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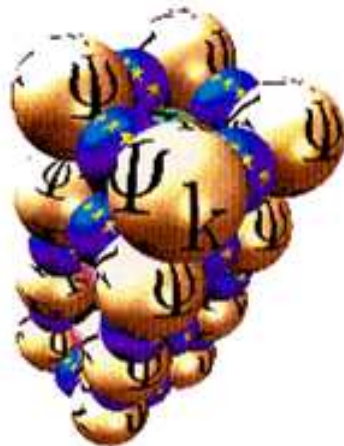
AB INITIO (FROM ELECTRONIC STRUCTURE) CALCULATION OF COMPLEX PROCESSES IN MATERIALS

Number 87   June 2008

Contents

1   Editorial

In this Psi-k Newsletter we have a letter from the Psi-k Chairman on the new organisational aspects of the Psi-k Network. Also, please do read the information on the Psi-k Portal and in particular how to subscribe to it, as from now on it will be the only means of receiving and sending information to the Psi-k community. Thus only members of the Psi-k Portal will be able to obtain and distribute information. Another item of importance in this Psi-k Newsletter is 'Call for Workshop Proposals for 2009'. If you would like to have your activity subsidised by the Psi-k Network, you need to respond to this call. Note that a poster with all the 2008 Psi-k Workshops can be found on or downloaded from the Psi-k Portal ('Psi-k Resources').

Other items are brief workshop reports, announcements of the International Workshop on "Computational Magnetism and Spintronics" in Dresden and the UK's CCP9 Conference in Cambridge, a few position announcements; in addition to those that you can find on the Psi-k Portal, a number of abstracts and most importantly the scientific highlight. The latter is by Gabriel Bester (MPI for Solid State Research, Sttutgart, Germany) on "Electronic Excitations in Nanostructures: An Empirical Pseudopotential based Approach".

The *Psi-k Network* has a home page on World Wide Web (WWW). Its *Uniform Resource Locator* (URL) is:

http://www.psi-k.org.uk/

From the above page you can also access the Psi-k Portal and all the information stored there.

Please submit all material for the next newsletters to the email address below.

	function
psik-coord@dl.ac.uk	**messages to the coordinators, editor & newsletter**

Dzidka Szotek, Martin Lüders and Walter Temmerman
e-mail: psik-coord@dl.ac.uk

2 General News

2.1 Letter from the Psi-k Chairman

Dear Members of the Psi-k Network,

With this letter I would like to inform you about some important changes in our organisation. As you might know, the Psi-k Network has been funded for two periods as an ESF Programme by the European Science Foundation (ESF), i.e. for a total of 10 years. This long period of stable funding was very good for us: Psi-k has strongly grown and our activities cover now nearly all fields in computational materials- and nano-sciences. During these years Psi-k has organised a total of 150 workshops, computer tutorials and summer schools. In the last years these were more than 20 activities every year, with more than 1000 participants. Equally successful were the large Psi-k Conferences in 2000 and 2005. The next one, Psi-k 2010, will be organised by Matthias Scheffler and his team in Berlin.

Unfortunately, 2 years ago the ESF told us that we cannot be funded any longer, since we are "too big and too diversified". Moreover this would have been our third funding period, which naturally represents a high barrier for any funding agency. On the other hand there is a strong need for a more permanent Psi-k organisation. Clearly workshops, training activities and networking will be needed for many years.

In this desperate situation without future funding we have tried the impossible: The Psi-k Steering Committee decided to found a legally independent, non-profit, science organisation, to be funded by financial contributions of the largest and financially strongest Psi-k groups in Europe. Therefore we have founded a "Company limited by guarantee" (In UK and Ireland this is the typical organisational form of charities and other non-profit organisations) with name "Psi-k", which is registered in England and Wales with Company No. 06440198 and has the office in Daresbury Laboratory. At present we are in the process of registering Psi-k Ltd as a charity.

Members of many European institutions have promised annual contributions between 2,000 and 10,000 Euros for a five year period, which amount to a total of about 150,000 Euros p.a. All 19 workshop activities in this year can be funded and already now we can say that in the next year we will also have no financial problem.

While the legal structure of the new Psi-k "Company" is very different from the one of an ESF Network, all important decisions will be obtained by consent in the "Scientific Advisory Committee" which replaces the "Steering Committee" of the ESF Network. The goals and tasks of the new Psi-k Network will be very much the same as the ones of the well proven Psi-k Programme funded by the ESF. In particular, also the new Network will be open for all European scientists, who e.g. can participate at Psi-k Workshops or make applications for Psi-k

activities. The management of the finances and the travel expenses will be similar to the ESF example and is handled by the Daresbury Laboratory.

The bottom-up funding of a Network from the budgets of its members is a novelty in Europe. It dramatically illustrates the success of our Network and that our members want to continue the Psi-k activities in the future. It also shows the strong cohesion in our Network, which was always typical for the "Psi-k Family" started with the Human Capital and Mobility (HCM) network in 1993.

For this reason we ask you to strongly collaborate with Psi-k also in the future in order to keep Europe leading in our field.

Last but not least I am glad to inform you that in the last months we obtained clear signals from the ESF encouraging us to apply for a new project with the ESF. Thus it is not unlikely that in the next years we might get funds from both the ESF as well as from our "Psi-k Ltd.".

With best regards,

Your Psi-k Chairman

Peter Dederichs

2.2 Call for Subscriptions to Psi-k Portal

As explained in the Psi-k Newsletter No 86, the April issue, the idea is that the Psi-k Portal replaces fully the existing Psi-k mailing list, so that no human intervention will be necessary to distribute announcements to the Psi-k community. As the summer is approaching, now is the right time to make the switch from the moderated Psi-k mailing list to the Psi-k Portal mode of operation. During the June-September period it is always difficult to maintain physical presence at one particular place and to approve promptly all e-mails sent to the Psi-k mailing list. So, the Psi-k Portal will fully take the role of maintaining electronic services to the Psi-k community. Thus from now on to receive information from or send it to the Psi-k community you need to join the Psi-k Portal. To have an information distributed, you need to upload it yourself and this will go by e-mail to all the Psi-k Portal members, only if for 'E-mail Notification' you will choose option 'High - to all addresses'. Otherwise, it will be saved on the Portal for all the members to view. Of course, you can choose the type of the information you want to upload from the menu, namely 'book, code/software, event, job, newsletter, other'. For viewing announcements saved on the Psi-k Portal, you can either choose 'all' or a specific one from among those enumerated.

To join the Psi-k Portal go to the Psi-k web page at

http://www.psi-k.org

and choose the option 'Login to Ψ_k Portal', and then 'New Account'. While filling in all the necessary spaces choose your full e-mail address as your 'id', followed by a suitable password. Of course, you need to fill in all the requested fields while joining the Portal. If your account was successfully created, then next time you access Psi-k Portal you just simply login to it with your 'id' and password. While logged in you will be put by default to 'PSI-K', where you will have access to all the information and functionality. In the 'PSI-K' you will have the whole menu at your disposal and then you will be able to upload, view, etc., any information. Please be patient when uploading information, like announcements, reports, etc., as it is sometimes slow, and by pressing multiple times on a 'submit/add' button, you keep on uploading the same information several times. The result being that your information will be sent to all the members of the Psi-k Portal as many times as you have pressed 'submit/add' button. Of course, you have a choice either to distribute your information by e-mail or just upload it to the Portal, for reference and viewing. In order not to have the information distributed you need to choose for the 'E-mail Notification' the option 'None'. For example, the workshop/meeting reports should not be distributed by e-mail, but should be uploaded to the Portal, for 'keeps' and an easy access for

everybody, by clicking on the 'Psi-k Resources'. After getting into 'Psi-k Resources' you need to open a folder with the name of your workshop, and then you should upload your report pdf-file or files into this folder. Please pay attention that there is no time limit set on the visibility of your folder, as after that date no-one would be able to see your report anymore.

It is also possible to choose 'My Workspace' while on the Psi-k Portal. One can switch from 'PSI-K' to 'My Workspace' by clicking on the required option at the top toolbar. There are a number of things you can do in your own workspace, and for details you should check on the Portal itself.

3 Psi-k Workshops

"Towards Atomistic Materials Design"

3.1 Call for Psi-k Workshop Proposals for 2009

Herewith we ask for proposals for workshops, small conferences, hands-on tutorials and summer schools in the field of ab-initio calculations to be held in 2009 and to be partially funded by the new Psi-k network.

The deadline for Psi-k proposals is 1. October 2008.

The 2009 year is the second year of the new Psi-k Network, being funded by financial contributions of the large European research groups in the ab-initio field. We all aim at excellent workshop activities and therefore we ask you to write a detailed and well founded proposal which will be refereed by members of the Scientific Advisory Committee. Training activities like computer tutorials and summer schools will be given some preference, but we hope for an excellent workshop program as in the past.

How to submit a proposal: You need to login to the Psi-k Portal, accessed from the Psi-k web pages (http://www.psi-k.org). First you will have to create an account (if you do not have it already) For this please use your e-mail address as userid. After the successful creation of an account you will end up in the PSI-K workspace. Click on the 'Workshop Proposal' button, and then click on the number 1 (left column) of the 'Call For Workshop Proposal List' to view its details, including the option to submit a proposal.

Then to submit a proposal for a workshop, click the 'Submit Workshop Proposal' button:

Fill in all form fields correctly and then you will be able to preview your proposal as a pdf-file by clicking on 'Preview(PDF)' button. If the preview button does not produce a pdf-file please check carefully that all input fields have been filled in, valid dates are used (format dd/mm/2009-dd/mm/2009) and budget (Euros) is provided. You can then make any changes to your proposal or 'Submit' your proposal as it is.

To view any proposals you have already submitted, first go to the relevant proposal page then click on the 'Show My Proposal(s)' button. You can view or modify your proposal, or download it as a pdf-file.

Collaboration with CECAM: As in the past years we strongly encourage joint CECAM/Psi-k Workshops as well as joint tutorials about electronic structure calculations, the latter ones funded partially by EU-Psi-k Training contract. The collaboration with CECAM is working very well and has effectively increased our funding substantially.

The deadline for CECAM proposals is 1. October 2008.

Due to a Council Decision, CECAM is in the process of moving from Lyon to Lausanne. A new CECAM director will be elected soon. A strong extension of the CECAM activities is planned and the available budget is expected to increase substantially. In addition to the Headquarter in Lausanne quite a few CECAM subnodes in different countries will be established which might also organise some activities of their own. New activities like Gordon Conferences or Santa-Barbara-like longer workshops are also feasible. We will inform you about new CECAM activities when decisions have been made.

