

Autopresentation

Małgorzata Wierzbowska

Scientific achievement:

***“Properties of novel materials obtained from first-principles
and contribution to the development of computational methods”***

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Scientific degrees

30th June 1994, Master of Science, Theoretical Physics,

Nicholas Copernicus University in Toruń, Poland,

subject: *Theoretical calculations of electronic structure of luminescence probes.*

supervisor - Prof. Wiesław Nowak

26th October 1994, Master of Science, Physical Basis of Microelectronics,

Nicholas Copernicus University in Toruń, Poland,

subject: *Hopping conductivity in the high frequency limit of external electric field.*

supervisor - Dr. hab. Jan Maćkowiak

7th June 2000, PhD in Theoretical Physics,

Nicholas Copernicus University in Toruń, Poland,

subject: *Ab Initio Calculations for the Adsorption of Oxygen and Potassium on the Cr₂O₃(0001) Surface.*

supervisor - Dr. hab. Jan Wasilewski

PhD fellowships and postdoctoral positions

- March 1998 – May 1998 (during PhD study)
Lehrstuhl fuer Theoretische Chemie, Ruhr-Universitaet Bochum, Germany
financed by Graduiertenkolleg "Dynamische Prozesse an Festkoerperoberflaechen – Adsorption, Reaktion, heterogene Katalyse", work with Prof. Volker Staemmler
- September 1998 – February 1999, May – June 1999, September – October 1999
Lehrstuhl fuer Theoretische Chemie, Ruhr-Universitaet Bochum, Germany
(during PhD study) Roman Herzog Fellowship, work with Prof. Volker Staemmler
- October 2000 – September 2001, Post doctoral position within THEONET II EU program,
Theoretical Chemistry Department, Chemical Center, University of Lund, Sweden
work with Ass. Prof. Roland Lindh
- October 2001 – February 2002, Hertie Fellowship, work with Prof. E.K.U. Gross
Universitaet Wuerzburg, Theoretische Physik I, Germany
- March 2002 – July 2002, work with Prof. Stefano de Gironcoli
SISSA, Condensed Matter Sector, Trieste, Italy
August 2002 October 2002, work with Prof. E. Tosatti
ICTP, Condensed Matter Sector, Trieste, Italy
- November 2002 November 2003, work with Prof. Stefano Sanvito
Trinity College, Physics Department, Dublin, Ireland (a few weeks stay in
Donostia Theoretical Centre, Spain, work with Dr. Daniel Sanchez-Portal)
- December 2003 February 2005, work with Prof. E. Tosatti
INFM, Condensed Matter Sector, Trieste, Italy
- July 2005 – May 2007, work with Prof. Maria Peressi
Trieste University, Condensed Matter Sector, Trieste, Italy

Recently

August 2011 – June 2014, researcher at the University of Warsaw,
Department of Theoretical Physics, Chair of Condensed Matter Physics,
work in project SiCMAT (<http://sicmat.materials.pl/>)

Bibliometric data

| | | |
|------------------------------------|------|---------------------------------|
| total impact factor | 51.4 | (after PhD 43) |
| total citations | 210 | (14 to arXiv, 22 autocitations) |
| averaged citations per publication | 10.5 | |
| Hirsch index | 7 | (+ 1 arXiv) |

Citations include only publications in Web of Science, not computer codes.
By autocitations, I understand the citations of all co-authors.

Publications before PhD

- [1] W. Nowak and **M. Wierzbowska**
“*A theoretical study of geometry and transition moment directions of flexible fluorescent probes– acetoxo derivatives of phenylanthracene*”
Journal of Molecular Structure (Theochem), vol. 368, p. 223-234 (1996)
Impact factor 1.453, cited 7 times (0 autocitation)
- [2] J. Szubiakowski, A. Balter, W. Nowak, A. Kowalczyk, K. Wiśniewski and **M. Wierzbowska**
“*Anisotropic reorientation of perylene and 3,9-dibromoperylene in glycerol: fluorescence anisotropy decay and quantum-mechanical study*”
Chemical Physics, vol. 208, p. 283-296 (1996)
Impact factor 2.059, cited 15 times (0 autocitation)
- [3] J. Wasilewski, S. Zelek and **M. Wierzbowska**
“*Modifications of Virtual Orbitals in the Limited CI Calculations for Electron-Rich Molecules*”
International Journal of Quantum Chemistry, vol. 60, p. 1027-1036 (1996)
Impact factor 1.306, cited 4 times (0 autocitation)
- [4] W. Zhao, G. Kerner, M. Asscher, X.M. Wilde, K. Al-Shamery, H.-J. Freund, V. Staemmler, and **M. Wierzbowska**
“*Interaction and diffusion of potassium on Cr₂O₃(0001)/Cr(110)*”
Physical Review B, vol. 62, p. 7527-7534 (2000)
Impact factor 3.603, cited 15 times (4 autocitations)

Publications after PhD

- [1] J. W. Krogh and **M. Wierzbowska**
“*The condensation energy of the homogeneous superconducting gas*”
Computer Physics Communications, vol. 150, p. 53-63 (2003)
Impact factor 3.212, cited 1 time (1 autocitation)
- [2] D. Ajitha, **M. Wierzbowska**, R. Lindh and P. A. Malmqvist
“*Spin-orbit ab initio study of alkyl halide dissociation via electronic curve crossing*”
Journal of Chemical Physics, vol. 121, p. 5761-5766 (2004)
Impact factor 3.176, cited 35 times (0 autocitation)
- [3] **M. Wierzbowska**, M. Lueders and E. Tosatti
“*Multiplet structures of charged fullerenes*”
Journal of Physics B: Atomic, Molecular and Optical Physics, vol. 37, p. 2685-2698 (2004)
Impact factor 2.031, cited 10 times (1 autocitation)
- [4] **M. Wierzbowska**, D. Sanchez-Portal and S. Sanvito
“*Different origins of the ferromagnetic order in (Ga,Mn)As and (Ga,Mn)N*”
Physical Review B, vol. 70, 235209-1-11 (2004)
Impact factor 3.603, cited 79 times (10 autocitations)
- [5] **M. Wierzbowska**, S. de Gironcoli, J. W. Krogh and P. Giannozzi
“*Condensation energy and T_c within the density functional theory for superconductors*”
AIP Conference Proceedings, vol. 789, p. 289-299 (2005)
proceedings from “IX Training Course in the Physics of Correlated Electron Systems and High- T_c Superconductors”, Vietri sul Mare (Salerno), Italy, 4-15 October, 2004
cited 0 times
- [6] **M. Wierzbowska** and J. W. Krogh
“*Condensation energy of the homogeneous electron gas from density-functional theory for superconductors*”
Physical Review B, vol. 71, 014509-1-9 (2005)
Impact factor 3.603, cited 1 times (1 autocitation)
- [7] **M. Wierzbowska**
“*Effect of spin fluctuations on T_c from density-functional theory for superconductors*”
The European Physical Journal B, vol. 48, p. 207-217 (2005)
Impact factor 1.282, cited 1 times (0 autocitation)
- [8] **M. Wierzbowska**, A. Delin and E. Tosatti
“*Effect of electron correlations in Pd, Ni, and Co monowires*”
Physical Review B, vol. 72, 035439-1-10 (2005)
Impact factor 3.603, cited 25 times (0 autocitation)
- [9] **M. Wierzbowska**, S. de Gironcoli and P. Giannozzi
“*Origins of low- and high-pressure discontinuities of T_c in niobium*”
ARXIV0504077, p. 1-15 (2006)
cited 14 times (1 autocitation)

