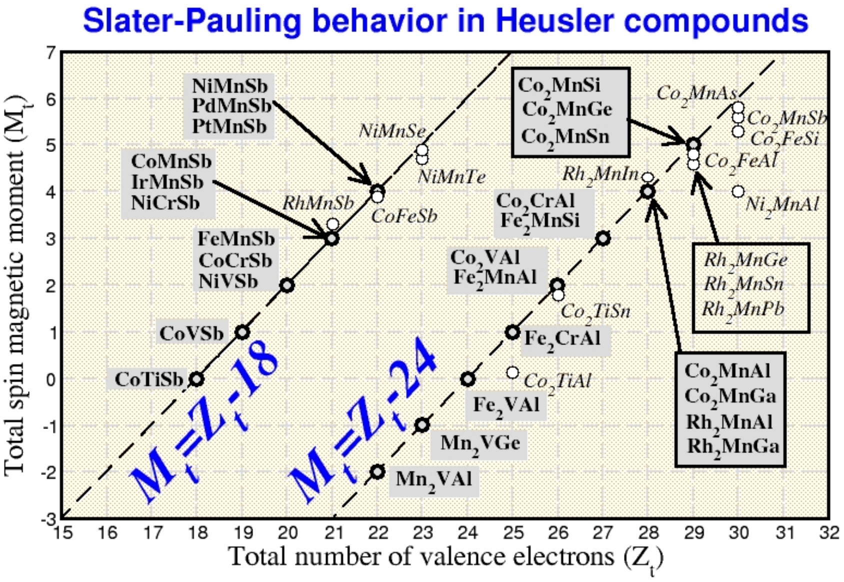
Half-metallic compounds – a new Class of Ferromagnets

One normally classifies crystalline materials as either metallic and conducting or as semiconductors/insulators with a gap at E_F, being non-conducting (at least without dopants or defects). However for ferromagnets a third class of materials can exist, being metallic for one spin-direction and having a band gap at E_F for the other spin-direction. These materials are known as half-metallic ferromagnets and they naturally exhibit a 100 % spin-polarisation at E_F and are therefore useful materials for spintronics. The existence of such hybrids between metals and semiconductors was first pointed out by R. A. De Groot and coworkers, who found by ab-initio calculations, that the Heusler alloy NiMnSb was half-metallic, having a band gap in the majority band (De Groot et al., 1983), which was confirmed experimentally for bulk crystals in middle 90's both with photoemission and positron annihilation experiments .

Today we know, that a large number of materials are half-metallic. There are first some so-called semi-(also known as half-)Heusler compounds like NiMnSb or CoMnSb, which crystallize in the cubic $C1_b$ structure, and some so-called full-Heusler compounds like Co_2MnAl, Co_2MnGe etc., crystallizing in the $L1_2$ structure which show this behaviour. Moreover half-metallicity is also exhibited by some zinc-blende and wurzite transition metal compounds (like CrAs), some double perovskites (Sr_2FeReO_6), some manganites or oxides (CrO_2) and some dilute magnetic semiconductors (GaMnAs etc.). In most of these cases both theory and experiments have confirmed the half-metallic character.



In principle, half-metallicity with a 100 % spin-polarisation at E_F cannot exist, since due to spin-orbit interaction both spin bands are coupled, so that due to spin-orbit induced hybridisation the gap of the minority states should be partially filled up by majority states, leading to a reduced spin-polarisation. However for most systems this effect is very small, so that in most cases a 99 % spin-polarisation is predicted for T = 0 and has been confirmed experimentally.

Typical for half-metallic compounds is that the magnetic moment M per unit cell (in units of Bohr magnetrons) is an integer. This follows directly from the fact, that the total number of valence electrons Z per unit cell is an integer and that moreover the number of electrons in the fully occupied minority valence band is an integer, too, being e.g. 9 for the semi-Heusler compounds and 12 for the full-Heusler compounds. Thus one finds a simple "Slater-Pauling" behaviour, leading to M = Z – 18 for semi-Heusler and M = Z - 24 for full-Heusler alloys

(Galanakis et al., 2002). These simple Slater-Pauling rules made it very easy to search for new half-metallic Heusler alloys. The alloys written with italic fonds have nearly integer moments, since the Fermi level does not lie in the gap, but close to the edges of the valence or conduction band.

The family of Heusler compounds form with more than 1000 members the largest class of half-metallic systems. Thus recent research focus both on studying the properties of well-known Heuslers as well as on designing of Heusler compounds with on demand magnetic properties. The half-metallic property has been predicted to exist also among the so-called inverse Heusler compounds like Cr_2CoGa (Skaftouros et al., 2013), and the LiPdMgSn-type Heuslers like CoFeCrSi (Ozdogan et al., 2013). Several such compounds have been already experimentally grown and their half-metallicity has been confirmed (Graf et al., 2009). In all these compounds several variants of the Slater-Pauling rule are obeyed as for the semi- and full-Heusler alloys discussed above.

For realistic applications in industry half-metallicity should be combined with other rare electronic and magnetic properties in order to maximize the efficiency of the devices (see review of Bai et al., 2012). A special case are half-metallic antiferro-magnets where the total magnetization is zero although the constituent atoms are magnetic leading to vanishing external stray fields. One can find the coexistence of antiferromagnetism and half-metallicity either among the usual Heusler compounds, e.g. the $Cr_{2+x}Se$ family (Galanakis et al., 2012), or in artificial heterostructures where various spacers of Heusler compounds are combined. Another special class of materials among the half-metallic Heusler compounds are the ones presenting an energy gap in both spin directions. If one of the two energy gaps is of vanishing width as for Mn_2CoAl, these materials are known as spin-gapless semiconductors (Skaftouros et al., 2013), otherwise they are known as ferromagnetic or antiferromagnetic semiconductors; typical examples are CoVTiAl and CrVTiAl respectively (Ozdogan et al., 2013). These materials allow to add the spin degree of freedom to the manipulation of the two kind of charges (electrons and holes) in devices leading to logic gates with enhanced capabilities.

There is still a long way till one can accurately control the magnetic, electronic and structural properties of half-metallic Heusler compounds. The research interest on these alloys intensifies as ab-initio calculations highlight new functionalities and enable the "a-la-carte" design of Heusler-based heterostructures suitable for advanced devices.