Funding for US participants: Very often the workshops have an American co-organizer, who can bring in additional support for US participants by funding from NSF or other agencies. As pointed out by Christian Elsaesser, European organizers can also apply for support of US participants from:

U.S. Office of Naval Research Global (http://www.onrglobal.navy.mil) European Office of Aerospace Research and Development (http://www.london.af.mil)

With best regards,

Peter Dederichs and Walter Temmerman
(Chair and Vice-chair, Psi-k)

3.2 Reports on Psi-k Workshops

Below we publish short reports on recent workshops subsidised by Psi-k. The complete reports, including also abstracts of presented papers, can be found on the Psi-k Portal, accessed from the Psi-k web pages

http://www.psi-k.org.

While on the Psi-k Portal you need to go to 'Psi-k Resources' to find the reports. If you have not subscribed to the Psi-k Portal yet, then you need to do so first, by opening a new account. In one of the beginning sections of this Psi-k Newsletter, we explain how to become a member of the Psi-k Portal.

3.2.1 Report on Advanced School on Quantum Monte Carlo Methods in Physics and Chemistry

ICTP, Trieste, Italy, 21/01/2008-02/02/2008

Organizers: C. Filippi, S. Moroni, S. Sorella, C. Umrigar, S. Zhang

Summary:
This Advanced School was sponsored by ICTP, SISSA, DEMOCRITOS and Psi-k, and focused on the latest developments in methodology and applications within quantum Monte Carlo (QMC) techniques. After briefly introducing the basics of the methods and giving a broad overview of the field, the lectures covered the current methodological developments, including efforts to incorporate molecular dynamics and improve geometry optimisation schemes, to find more efficient ways of optimising trial wave functions, and to develop new algorithms alternative to the fixed-node diffusion Monte Carlo method. The invited lecturers were leading figures in the field, being involved both in methodological developments as well as in pushing the frontier of applications to complex systems.

The main topics covered in the school were:

- Introductory material: Random walks, Variational Monte Carlo, Projection Monte Carlo. (Ceperley, Filippi, Foulkes)

- Improved wave functions: Multideterminant, Pfaffian, Geminal, Backflow. (Sorella, Schmidt)

- Low-variance derivatives: Progress in wave function optimization, Forces. (Umrigar, Sorella)

- Progress in Projection Monte Carlo: Lattice Regularized Diffusion Monte Carlo and Non-Local Pseudopotentials, Auxiliary-Field Monte Carlo for any single-particle basis set. (Sorella, Moroni, Zhang, Schmidt)

- Finite temperature: Introduction to Path Integral Monte Carlo, Coupled Electron-Ion Monte Carlo. (Ceperley)

- Diagrammatic Monte Carlo and Worm algorithm. (Prokof'ev)

The lectures were held during the morning sessions while the afternoon sessions were devoted to hands-on tutorials held in the Computer Laboratory of the ICTP. The school was followed by a mini-workshop on recent applications of quantum Monte Carlo to problems of relevance to material science, condensed matter, physical chemistry as well as nuclear physics (Assaraf, Casula, Needs, Pierleoni, Prokof'ev, Schmidt, Senatore, Umrigar).

The school was very timely to fully capitalize on the recent exciting developments and on the potential of QMC as testified by the very large number (about 250) of applications we received. Among these applications, we accepted 73 participants from over 20 countries, who were actively engaged in the school through the hands-on sessions as well as a poster presentation. The participation was substantially larger than anticipated, and essentially at peak capacity of the ICTP computer laboratory.

The school was successful in its primary goal to train young researchers who have just entered or are interested in entering the field. Moreover, the lecturers provided the participants with real, full-fledged codes where state-of-the-art algorithms were implemented. Finally, also the talks at the workshop following the school were mainly intended for the participants and therefore tuned to a non specialized audience.

Full lecture notes available at

http:cdsagenda5.ictp.trieste.it full_display.php?email=0&ida=a07138

Programme

School: Week 1	
21 January 2008	
08:30 - 09:50	Registration
09:50 - 10:00	Opening remarks
10:00 - 11:30	Intro on random walks and error analysis
	D. Ceperley/University of Illinois at Urbana-Champaign
11:30 - 13:00	VMC and trial wave functions
	C. Filippi/Leiden University
13:00 - 15:00	Lunch break
15:00 - 17:00	Statistical analysis of computer simulation data
	B. Clark/University of Illinois at Urbana-Champaign

22 January 2008

09:00 - 10:30	Optimization of many-body wave functions
	C.J. Umrigar/Cornell University
10:30 - 11:00	Coffee break
11:00 - 11:45	DMC 1
	C. Filippi/Leiden University
11:45 - 12:30	DMC 2
	W.M.C. Foulkes/Imperial College London
12:30 - 15:00	Lunch break
15:00 - 17:00	Optimization of trial wave functions
	C. Filippi/Leiden University

23 January 2008

09:00 - 10:30	Solids 1
	W.M.C. Foulkes/Imperial College London
10:30 - 11:00	Coffee break
11:00 - 11:45	Solids 2
	W.M.C. Foulkes/Imperial College London
11:45 - 12:30	Informal discussions/questions by partecipants
12:30 - 15:00	Lunch break
15:00 - 17:00	Introduction to CASINO
	N. Drummond/University of Cambridge

24 January 2008

09:00 - 10:30	PIMC 1 Intro
	D. Ceperley/University of Illinois at Urbana-Champaign
10:30 - 11:00	Coffee break
11:00 - 12:30	PIMC 2 Bosons
	D. Ceperley/University of Illinois at Urbana-Champaign
12:30 - 15:00	Lunch break
15:00 - 17:00	Pair density matrix, simple PIMC
	B. Clark/University of Illinois at Urbana-Champaign

25 January 2008

09:00 - 10:30	PIMC 3 Fermions
	D. Ceperley/University of Illinois at Urbana-Champaign
10:30 - 11:00	Coffee break
11:00 - 12:30	RVB-JAGP and pfaffians
	S. Sorella/DEMOCRITOS, SISSA
12:30 - 15:00	Lunch break
15:00 - 17:00	PIMC++
	B. Clark/University of Illinois at Urbana-Champaign

School: Week 2

28 January 2008

09:00 - 10:30	AFDMC 1
	S. Zhang/College of William and Mary
10:30 - 11:00	Coffee break
11:00 - 12:30	LRDMC and beyond locality approximation
	S. Sorella/DEMOCRITOS, SISSA
12:30 - 15:00	Lunch break
15:00 - 17:00	LRDMC lab
	F. Sterpone/CASPUR

29 January 2008

09:00 - 10:30	RQMC
	S. Moroni/DEMOCRITOS, SISSA
10:30 - 11:00	Coffee break
11:00 - 12:30	AFDMC 2
	S. Zhang/College of William and Mary
12:30 - 15:00	Lunch break
15:00 - 17:00	AFDMC lab
	S. Zhang/College of William and Mary

30 January 2008

09:00 - 10:30	Spin/isospin 1
	K.E. Schmidt/Arizona State University
10:30 - 11:00	Coffee break
11:00 - 13:00	Worm Algorithm
	N. Prokofiev/University of Massachusetts
13:00 - 15:00	Lunch break
15:00 - 17:00	Worm Algorithm lab
	N. Prokofiev/University of Massachusetts

31 January 2008

09:00 - 11:00	Diagrammatic Monte Carlo
	N. Prokofiev/University of Massachusetts
11:00 - 11:30	Coffee break
11:30 - 13:00	Spin/isospin 2
	K.E. Schmidt/Arizona State University
13:00 - 15:00	Lunch break
15:00 - 17:00	Diagrammatic Monte Carlo lab
	B. Capogrosso/University of Massachusetts

	Mini-workshop

1 February 2008

09:20 - 09:30	Opening remarks
09:30 - 10:15	R. Needs/University of Cambridge
	Some applications of diffusion quantum Monte Carlo
10:15 - 11:00	C. Pierleoni/University of L'Aquila
	Coupled electron-ion Monte Carlo simulation of high pressure hydrogen
11:00 - 11:30	Coffee break
11:30 - 12:15	G. Senatore/University of Trieste
	Modelling the two-dimensional electron gas in solid state devices
12:15 - 14:30	Lunch break
14:30 - 15:15	K.E. Schmidt/Arizona State University
	Quantum Monte Carlo studies of superfluid Fermi gases
15:15 - 17:00	Poster session

2 February 2008

09:00 - 09:45	C. Umrigar/Cornell University
	Correlations and localization in planar quantum dots
09:45 - 10:30	R. Assaraf/University Pierre et Marie Curie (Paris VI)
	Extending QMC accuracy from total energies to observables and small energy differences
10:30 - 11:00	Coffee break
11:00 - 11:45	N. Prokofiev/University of Massachusetts
	Stochastic summation of self-consistent Feynman diagrams. A generic technique for polaron (and many-body?) problems
11:45 - 12:30	M. Casula/University of Illinois at Urbana-Champaign
	One dimensional trapped fermions with attractive contact interaction

Final List of Participants

FILIPPI Claudia; filippi@lorentz.leidenuniv.nl

MORONI Saverio; moroni@sissa.it and moroni@democritos.it

SORELLA Sandro; sorella@sissa.it

UMRIGAR Cyrus J., cyrus@ccmr.cornell.edu

ZHANG Shiwei; shiwei@physics.wm.edu

CEPERLEY David M.; ceperley@ncsa.uiuc.edu

FOULKES William Matthew; wmc.foulkes@imperial.ac.uk

PROKOFIEV Nikolai Viktorovich; prokofev@physics.umass.edu

SCHMIDT Kevin; kevin.schmidt@asu.edu

ASSARAF Roland; assaraf@lct.jussieu.fr

CASULA Michele; casula@uiuc.edu

NEEDS Richard James; rn11@cam.ac.uk

PIERLEONI Carlo; Carlo.Pierleoni@aquila.infn.it

SENATORE Gaetano; SENATORE@TS.INFN.IT

ATTACCALITE Claudio: claudio.attaccalite@gmail.com

CAPOGROSSO SANSONE; capogros@physics.umass.edu

CLARK Bryan K., Urbana, USA

DRUMMOND Neil David; ndd21@cam.ac.uk

ESLER Kenneth; esler@uiuc.edu

MCMINIS Jeremy Beeman; mcminis2@uiuc.edu

STERPONE Fabio; f.sterpone@caspur.it

AMBROSETTI Alberto; ambrosetti@science.unitn.it

AMOVILLI Claudio; amovilli@dcci.unipi.it

AUGUSTINSKY Pavel; august@fzu.cz

BALAZ Antun; antun@phy.bg.ac.yu

BAXEVANIS Benjamin; benjamin.baxevanis@physnet.uni-hamburg.de

BERARDI Fulvio; naviglioblu@gmail.com

BORGHI Giovanni; borghi@sissa.it

CARLEO Giuseppe, Roma, Italy CARRASQUILLA ALVAREZ Juan Felipe, jfcarras@unalmed.edu.co
(carrasqu@sissa.it, until 01.11.2009)