- [10] **M. Wierzbowska** and A. Fleszar
“*Density functional theory calculations for a single Re impurity in silicon*”
Physical Review B, vol. 83, 184418-1-6 (2011)
Impact factor 3.603, cited 2 times (2 autocitations)
- [11] **M. Wierzbowska** and J. Majewski
“*Forces and atomic relaxation in density functional theory with the pseudopotential self-interaction correction*”
Physical Review B, vol. 84, 245129-1-9 (2011)
Impact factor 3.603, cited 2 times (2 autocitations)
- [12] **M. Wierzbowska**
“*Exchange interactions and Tc in rhenium-doped silicon: DFT, DFT+U and Monte Carlo calculations*”
Journal of Physics Condensed Matter, vol. 24, 126002-1-7 (2012)
Impact factor 2.355, cited 0 times
- [13] **M. Wierzbowska**
“*Poisoning of magnetism in silicon doped with Re, caused by a charge transfer from interstitials to substitutionals, by means of the self-interaction corrected density-functional approach*”
Journal of Applied Physics, vol. 112, 013919-1-6 (2012)
Impact factor 2.210, cited 0 times
- [14] **M. Wierzbowska**, A. Dominiak and K. Tokar
“*CVD formation of graphene on SiC surface in argon atmosphere*”
Physical Chemistry Chemical Physics, vol. 15, 8805-8810 (2013)
Impact factor 3.829, cited 0 times
- [15] K. Z. Milowska, M. Wońska and **M. Wierzbowska**
“*Contrasting elastic properties of heavily B- and N-doped graphene with random impurity distributions including aggregates*”
The Journal of Physical Chemistry C, vol. 117, p. 20229-20235 (2013)
Impact factor 4.814, cited 0 times
- [16] K. Z. Milowska and **M. Wierzbowska**
“*Hole sp^3 -character and delocalization in (Ga,Mn)As revised with pSIC and MLWF approaches - newly found spin-unpolarized gap states of s-type below 1% of Mn*”
Chemical Physics, vol. 430, p. 7-12 (2014)
Impact factor 2.059, cited 0 times
- [17] I.N. Demchenko, T. Tyliczszak, M. Chernyshova, K.M. Yu, J.D. Denlinger, D. Speaks, W. Walukiewicz, **M. Wierzbowska**, and K. Ławniczak-Jabłońska
“*Electronic structure of irradiated CdO thin films*”
ISSRNS 2012: Synchrotron Radiation in Natural Science Vol. 10, No. 1 - 2 (2012)
cited 0 times

Contributions to large computer codes:

K. Andersson, M. Barysz, A. Bernhardsson, M. R. A. Blomberg, Y. Carissan, D. L. Cooper, M. Cossi, T. Fleig, M. P. Fuelscher, L. Gagliardi, C. de Graaf, B. A. Hess, G. Karlstrom, R. Lindh, P.-A. Malmqvist, P. Neogrady, J. Olsen, B. O. Roos, B. Schimmelpfennig, M. Schuetz, L. Seijo, L. Serrano-Andres, P. E. M. Siegbahn, J. Stalring, T. Thorsteinsson, V. Veryazov, **M. Wierzbowska**, P.-O. Widmark. **MOLCAS Version 5.2.** Dept. of Theor. Chem., Chem. Center, University of Lund, P.O.B. 124, S-221 00 Lund, Sweden, 2001.

SIESTA package (first versions of LDA+U and pSIC methods)

Quantum ESPRESSO package (pSIC method and accurate el-ph calculation, pw2wannier)

Own codes:

CHS: Condensation energy of homogeneous gas (parallelized by J. W. Krogh)

Tc-SCDFT: Tc of superconductors from SC-DFT, including Eliashberg function and spin-fluctuations

Scientific achievement:

“Properties of novel materials obtained from first-principles and contribution to the development of computational methods”

List of publications in the basis of habilitation procedure

- [1] **M. Wierzbowska**, D. Sanchez-Portal and S. Sanvito
“Different origins of the ferromagnetic order in (Ga,Mn)As and (Ga,Mn)N”
Physical Review B, vol. 70, 235209-1-11 (2004)
- [2] K. Z. Milowska and **M. Wierzbowska**
“Hole sp^3 -character and delocalization in (Ga,Mn)As revised with pSIC and MLWF approaches - newly found spin-unpolarized gap states of s-type below 1% of Mn”
Chemical Physics, vol. 430, p.7-12 (2014)
- [3] **M. Wierzbowska** and A. Fleszar
“Density functional theory calculations for a single Re impurity in silicon”
Physical Review B, vol. 83, 184418-1-6 (2011)
- [4] **M. Wierzbowska**
“Exchange interactions and T_c in rhenium-doped silicon: DFT, DFT+U and Monte Carlo calculations”
Journal of Physics Condensed Matter, vol. 24, 126002-1-7 (2012)
- [5] **M. Wierzbowska**
“Poisoning of magnetism in silicon doped with Re, caused by a charge transfer from interstitials to substitutionals, by means of the self-interaction corrected density-functional approach”
Journal of Applied Physics, vol. 112, 013919-1-6 (2012)
- [6] **M. Wierzbowska**, A. Delin and E. Tosatti
“Effect of electron correlations in Pd, Ni, and Co monowires”
Physical Review B, vol. 72, 035439-1-10 (2005)
- [7] J. W. Krogh and **M. Wierzbowska**
“The condensation energy of the homogeneous superconducting gas”
Computer Physics Communications, vol. 150, p. 53-63 (2003)
- [8] **M. Wierzbowska** and J. W. Krogh
“Condensation energy of the homogeneous electron gas from density-functional theory for superconductors”
Physical Review B, vol. 71, 014509-1-9 (2005)
- [9] **M. Wierzbowska**
“Effect of spin fluctuations on T_c from density-functional theory for superconductors”
The European Physical Journal B, vol. 48, p. 207-217 (2005)

- [10] **M. Wierzbowska**, M. Lueders and E. Tosatti
“*Multiplet structures of charged fullerenes*”
Journal of Physics B: Atomic, Molecular and Optical Physics, vol. 37, p. 2685-2698 (2004)
- [11] **M. Wierzbowska**, A. Dominiak and K. Tokar
“*CVD formation of graphene on SiC surface in argon atmosphere*”
Physical Chemistry Chemical Physics, vol. 15, 8805-8810 (2013)
- [12] **M. Wierzbowska** and J. Majewski
“*Forces and atomic relaxation in density functional theory with the pseudopotential self-interaction correction*”
Physical Review B, vol. 84, 245129-1-9 (2011)

Scientific achievement:***“Properties of novel materials obtained from first-principles and contribution to the development of computational methods”*****• Magnetism – dilute magnetic semiconductors and nanomagnetism**

Semiconductors doped with transition metals very often are ferro- or antiferromagnetic, however, we find very rarely reports about measured Curie temperatures exceeding the room temperature and there is no reproducibility of such experiments. The impact of dilute magnetic semiconductors in spintronics, due to the possibility of spin manipulation as a logic element, deserves for great effort in basic research. The most popular dilute magnetic semiconductor is (Ga,Mn)As with Curie temperature 110-160 K; this system serves as a prototype. In thin layers of (Ga,Mn)N, the ferromagnetism has been found in room temperature. The same as in silicon doped with rhenium. I deal with these systems using the computational methods within and beyond popular density functional theory (DFT).