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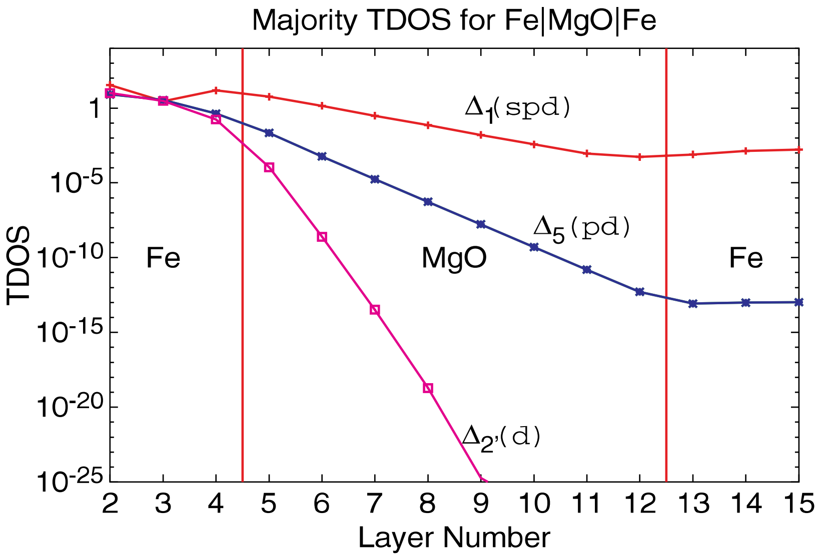
Written by Peter H. Dederichs and Iosif Galanakis

Tunnel Magnetoresistance and the MgO Barrier

The Giant Magnetoresistance (GMR) was discovered independently in 1988 by A. Fert and P. Gruenberg (Nobel Prize 2007). It has lead to a revolution in magnetic memory storage, since it allowed increasing the storage density by a huge factor. While the GMR effect applies to systems, where two ferromagnetic layers are separated by a non-magnetic metallic layer (e.g. Fe/Cr/Fe), the so-called Tunnel Magnetoresistance (TMR) refers to an insulating “spacer” layer acting as a spin-dependent barrier to electron transmission. First experiments by T. Miyazaki (1993, 1995) and J.S. Moodera (1995) used an amorphous Al_2O_3 barrier; but the spin polarization of about 20-70% achieved for these systems was not much larger than the one obtained by the GMR effect for metallic spacers (about 5-20%). Here and in the following the spin-polarization is defined by the magneto-resistance ratio $(R_{ap}-R_p)/R_p$ where R_{ap} is the electrical resistance for the antiparallel alignment of the magnetic layers and R_p the resistance for the parallel state.

However, in 2001 W.H. Butler and coworkers (1) and J. Mathon and A. Umerski (2) could show independently by ab-initio calculations that the epitaxial Fe/MgO/Fe(001) system should show for thick MgO layers an infinitely high magnetoresistance ratio of the transmitted current, being orders of magnitude larger than the polarization achieved by the Al_2O_3 barrier and by metallic spacers. The reason for the high spin-polarization had already been discussed by Ph. Mavropoulos et al. (3). In a large range of insulator barriers (incl. MgO) the states with the slowest decrease in the insulator are states with normal incidence of the electron and the full symmetry Δ_1 with respect to the vertical axis. For Fe only majority electrons have states of Δ_1 symmetry at the Fermi energy.



In order to demonstrate the symmetry effect for the tunnel magneto resistance, the above figure shows the majority tunnel density of states (TDOS) for the Fe/MgO/Fe(001) junction for perpendicular incidence and for ferromagnetic alignment of the Fe layers. One sees that states with Δ_1 symmetry, having s, p_z and d_{z^2} admixtures, are for a MgO thickness of 8 layers only weakly attenuated by the barrier, while states with Δ_5 and other symmetries are strongly reduced by a factor 10^{-10}. Thus only the majority Δ_1 states can penetrate the barrier.

Several years later, in 2004 and inspired by the theoretical work, Yuasa et al. (4) and Parkin et al. (5) could achieve for the Fe/MgO/Fe(001) system a relative resistance change(TMR value) of 200%. Since then TMR values of up to 600 % at room temperature have been obtained. In previous experiments the Fe/MgO/Fe films always had an FeO interface layer which prevented the high spin-polarization. For practical applications CoFeB/MgO/CoFeB junctions have important advantages, while showing similar high TMR values (S.Yuasa et al., APL 2005).

This progress has had a strong impact on technology: Since the years 2006/2007 all read-out sensors of modern magnetic hard disk drives (HDD) are based on the CoFeB/MgO/CoFeB system, which completely replaced the GMR sensors and allowed, due to the much larger sensitivity, a considerable further increase of the storage density. The impact can be characterized by two numbers: In 2012 the world market for hard disk drives amounted to 37 billion dollars, to which the read-out heads alone contributed about 7-8 billion dollars. About 98% of the digital information in the world is stored in hard disk drives (mainly in data centers).

At present there are strong indications that in the future the “Giant Tunneling Magnetoresistance” of the MgO barrier will have another large impact on technology. Magnetic Random Access Memories (MRAM) using the MgO tunnel barrier are likely to replace in the future the presently used Dynamic RAM (DRAM) and in the longer run also the Static RAM (SRAM) of our computers. Basically two advances have lead to this progress: Firstly the CoFeB layers have in addition to the large TMR value also a strong uniaxial anisotropy, thus fixing the magnetization perpendicular to the layer, leading to a larger stability and allowing an important reduction of the memory cell. Secondly the switching of the magnetization of the “free layer”, previously achieved by the magnetic field of an external current line, is now achieved by the Spin-Transfer-Torque method (STT-MRAM), i.e. by a spin polarized current incident on the junction with a magnetization oblique to the magnetization of the free layer. When penetrating this layer the spin polarization of the current relaxes to the magnetization direction of the free layer, in this way transferring a torque on the free-layer- magnetization, which in the end switches the magnetization due to the transferred torque. This switching method was proposed independently by J. Slonczewski (6) and L. Berger (7). It allows a very fast switching with a very small current, considerably reducing the power consumption of the MRAM as compared to the DRAM.

It is fair to say that all these activities were initiated by ab-initio calculations.

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Written by Peter H. Dederichs

Crystal structure prediction and computational materials discovery – solving the “intractable” problems

> *One of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition. Who, for example, would guess that graphite, not diamond, is the thermodynamically stable allotrope of carbon at ordinary temperature and pressure? Solids such as crystalline water (ice) are still thought to lie beyond mortals’ ken.*
>
> John Maddox, “Crystals from first principles”, Nature 335, 201 (1988).