CERESOLI Davide; ceresoli@sissa.it

CHEN Shiyou; chensy@fudan.edu.cn (coccia@caspur.it)

CONCEICAO DE SOUZA Andre Mauricio; AMCSOUZA@UFS.BR

CRESPO HERNANDEZ Yanier; crespo@sissa.it (until 31 October 2009)

CUANSING Eduardo Chaves Jr.; cuansinge@dlsu.edu.ph

DAI Zhenxiang; zxdai@theory.issp.ac.cn

DANDREA Lucia; ldandrea@science.unitn.it

DATTA DAS Sumita; sumita@bose.res.in, sumitad@gmail.com

DI TOMMASO Devis; uccaddi@ucl.ac.uk

ESMAEILI SERESHKI Leila; lilyes81@yahoo.com

FILINOV Alexey; filinov@theo-physik.uni-kiel.de (until 1 October 2009)

FLORIO Giuseppe; giuseppe.florio@ba.infn.it

FLORIS Franca Maria; floris@dcci.unipi.it

FONTANA MICHELON Mateus; michelon@ifi.unicamp.br

GANDOLFI Stefano; gandolfi@sissa.it (until 31 December 2009)

GARCIA DE GURTUBAY Idoia; idoia.gurtubay@ehu.es

GENTILE Paola; gentilep@sissa.it

GHOSH Prasenjit; prasenjit@jncasr.ac.in

HARTMANN Peter; hartmann@sunserv.kfki.hu

HEIDARIAN Dariush; dariush@theory.tifr.res.in

HOLZMANN Markus; markus@lptl.jussieu.fr

HUEBENER Robert; robert.huebener@uibk.ac.at

JAFARI Seyed Akbar; sa.jafari@cc.iut.ac.ir, akbar.jafari@gmail.com

KAROLAK Michael; mkarolak@physnet.uni-hamburg.de

KONSTANTINOVA Elena; konst@fisica.ufjf.br

KRYVOHUZ Maksym; maximian@mit.edu

KUCUKBENLI Emine, Turkey

KYLANPAA Ilkka Torsti; ilkka.kylanpaa@tut.fi

LE Duc Thong; ducthong@gmail.com

LEE Mal-Soon; mslee@unipune.ernet.in (until 31 July 2009) LIBERATORE Elisa, Roma, Italy

MADARASZ Adam; madaram@gmail.com

MALEKI Armin; amaleki@sissa.it

MARCHI Mariapia Corrada: marchi@ts.infn.it, marchi@sissa.it

MARTINEZ MESA Aliezer; aliezer@fisica.uh.cu

MATEO VALDERRAMA David; dmateo@ecm.ub.es, david.mateo.v@gmail.com

MAYRHOFER Johannes; JohannesMayrhofer@gmx.at

MIRANDA MENA Joaquin Gabriel; joaquin.miranda@ijs.si

MOHAMMADI ZADEH Mohammad Reza; mohammadi@khayam.ut.ac.ir, zadeh@ut.ac.ir

MONES Letif; molet@enzim.hu

NEEK-AMAL Mehdi; mm_nikamal@yahoo.com

NGUYEN Hoang Tuyen; nguyenhoangtuyen@gmail.com

PEKOZ Rengin; rpekoz@newton.physics.metu.edu.tr

PELLEGRINI Franco, Trieste, Italy

PERDOMO ORTIZ Alejandro; perdomo@fas.harvard.edu

PEZZOLI Maria Elisabetta; pezzoli@sissa.it

RAMANAN Sunethra; suna@cts.iisc.ernet.in

RINGEL Matous; ringel@fzu.cz

SAKHEL Asaad Raji asakhel@hotmail.com, asakhel@fet.edu.jo

SCHIRO' Marco; schirom@sissa.it

SIL Amar Nath; ansil05@gmail.com; amar@mpipks-dresden.mpg.de

SILVI Pietro, Trieste, Italy

SKRBIC Tatjana; skrbic@sissa.it

SUBASI Ahmet Levent; subasi@fen.bilkent.edu.tr

TANASKOVIC Darko; tanasko@phy.bg.ac.yu

TANATAR Bilal; tanatar@fen.bilkent.edu.tr

TOCCHIO Luca Fausto; tocchio@sissa.it

TRAN Huan Doan; tdhuan-iep@mail.hut.edu.vn; tran@magnet.fsu.edu

TYAGI Pawan; ptyag2@uky.edu

URANGA-PINA Llinersy; llinersy@fisica.uh.cu

VARINI Nicola; nicola.varini@gmail.com

VENTURELLI Davide, Trieste, Italy

ZIDI Zouhaier Ben Sellami; zouhaier.zidi@fst.rnu.tn

3.2.2   Report on the 2008 "Computational Physics and Materials Science" - Mini-Workshop in Bonn, Germany

International Workshop on
Computational Physics and Materials Science:
"Progress in Computational Electronic Structure Theory"

10-12 January 2008

Gustav-Stresemann-Institut, Bonn, Germany

Sponsored by:

Forschungszentrum Jülich

European Science Foundation, Psi-k network

Institute for Complex Adaptive Matter

Organizers:

Erik Koch and Eva Pavarini

Institut für Festkörperforschung, FZ-Jülich

Web page:

http://www.i2cam.org/conference/cpest/

The workshop was part of the series of International Workshops on Computational Physics and Materials Science, which started in Oxford (1983) and Braunschweig (1984), and is continued biennially in Trieste (1987, ..., 2007), with mini-workshops in the intervening years (2004: Paris, 2006: Cambridge). The 2008 edition was organized with the help of the Forschungszentrum Jülich at the Gustav-Stresemann-Institut (GSI) in Bonn, Germany.

As the previous workshops, this year's meeting served to survey the state-of-the-art of computational methods for the calculation of the electronic structure of real materials. A special focus was recent progress in the understanding of correlated systems beyond simple model systems. The aim was to bring together practitioners from different parts of the electronic structure community and to enable the exchange of ideas between the fields ranging from method development to applications.

The workshop was attended by 43 participants staying at the GSI plus 8 students commuting from Bonn University and Jülich. Thanks to financial support from the the Forschungszentrum Jülich, the European Science Foundation (ESF) through Psi-k, and the Institute for Complex Adaptive Matter (ICAM), we could cover the local costs of all participants. In addition, with the help of ICAM Junior Travel Awards, we were able to cover the travel expenses of three young participants, a PhD student from China as well as two postdocs, one from Bangladesh and one from the United States.

The program consisted of 20 invited talks (50 minutes with ample time for discussion) that

presented recent advances in the field. The chairs played the key role of stimulating and directing the animated discussions on the work and its perspective in the field. All presentations are available at http://i2cam.org/conference/cpest/. The program also involved a lively poster session with 13 contributions. The GSI, with all facilities (lecture room, accommodation, and cafeteria) located in the same building, proved to stimulate discussions to extend well beyond the regular workshop program.

The talks provided a rich sampling of recent developments in electronic structure theory with a certain focus on new methods for systems with electron correlations.

The first session was devoted to quantum Monte Carlo, where in the context of traditional diffusion Monte Carlo J. Toulouse presented a new approach to wave-function optimization while M. Casula discussed how to deal with non-local pseudopotentials. New developments in determinant-based methods were S. Zhang's auxiliary-field Monte Carlo for ground- and even excited states as well as the continuous-time QMC approach developed by A. Rubtsov, which is establishing itself as the solver of choice for dynamical mean-field theory.

The afternoon was devoted to large systems and surfaces: L. Genovese demonstrated how a wavelet basis can be used for efficient bigDFT calculations. Applications to processes at surfaces were presented by M. Bernasconi, discussing the dynamics of silyl radicals on silicon, D. Alfè, who presented a technique for computing thermal desorption rates and gave an outlook on how to include nuclear quantum effects. Finally J. Behler demonstrated how to treat non-adiabatic effects using constrained DFT.

On friday morning the focus was on excited states. The strength of combining methods for the calculation of optical spectra was demonstrated by O. Pulci for the combination of many-body perturbation theory and molecular dynamics and by R. Gebauer combining time-dependent DFT with Lanczos. Going to finite temperatures, A. Marini showed how to calculate excitons a experimental temperatures, while M. Verstraete presented an extension of the space-time formulation of GW to finite-T, giving applications to metallic systems.

In the afternoon new methods for strongly correlated electrons were discussed. F. Aryasetiawan explained how to determine ab-initio parameters for model Hamiltonians and gave exciting examples. I. Souza demonstrated the amazing accuracy of Wannier interpolation techniques. Focusing on many-body physics, S. Savrasov discussed the locality of the self-energy in real space, which is so central to methods based on dynamical mean-field theory, while M. Potthoff gave an introduction to his new self-energy functionals.

The final session on Saturday was devoted to applications to strongly correlated materials. After a comprehensive overview of the current state-of-the art of the field by A. Lichtenstein, K. Haule discussed how heavy Fermion systems can be realistically modeled. R. Valenti discussed the intricacies of orbital ordering in a frustrated spinel. Going beyond bulk systems, R. Pentcheva presented the interesting physics that makes the interface between two insulators metallic.