Mechanisms of ferro- and antiferromagnetism in doped semiconductors are diverse – recently one may identify them theoretically on the basis of the electronic structure. When I started to deal with these systems, in 2002, the descriptions of these mechanisms based on tight-binding approximation and two Zener models: for large $sp-d$ coupling with very delocalized holes, and for strongly localized hole at d -states. In the first case, the ferromagnetism is mediated between the impurities on large distances due to the coupling between magnetic ions and the spins of free carriers which are holes. The critical temperatures are proportional to the spin splitting of the top of valence band (or bottom of the conduction band for electron mediated ferromagnetism). In the second type of dilute magnetic semiconductors, the strong interactions between transition metal ions are short range and the critical temperatures are described by the percolation model. In this case, only the high concentrations of impurities may lead to the total magnetization of samples. Usually, there is clustering of impurities in such compounds, and the magnetic domains form. The electronic structure of such system is characterized by thin impurity band localized at the Fermi level, and the top of the valence band does not spin split. On the basis of these models, Dietl and Ohno explained the mechanisms of ferromagnetism in very dilute (Ga,Mn)As and predicted the high critical temperature in (Ga,Mn)N. Under the electron doping, both types of these systems behave similarly: when holes are completely compensated and the Fermi level is within the gap between the occupied and unoccupied states, then the spin polarization of bands remains, but the antiferromagnetic couplings dominate and the so-called superexchange mechanism is valid. In 2010, all aforementioned mechanisms were presented in detail by Sato et al. in a comprehensive article in Review of Modern Physics.

At the begin, when I started to work on this field, there was very few data on material parameters obtained from first principles. Dilute magnetic semiconductors were not a preferable systems for calculations due to the necessity of using large elementary cells at low impurity concentrations. And also for the reasons of failure of the density functional theory in local density approximation (or gradient corrected too), which could not describe the localized states, which are the atomic orbitals of d and f -shells. The method underestimates the band gaps and the bond lengths in the systems. These problems of the method have large influence on obtained magnetic properties in the so-called strongly correlated materials (with strong electronic correlations on the localized orbitals); dilute magnetic semiconductors belong to this class. Most of calculations was

performed using the local density approximation (LSDA), or with gradient corrections (GGA), and applied corrections for the Coulomb interactions in the strongly correlated atomic shells using the DFT+U method; the systems were restricted to small elementary cells, which means to high concentrations. Application of a very accurate method such as GW or GW+EXX for systems with large elementary cells is still impossible. Corrections for the self-interaction within the pseudopotential formulation has been published at the time when I just started my work on DMS.

My first publication about dilute magnetic semiconductors with Stefano Sanvito and Daniel Sanchez-Portal: *“Different origins of the ferromagnetic order in (Ga,Mn)As and (Ga,Mn)N”* was prepared using the computer code SIESTA, in which only the DFT method has been implemented. First step, which I have done within that project, was implementation of the DFT+U method. In the next step, I checked this implementation for the systems whose results with this method were known and published, such as: MnO, NiO, FeO. With this code, I could then perform calculations for (Ga,Mn)As and (Ga,Mn)N: to find the electronic structure, density of states projected on the $3d$ orbitals of Mn, to analyze Mulliken population numbers. On that set of data, it was possible to differentiate investigated systems. I applied the LDA+U method with $U=4.5$ eV and $J=1$ eV, where the parameters were chosen in such a way that the $3d$ -states of Mn in the band structure took the place below the Fermi level in the position of the results of photoemission measurement. This enabled us to draw conclusions, without any doubt, that the magnetic state of (Ga,Mn)As is d^5 at Mn with a hole coupled antiferromagnetically – which sets the total magnetic moment at $4\mu_B$. In contrast, the situation in (Ga,Mn)N is closer to the configuration d^4 than $d^{3.5}$, as it was in the LSDA method. The critical temperature (Ga,Mn)As is linearly proportional to the exchange parameter N_β , which is dependent on the spin splitting of the top of the valence band – overestimated in the LSDA method. The value, which we obtained from the LSDA+U, i.e. -2.8 eV, fits better the p - d exchange Zener model than the larger value obtained from the LSDA method. The dependence of the parameter N_β on the concentration of dopants is linear only for $U=4.5$ eV. In the limit of pure GaAs crystal without impurities, the correct result of vanishing spin polarization is also obtained only for $U=4.5$ eV; for other parameters U and for the LSDA method the value of N_β is nonzero in this limit. The magnetic coupling between impurities as a function of the distance between them is ferromagnetic for both materials, for short and long inter-impurities separations. The main difference in these couplings, in studied materials, is that the range of magnetic couplings is large in (Ga,Mn)As, and it is short in (Ga,Mn). After the difference in the band structures, this is the next proof that the mechanism of magnetism in the investigated systems is different: ferromagnetism mediated by the holes in gallium arsenide, and the double-exchange in gallium nitride.

After a decade, one could expect that everything about (Ga,Mn)As has been said. However, we returned to this subject together with Karolina Milowska in publication: *“Hole sp^3 -character and delocalization in (Ga,Mn)As revised with pSIC and MLWF approaches - newly found spin-unpolarized gap states of s -type below 1% of Mn”*. The new reasons for the return to the (Ga,Mn)As crystal were stimulated by new computational methods, which describe better chemical bonds and enable to analyze in detail the investigated system. One of these methods was the pseudopotential correction for the self-interaction of the electrons on each atomic shell (pSIC) – not only d or f shells, as it was in the LSDA+U method. In the past, I coded the pSIC method to the SIESTA code and then to the Quantum ESPRESSO package. The latter package has been used in described publication. Moreover, meantime, a new “branch of computational industry” developed – namely the application of maximally-localized Wannier functions (MLWF). Last years, more experimental data have been obtained for small concentrations of impurities, and some of these experiments were interpreted in a wrong way. These experiments concerned the impurity states which exist in the energy gap, their spin-polarization and orbital content, whether

the $3d$ -states of Mn prevail in these states or not, and whether these states separate from the top of the valence band. These are the key questions, because they explain the mechanism of ferromagnetism and point to the one of two aforementioned Zener models, which should be used to describe (Ga,Mn)As. In very recent publication, we extended the range of investigated concentrations to 1% of Mn (which means the necessity to use the elementary cells larger than 200 atoms). The analysis of states projected on Mn atomic-shells and its neighbors – close and very distant – and the occupation numbers of obtained MLWFs, clearly showed that the delocalization of the hole density function extends even to the middle part of the largest cells. This tendency is even more pronounced in the DFT+pSIC method than in the DFT. Moreover, the shape of the hole density function, depicted by MLWFs, points to the sp^3 character with the substantial contribution of the $4p$ -Mn atomic orbitals. It reveals, that the t_{2g} orbitals, built by $3d$ -states of Mn, do not hybridize so strongly with the $4p$ -states of neighboring As atoms as it was believed in the community. Unexpectedly, at small concentrations of Mn, we concluded that the impurity states within the energy gap separate from the bottom of the conduction band, not from the top of the valence band as it was established in experimental groups. And these states are purely of the s -type not containing orbitals of p or d -type – and are spin-unpolarized impurity states. This is completely new result, which needs to be confirmed by more exact GW method – I have further plans concerning this subject. The new states are completely empty, and the Fermi level still cuts through the states just below the top of the valence band, which remain spin-polarized. Therefore, the ferromagnetism at low concentrations still remains. Experimentally, lack of magnetism in the rarely doped samples can be explained with the fact, that the holes are compensated with double-donor interstitial dopants, which are always present in the systems due to the close formation energies of the substitutional and interstitial impurities. Thus, the hole mediated mechanism of the ferromagnetism in (Ga,Mn)As remains true even at very low concentrations of impurities.