For decades, the problem of crystal structure prediction was considered to be intractable, largely due to its unsurmountable combinatorial complexity – there are an astronomic number of distinct ways to place atoms in space, and finding the most stable one by sampling all possibilities is impractical. This problem is in the heart of computational materials discovery: only by being able to predict the crystal structure can one approach the problem of predicting materials with needed properties. In 2004 our group has started developing an evolutionary algorithm for crystal structure prediction, which has resulted in a powerful algorithm USPEX for crystal structure prediction. USPEX merges our evolutionary algorithm for global exploration of the energy landscape with ab initio total energy calculations. This approach can work with any method for computing total energies, but for many systems density-functional calculations using standard approximations (GGA, LDA) are sufficiently reliable and efficient. This algorithm has evolved with time and is at the core of our freely distributed USPEX code, which we started distributing in late 2010 and which is now used by more than 1400 researchers worldwide. Major discoveries made with this method include a partially ionic superhard form of boron (Fig. 1) and a transparent phase of sodium, and both of these predictions were confirmed by experiments. Furthermore, a new allotrope of carbon (M-carbon) was predicted and later established both by experiment and theory.

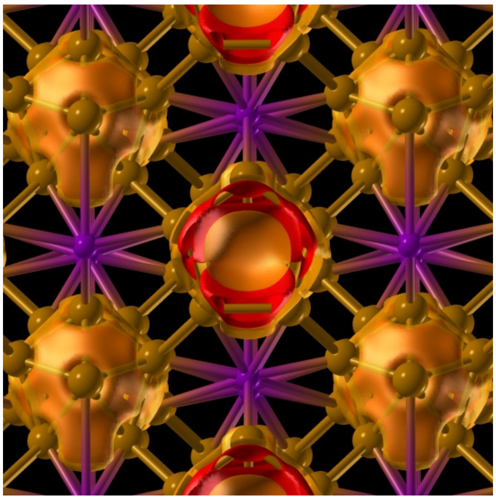

Fig. 1. Crystal structure and distribution of lowest-energy valence band electrons in the newly discovered structure of γ-B_{28} allotrope of boron.

Building on that development, it is now possible to predict structures containing up to a few hundred atoms in the unit cell, for bulk crystals, crystalline surfaces, polymers, and nanoparticles. It is also possible now to predict simultaneously the chemical composition, and crystal structures of all stable compounds in a given variable-composition chemical system. It is also possible to predict the chemical composition, and crystal structure of a material with desired target properties. It has been shown, for example, that diamond is the hardest possible phase of carbon. Even more surprisingly, for Na-Cl and Mg-O systems, a number of exotic compounds (such as $NaCl_3$ and Na_3Cl, or Mg_3O_2) were predicted to become thermodynamically stable at high pressure, and this prediction has already been verified experimentally for Na-Cl phases. This challenges traditional chemical models and rules and marks the beginning of a new chapter in chemistry.

USPEX has developed from implementation of a single algorithm (2004-2010) for predicting stable structures of bulk crystals to a multi-method general-purpose platform (2011-) enabling prediction of stable stoichiometries, studies of low-dimensional and molecular systems, and even phase transition mechanisms. One new algorithm, particularly suitable for not only prediction of thermodynamically stable structures, but also for harvesting numerous low-energy metastable structures and rough prediction of phase transformation mechanisms, is evolutionary metadynamics – a marriage between Martonak-Laio-Parrinello's MD metadynamics and evolutionary algorithm USPEX. Other methods (random sampling, particle swarm optimization) are available in USPEX as well, but compared to the evolutionary approach and evolutionary metadynamics, their efficiency is demonstrably much lower in all existing implementations – however, some hope remains and we are exploring the possibilities of improving this.

The success of crystal structure prediction has sparked numerous efforts across the field. With these developments, the dream of computational materials discovery has become closer than ever.

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Written by Artem R. Oganov

Computational Mineral Physics

The Earth's radius is ~6380 km. We can sample it directly, by drilling, only to about 15 km depth. There are some samples from the Earth's mantle, such as inclusions in "ultra-deep" diamonds, but the data derived from these rare samples provides an insufficiently broad data basis. The lack of data is even more apparent for the other planets in our solar system, and so essentially all of our knowledge about the deep Earth and the interior of planets is based on the interpretation of seismic signals, gravitational measurements and spectroscopic observations.

In order to interpret these data and establish reliable models of the Earth and other planets, we need to understand phase relations and structure-property relations of minerals and planetary materials at extreme (pressure, temperature)-conditions. While enormous progress has been made in the last few decades in generating extreme (pressure, temperature)-conditions in laser heated diamond anvil cells, it is still extremely challenging to measure properties at Mbar pressures and a few thousand Kelvin. Hence, parameter-free atomistic model calculations offer a unique approach to provide much needed data and to allow us to understand the structures of high pressure phases, their properties and the relevant processes. Therefore, DFT-based models have been extensively used in the geoscience community for the last two decades.

Highlights of DFT-based atomistic model calculations include studies of the melting of iron at Earth's core conditions and predictions of properties in the interior of gas planets (see review by Gillan et al., 2006). Another group of important papers were concerned with structures and properties of lower mantle minerals, such as the "post-perovskite" phase (Gillan et al., 2006).