Program

Thursday, 10 January 2008

8:45 Welcome

chair: R. Needs

9:00 S. Zhang: *Recent progress in auxiliary-field electronic-structure methods*

9:50 J. Toulouse: *Optimization of quantum Monte Carlo wave functions by energy minimization*

10:40 coffee

11:00 M. Casula: *Diffusion Monte Carlo methods with non-local potentials*

11:50 A. Rubtsov: *Continuous time QMC methods: Applications for DMFT and beyond*

12:40 lunch

chair: X. Gonze

14:30 L. Genovese: *Daubechies wavelets as a basis set for density functional pseudopotential calculations: the BigDFT project*

15:20 M. Bernasconi: *Adsorption, diffusion and decomposition of silyl radicals at clean and hydrogenated Si(100) surfaces by ab-initio simulations*

16:10 coffee

16:40 J. Behler: *Non-adiabatic effects in the oxygen dissociation at the Al(111) surface*

17:30 D. Alfè: *Absolute rate of thermal desorption form first-principles simulations*

20:00 Poster session

Friday, 11 January 2008

chair: X. Gong

9:00 A. Marini: *Ab-initio finite temperature excitons*

9:50 O. Pulci: *Optical spectrum of water: many-body perturbation theory meets molecular dynamics*

10:40 coffee

11:00 R. Gebauer: *A Lanczos-based recursion scheme for the direct calculation of optical spcetra in TD-DFT*

11:50 M. Verstraete: *The GW space-time formalism at finite temperature for metallic systems*

12:40 lunch

chair: D. Vanderbilt

14:30 S. Savrasov: *Are self-energies local? Insights from LDA+DMFT and GW+DMFT*

15:20 M. Potthoff: *Lanczos-based cluster methods for strongly correlated electron systems*

16:10 coffee

16:40 F. Aryasetiawan: *Calculating the Hubbard U from first principles: Constrained RPA*

17:30 I. Souza: *Wannier interpolation and its application to the calculation of anomalous Hall conductivity*

20:00 Conference dinner

Saturday, 12 January 2008

chair: M. Gillan

9:00   A. Lichtenstein: *Spectral density functionals: LDA+DMFT*

9:50   K. Haule: *Modeling the localized-to-itinerant electronic transition in the heavy Fermion system $CeIrIn_5$*

10:40   coffee

11:00   R. Pentcheva: *Compensation mechanisms and functionality of perovskite interfaces*

11:50   R. Valenti: *Orbital order in the frustrated spinel ZnV_2O_4*

Participants

Alfè, Dario	University College London, UK
Aryasetiawan, Ferdi	AIST, Tsukuba, Japan
Behler, Jörg	Ruhr-Universität Bochum, Germany
Bernasconi, Marco	Università di Milano-Bicocca, Italy
Blügel, Stefan	Forschungszentrum Jülich, Germany
Casula, Michele	University of Illinois at Urbana-Champaign, USA
Chen, Shiyou	Fudan University Shanghai, PR China
Dolfen, Andreas	Forschungszentrum Jülich, Germany
Freimuth, Frank	Forschungszentrum Jülich, Germany
Gatti, Matteo	École Polytechnique, France
Gebauer, Ralph	ICTP Trieste, Italy
Genovese, Luigi	CEA Grenoble, France
Gillan, Mike	University College London, UK
Gong, Xingao	Fudan University Shanghai, PR China
Gorelov, Evgeny	Universität Hamburg, Germany
Gonze, Xavier	Université catholique de Louvain, Belgium
Haule, Kristjan	Rutgers University, USA
Heilmann, David	Forschungszentrum Jülich, Germany
Hozoi, Liviu	MPI-PKS, Dresden, Germany
Islam, Fakir Nazrul	University of Rajshahi, Bangladesh
Koch, Erik	Forschungszentrum Jülich, Germany
Lichtenstein, Alexander	Universität Hamburg, Germany
Marini, Andrea	Università di Roma "Tor Vergata", Italy
Monien, Hartmut	Universität Bonn, Germany
Mokrousov, Yuri	Universität Hamburg, Germany
Needs, Richard	Cambridge University, UK
Pavarini, Eva	Forschungszentrum Jülich, Germany
Pentcheva, Rossitza	LMU München, Germany
Potthoff, Michael	Universität Hamburg, Germany
Pulci, Olivia	Università di Roma "Tor Vergata", Italy

Rosner, Helge	MPI-PKS Dresden, Germany
Rubtsov, Alexey	Moscow State University, Russia
Sangiovanni, Giorgio	MPI-FKF Stuttgart, Germany
Savrasov, Sergey	UC Davis, USA
Souza, Ivo	UC Berkeley, USA
Toschi, Alessandro	MPI-FKF Stuttgart, Germany
Toulouse, Julien	Université Pierr et Marie Curie, France
Vanderbilt, David	Rutgers University, USA
Valenti, Roser	Universität Frankfurt, Germany
Verstraete Matthieu	University of York, UK
Wan, Xiangang	UC Davis, USA
Wortmann, Daniel	Forschungszentrum Jülich, Germany
Zhang, Shiwei	College of William and Mary Williamsburg, USA

3.3 Psi-k Workshop/Conference Announcements

3.3.1 International Workshop on Computational Magnetism and Spintronics

**November 03 - 07, 2008, Dresden, Germany**

Scientific Coordinators:

Olle Eriksson (University of Uppsala, Sweden)
Ingrid Mertig (Martin-Luther-Universität Halle-Wittenberg , Germany)
Peter Zahn (Martin-Luther-Universität Halle-Wittenberg, Germany)

Organisation:

Mandy Lochar (MPI PKS Dresden, Germany)
Marita Schneider (MPI PKS Dresden, Germany)

Spintronics and magnetism are currently among the most dynamic research themes in solid state physics. The progress of these topics is impressive and they also branch into wider areas, which include strongly-correlated electron materials, multiferroic materials, and semiconductors, including graphene. The conference is intended to provide an overview of our current understanding of spin phenomena, like spin dynamics and spin Hall effect, both from experiment and theory. The theoretical contributions are devoted particularly to state-of-the-art first-principles calculations. Besides fundamental physical properties of these systems, advances in the design of new materials and device-concepts will be highlighted. The conference is the second of the European series CompMag, opened in Jülich in 2006, and it is co-sponsored by the Psi-k network.
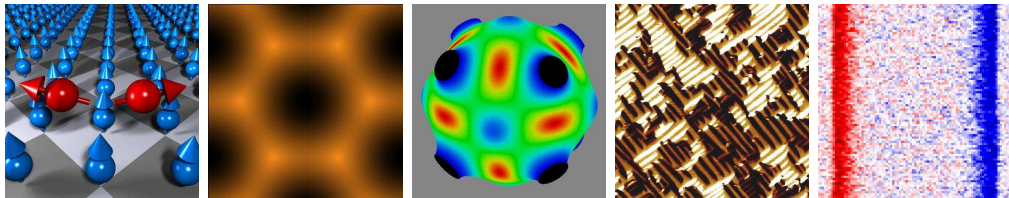
List of Invited Speakers

A. Barthélémy (Palaiseau, France)	S. Blügel (Jülich, Germany)	P. Bruno (Grenoble, France)
K. Dörr (Dresden, Germany)	H. Ebert (Munich, Germany)	C. Ederer (Dublin, Ireland)
C. Heiliger (Gaithersburg, USA)	P. Kelly (Twente, Holland)	M. Katsnelson, (Nijmegen, Holland)
A. Liechtenstein (Hamburg, Germany)	L. Molenkamp (Würzburg, Germany)	R. Nieminen (Helsinki, Finland)
Q. Niu (Austin, USA	L. Nordström, (Uppsala, Sweden)	S. Picozzi (L'Aquila, Italy)
R. Ramesh (Berkeley, USA)	P. Ravindran (Oslo, Norway)	B. Sanyal (Uppsala, Sweden)
K. Sato (Osaka, Japan)	T. Schulthess (Oak Ridge, USA)	J. Sinova (TAMU, USA)
N. Stern (Santa, Barbara, USA)	W. Temmerman (Daresbury, UK)	I. Turek, (Praha, Czech Republic)
B. van Wees (Groningen, Holland)	W. Wulfhekel, (Karlsruhe, Germany)	

Applications are welcome and should be made by using the application form on the web page below. The number of attendees is limited. The registration fee for the conference is 100

Euro. Costs for the accommodation and meals will be covered by the Max Planck Institute. In exceptional cases, funding is available to partially cover travel expenses.

Deadline for applications is August 31, 2008.

For further information please see

`http://www.mpipks-dresden.mpg.de/~ccms08/`
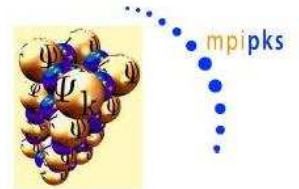
or email to ccms08@mpipks-dresden.mpg.de

Contact address:
Visitors Programme - Marita Schneider & Mandy Lochar
Max-Planck-Institut fü Physik komplexer Systeme
Nöthnitzer Str. 38, D-01187 Dresden, Germany
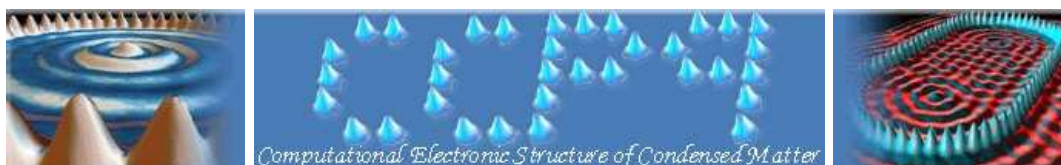Tel.: +49-351-871-2197; Fax: +49-351-871-2199

4 News from UK's CCP9 Programme

UK's Collaborative Computational Project 9 (CCP9) on "Computational Studies of the Electronic Structure of Solids"

4.1 CCP9 Conference Announcement

Cambridge, 4-5 September 2008

General Information

The Conference will be held at Robinson College in Cambridge on 4th and 5th September 2008. The scope of the Conference is all ab-initio and materials specific calculations of the electronic properties of condensed matter systems such as metals, semiconductors, magnets, superconductors, biological systems, minerals, surfaces etc. Topical areas incorporated in the Conference are magno-electronics, catalysis, nanotechnology, high temperature superconductors, novel wide band gap semiconductors etc. Techniques covered by the Conference include QMC, DFT, GW, TD-DFT, DMFT, SIC-LSDA, LSDA+U. We welcome all contributions dealing with the solution of the Schrodinger/Dirac equation in condensed matter systems.