One of very few reports on the semiconductor doped with a transition metal, which is ferromagnetic at room temperature – not confirmed by the experimental publication – has been given to us in private communication by Prof. R.R. Gałazka, and concerned silicon doped with Re. We decided with Andrzej Fleszar to deal with this system in the publication: ***“Density functional theory calculations for a single Re impurity in silicon”***. Rhenium is the element placed in the same column of the periodic table as Mn, and filling the atomic shells $5s$ i $5d$. However, similarly to technet – as I checked – rhenium possesses low magnetization as the substitutional impurity in silicon. The advantage of Re in comparison to Mn, as an impurity in silicon, is its stronger p - d coupling with Si. In each new system, it is important to know which of doping sites characterizes by the lowest formation energy – for Si:Re, we checked the sites: substitutional, interstitial tetrahedral and hexagonal, and “exchanged” with Re in the tetrahedral interstitial site and vacans in the neighboring Si site, and the configuration with the two vacancies in neighboring Si sites and rhenium atom placed in the middle of removed bond. It came out that the most favored positions for the doping are substitutional and interstitial tetrahedral. Magnetization of Re in silicon amounts to $1\mu_B$ in the substitutional position, and in the tetrahedral interstitial position the impurity is diamagnetic; above results are obtained from the GGA method. In contrast to Mn in GaAs and GaN, the impurity states in Si:Re are of the e_g type at the Fermi level, and not the t_{2g} type. Besides, the half-metallicity is in the minority spin, and in the majority spin there is an insulating phase. For the interstitial impurity, the Fermi level is placed just above the bottom of the conduction band, and this fact causes the demagnetization of Re. The results of the DFT+U do not differ from those obtained with the DFT method, since the change of Coulomb potential within the d -shell is not able to move the states which lay exactly on the Fermi level (the correction increases with the separation of the states from the E_F). Doping of the system with electrons or holes is energetically possible only for the n-type in the case of substitutional Re and p-type in the case of tetrahedral impurity; in the both cases, it gives the diamagnetic state.

I performed further investigations for Si:Re, independently, in the publication: ***“Exchange interactions and Tc in rhenium-doped silicon: DFT, DFT+U and Monte Carlo calculations”***. From the simulations for one impurity in the cell one is not able to conclude, without any doubt, about the mechanism of magnetism. Although, the band structure of Si:Re would suggest the hole mediated global ferromagnetism in the sample. I analyzed magnetic interactions between impurities in the substitutional pairs, within the DFT and DFT+U methods in a large range of impurity separations and for all symmetry configurations in elementary cells up to 256 atoms – the exchange couplings were smaller than 1 meV at the most distant separations in the largest elementary cell. I presented also the formation energies of the pairs of impurities and their magnetic moments per Re obtained with two types of the starting magnetic order: ferro- or antiferromagnetic. The most favorite energetically were dimers Re-Re in neighboring sites in silicon, but their magnetic moment vanished in the case of the DFT method, and remained for pairs in ferromagnetic configuration calculated with the DFT+U method. All magnetic couplings, in cases of more distant pairs than close neighbors, were positive which means ferromagnetic, and the largest values of the exchange couplings were obtained for pairs along 110 axis in the crystal – the bridges Re-Si-Re strengthen the magnetic couplings. Anisotropy has been more pronounced in the DFT+U method. In the next step, I used the exchange couplings, calculated within the DFT and DFT+U methods, in the Monte Carlo simulations of Ising model – using my own MC code for the crystal symmetry of the zinc blende with randomly distributed spins. The results were then averaged over many geometric configurations. Critical temperatures for ferromagnetic phase exceeded room temperature for impurities concentrations 7% in the case of magnetic couplings obtained with the DFT method, and for concentrations 3% in the case of parameters obtained with the DFT+U method. The most interesting effect – superparamagnetism – I found for statistical samples with the DFT+U couplings at temperatures much lower than critical temperature. In this phenomenon the magnetic domains formed, in contrast to the total magnetization of samples in the ferromagnetic state. The origin of superparamagnetic effect, with the homogenous (not clustered) impurity distributions, is in the very long-range magnetic coupling of pairs Re-Re. Magnetization inside the “cluster” of impurities in the sphere of nonvanishing couplings is so strong, that the spin reversal of the whole “cluster” costs too large energy, which cannot be overtaken by the vicinity of the next magnetic domain in the antiferromagnetic configuration. We cannot close the subject with these very optimistic results, because the corrections for the self-interaction of electrons in the *s* and *p* shells – not only in the *d*-shell like in the DFT+U – might change the magnetism in the system.

After the implementation of the pSIC method to the Quantum ESPRESSO code, I returned to the Si:Re DMS, in publication: ***“Poisoning of magnetism in silicon doped with Re, caused by a charge transfer from interstitials to substitutionals, by means of the self-interaction corrected density-functional approach”***. Taking into account the pSIC effect in silicon corrects a bit the energetic gap, by opening it slightly by such amount that the *3d*-states of Re in the interstitial configuration are positioned just below the conduction band. This slight difference in the position of impurity states with respect to the host band structure causes spectacular difference in magnetism: rhenium in the tetrahedral interstitial position becomes magnetic. In addition, Re in the interstitial position is a single donor with respect to Re in the substitutional position, and both cases have similar formation energies – thus, they compensate each other magnetically. I calculated the formation energies of all Re-Re pairs, in which both impurities are substitutional, or interstitial, or the pairs are mixed; I did it for elementary cells up to the same size which were calculated in the previous publication. In the result, magnetic moments of all mixed pairs vanished, and in the pairs of the same type the magnetizations were about 0.7-1.0 μ_B per one rhenium atom. It came out, that the most favorite were mixed pairs. To preserve the magnetism in

the system, one would need to completely control the formation process such that only one type of impurities forms. Fortunately, there is an easier way: one can co-dope the system with electrons or holes and in such case the magnetization also retains.