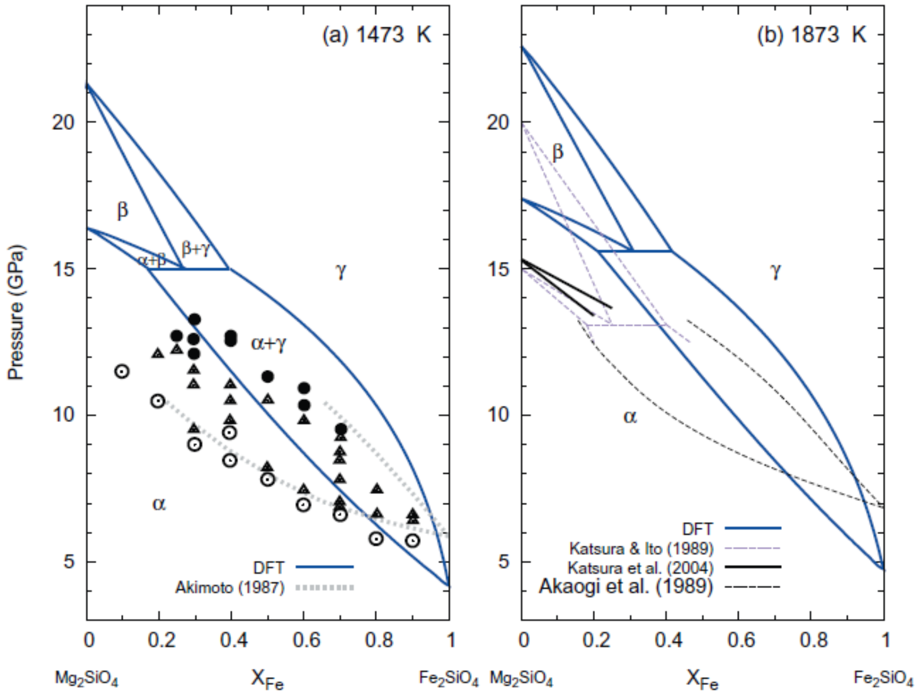

Fig. 1 (from Yu et al., 2013) Binary phase loops of α-β-γ(Mg,Fe)$_2$SiO$_4$ from DFT + U_{sc} calculations (solid blue lines) compared to experiments, at (a) 1473 K and (b) 1873 K.

The introduction of the quasi-harmonic approximation, QHA, improves the models so that realistic values of the elasticity of minerals at geophysically relevant (temperature, pressure)-conditions can be obtained (see review by Wentzcovitch et al., 2010). In order to extend these calculations to geophysically relevant compositions, where 10 – 20% iron is present in the silicates and oxides, DFT+U calculations are now employed (Hsu et al., 2010). This is of fundamental importance as it is a prerequisite for an understanding of pressure-induced spin-transitions in mantle minerals (Wu et al., 2013). The combination of these approaches has recently allowed us to compute the complete phase diagram of the Mg_2SiO_4- Fe_2SiO_4 solid solution (Fig. 1), where DFT + self-consistent U calculations within the QHA and the virtual crystal approximation yielded the correct phase relations (Yu et al., 2013), which earlier approaches failed to achieve.

A recently terminated NASA mission, in which the Kepler space observatory has identified more than 100 exoplanets and several thousand candidate planets, has highlighted the need to better understand the behavior of phases such as water and ammonia, which are thought to be major components of the giant planets, at extreme pressure and temperature conditions. An early highlight in this area were ab initio molecular dynamic simulations of water and ammonia at pressures to 300 GPa and temperatures to 7000 K, used to study the superionic and metallic states of these phases (Cavazzoni et al., 1999).

In summary, DFT-based atomistic model calculations are a unique tool to understand planetary interiors and can be used to address questions which are currently out of reach of experimental endeavors.

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Written by Björn Winkler

Getting Real!

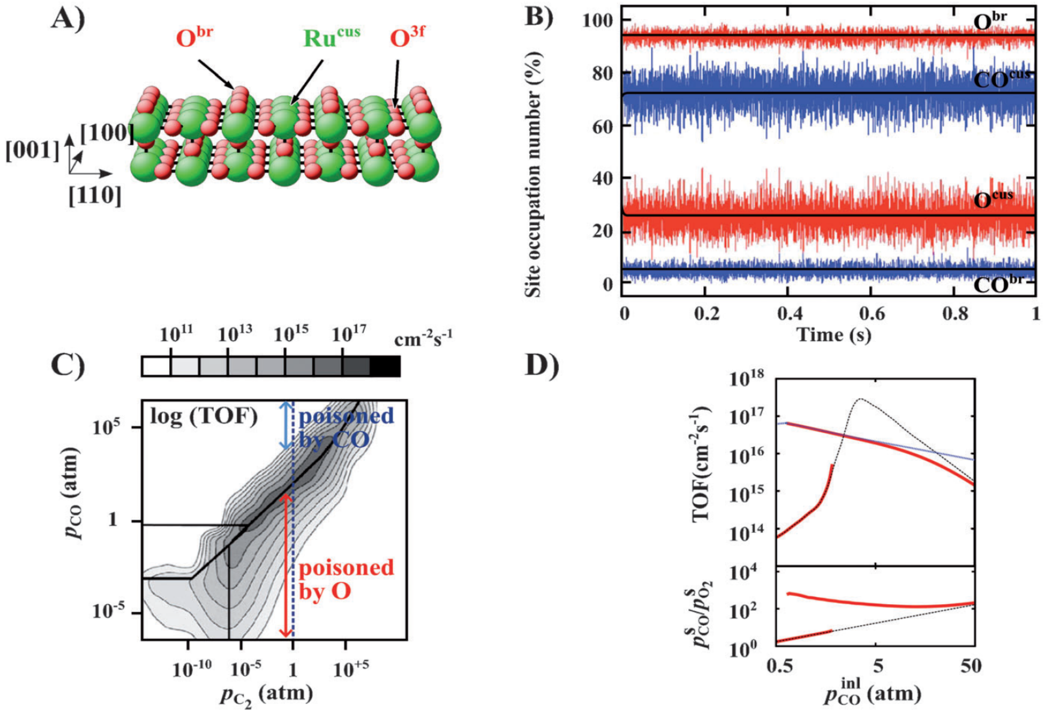
Thermodynamics and Statistical Mechanics from First Principles

Starting in the 1980s with theoretical work on defects in bulk semiconductors and at interfaces, density-functional theory total-energy calculations were systematically linked to thermodynamic reservoirs.[Ref 1 and references therein] In this way it became possible to calculate the Gibbs free energy for doped semiconductors (changing the numbers of electrons or holes) and the contact of materials with a gas- or liquid-phase environment (changing the atomic composition). In both cases, thermodynamic reservoirs enter the theory via their chemical potentials. For atoms, these chemical potentials sensitively depend on temperature and partial pressures. By now, this concept is known as "*ab initio* (atomistic) thermodynamics".[1] It became instrumental for calculating the concentration of native defects and impurities in solids and the geometric structure and composition of interfaces and surfaces (reconstructions and relaxations) under realistic (*p, T*) conditions. It covers situations from ultra-high vacuum to ambient and higher pressures and elevated temperatures.[1]

A*b initio* (atomistic) thermodynamics [1] has evolved into a standard practice in application areas as important as defects in materials doping, materials growth, corrosion or sensing. Important ramifications have furthermore established its use in heterogeneous catalysis [2] and electrocatalysis [3]. They introduce the concept of "constrained" equilibria to account for the kinetic hindrance of certain processes.[1,2]

In numerous applications and for a wide range of different materials the approach has served to predict novel surface terminations in the technologically relevant environment. This comprises the formation of new surface phases like ultrathin oxide films under oxidizing conditions, or alloy segregation profiles that are sensitively affected by reactive gas-phase species. Next to the work on low-index single crystal surfaces, *ab initio* atomistic thermodynamics has been employed for the structure determination of solid-solid interfaces or nanoscale atomic clusters, as well as to assess the equilibrium shapes of nanoparticles or the stability against reconstruction e.g. through faceting. Thanks to its efficiency in practical calculations, its use is not restricted to expert *ab initio* groups, but extends increasingly to in- and outside academia. Recent advances in the fully *ab initio* description of anharmonic and magnetic entropy contributions together with multiscale approaches allowed to successfully describe the thermodynamics and the atomistic deformation mechanisms in next-generation steels [4].