Plenary Speakers

Hardy Gross (FU Berlin, Germany)

Nicola Marzari (MIT, USA)

David Ceperley (University of Illinois, USA)

Gustavo Scuseria (Rice University, USA)

Vladimir Anisimov (Ekaterinberg, Russia)

Invited Speakers

Hubert Ebert (LMU Muenchen, Germany)

Leon Petit (University of Aarhus, Denmark)

Dario Alfe (UCL, UK)

Neil Drummond (University of Cambridge, UK)

Jonathan Yates (University of Cambridge, UK)

Massimiliano Stengel (Santa Barbara, USA)

Marcus Neumann (AVMATSIM)

Robert Laskowski (TU Wien, Austria)

Important Dates

Submission of Abstracts: by 1st July 2008

Registration and Fees: paid by 15th July 2008

Conference Dates: 4th and 5th September 2008

Talks and Posters

We welcome your contributions. Please submit an abstract by 1 July 2008

Registration & Fees

We will open soon an online registration for this event.

Registration Fees are £200 and include two nights accommodation at Robinson College (Wednesday 3rd and Thursday 4th September), all meals and refreshments. Extra accommodation can be booked at the delegates' own expense - please contact Damian Jones (D.R.Jones@dl.ac.uk) to extend your accommodation booking.

A substantial number of Scholarships will be made available from CCP9/Psi-k. These scholarships are especially for UK based young researchers. The Scholarship will take the form of full reimbursement of fees - no support will be provided for travel. If you would like to apply for a Scholarship please tick the relevant box on the online registration form. Successful applicants will be notified by email at the end of July.

Further up-to-date information can be obtained from

`http://www.ccp9.ac.uk/ccp9workshops_2008_cambridge_sept.shtml`

5   General Job Announcements

Postdoctoral Positions

Department of Chemistry and Chemical Biology

Harvard University

The Aspuru-Guzik group (Department of Chemistry and Chemical Biology, Harvard University), in collaboration with Dr. Michael Stopa of the Center of Nanoscale Science (Harvard University) are looking for one or two postdoctoral researchers for the theoretical study of the chemical enhancement in Surface Enhanced Raman Spectroscopy using electronic structure methods. The positions are available immediately, and all things being equal, preference will be given to those with earlier start dates. The researchers will be co-supervised by Drs. Stopa and Aspuru-Guzik.

The postdoctoral researchers will be part of a DARPA-funded collaboration between experiment (Eric Mazur, Ken Crozier, Harvard Univerty) and theory (Stopa, Aspuru-Guzik).

Qualifications required:

- Ph.D. in Theoretical Physical Chemistry, Theoretical Condensed Matter Physics or related discipline obtained at the time of the beginning of the appointment.
- Experience both as a developer and an user of molecular or solid-state electronic structure packages.
- Strong communication skills.
- Strong leadership ability.
- Two letters of recommendation sent to aspuru@chemistry.harvard.edu and stopa@deas.harvard.edu.
- Online application filled at the Aspuru-Guzik group website:

`http://aspuru.chem.harvard.edu/About/Postdoctoral_positions/`

Please mention this ad in the cover letter.

We have a preference for people with previous experience in computational spectroscopy, but all qualified applicants are welcome.

Alan Aspuru-Guzik
Assistant Professor
Department of Chemistry and Chemical Biology
12 Oxford Street
Harvard University
Cambridge, MA 02138

Tel: (617)384-8188
Group URL: http://aspuru.chem.harvard.edu

PhD Position in Theoretical Chemistry

Center for Theoretical Chemistry, Ruhr-University Bochum, Germany

A PhD fellowship in theoretical chemistry is available at the Ruhr-University in Bochum. The work will involve the use of density-functional theory and the development of modern methods for the construction of potential-energy surfaces. The potentials will be applied to describe structural and mechanistic aspects of complex chemical reactions at metal surfaces in the context of heterogeneous catalysis. A close collaboration with international experimental and theory groups is part of the project. The candidate will work in a motivated team and will benefit from the excellent working environment and computational equipment of the Center for Theoretical Chemistry.

Please send your application including CV (preferably by email) to

Dr. Jörg Behler
Lehrstuhl für Theoretische Chemie
Ruhr-Universität Bochum
D-44780 Bochum
Germany
Email: joerg.behler@theochem.rub.de

Consideration of candidates will begin immediately and continue until the position is filled. The University particularly welcomes applications from women.

PhD Studentship

Max Planck Institute of Microstructure Physics, Halle (Saale), Germany

At the Theory Department of the Max Planck Institute of Microstructure Physics in Halle (Saale), Germany, a **position for a PhD student** in the field of **Magnetoelectric Coupling in Multiferroic Heterostructures** is available immediately. The position is associated with the project B2 of the Collaborative Research Initiative (*Sonderforschungsbereich*) 762, 'Functionality of Oxidic Interfaces' of the German Research Society (*Deutsche Forschungsgemeinschaft*; for details, `http://www.physik.uni-halle.de/sfb762/`).

The aim of the project is to understand the magnetoelectric effect at interfaces between ferroelectric and ferromagnetic materials on a microscopic scale, using methods of Computational Physics.

The Max Planck Institute of Microstructure Physics is an internationally highly competitive institution. For details, see `http://www.mpi-halle.mpg.de/~theory`. The MPI is embedded in a stimulating environment, comprising in particular the International Max Planck Research School for Science and Technology of Nanostructures and the Martin Luther University Halle-Wittenberg. The graduation will be at the Martin Luther University Halle-Wittenberg.

The Max Planck Society is interested in increasing the proportion of women among its scientists and strongly encourages women to apply to the position. Applications from disabled candidates are encouraged and will be given priority in case of equal qualification.

An application, to be sent by electronic mail as a single pdf file to PD Dr. Jürgen Henk, should include a cover letter, a resume, and a statement of qualifications relevant for the position. Applications will be scanned until the position is filled.

Contact: PD Dr. Jürgen Henk, Theory Department, Max Planck Institute of Microstructure Physics, Weinberg 2, D-06198 Halle (Saale), Germany. Electronic address: `henk@mpi-halle.de`.

Postdoc Position/Research Associate Position:
Quantum Simulation of Complex Molecular Systems
Center for Theoretical Chemistry, University of Bochum, Germany

Applications are invited for a research associate position that is expected to become available in early Summer 2008.

The ideal candiate should have significant experience in path integral MC/MD methods, electronic structure calculations, and computer simulation techniques. A PhD in theoretical chemistry or physics is required.

The position is focused on applying and improving our novel ab initio Quantum Monte Carlo technique based on path integrals and will strongly benefit from collaborations with experimental groups. In addition, you are most welcome to get involved in other challenging research projects including both method development and large-scale applications.

Information on the techniques used and developed at CTC is accessible via

http://www.theochem.rub.de/go/cprev.html.

The Center for Theoretical Chemistry at RUB offers an exciting interdisciplinary research environment and excellent facilities including several high-performance parallel platforms in house, see www.theochem.rub.de/go/jobs.html.

Candidates should send a detailed resume including an outline of their research achievements and interests as well as contact information to obtain academic references to:

```
Professor Dominik Marx
Lehrstuhl fuer Theoretische Chemie
Ruhr-Universitaet Bochum
44780 Bochum, Germany
Email: office@theochem.rub.de
```

Consideration of candidates will begin immediately and continue until the position is filled. The University particularly welcomes applications from women.

Junior Research Group Leader/Research Associate Position:
Ab Initio Biomolecular Simulation
Center for Theoretical Chemistry, University of Bochum, Germany

Applications are invited for a research associate position starting in mid 2008 or later. Depending on the applicant there will be the opportunity for establishing a Junior Research Group and for academic qualification in the framework of Habilitation.

The ideal candidate should have significant experience in electronic calculations of complex biomolecular systems and reactions, including preferentially multiscale QM/MM–type approaches. A PhD in theoretical physics or chemistry is required, as well as research experience as a postdoc. She or he will be involved in a number of challenging projects in the realms of ab initio biomolecular simulation (see e.g. some of our recent papers: JACS Commun. **130**, (2008) 2768; PNAS **104** (2007) 20725; PNAS **104** (2007) 6980; JACS **128** (2006) 13815).

Information on the techniques used and developed at CTC is accessible

http://via www.theochem.rub.de/go/cprev.html.

The Center for Theoretical Chemistry at RUB offers an exciting interdisciplinary research environment and excellent facilities including several high-performance parallel platforms in house, see

http://www.theochem.rub.de/go/jobs.html.

Candidates should send a detailed resume including an outline of their research achievements and interests as well as contact information to obtain academic references to:

```
Professor Dominik Marx
Lehrstuhl fuer Theoretische Chemie
Ruhr-Universitaet Bochum
44780 Bochum, Germany
Email: office@theochem.rub.de
```

Consideration of candidates will begin immediately and continue until the position is filled. The University particularly welcomes applications from women.

PhD Studentship

"Atomistic Simulation of H-Storage Materials"
University of Salford, UK

A fully funded EPSRC studentship is available within the Institute for Materials Research at the University of Salford

(http://www.imr.salford.ac.uk/)

in the general area of first principles atomistic modelling of materials. The funding is for four years and incorporates study and training at the Edinburgh Parallel Computer Centre (EPCC) that will lead to the award of an MSc in High Performance Computing as well as the Salford PhD.

The project will participate in the UKCP consortium

(http://www.cse.scitech.ac.uk/cmg/NETWORKS/UKCP/)

of 15 leading UK Chemistry, Physics and Materials departments for large-scale simulations of materials on HECToR (www.hector.ac.uk), the new 11328-processor UK national supercomputer.

The project will use first principles quantum mechanical simulation methods as employed in the castep code (www.castep.org). Specifically the project will be concerned with implementation and application of methods to simulate diffusion processes in novel hydrogen storage materials. This research is being done as part of the European project NESSHY

(http://www.nesshy.net/).

Applications are invited from holders of a first degree in all areas of the physical sciences. The studentship is open to all EU nationals.

Please contact Prof. Ian Morrison (email: i.morrison@salford.ac.uk, Tel +44 161 2955303) for informal enquiries. Applicants should submit a CV in the first instance.