In addition to dilute magnetic semiconductors, I worked also with other systems, which showed magnetization. Although their nature was not stable. These systems are monatomic metallic nanowires, obtained as transient objects in very fast experiments. It is possible to stabilize such objects inside other nanostructures. Sharing the office in Trieste with Dr. Anna Delin and the work with Prof. Tosatti led to the publication: "*Effect of electron correlations in Pd, Ni, and Co monowires*". Nanowires of transition metals could be a part of electronic chips, not only because of electrical conductivity, but also due to their magnetization, which may be used as additional logic element. In transition metals, it is important to take care of the relations between electronic occupations of s - and d -shells. These relations influence the magnetism and conductivity. The theoretical description of such systems is difficult, because it is related to the problem of aforementioned electronic strong correlations within the localized orbitals. The DFT+U, or DFT method with the correction for the self-energy (pSIC) can be classified as so-called methods with the static correlations, because the corrections do not depend on the Matsubara frequency. In contrast to the methods with dynamic correlations such as the dynamical mean field theory (DMFT), which has other disadvantage: it is, in its construction, not suited for low dimensional systems. After the postdoctoral position in Dublin and a few weeks spent in San Sebastian, working with one of main SIESTA developers – Dr. Daniel Sanchez-Portal – where I implemented first version of the pSIC method, I used this code and applied the DFT+U and pSIC methods to the problem of metallic nanowires Pd, Co and Ni. The results showed that the occupation of s -shells increases slightly when the corrections were switched on. This led to the pronounced decrease of the number of transport channels, and the reduction of the ballistic conductance. Calculations for the atomic separations obtained at the minimum of total energy of the system, and at much larger separations – in the breaking point of the nanowires – led to the increase of magnetization in Pd and vanishing effect of electronic correlations on magnetization in Ni and Co. Systematic strengthening of the electronic correlations in the d -shell causes the continuous reduction of the number of conduction channels. However, for both – the DFT+U method, and the pSIC method with corrections in s - and d -shells – the two conduction channels of s -type and both spins always remain; s -type channels are wider and more efficient for transport than thin d -type channels (for all studied nanowires). For very low dimensional systems, the pSIC correction is too weak and it does not depend on the interatomic distances (the Hartree and exchange-correlation potentials depend on the orbital densities and not on the total density, and only the occupation numbers may change with the distance). In the DFT+U method, it is possible to estimate the U parameter for given system at different atomic separations. It is convenient to use the linear response method for this. In this method the orbital occupation numbers adjust to the change of the perturbation parameter in the Kohn-Sham equation with constraints. I calculated the U parameter for all nanowires at the breakpoint, and at very large atomic separation – which gave very high values growing with the inter-atomic distances. Intuitively, this trend is not surprising. However, so high values of U might seem strange. On the other hand, in such unstable case like nanowires of transition metals, these numbers might be correct – one needs to check them experimentally.

- **Superconductivity – electronic, phononic and spin-fluctuations contributions, model parameters for C_{60}**

Superconductivity is an effect, which is modeled theoretically using many parameters – usually these parameters are fit to the experiment. Despite a few formulations within the *ab initio* methods, there is no tool, which enables comfortable studies of superconductors on the same level as magnetic systems – I mean the method completely free of parameters for the Cooper pairs. Within the density functional theory, the ground for the description of superconductors has been led by two equations, similar to Bogoliubov-de Gennes, and taking into account the dependence of the exchange-correlation functional on both the normal and the anomalous densities. In other words: via equations contained the dependence on the potential of the interaction with nuclei and the pairing potential. This formulation has been led in the publication by Olivera, Gross and Kohn (OGK) in 1988. To this day, the parametrization of the exchange-correlation functional for both densities in superconductors is missing – on such grounds as it was done for spin-densities by Ceperley-Alder in quantum Monte Carlo simulations, and followed by other authors within the framework of the perturbation theory. Only very complicated formulas for the exchange-correlation functional exist in the case of the homogenous gas. This formula rests on the random phase approximation (RPA). Other contributions to the total energy contain the first order terms with respect to the electron-phonon and electron-magnon interactions. One trial of giving the form of density functional for inhomogeneous systems has been done, in phenomenological way, by Gyorffy, Temmermann and Szotek who fit the parameters in such a way that they reproduced the experimental T_c for YBCO.

In its ground, the DFT method rests on the minimum of the total energy obtained with variation to the parameters of the density (usually represented in the basis of plane waves or localized functions). Although, the differences of the total energies for two states of the system are difficult to measure, the total energy is a very convenient object for theoretical comparison of two phases, e.g. magnetic states, crystal structures, chemical reactions. For magnetic systems, one can calculate the total energy for the ferromagnetic and antiferromagnetic, or paramagnetic order and compare them in order to draw conclusions about the ground state. In the case of superconductivity, the condensation energy is a very convenient object – this is a difference of the total energies at vanishing and nonvanishing pairing potential. This way, one can find the ground state. But even more interesting is to see, how deeply in the superconducting state or how far from it is the investigated system, when we switch on the interactions: purely electronic, phononic, magnetic; and analyze contributions from these interactions as a function of temperature.

Kohn and Luttinger, in the publication in 1965, analyzed in a model way the condensation energy of homogeneous gas at the pairing potential with various amplitudes and symmetries (for orbital quantum numbers $l=0,1,2,3$). They considered the model correlation interactions for Friedel oscillations. In our publications with Jesper Krogh, we analyze the condensation energy of homogenous gas, strictly within the formulation for DFT for superconductors and the perturbative expansion of the electronic interactions; developed by PhD students of Professor E.K.U. Gross.

In the publication: “*The condensation energy of the homogeneous superconducting gas*”, printed in Computer Physics Communications, we gave to common use the computer code CHS. It may be used as a tool for parametrization of the exchange-correlation functional for inhomogeneous gas, basing on the data collected for a representative set of parameters fixed for the homogeneous gas at various densities. The density parameter is r_s , radius of free electron, and the pairing potential parameters are its amplitude and orbital quantum number describing the symmetry, in the representation of Legendre polynomials. Two-electron interactions depend on two vectors and two Matsubara frequencies, therefore we deal with 8-dimensional space for the

numerical quadrature. Fortunately, one Matsubara frequency can be summed analytically in the total energy expression, thus leaving the 7-dimensional space for numerical sampling. Not only high dimensionality is complicated. But main difficulty is in singularities, moving in the configuration space with the interaction vector between the electrons. To be specific, these singularities lay on a torus, whose plane is perpendicular to the interaction vector, and its shape is described by the two electronic vectors. In such cases, it is not possible to use the constant grids, but the statistical sampling in the Monte Carlo method is very convenient. I wrote the computer code in order to accurately perform the numerical quadrature. This code was serial, for one processor. Meeting Jesper Krogh, who taught me the programming method Fortran MPI and rewrote my code to the parallel version, was the key step in this project. I benefitted from that many times in my following projects.

Theoretical basis and the physical picture drawn from data collected from the CHS code, we discussed in the following publication: "*Condensation energy of the homogeneous electron gas from density-functional theory for superconductors*"; printed in Physical Review B. We used our code to complete results for a set of density parameters and parameters of the pairing potential. We exactly included the exchange energy for the normal and anomalous densities, and the correlation energy was treated on the level of random phase approximation (RPA). I presented the Feynmann diagrams for OGK theory and compared them with earlier work by Kohn-Luttinger 1965, Takada 1978 and Rietschel-Sham 1983. Main difference between our diagrams and earlier results is in the fact that we considered all lowest order contributions from Green's functions for the anomalous density (F) and normal density (G). This is crucial, since normal density in superconductors also depends on the pairing potential, and its contribution to the total energy is of the same order as contributions from the anomalous density F. Both exchange energies and the kinetic energy are always positive, and the contribution from the correlation energy is negative – It was important for us to know whether the negative contribution was larger for some set of parameters, whether it would be possible to obtain superconductivity from purely electronic interactions. It was known that in high- T_c superconductors, the critical temperature grows with number of nodes in the energy gap. We assumed the singlet pairing in our code, but for triplet pairing the considerations would be analogical – there is no such restriction for the parity in the DFT for superconductors. However, at the moment there are restrictions due to the lack of corrections for strong electronic correlations in the system. One could include such corrections on the level of the DFT+U and the DFT+DMFT. Our results show, that the condensation energy is positive almost everywhere in the configuration space, and this energy decreases with orbital quantum number l – as we expected. The most interesting are negative values of the condensation energy for pairing potential of f symmetry and very small densities ($r_s=10, l=3$).