Fig. 1: A) Surface structure of RuO_2 (110) under UHV conditions as predicted by DFT calculations and observed experimentally. The bridge sites (occupied by O^{br}), the naked Ru^{cus} atoms (cus =coordinatively unsaturated site), and the second layer threefold (3f) coordinated O^{3f} atoms are labeled. B) Time evolution of the occupation of the two prominent adsorption sites, bridge and cus, by O atoms and CO molecules. The assumed temperature and pressure conditions (T =600 K, p_{CO} =7 atm, p_{O2} =1 atm) correspond to the optimum catalytic performance. Under these conditions a kinetic steady-state surface population is built up in which O and CO compete for both types of sites at the surface. The fluctuations in the site occupations within the (20x20) simulation cell are significant. Note the time range for the "induction period" until the steady-state populations are reached when starting from a fully oxygen-covered surface. C) Map of calculated turn over frequencies (TOFs) at T=600 K. The plot is based on 400 kMC simulations for different (p_{CO}, p_{O2}) conditions. D) Comparison of intrinsic TOFs (blue dotted line, see text) with observable TOFs (red solid line) for the CO oxidation at RuO_2(110) in a stagnation flow reactor. At the high TOFs reached at the nominal inlet temperature of 600 K, the observable TOF is for most pressures very close to the upper limit set by mass transfer through the boundary layer of products above the surface (blue line). This limit is a reactor property, independent of the employed catalyst. For a movie see http://www.youtube.com/watch?v=PD3d1GLLj4o .[6,7]



Since the late 1990s the above method is being complemented by what is called the "*ab initio* kinetic Monte Carlo" approach [5], enabling the correct description of the kinetic processes that govern diverse technologically important processes and/or the function of materials.[1] For short time scales *ab initio* molecular dynamics helps to identify the relevant processes, but its time span is limited to about one nano second. The *ab initio* kinetic Monte Carlo approach then reaches the realistic range (seconds, minutes, and longer). This enabled the first-principles description and understanding of crystal growth [5] and heterogeneous catalysis [6,7] (s. Fig. 1).

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Written by Karsten Reuter, Jörg Neugebauer, and Matthias Scheffler

Theoretical Spectroscopy:
How to unravel chemical and physical properties of materials

Every observation is based on the interaction of materials with light, electron beams, or other sources, creating excitations. Our understanding of the interaction between radiation (such as visible or ultraviolet light, X-rays, and electron beams) and matter, coupled with our capability to analyze and predict the reaction of materials as a consequence of the electronic response, conditions our ability to design new materials, add new functionalities, improve devices, or simply understand our environment. For example, with the help of new light sources, scientists can explore the nature of chemical bonds in a new compound, investigate the adsorption of molecules on surfaces, probe the arrangement of atoms in a biological macro-molecule, provide images of tissues, or etch nanometer-scale patterns for industrial applications. In short, electronic excitations are at the origin of a wide range of phenomena, processes and problems such as the color of materials, photosynthesis, or radiation defects.

Today, calculations from first principles are able to describe, analyze and predict a wealth of problems in physics, chemistry, biology or technological applications. A large majority of questions that have been successfully treated involve the electronic ground state: lattice parameters of crystals, the geometry of molecules, surface reconstructions, phonon frequencies, mechanical properties, and much more, are determined by the equilibrium distribution of electrons. Density Functional Theory (DFT), has played an essential role in this success story. As has been outlined above, a huge number of interesting problems demand for the description of electronic excitations. A strong effort has hence been made in the last decades to boost the possibilities of ab initio calculations of electronic excited states.

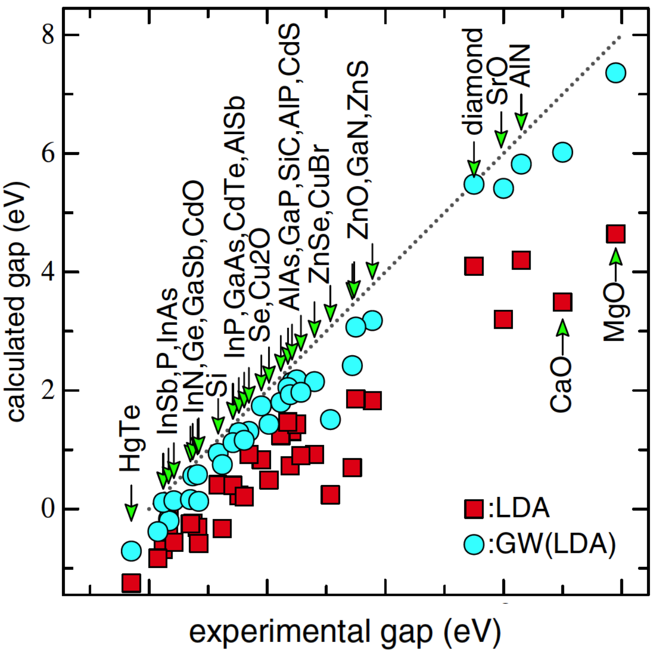

Fig. 1: Comparison of the experimental and theoretical fundamental band gaps of sp compounds from LDA (squares) and $G_{LDA}W_{LDA}$ *(circles) calculations.*
(M. van Schilfgaarde, T. Kotani, and S. Faleev, Phys. Rev. Lett. 96, 226402 (2006))

Excited states calculations have hence clearly entered the range of questions of challenging fundamental or technological interest. This is noteworthy especially considering the fact that only 25 years ago the ab initio determination of the bandgap of a simple semiconductor with 2 atoms per unit cell constituted a spectacular success [1] . Much of the progress has been possible thanks to the adoption by the community of suitable theoretical approaches (similar to the adoption of DFT for ground state problems): When excited states are involved, accurate description can be obtained by combining DFT ground state calculations with many-body perturbation theory (MBPT) or, alternatively, time-dependent density-functional theory (TDDFT) [2], both of which have witnessed impressive advances in recent years [3]. The two approaches are complementary and follow different philosophies, but both open, in principle, a pathway to the exact excitation spectra.