Prof. Ian Morrison
Joule Physics Laboratory and Institute for Materials Research
University of Salford, Salford, M5 4WT, UK
tel: +44 161 2955303
mobile: +44 7974795056
email: i.morrison@salford.ac.uk

6 Abstracts

Electronic structure investigation of the exchange-spring behavior during the magnetic reversal process

V.M. Uzdin

Departamento de Física Teórica, Atómica y Óptica, Universidad de Valladolid,
E-47011 Valladolid, Spain
St. Petersburg State University, Universitetskaya nab. 7/9,
St. Petersburg, 199178 Russia

A. Vega

Departamento de Física Teórica, Atómica y Óptica, Universidad de Valladolid,
E-47011 Valladolid, Spain

Abstract

We present an atomic scale quantum-mechanical theory based on a non-collinear Tight-Binding formalism for self-consistent calculations of electronic and magnetic structure of d-metallic systems in an external magnetic field. The theory is applied to the description of the magnetic reversal process in exchange spring magnets with Fe as the soft magnetic material. From the magnetic spin configuration obtained through the electronic structure calculation in different external fields, we have determined the average magnetic moment and the reversible part of the hysteresis loop. The calculations reproduce all the main features of the exchange spring behavior. The theory is suitable for the study of more complex systems with interface roughness, interdifussion and non-coplanar magnetic ordering.

Interface magnetism in Fe_2O_3/$FeTiO_3$-heterostructures

Rossitza Pentcheva and Hasan Sadat Nabi

Department of Earth and Environmental Sciences, University of Munich,

Theresienstr. 41, 80333 Munich, Germany

Abstract

To resolve the microscopic origin of magnetism in the Fe_2O_3/$FeTiO_3$-system, we have performed density functional theory calculations taking into account on-site Coulomb repulsion. By systematically varying the concentration, distribution and charge state of Ti in a hematite host, we compile a phase diagram of the stability with respect to the end members and find a clear preference to form layered arrangements as opposed to solid solutions. The charge mismatch at the interface is accommodated through Ti^{4+} and a disproportionation in the Fe contact layer into Fe^{2+}, Fe^{3+}, leading to uncompensated moments in the contact layer and giving first theoretical evidence for the *lamellar magnetism hypothesis*. This interface magnetism is associated with impurity levels in the band gap showing halfmetallic behavior and making Fe_2O_3/$FeTiO_3$ heterostructures prospective materials for spintronics applications.

An Improved Real–Space Genetic Algorithm for Crystal Structure and Polymorph Prediction

N.L. Abraham and M.I.J. Probert

Department of Physics, University of York, Heslington, York, YO10 5DD, UK

Abstract

Existing Genetic Algorithms for crystal structure and polymorph prediction can suffer from stagnation during evolution, with a consequent loss of efficiency and accuracy. An improved Genetic Algorithm (GA) is introduced herein which penalizes similar structures and so enhances structural diversity in the population at each generation. This is shown to improve the quality of results found for the theoretical prediction of simple model crystal structures. In particular, this method is demonstrated to find three new zero–temperature phases of the Dzugutov potential that have not been previously reported.

Reduced band-gap due to phonons in SrTiO$_3$ analyzed by ab initio calculations

Wilfried Wunderlich

Tokai University, Graduate School of Engineering, Material Science Department,
259-1292 Kanagawa-ken, Hiratsuka-shi, Kitakaname 1117, Japan

Abstract

Phonons change remarkable the interatomic bond length in solids and this work suggest a novel method how this behavior can be displayed and analyzed. The bond length spectrum is plotted for each of the different atomic bonding types. When comparing the bond length to an undeformed crystal by the so-called difference bond length spectrum, the effect of phonons is clearly visible. The Perovskite lattice of SrTiO$_3$ is used as an example and several lattice vibration modes are applied in a frozen phonon calculation in a 2 2 2 supercell. Ab initio DFT simulations using the Vasp software were performed to calculate the density of states. The results show the important finding reported here first, that certain phonon interactions with shorter Ti-O bonds decrease the band-gap, while changes in the Sr-Ti bond length enlarge the band-gap.

Popular density functionals strongly overestimate many-body interactions in van der Waals systems

Alexandre Tkatchenko

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6,
D-14195 Berlin-Dahlem, Germany

O. Anatole von Lilienfeld

Multiscale Dynamic Materials Modeling Department, Sandia National Laboratories,
Albuquerque, New Mexico 87185-1322, USA

Abstract

We find spuriously large repulsive many-body contributions to binding energies of rare gas systems for all rungs of "Jacob's Ladder" within Kohn-Sham density functional theory. While the description of van der Waals dimers is consistently improved by the pairwise London $C_6 R^{-6}$ correction inclusion of a corresponding threebody Axilrod-Teller C9/R9 term only increases the repulsive error. Our conclusions, based on extensive solid state and molecular electronic structure calculations, are particularly relevant for condensed phase van der Waals systems.

Theory of Ultrafast Dynamics of Electron-Phonon Interactions in Two Dimensional Electron Gases: Semiconductor Quantum Wells, Surfaces and Graphene

Marten Richter, Stefan Butscher, Norbert Bücking, Frank Milde, and Andreas Knorr

Institut für Theoretische Physik, Technische Universität Berlin,
Hardenbergstr. 36, 10623 Berlin, Germany

Carsten Weber

Mathematical Physics, Lund University, Box 118, 22100 Lund, Sweden

Peter Kratzer

Fachbereich Physik, Universität Duisburg-Essen,
Lotharstr. 1, 47048 Duisburg, Germany

Matthias Scheffler

Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Faradayweg 4–6, 14195 Berlin, Germany

Abstract

Two-dimensional semiconductors are ideal model systems for investigating the dynamics of the electron-phonon interaction under spatial confinement of electronic excitations. In this contribution, the simultaneous quantum dynamics of electrons and phonons on ultrafast timescales is theoretically addressed. Typical examples include the ultrafast electron transfer at silicon surfaces, optical intersubband transitions in doped quantum wells, and non-equilibrium phonon generation in graphene.

Phonon transmission through defects in nanotubes from first principles

N. Mingo[1,2], D. A. Stewart[2], D. A. Broido[3], and D. Srivastava[2]

(1) CEA-Grenoble, 17 Rue des Martyrs, Grenoble 38054, France

(2) Department of Electrical Engineering, University of California,
Santa Cruz, CA 95064, USA

(3) Cornell Nanoscale Facility, Cornell University, Ithaca, NY, 14853, USA

(4) Department of Physics, Boston College, Chestnut Hill, MA 02467, USA

Abstract

We compute the effect of different isolated defects on the phonon transmission through carbon nanotubes, using an ab initio density functional approach. The problem of translational and rotational invariance fulfillment in the nonperiodic system is solved via a Lagrange-multiplier symmetrization technique. The need for an ab initio approach is illustrated for the case of phonon transmission through a nitrogen substitutional impurity, for which no reliable empirical interatomic potentials exist. This opens an avenue for the accurate parameter-free study of phonon transport through general systems with arbitrary composition and structure, without any need for semiempirical potential descriptions.

Ab-initio investigation of phonon dispersion and anomalies in palladium

Derek A. Stewart

Cornell Nanoscale Facility, Cornell University, Ithaca, NY 14853, USA

Abstract

In recent years, palladium has proven to be a crucial component for devices ranging from nanotube field effect transistors to advanced hydrogen storage devices. In this work, I examine the phonon dispersion of fcc Pd using first-principle calculations based on density functional perturbation theory (DFPT). While several groups in the past have studied the acoustic properties of palladium, this is the first study to reproduce the full phonon dispersion and associated anomaly in the [110] direction with high accuracy and no adjustable parameters. I will show that the [110] anomaly is a Kohn anomaly due to electron−phonon interactions and that paramagnons play no significant role in the [110] phonon dispersion.

Ab-initio study of polarizability and induced charge densities in multilayer graphene films

Eric K. Yu[1], Derek A. Stewart[2], and Sandip Tiwari[1]

(1)Department of Electrical and Computer Engineering, Cornell University, Ithaca, NY 14853

(2)Cornell Nanoscale Facility, Cornell University, Ithaca, NY 14583, USA

Abstract

We present an ab initio analysis of polarization of multilayer graphene systems under applied electric fields. The effects of applied electric fields are calculated using a Berry phase approach within a plane-wave density functional formalism. We have determined polarizability values for graphene films and carbon nanotubes and found that the polarizability of graphene films follows a linear relationship with the number of layers. We also examined changes in the induced charge distribution as a function of graphene layers. We focus, in particular, on the bilayer graphene system. Under applied electric fields, we found the Mexican hat band structure near the K point reported by previous groups. We found that the induced charge primarily accumulated on the B sublattice sites. This observation is supported by additional calculations with a tight-binding Green's function model. By examining the local density of states at the Fermi energy, we found a high density of states at the B sites at the Fermi energy. In contrast, coupling between A sites in neighboring graphene layers leads to negligible density of states at the Fermi level. This high density of states at the B sites results in greater induced charge under applied electric fields. This scenario of preferential induced charge on the B sublattice sites under applied electric fields could impact the stability of atoms and molecules absorbed on bilayer graphene.

Intrinsic lattice thermal conductivity of semiconductors from first principles

D. A. Broido[1], M. Malorny[2], G. Birner[2], N. Mingo[3], and D. A. Stewart[4]

(1) Department of Physics, Boston College, Chestnut Hill, MA 02467, USA

(2) Department of Physics, University of Regensburg,

D−93040 Regensburg, Germany

(3) CEA-Grenoble, 17 Rue des Martyrs, Grenoble 38054, France

& Department of Electrical Engineering, University of California,

Santa Cruz, CA 95064, USA

(4) Cornell Nanoscale Facility, Cornell University, Ithaca, NY, 14853, USA

Abstract

We present an *ab initio* theoretical approach to accurately describe phonon thermal transport in semiconductors and insulators free of adjustable parameters. This technique combines a Boltzmann formalism with density functional calculations of harmonic and anharmonic interatomic force constants. Without any fitting parameters, we obtain excellent agreement ($<5\%$ difference at room temperature) between the calculated and measured intrinsic lattice thermal conductivities of silicon and germanium. As such, this method may provide predictive theoretical guidance to experimental thermal transport studies of bulk and nanomaterials as well as facilitating the design of new materials.

7 SCIENTIFIC HIGHLIGHT OF THE MONTH: "Electronic Excitations in Nanostructures: An Empirical Pseudopotential based Approach

---

Electronic Excitations in Nanostructures: An Empirical Pseudopotential based Approach

Gabriel Bester

Max-Planck Institut für Festkörperforschung, Heisenbergstr. 1, D-70569 Stuttgart

Abstract

Physics at the nanoscale has emerged as a field where discoveries of fundamental physical effects lead to a greater understanding of the solid state. This area of research is additionally driven by high hopes for technological relevance and a high pace of experimental achievements in fabrication and characterization has been witnessed in the last decade. From the side of theoretical modeling —so successful in solid state physics in general, since the emergence of density functional theory— we must acknowledge a weak connection to state of the art experimental achievements in the realm of nanostructures. The cause for this partial disconnect resides in the difficulty of the matter. Nanostructures being small in size but large in the number of atoms constituting them, and the relevant observables being accessible only through proper treatment of excitations. The large number of atoms and the need for excited sate properties makes this a challenging task for theory and modeling.