Publication: "*Condensation energy and T_c within the density functional theory for superconductors*", printed in AIP Conference Proceedings from the Summer School in Vietri Sul Mare devoted to superconductivity and strongly correlated systems, compiles the publication about the condensation energy of homogeneous gas, and results collected for Nb under pressure with the electron-phonon interactions included to the model for critical temperature, within the formulation of the density functional theory for superconductors. I presented, during the School, the introduction to the formulation of DFT for superconductors and described the examples for the condensation energy and T_c . In this model, the critical temperature is obtained from the so-called gap equation (incorporating both potentials: of atomic nuclei and pairing potential) for the superconducting state. This equation is derived from the Bogoliubov-de Gennes equations after application of the decoupling approximation for electronic and superconducting scales of energy. Then, the gap equation can be linearized and solved. The critical temperature is the one, at which the pairing potential vanish. As one can see, the condition for critical temperature assumes that we

deal with the conventional superconductors; this assumption excludes the high- T_c cases with the pseudogap – however, the general OGK theory does not possess such restriction. I implemented the gap equation, and collected the results with electron-phonon coupling using the Eliashberg function, calculated with the Quantum ESPRESSO package; where phonons are obtained from the linear response of the Kohn-Sham potential to the atomic distortions. I made the calculations of the el-ph coupling in the PHONON code of ESPRESSO package more efficient – what will be described in the next publication. Critical temperatures obtained from the phenomenological formula of McMillan and Allen-Dynes fit more/less the experimental results at ambient pressure, but they fail in the description of trends for a material under pressure. Such curves with respect to pressure were reproduced from the DFT for superconductors, which includes the full Eliashberg function; not only the simple electron-phonon constant like it is in the phenomenological formulas.

The contribution from the electron-phonon coupling to the superconductivity often plays a key role, if not crucial. It is also important to take it into account the el-ph in the transport phenomena. In Quantum ESPRESSO package, there is a tool PHONON, which enables the electron-phonon calculations. Accurate calculation is very demanding due to the necessity of numerical quadrature in 3-dimensional space over electronic and phononic vectors, which gives in total 6-dimensional configuration space. In addition, this integrand contains Dirac's double-delta close to the Fermi energy. Since Fermi surfaces are very different for each material, it is not convenient to make the grid denser for chosen parts of the Brillouin zone (BZ) – the grids for numerical quadrature must be dense in whole configuration space. For this aim, I implemented the interpolation scheme for denser grids for the el-ph matrix elements in the whole Brillouin zone for electronic vectors, and used the symmetry operations to interpolate phonon vectors known in the irreducible wedge of the BZ. The second summation over the phononic vectors, we interpolate using the double Fourier transform from the reciprocal to real space and back. Phonons, dynamical matrix and matrix elements of the electron-phonon coupling are calculated from the linear response of the Kohn-Sham potential to the change of atomic coordinates (the DFT perturbation theory, DFTPT). I checked the routines for the changes of the electron-phonon coupling and the critical temperature for the superconductivity of Nb under pressure. These calculations led to our report with Stefano de Gironcoli and Paolo Giannozzi: *“Origins of low- and high-pressure discontinuities of T_c in niobium”*. We noticed, that sudden fall of the electron-phonon coupling and critical temperatures at atmospheric pressure and slow continuous fall with higher pressures are connected to the nesting of the electronic bands close to the Fermi level. The manuscript has been sent to Phys. Rev. B, but the referee disagreed with the direct conclusion about the el-ph coupling, which was drawn from the nesting. Thus, the manuscript was rejected and remains only on ARXIV. The method of el-ph calculation made more efficient is described in that report and is a part of official Quantum ESPRESSO distribution. Since it is useful for users, it got citations.

Besides the purely electronic or electron-phonon interactions, one of the most important elements of the superconductivity are spin-fluctuations. They might be longitudinal and cause increase of the critical temperature, and transverse (paramagnons) and cause decrease of the T_c . Therefore, I derived the equations for the contribution of spin-fluctuations to the formulation of DFT for superconductors, and implemented them to my own code for the critical temperatures, and applied these equations to simple metals. This is the content of the publication: *“Effect of spin fluctuations on T_c from density-functional theory for superconductors”*. In order to give details of the paramagnon contributions, it turned to be necessary to discuss the implementation of phonons to the DFT for superconductors. In the next step, I introduced the spin-fluctuations. Function Green-Nambu is in this case 4-dimensional, the same as matrix of the self-energy. In case of paramagnons, Green's function for spin-fluctuations is the transverse spin-susceptibility, and

the interaction in vertices of the Feynmann diagrams is the electron-paramagnon exchange constant I_{ex} , obtained from the magnon-dependent function averaged over interaction vectors. In analogy to phononic spectral function, so-called Eliashberg function, the spectral function of paramagnons is also dependent on frequencies (interaction energies), but obtained from the random phase approximation and averaged over the momentum space. Thus, the formulation is not fully *ab initio* – with spin-fluctuations calculated as phonons from the variation of Kohn-Sham potential in linear response to the perturbation – but it is a mixed approach with model dependence on the frequency and material dependent exchange constant. I derived the gap equation for superconductivity with the spin-fluctuation spectral function. I calculated both spectral functions for phonons and paramagnons and obtained the critical temperatures for the superconductivity for a few simple metals: Ta, Mo, V, Pd-fcc and Pd-bcc for the optimized lattice constant, and the dependence of the superconducting parameters for Nb under pressure. I compared the critical temperatures obtained from the DFT for superconductors and the Eliashberg model, including phonons and both phonons and paramagnons. The results with included spin-fluctuations fit the experimental data much better than just the phononic part, and the OGK theory is much closer to the measurement of T_c than the Eliashberg model. In the past, similar calculations have been performed by Chubukov within the Eliashberg model, also for the condensation energy. The main focus of theoreticians interested in superconductivity moved to the effects of strong electronic correlations and to the DFT+DMFT method. This way the number of difficult theoretical subjects to be solved increased, and the interest in the development of DFT for superconductors moved down on the priority list. I hope, however, that the interest in this approach will come back, because in the history of physics, the *ab initio* methods – due to their complication – always developed a few steps after simpler models.

Aforementioned, electronic strong correlations, so characteristic for superconductors, are in the main focus of our common publication with Dr. Martin Lueders and Prof. Erio Tosatti: “**Multiplet structures of charged fullerenes**”. Fullerene C_{60} doped with holes is superconducting as a molecular crystal in the bcc lattice. As a molecule, C_{60} has 5-fold degenerate highest occupied orbitals (HOMO) and 3-fold degenerate lowest unoccupied orbitals (LUMO). Under doping, the Hund’s exchange rules and the Jahn-Teller effects interplay, which leads to the complicated phase diagrams in this system. Therefore, it is important to find the exact parameters for the Coulomb U and exchange J for the Hubbard model and the DMFT. Earlier works for C_{60} in Trieste condensed matter group used the Quantum ESPRESSO code for DFT periodic calculations in the plane-waves basis set. DFT for crystals is not designed to reproduce the excitation energies in molecules. Therefore, being witness of discussions on C_{60} , I proposed the CAS SCF method and GAMESS code, which I used during preparation of my PhD thesis. DFT rests on the electronic density only. On the other hand, in order to find the excitation energies of all multiplets, one needs to include all electronic excitations within a few degenerate orbitals. Such energies might be obtained only with a combination of Slater determinants and exact exchange energy. The CAS SCF method (complete active space self-consistent field) includes all electronic configurations in the restricted configuration space, and it is so-called method with static correlations. In contrast to the perturbation methods, which take into account so-called dynamical correlations. In our calculations, in case of positive charged states, the active space has been spanned by five HOMO, and in case of negative ions, three LUMO. All multiplet energies were calculated at the geometry of neutral system (closed shell). Ionization of the system causes not only changes within the HOMO or LUMO orbitals, but it makes the deeper orbitals to relax or expand. Such effects might be taken into account by assuming the reference state for the CAS SCF calculations to be obtained from the ROMP2 method (restricted open-shell Moeller-Plesset perturbation theory of 2nd order). We checked also the effect of inclusion of five deeper orbitals HOMO-1 and three higher orbitals LUMO+1, and in the result, these effects were very small and neglected in further calculations.