In MBPT, excitations are described by defining the propagation of effective particles or groups of particles, and holes. One situates in this context the prominent GW approximation, and approach introduced by Lars Hedin [4] that provides a very good description of the spectral properties of wide-range of electronic systems. An example for the success of this method for the band gaps of sp compounds is given in the above figure. Moreover, the calculation of response functions (response to light, X-rays, electrons etc.) requires the description of electron-hole pairs, which is obtained via the solution of a two-particle Bethe-Salpeter equation (BSE). Since the first fully ab-initio Bethe-Salpeter calculation performed more than 15 years ago, the method has been by now also applied to complex systems, like transition metal oxides, semiconductor surfaces, biomolecules, nanotubes, or liquids [3]. Dynamical mean field approaches have been shown to be very efficient in describing strongly correlated systems when combined with standard density functional schemes (e.g LDA+DMFT), but in the last years there has been an important progress in combining DMFT with GW. [5]

TDDFT, on the other hand, deals directly with density-fluctuations resulting from external perturbations. It is therefore suitable for the description of neutral excitations mimicking in the computer the process of excitation in experiments. Excellent results have been obtained for optical, energy loss and time-resolved spectroscopies (at the femto- and atto-second scales) for finite systems, including proteins and nanostructures. [6]

These advances have led to predictive results of unprecedented accuracy and new insights on the spectroscopic properties of numerous systems. They have transformed computational materials physics and spawned worldwide activities in the lasts years. An example is the recent establishment of the European Theoretical Spectroscopy Facility (ETSF) [7] that now provides services for the experimental spectroscopy community using advanced methods for quantum-mechanical spectroscopy calculations. The ETSF (theoretical synchrotron) is a unique idea that sets a new philosophy in the joint work between experiment, which pushes forefront developments in theory and numerical simulations.

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7. See http://www.etsf.eu

Written by Angel Rubio

Exploring the catalyst genome
– New non-precious catalysts for (photo-)electrochemical hydrogen production

The set of instruction that define the surface catalytic properties – also known as the catalyst genome – is in general incorporated in the electronic structure of the catalyst material. The problem is that the electronic structure in its entirety is too complex to be useful in charactering the material. If we can find descriptors, a few essential parameters, that determine the catalytic activity or selectivity, we are in a position to understand variations form one system to the next and to use computational methods to identify new, interesting catalysts.

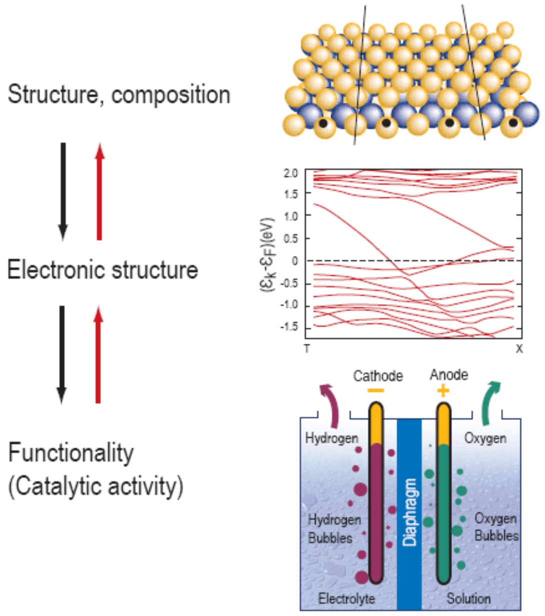

Fig. 1 *The electronic structure of a material contains the information that defines its functionality. Changing the functionality can be achieved by engineering the electronic structure through changes in structure and composition. The example shown is a MoS_2 sheet, a few atoms wide, where new electronic states at the edges cross the Fermi level and give rise to catalytic activity, for instance in electrochemical hydrogen evolution.[1] Adapted from Ref. 2 .*

One example of such an approach is the discovery that nano-structured MoS_2 is an alternative to expensive noble metals as a catalyst for electrochemical and photo-electrochemical hydrogen evolution. Figure 2 suggests that the free energy of hydrogen adsorption is a good descriptor for activity. It binds atomic hydrogen strongly enough for it to adsorb but not so strongly that it cannot desorb as molecular hydrogen. The same analysis of biological hydrogen evolution catalysts, hydrogenases[3] and nitrogenases[4] shows that the descriptor approach also applies to the active centers of enzymes[1,5] see Fig. 2. An analysis of a broad range of calculated hydrogen adsorption energies suggested that the edge of MoS_2 slabs or nanoparticles also has a favorable hydrogen adsorption energy. These structures are well-known as hydro-desulfurization catalysts used in removing sulfur-containing molecules from oils products[6,7]. Since then a large number of experimental studies has shown MoS_2 edge steps to be very active,[1,8,9,10], and most recently a paper by Jaramillo and co-workers showed activities are that within ca. an order of magnitude of the noble metals.[10]

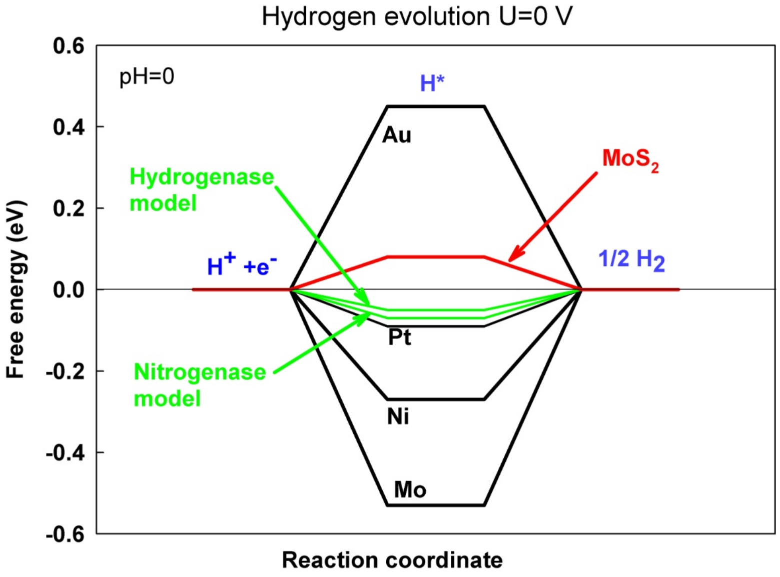

Fig. 2. *Calculated free energy diagram of hydrogen evolution at zero potential and zero pH for Au, Pt, Ni, Mo close-packed surfaces, the MoS_2 edge, and the active centers in hydrogenase and nitrogenase. The closer the binding free energy of the intermediate, adsorbed H (denoted H*) is to zero the higher the activity. Adapted from ref. 2.*

The approach illustrates that the identification of descriptors form electronic structure calculations can rationalize large amounts of experimental data and provides avenues for exploring completely new classes of catalysts.