In this contribution we will outline the framework, based on empirical pseudopotentials and configuration interaction, to obtain quantitative predictions of the excited state properties of semiconductor nanostructures using their experimental sizes, compositions and shapes. The methodology can be used to describe colloidal nanostructure of few hundred atoms all the way to epitaxial structures requiring millions of atoms. The aim is to fill the size gap existing between *ab initio* approaches and continuum descriptions. Based on the pseudopotential idea and the developments of empirical pseudopotentials for bulk materials in the early 60's, the method has evolved into a powerful tool where the pseudopotential construction has lost some of its empirical character and is now based on modern density functional theory. We will present the construction of these potentials and the way the ensuing wave functions are used in a subsequent configuration interaction treatment of the excitation. We will illustrate the available capabilities by recent applications of the methodology to unveil new effects in the optics of nanostructures, quantum entanglement and wave function imaging.

1 Introduction

The new class of materials formed by semiconductor nanostructures has a **large and mostly unexplored ensemble of possible applications**. For instance, colloidal semiconductor nanostructures are used today in biology and medicine as light-emitting markers that remain inert in the bio-environment. They can help to resolve structures and processes within the cells and can tag body substances. In the area of *classical* information science and technology they have a strong potential for providing efficient tunable light sources and light detectors. In general, optoelectronics could profit from the developments of semiconductor nanostructures. Following a rather long-term goal, in the area of *quantum* information science and technology (towards the realization of single-photon sources, sources of entangled photons, or quantum gates and register all the way to a quantum computer), the use of quantum dots is one of the most promising concepts and is lead by a world-wide effort.

As a general remark one could note that the field of nanostructure science is driven by a high pace of experimental achievements. Experimentalists are now able to grow nanostructures of high quality from **diverse semiconductor materials** [1] with the ability to dope them [2–9]. The area of characterization reveals increasingly **complex behavior**, including the appearance of high-energy excited excitons [10], charged excitons [11], multi excitons [12], exchange-induced splittings [13], Coulomb blockade in addition spectra [14, 15], spin blockade [16], quantum entanglement [17], enhancement of electron-hole exchange interactions [18], carrier relaxation and multiplication via Auger processes [19], and the observation of quasiparticle wave functions through magnetotunneling experiments [20] and scanning tunneling microscopy [3, 21, 22].

Nanostructures have therefore potential for applications, they cover a diverse set of materials and structures, and they revel complex behavior revealed through a growing number of characterization methods leading to interesting and fundamental physical effects. At this point we should emphasize that the nanometer-scale that is the focus of *nanotechnology* describes structures with dimensions of several nanometers up to hundreds of nanometers. While these structures are "small" they do comprise thousands up to hundred thousands of atoms. In short: **nanometer-scale means thousands of atoms.** Smaller structures are referred to as *clusters* and are often of poor quality, showing broad size and shape distributions, poor surface passivations and optical properties. We must conclude that to address the relevant size regime and the relevant physical observables, we need to be able to address a large number of atoms, including excitations and many-body effects.

The current status of theoretical capabilities for describing the electronic and optical properties of semiconductor nanostructures is as follows. Optical properties can be calculated from atomistic **first-principles** (Quantum Monte Carlo, time-dependent density functional theory, GW and Bethe Salpeter,...) for nanosystems containing few to 200 atoms (depending on the level of approximation). Pending a revolutionary change in our current approach to many body physics, extensions of these approaches are unlikely to be able to address the size regime described above. However, the development of first principles *ab initio* methods is important since it gives many insights into the physics in strong confinement and can often be used as benchmark. **Continuum models** such as effective-mass and $\mathbf{k} \cdot \mathbf{p}$ [23], can handle macroscopic nano systems but fail to address nanostructure where atomistic effects become important [24–26]. **Empirical**

Tight binding models [27, 28] can presently deal with millions of atoms but lack atomistic wave functions (since the Hamiltonian is directly parametrized) which constitute the essence of the many-body problem.

In this contribution we will present the empirical- and semiempirical-pseudopotential methods that can be used in conjunction with configuration interaction to obtain many-body wave functions of structures with millions of atoms. More than the bare empirical pseudopotential construction, we will survey the different steps that can lead to the calculation of the observables relevant to modern experiments, using the experimental nanostructure geometry. We will conclude by presenting three recent applications of the developed formalism.

2 Method

A summary of the methodology is given in Figure 1 in the form of a flowchart summarizing the different components of our current approach. Figure 1 is divided into three logical segments, labelled as *Ground State*, *Excitations* and *Observables*, feeding into each other. The calculation of the ground state requires the input of the geometry and relaxation of the atomic positions to minimize strain. The generation of empirical pseudopotentials is the prerequisite for the construction of the total crystal potential that is subsequently used in the Schrödinger equation. The ensuing eigenfunctions are fed into a configuration interaction treatment to obtain excitations. Finally, from the many-body wave functions, observables can be obtained through the use of post processor tools. These different components will be introduced by using Figure 1 as the thread of the discussion.

2.1 Input geometry and geometry relaxation

In the first step of the flowchart in Fig. 1, *Input Geometry*, we construct a supercell containing the nanostructure. The shape, size and composition are taken as initial input from experiments and the atoms are placed, at first, on a regular grid representing an initial guess for the final atomic positions to be obtained in the next step. The atoms within the supercell are then allowed to relax in oder to minimize the strain energy. In most cases, the system of interest is too large to be handled by standard density functional theory and we make use of a classical atomistic force field model [29–31], the Valence Force Field (VFF) method, including bond bending, bond stretching and bond bending-bond stretching interactions:

$$
\begin{aligned}
E_{VFF} &= \sum_i \sum_j^{nn_i} \frac{3}{8}[\alpha_{ij}^{(1)}\Delta d_{ij}^2 + \alpha_{ij}^{(2)}\Delta d_{ij}^3] + \sum_i \sum_{k>j}^{nn_i} \frac{3\beta_{jik}}{8d_{ij}^0 d_{ik}^0}[(\mathbf{R}_j - \mathbf{R}_i) \cdot (\mathbf{R}_k - \mathbf{R}_i) \\
&- cos\theta_{jik}^0 d_{ij}^0 d_{ik}^0]^2 + \sum_i \sum_{k>j}^{nn_i} \frac{3\sigma_{ijk}}{d_{ik}^0}\Delta d_{ij}[(\mathbf{R}_j - \mathbf{R}_i) \cdot (\mathbf{R}_k - \mathbf{R}_i) - cos\theta_{jik}^0 d_{ij}^0 d_{ik}^0] \quad , (1)
\end{aligned}
$$

where $\Delta d_{ij}^2 = \left[[(R_i - R_j)^2 - d_{ij}^{0\,2}]/d_{ij}^0\right]^2$. Here $\mathbf{R}_i$ is the coordinate of atom i and d_{ij}^0 is the ideal (unrelaxed) bond distance between the atoms i and j. Also, θ_{jik}^0 is the ideal (unrelaxed) angle of the bond angle $j - i - k$. The $\sum^{nn_i}$ denotes summation over the nearest neighbors of atom i. The bond stretching, bond angle bending, and bond-length/bond-angle interaction coefficients
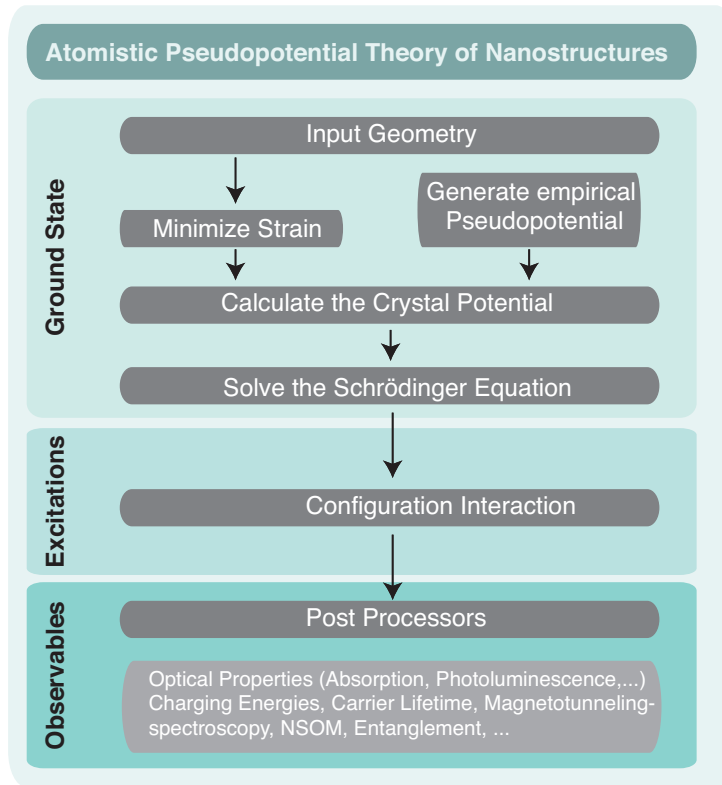
Figure 1: Flowchart of the methodology underlying the atomistic calculation of various observables for semiconductor nanostructures. The flowchart is divided into three logical sections: Ground State, Excitations (many-body part), and Observables. The different computational parts are described in the text.

$\alpha_{ij}^{(1)} (\equiv \alpha)$, β_{jik}, σ_{jik} are directly related to the elastic constants in a pure zincblende structure [32]. The second-order bond stretching coefficient $\alpha^{(2)}$ is related to the pressure derivative of the Young's modulus by $\frac{dB}{dP}$, where $B = (C_{11} + 2C_{12})/3$ is the Young's modulus.

An atomic force field is similar to continuum elasticity approaches [30] in that both methods are based on the elastic constants, $\{C_{ij}\}$, of the underlying bulk materials. However, atomistic approaches are superior to continuum methods in two ways, (a) they can contain anharmonic effects, and (b) they capture the correct point group symmetry. The calculation of the energy and forces from expressions such as Eq. (1) can be performed within seconds for millions of atoms, allowing for a manageable strain minimization of large nanostructure.