Due to the fact that the GAMESS code did not allow for the use of icosahedral symmetry, we applied D5 and D3 symmetries in the calculations, but the geometry possessed the full icosahedral symmetry. The Coulomb parameter U has been obtained for ions in two ways: from the total energies of the ground states, and from averaged multiplet energies. The Hund's exchange parameter J has been found from the model using the multiplet energies for ionized cases. We compared our results with the data obtained from the DFT, semiempirical methods and methods of quantum chemistry – where such data existed. Ionization potentials were compared with the spectroscopic data. Our parameters have been cited by works which used the DMFT method (Millis, Werner, Siegrist).

- **Graphene**

Within my research position in Warsaw, in the project SiCMAT (<http://sicmat.materials.pl/>), the main focus of my work was in graphene at the silicon carbide surface. The subject was done in the collaboration with ITME, where large graphene wafers of high quality are produced – in high temperature and in argon atmosphere, in the chemical vapor deposition (CVD) process. The propane molecule, C_3H_8 , as carbon precursor is used. It is interesting to know how these components react in the formation process of graphene deposited on SiC, and how the dehydrogenation occurs, and what is the role of argon. Together with Adam Dominiak and Kamil Tokar, we performed the calculations, which led to the publication: “*CVD formation of graphene on SiC surface in argon atmosphere*”. Argon, as a noble gas, does not make chemical bonds in the ground state, only forms Van der Waals complexes. On the other hand, in the excited state to the triplet spin, argon forms a few molecules: $HArF$, $HArCl$, $FArCCH$, $FArSiF_3$. Ionized noble gases form complexes with hydrogen; the known are: ArH^+ , HeH^+ , NeH^+ , KrH^+ , XeH^+ . In addition, it has been observed in the Raman spectra, that after the epitaxy of graphene, the SiC surface is negatively charged. We asked the question whether argon takes a part in the chemical reactions with proton. We performed the quantum chemistry calculations for molecules, with the GAMESS code, using the Hartree-Fock, MP2 and DFT methods. We focused on sequential reactions of deprotonation of propane and its subsequent dehydrogenated forms and the dissociation of ArH^+ . In the next step, using the Quantum ESPRESSO package, we performed the stream of calculations using the DFT method for $4H$ -SiC(0001) surface (for hexagonal forms of SiC in the stacking with period 4) with hydrogen, propane and all transition forms of propane after dissociation of following hydrogens or protons – for neutral and negatively ionized forms. We found the barriers for the dehydrogenation within the climbing-image nudged-elastic-band method (NEB), and we estimated the catalytic effect of the surface for the reactions in two ways (adsorption or desorption). The final conclusion is that at low temperatures, the deprotonation reaction does not occur with the help of argon. Kamil Tokar performed also pilot calculations with molecular dynamics (MD) method in the temperature of 1500 K for propane molecule at SiC, but without argon atmosphere, in order to confirm the catalytic effect of the surface; he used the SIESTA code. In both numerical experiments, NEB and MD, hydrogens after dissociation from hydrocarbons, adsorbed at the SiC surface closely to the adsorbed groups C_3H_x ($x=8, \dots, 0$). Therefore in our simulations, the SiC surface remained always “poisoned” by hydrogens, what makes the total coverage by the clean graphene layer difficult. We studied the SiC terminated with Si, not with C. In the experiments, the graphene at Si-terminated surface grows as a monolayer with variable distances between graphene carbons and Si atoms, which indicates existence of some hydrogen islands between SiC and graphene.

Graphene as a metal in the one k-point in BZ, called Dirac point, cannot be used in electronic elements as a semiconductor. Therefore, it is important to functionalize this material and open an energy gap. This might be achieved by doping with bohr or nitrogen. Since the elastic properties of graphene are excellent, it is important to ask whether after doping these properties remain. Karolina Milowska and Magdalena Wońska set this aim for their investigations, and used the SIESTA code to perform all calculations and wrote the first version of the publication. Then, not having the degree, they asked me for corrections of the English text and taking the role of corresponding author to J. Phys. Chem. C.

Recently, we work on two following manuscripts about graphene deposited on silicon carbide: M. Wierzbowska, Adam Dominiak and Giovanni Pizzi: *“Effect of C-face 4H-SiC(0001) deposition on thermopower of single and multilayer graphene in AA, AB and ABC stacking”* and *“Longitudinal spin-Seebeck effect in graphene doped with H or F, free-standing and deposited on C-face 4H-SiC(0001); huge growth of thermopower and thermoelectric efficiency (ZT) at the band edges”*. These subjects have been presented on MRS Fall Meeting, Warsaw, 2013 – for pure graphene, graphene multilayers and doped graphene, all cases free-standing. After the conference, I calculated the effect of deposition on SiC, and wrote the manuscript which is now with coauthors. Interesting conclusions from these works are: 1) enhancement of Seebeck effect after the deposition on SiC, 2) AB and ABC stackings are thermoelectrically more efficient than the AA stacking due to the Van der Waals forces, 3) doping graphene with H and F causes the spin-dependent Seebeck effect with opposite transport for electrons with opposite spins in these magnetic systems. The most important are “band-edge” and “energy-gap” effects, where the enhancement of thermoelectric effects is gigantic. In the manuscripts, we used the Boltzmann equations implemented on top of accurate interpolation of energetic bands using the maximally-localized Wannier functions; Dr. Giovanni Pizzi is the main author of this code. This enabled fast calculations of thermoelectric parameters on the fine grids of 2500 k-points in each of two directions in the Brillouin zone.

- **Contribution to the development of computational methods and codes**

During my PhD studies, I implemented a few utilities to the codes: the point charge field simulating the surfaces of ionic crystals to the GAMESS package and the UHF (unrestricted Hartree-Fock) method to the code of Prof. Staemmler.

My first postdoctoral research position in Lund was in the group, which developed the MOLCAS package. In that time, they planned to develop the method, which would be as accurate as CAS PT2 and as fast as DFT. It was DFT for open-shell states – which has been later published in general formulation including examples a few years after my stay in the group. My task was to help in the implementation of the DFT to this huge package of codes for quantum chemistry. Earlier, I wasn't even a user of this package and my experience with fortran90 did not allow quickly finish the coding. Prof. Roland Lindh taught me in that time a lot, showed me how to code new functionality to the existing package, and practically he wrote everything himself. I just watched and learned, and tested new parts of the code, correcting only little mistakes – I made so-called debugging. Experience with the MOLCAS package helped me to implement, independently, the new methods to the SIESTA and Quantum ESPRESSO packages. During that work with MOLCAS code in Lund, I performed preliminary calculations for the dissociation of molecules CH_3X , $\text{X}=\text{Cl}, \text{Br}, \text{I}$, including the spin-orbit coupling. This coupling lifts the rules not allowing for the transitions with the change of spin multiplicity. In effect, the molecules dissociated to the two spin channels splitted proportionally to the spin-orbit coupling. Further

detailed studies performed by Dr. Ajitha, Dr. Malmqvist and Prof. Lindh led to the publication: *“Spin-orbit ab initio study of alkyl halide dissociation via electronic curve crossing”*.