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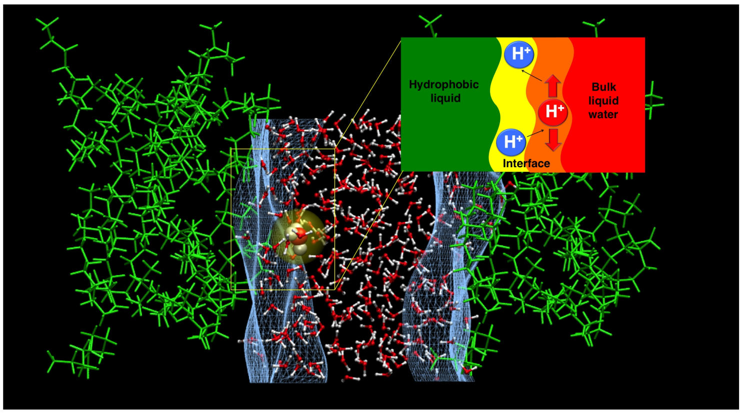
Written by J. K. Nørskov, T. Bligaard, F. Studt, and F. Abild-Pedersen

Biochemistry à la Car-Parrinello: Recent applications

1. Introduction. Car-Parrinello Molecular Dynamics (CPMD) is revealing itself as an efficient and powerful approach for biomolecular simulations [1,2]. Either embedded in explicit molecular mechanics (MM)-based framework (the so-called Quantum Mechanics/Molecular Mechanics (QM/MM, or here CPMD/MM) method) or even fully from first principles, CPMD allows to describe a variety of key electronic biological processes such as enzymatic reactions, photoinduced electronic excitations, charge transfer or the action of transition metal ion's biomolecules [1,2,3]. Here we present a couple of recent applications from us. These are meant to illustrate the power of current applications of the methods [4-6].

2. Protons race at cell membranes. Without protons' gradients at cell membranes, life as we know it would cease to exist. Hence, how protons diffuse *across and along* the membrane is an absolutely crucial biological question. Recent measurements suggest that, very intriguingly, protons can simultaneously travel across the cell's surface at about half the speed they travel through water, but they also bind to the membrane surface. Recent full CPMD calculations have succeeded in solving this riddle. A minimalistic model interface consisting of an excess proton between an apolar hydrophobic phase (*n*-decane) and an aqueous phase was used to mimic the biological pathway for lateral proton migration [4]. The calculated free energy profile revealed that protons preferentially do stick to the hydrophobic surface thus experiencing reduced mobility. However, those located only one water layer away from the surface migrate very quickly and yet experience sufficient attractive forces to prevent release to the bulk water (Fig. 1a). These are the protons that allow for fast diffusion along biological membranes. Such peculiar proton attraction while retaining fast surface proton diffusion is expected to be an intrinsic property of all water/hydrophobic interfaces. These findings may have far-reaching implications beyond membrane transport, i.e. not only for our understanding of bioenergetics processes, but also for drug discovery.

a)



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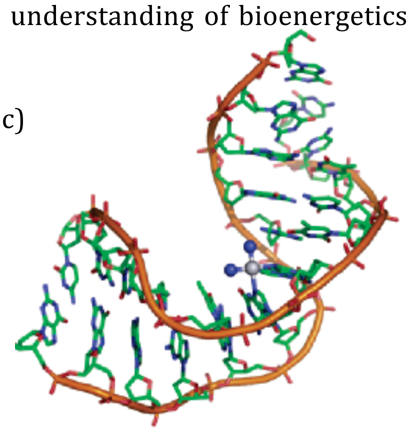

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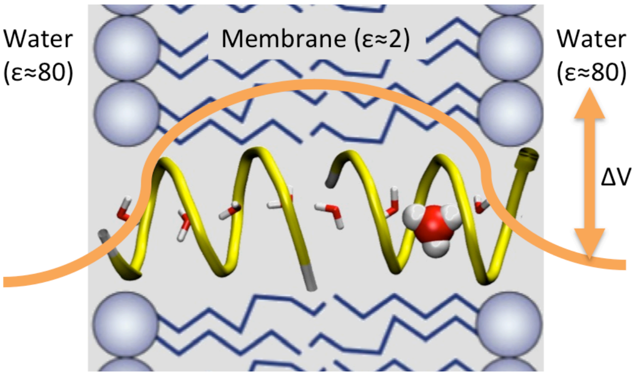

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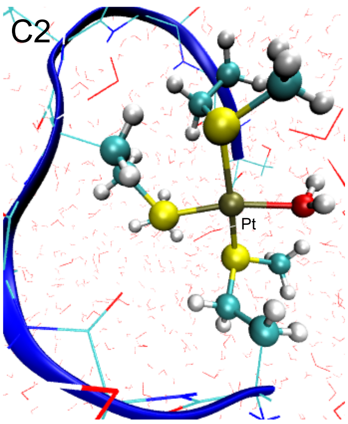

Figure 1. (a) Excess proton (yellow sphere) on an interface of water and a hydrophobic surface (dotted blue grid) formed by n-decane (green sticks). Inset: CPMD calculations suggest a mechanism of fast proton migration in the second water layer (orange), whereas protons in the first layer (yellow) stick to the surface [4]. (b) The rise of the membrane dipole potential ΔV (orange) at the gramicidin A channel (yellow) entrance contributes to the free energy barrier [5]. (c) Platinated DNA [7, 8] and protein [6] adducts formed by the drug cisplatin (in ball-and-sticks), predicted by CPMD/MM calculations.

If one wants to study really efficient proton transport across membrane, the system of choice is arguably the ion channel gramicidin A (gA). In spite of the low relevance of tunneling effects, gA permeates H^+ ions at the stunning rate of 2×10^9 H^+ s^{-1}, faster than any other membrane channel. Experiments suggest that the potential generated by a dipole formed by the mismatch of the water and membrane dielectric (see Fig. 1b) plays a role for the proton conduction's free energy barrier: for instance, application of a transmembrane voltage opposing to this dipole increases the rate of proton conduction. Yet, it has been recognized that dipole potentials cannot be described properly by current widely used biomolecular force fields, which lack electron polarization. This issue has now been addressed by CPMD simulations. The latter have been carried out on gA embedded in a solvated 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC) model membrane environment (about 2,000 atoms) [5]. The calculated membrane dipole potential ΔV rises at the channel mouth by ~0.4 V (Fig. 1b). A similar value has been measured for gA embedded in a DMPC monolayer. The calculated free energy barrier is located at the channel entrance, consistently with experiments comparing gA proton conduction in different bilayers. Hence, the dipole potential generates an electrostatic potential opposing to permeation at the mouth of the channel. This feature impacts most likely on the permeation of ions also in channels other than gA.

3. Action of anti-cancer drugs. Drugs exert their beneficial effect by reaching specific target receptors. Unfortunately, before doing so, they are likely to bind to a myriad of proteins present in the cell, other than the target. This may greatly reduce their efficacy. The drug cisplatin, widely used in anti-cancer therapy, suffers severely from this problem. This drug kills cancerous cells by binding to their DNA – indeed CPMD/MM have elucidated the structural determinants of cisplatin/DNA interactions [7, 8] – yet only a small percentage of it reaches the DNA target. The rest is either excreted, or, very unfortunately, binds to proteins with severe toxic side effects such as nephrotoxicity, neurotoxicity, or nausea. Designing cisplatin derivatives with improved affinity to DNA relative to undesired cisplatin's cellular partners requires a molecular understanding of how cisplatin enters the cell. Experimentally, it is known that cisplatin uses copper transport proteins such as the high-affinity copper transporter 1 (Ctr1). It binds to methionine-rich motifs located at Ctr1's extracellular domain. CPMD/MM simulations predict the structural determinants of a realistic model of the platinated protein (Fig. 1c) [6]. The cisplatin binding region is taken as QM part, whereas the rest is treated with the AMBER Force field. The simulations allow for an accurate treatment of the transition metal ion's coordination geometry, which is dictated by the electronic structure. Comparison with spectroscopic data (CD, EXAFS, and NMR) establishes the accuracy of the prediction [6]. The CPMD/MM simulations provide the basis for applying the force-matching technique to derive force field parameters for the platinated moiety. The latter allow for long time scale classical MD simulations to study the large-scale motion of the system. Encouraged by these promising results, the challenge is now to characterize the entire pathway of cisplatin in the cell at the molecular level.

4. Conclusions. CPMD is an excellent weapon in the arsenal of current tools for biological simulations. The use of supercomputer facilities at the Supercomputing Center in Jülich, made possible by the PRACE EU initiative for HPC, enables today to perform CPMD studies for systems in laboratory realizable conditions, such as those which are described in this article. We expect that with increasing progress in algorithms combined with the ever-growing power of parallel computing, CPMD will become the method of choice for a variety of biologically relevant problems.

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Written by Jens Dreyer and Paolo Carloni

Materials for solar energy harvesting and storing

Ab initio calculations of the intrinsic properties of solid-state materials and organic molecular systems have undoubtedly helped deepening the knowledge of materials traditionally used in solar cells, especially those used as absorber layers. The most remarkable example refers to inorganic photovoltaics of the CIGS family for which pioneering work successfully complemented experiment by shedding light into the crucial effects of point defects and dopants [1].

More recently, the need to find novel, less expensive, materials with suitable energy gaps for solar-cells applications spurred an enormous amount of computations using the modern tools of electronic structure calculations, from TDDFT to GW and diverse approximations for the DFT exchange-correlation functional. On one side, self-consistent GW calculations continue to assist experiment by enabling to understand e.g., the observed influence of the lack of stoichiometry on the energy gaps of the CIGS [2]; on the other hand, TDDFT combined with advanced exchange-correlation functionals [3] appears to lead the path towards the modeling of organic photovoltaics [4]. Moreover, it is worth mentioning that quantum chemical calculations of diverse levels of sophistication (see, e.g., [5]) have steadily accompanied progress in the development of dye-synthesized (Grätzel) solar cells (DSC).

The most recent and exciting discovery in solid-state solar cells exploits hybrid organic-inorganic perovskites as harvesting materials. Also in this case, useful characterization has come from – still traditional – DFT calculations [6]. However, the crucial step leading to an unprecedented increase of efficiency of DSC has come from the application of a new processing route [7]. Indeed, the choice of the processing-method is known to play a critical role for the fabrication and optimization of solar cells in general: these results emphasize the need of atomistic simulations to propose new and rationally based criteria for the tuning of processing procedures.

A remarkable example of atomistic simulations leading to patents related to device fabrication concerns solar cells based on hydrogenated amorphous silicon (a-Si:H) [8-10]. The theoretical approach consisted of a combination of large-scale classical and DFT-based molecular dynamics followed by extensive analysis of the electronic properties. The key challenges in a-Si:H technology were addressed, namely the need for increasing hole mobility and reducing the light-induced degradation (known as the Staebler-Wronski effect). This work [8] allowed for an unambiguous identification of the nature of the defect structures responsible for valence band-tails, midgap states and limitation in the hole mobility, and also unraveled the role of hydrogen. Inspired by these results, new routes for the increase of cell performance were then explored, thus providing two patents: in one [9] compressive strain is proposed as method for reducing light-induced degradation via reduction of stretched bonds; in the other [10], a specific band-stop filter is designed so as to avoid specific (detrimental) electronic excitations from valence band tails to the conduction band of the amorphous material.

Regarding the storing of solar energy, chemicals offer clear advantages because, in particular, they can store it for long time. The realization of this concept has long been hampered by the rapid degradation of available materials and/or the presence of ruthenium, a rare and very expensive element. DFT calculations, [11] have led to a patent [12] proposing a new solar fuel, which consists of carbon nanotubes functionalized with azobenzene and has volumetric energy density comparable to that of Li-ion batteries.

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