I wrote the serial version of the CHS code for the calculation of contributions to the condensation energy of the superconducting state in the approximation of the homogeneous gas. Dr. Jesper Krogh (who was that time a PhD student in Lund) rewrote my code to the parallelized version, and taught me how to use Fortran MPI – which helped me in the future to implement further methods. The CHS code serves for the parametrization of the exchange-correlation functionals for the superconductors within the DFT formulation. The code has been also used to compare the OGK theory with earlier work by Kohn-Luttinger, Rietschel-Sham and Takada. I described it in detail in the chapter “Superconductivity” and in the publications nr 1, 5, 6, and 7 from the list after PhD.

In the OGK theory (DFT for superconductors) one can apply the decoupling approximation for normal phase and variables describing the Cooper pairs. In effect, only one equation describes the energetic gap for the superconductivity and the other is a simple Kohn-Sham equation. The gap equation can be linearized and the critical temperature of the system would be the one, at which the gap vanishes. Such equation contains the contributions from the exchange energy for normal density and anomalous density, the correlation energy, the energy of the electron-phonon coupling, the spin-fluctuations energy. I implemented these contributions to my own code for T_c and used it in the publications nr 5 and 7 from the list after PhD.

I derived the equations for the contribution of the spin-fluctuations (paramagnons) to the total energy and the pairing potential within the DFT for superconductors. The details are described in the section “Superconductivity” and they are connected to the publication nr 7 from the list after PhD. New contributions were introduced to the code for the energetic gap and the critical temperature.

Calculation of the electron-phonon coupling needs very accurate numerical quadrature in the 6-dimensional space with Dirac’s double-delta functions close to the Fermi surface. Therefore, I made the PHONON code in Quantum ESPRESSO package more efficient – which is described in the section „Superconductivity”. The results and the description of the modified scheme is in the report 9 from the list. I used this part of the package for calculations in the publications 5 and 7 from the list after PhD.

I implemented the LDA+U method and the first version of the self-interaction correction within the pseudopotential method (pSIC) to the SIESTA package. Details of the implementation and the results with the LDA+U method for the dilute magnetic semiconductors are published in the work nr. 4 in the list after PhD, and described in the section “Magnetic semiconductors”. Implementation of the pSIC in the SIESTA package has been used in the publication nr. 8 in the list after PhD, and described for an example of nanomagnetism in the section “Magnetic semiconductors and nanomagnetism”. In that publication (nr. 8), at the end, I described the method for the estimation of U parameter from first principles, from the linear response of occupation numbers to the perturbation added to the Kohn-Sham equation. This is very useful method, since obtained parameter U fits studied material in fixed geometry, with used pseudopotentials and other parameters, which should not change when we use this U parameter in the calculations. The most important in the LDA+U method is not U alone, but the multiplication of U with the orbital occupation numbers. The dependence of U, obtained from that linear response method, on the geometry of the system is interesting in itself, especially for low-dimensional systems. I implemented this method in the SIESTA code for my own use.

Taking care for the corrections to the DFT method for the strong electronic correlations in the systems with localized orbitals, in low dimensional systems, and for the self-interaction, is often necessary in order to draw meaningful physical conclusions. The pSIC method is independent on parameters, in contrast to the DFT+U. The pSIC is much simpler method for computations than exact exchange (EXX). But not only economic reasons give an advantage to the pSIC. The correction is embedded in the exchange-correlation functional, while in the EXX, the exact exchange in the place of a simpler form, which was unified with the correlation, might not fit to this correlation. The EXX for crystals very often gives two high band gaps as it is in the Hartree-Fock method for molecules in a sense of HOMO-LUMO gaps. The pSIC contains the self-interaction energy within all atomic orbitals of all atoms in the system. The form of this correction is not complicated – this is the Hartree and the exchange-correlation potential on orbital density of the atomic pseudopotential. Therefore, I implemented the pSIC method also in the Quantum ESPRESSO package. I finished the whole implementation of the pSIC before starting the work in Warsaw, and we compared the results with Dr. Andrzej Fleszar, who in the same time coded this method in his mixed basis code. In the publication nr 13 from the list after PhD, the pSIC was necessary and not possible to be replaced by the DFT+U method.

I derived equations for interatomic forces within the DFT+pSIC scheme. After the comparison of these formulas with those published earlier by Alessio Filippetti et al., I realized that a few terms proportional to the derivatives of the occupation numbers are missing in the published work. Thus, I implemented derived terms for forces to the Quantum ESPRESSO package. In this code, there are two types of pseudopotentials (PP) used: norm conserving (NC) and ultrasoft (of Vanderbilt type) – the last case needs some additional terms in each implementation due to the norm corrections for the electronic density. In the next step, I checked the equations in the module of geometry optimization and collected the results for ZnO, CeO₂, perovskites in the P_{nma} structure (20 atoms in the elementary cell with Jahn-Teller distortions) LaTiO₃, YTiO₃, LaMnO₃, and magnetic semiconductors Si:Mn and Si:Re with two impurities in the elementary cell. Implementation includes also gradient corrections within the GGA method, in the part of the pSIC self-consistent method and the optimization of geometry using the method of minimal absolute values of forces (which is equivalent to the minimum of the total energy). I chose the examples and wrote the publication: *“Forces and atomic relaxation in density functional theory with the pseudopotential self-interaction correction”*. Then I asked Prof. Majewski for corrections and comments to the manuscript, since he has the experience with other methods with self-interaction correction. Further I used the method and code to obtain results in publications 13 and 16 from the list after PhD.

During my postdoctoral research in Trieste, in the same time, the group from MIT developed the code wannier90 for maximally-localized Wannier functions (MLWF). This code uses the start from the crystal data and the optimized, within the self-consistent DFT method, Hamiltonian vectors, so-called Bloch functions. I was involved in writing the interface from the Quantum ESPRESSO package to the wannier90 code – pw2wannier; information about it is in the history of the code in www.wannier.org Following, I used this code in publication number 16 in the list and in the manuscripts about thermoelectric effects in pure graphene, multilayers and doped graphene on SiC. I plan to use the wannier90 code in future projects.

Projects in progress

Using the MLWFs for the interpolation of bands or Hamiltonian matrix elements enables to calculate many interesting and complicated observables defined by the solution of DFT method. One of these phenomena is the anomalous Hall conductivity, which is interesting for me in application to the thin layers of (Ga,Mn)As. I presented results for small elementary cells up to 64 atoms during the MRS Fall Meeting, Warsaw, 2013. For larger elementary cells, which are necessary to define 2D layers with various surface reconstructions, one needs powerful supercomputers and still some code development.

Second interesting for me class of materials is the group of 2D organometallic semiconductors possessing many properties desired for future electronics, spintronics and opto-electronics.

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