2.2 Pseudopotentials

It is advantageous to split the electrons into core and valence electrons. The valence electrons occupy the outer shells and interact with the potentials of the neighboring atoms. They are responsible for the interatomic binding, in contrast to the atom-localized core electrons. In the *frozen core* approximation, the core electrons are assumed to be unperturbed by their environment and the Schrödinger equation has to be solved only for the valence electrons. The assumption that the core electrons are independent of their surroundings is poorly fulfilled [33], but the change in energy vanishes in the first order of density change [33,34] making this approximation practical. The frozen core approximation is the founding assumption of pseudopotentials.

The Pauli principle requires from the valence wave functions to be orthogonal to the core wave functions leading to valence wave functions that are fast oscillating in the core region with high kinetic energy. This behavior can be pictured with a virtual repulsive potential at the ion cores. It turns out that this repulsion is nearly perfectly compensated by the attractive core potential, both effects leading to a weak effective potential acting on the valence electrons[1].

Following the formulation of Phillips and Kleinman [35] the formal justification of pseudopotentials can be given as follows. $|\psi\rangle$ represents the valence wave functions and $\{|\chi_n\rangle\}$ the core wave functions with eigenvalues $\{E_n\}$. The aim is to construct a node-free pseudo–wave function $|\phi\rangle$. Initially, we assume:

$$|\psi\rangle = |\phi\rangle + \sum_n c_n |\chi_n\rangle \quad . \tag{2}$$

From the orthonormality relation we obtain:

$$\langle \chi_n |\psi\rangle = 0 = \langle \chi_n |\phi\rangle + c_n \longrightarrow c_n = -\langle \chi_n |\phi\rangle \tag{3}$$

and

$$|\psi\rangle = |\phi\rangle - \sum_n |\chi_n\rangle\langle \chi_n |\phi\rangle \quad . \tag{4}$$

This expression for the valence wave functions is used in the Schrödinger equation $\widehat{H}|\psi\rangle = E|\psi\rangle$:

$$\widehat{H}|\psi\rangle = \widehat{H}|\phi\rangle - \sum_n \widehat{H}|\chi_n\rangle\langle \chi_n |\phi\rangle = \widehat{H}|\phi\rangle - \sum_n E_n |\chi_n\rangle\langle \chi_n |\phi\rangle = E|\psi\rangle \tag{5}$$

$$= E|\phi\rangle - \sum_n E|\chi_n\rangle\langle \chi_n |\phi\rangle \quad , \tag{6}$$

and the terms are rearranged:

$$\widehat{H}|\phi\rangle + \sum_n (E - E_n)|\chi_n\rangle\langle \chi_n |\phi\rangle = E|\phi\rangle \quad . \tag{7}$$

The node-free pseudo–wave functions fulfill a Schrödinger equation with an additional energy dependent non-local pseudopotential $\widehat{V}_{nl}$:

$$\widehat{T}|\phi\rangle + \left\{ \widehat{V} + \underbrace{\sum_n (E - E_n)|\chi_n\rangle\langle \chi_n|}_{\widehat{V}_{nl}} \right\}|\phi\rangle = E|\phi\rangle \quad , \tag{8}$$

where $\widehat{H}$ has been split into kinetic $\widehat{T}$ and potential $\widehat{V}$ terms. The expression in curly brackets is the pseudopotential, which is made of a positive attractive part $\widehat{V}$ and a negative repulsive part $\widehat{V}_{nl}$. The eigenvalues of the Schrödinger equation for the real– and the pseudopotential are identical since Eq. (7) can be rewritten as:

$$\langle \psi |H|\phi\rangle + \sum_n (E - E_n)\langle \psi |\chi_n\rangle\langle \chi_n |\phi\rangle = E\langle \psi |\phi\rangle \quad , \tag{9}$$

and the core and valence states must be orthogonal: $\langle \psi |\chi_n\rangle = 0$.

The pseudopotential at this point is not necessarily soft since $\widehat{V}_{nl}$ includes core states but it is not unique, since $(E - E_n)$ can be arbitrarily replaced. This non-uniqueness will be used to generate

---

[1]This compensation is only effective when electrons with the angular momentum of the valence electrons are present in the core. A lack of thereof lead to strong (or hard) pseudopotentials.

soft pseudopotentials. The pseudopotential is also non-local since the projector $|\chi_n\rangle\langle\chi_n|$ applied on the pseudo-wave functions yields a volume integration $|\chi_n\rangle\langle\chi_n|\phi\rangle$. The pseudopotential also depends on energy and acts mainly in the core region.

At this point where we have established the partial cancellation of attractive and repulsive parts of the potential [35, 36] and given a formal derivation for weak pseudopotentials, there are two possible routes.

- The construction of ionic pseudopotentials where the interaction of valence electrons is explicitly taken into account. This route has been very successful, especially when *ab initio* calculations for the atom have been used to construct transferable and accurate pseudopotentials. One of the requirements for such pseudopotentials is to deliver pseudo-wave functions identical to the real all-electron wave functions outside of a certain cut-off radius. This guarantees to obtain accurate binding properties. There are several implementations of ionic pseudopotentials starting with norm-conserving pseudopotentials where the generalized eigenvalue problem of Eq. (8) (the pseudo-wave function are not orthogonal, Eq. (4)) is transformed to a standard eigenvalue problem where the pseudo-eigenfunctions satisfy the orthonormality condition. The norm conservation guarantees that the important scattering properties only change in second order with a change in energy [37–40] which is the key ingredient for the good transferability of these potentials. The most common construction procedures are due to Vanderbilt [41], Hamann, Schlüter and Chiang [40, 42] , Troullier and Martins [43], and von Kerker [44]. Another type of ionic pseudopotentials are *ultrasoft pseudopotentials (US)* [45, 46] where the norm-conservation is not explicitly required for the pseudo valence wave functions at the expense of introducing an auxiliary function acting at the ionic cores. Yet another type of ionic pseudopotentials are used in the *projector augmented waves (PAW)* [47] method. Like for ultrasoft pseudopotentials, projectors and auxiliary functions are introduced but the all-electron wave function is kept. This involves in the calculation of the integrals smooth functions extending outside the core region and functions localized inside of muffin-tin spheres.

- The construction of total pseudopotentials that include the interaction of not only the core electrons but of all electrons. This is the route taken in the construction of empirical and semiempirical pseudopotentials, as described in the next section.

2.3 Empirical pseudopotentials and their construction

The empirical pseudopotential method (EPM) (see Ref. [48] and references therein for a more detailed review of the method and a historical introduction) involves a fit of the reciprocal space pseudopotential $V(\mathbf{G})$ to experimentally known quantities, such as certain points of the band structure. The first assumption is that the self-consistent effective pseudopotential of the crystal (we use capital V for crystal potentials and lower-case v for atomic potentials) can be written as a sum of atom-centered pseudopotentials:

$$V(\mathbf{r}) \quad = \quad \sum_{\alpha,j,n} v_\alpha(\mathbf{r} - \mathbf{R}_n - \mathbf{r}_{\alpha,j}) \quad , \tag{10}$$

where n is the index for the primitive unit cells and $\mathbf{R}_n$ the corresponding lattice vector. α stands for the atom type and j is the atom index. $\mathbf{r}_{\alpha,j}$ is therefore the basis vector for the atom

j of type α. Simplifying, at first, to a crystal with only one type of atoms (e.g. Si), v, we can write the potential in reciprocal space as

$$V(\mathbf{r}) \;=\; \sum_{\mathbf{G}} v(\mathbf{G}) S(\mathbf{G}) e^{i\mathbf{Gr}} \quad , \tag{11}$$

with the structure factor

$$S(\mathbf{G}) = \frac{1}{n} \sum_{j} e^{-i\mathbf{Gr_j}} \quad , \tag{12}$$

where n is the number of basis atoms. The structure factor only depends on the geometry. The potential $v(\mathbf{G})$, also called the form factor, is treated in the EPM as disposable parameter.

To illustrate the practical implications of this formalism, we take the example of Si in the diamond structure. The lattice vectors in real and reciprocal space are given by $\mathbf{A}$ and $\mathbf{B}$ and the vectors of the two basis atoms by $\mathbf{r}$ and $-\mathbf{r}$:

$$\mathbf{A} = \frac{a_0}{2} \begin{pmatrix} 1 & 1 & 0 \\ 0 & 1 & 1 \\ 1 & 0 & 1 \end{pmatrix} \quad , \quad \mathbf{B} = \frac{2\pi}{a_0} \begin{pmatrix} 1 & 1 & -1 \\ -1 & 1 & 1 \\ 1 & -1 & 1 \end{pmatrix} \quad , \quad \mathbf{r} = \frac{a_0}{8} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \quad . \tag{13}$$

In this case, the structure factor from Eq. (12) simplifies to

$$S(\mathbf{G}) = \cos(\mathbf{G} \cdot \mathbf{r}) \quad . \tag{14}$$

A few reciprocal lattice vectors sorted according to their length are given in Table 1. According

Table 1: Reciprocal lattice vectors $\mathbf{G}$ with smallest length in diamond structure with lattice constant a_0.

$\frac{a_0}{2\pi}\mathbf{G}$	$\left(\frac{a_0}{2\pi}\mathbf{G}\right)^2$	$\mathbf{G} \cdot \mathbf{r}$
000	0	0
{111}	3	$3\pi/4$
{200}	4	$\pi/2$
{220}	8	π
{311}	11	$5\pi/4$

to Eq. (14) and Table 1 the structure factor for $\mathbf{G}^2 = 4(2\pi/a_0)^2$ vanishes. It turns out that for Si and most conventional group IV, and III-V semiconductors the potential $\mathbf{G}$ becomes week for reciprocal vectors larger than $\mathbf{G}^2 = 11(2\pi/a_0)^2$, so that truncating the expansion at this point turns out to be a reasonable approximation. The $\mathbf{G}=0$ component of the form factor simply gives the averaged potential and shifts the band structure rigidly along the energy axis. If we further assume that $v(\mathbf{r})$ is spherically symmetric the form factor takes the form $v(G)$ and only three different form factors remain. These three factors, v_{111}, v_{220} and v_{311} are used as adjustable parameters to reproduce experimental results, such as the band structure. Early applications of the method were done for Si and Ge [49, 50] and soon extended to fourteen different semiconductors [51] with surprisingly accurate results, considering the limited input. The band structure of most semiconductors can be fitted to high accuracy using this procedure

giving us the hint that a local potential $V(r)$ can be used as a mean field to describe the complex many-body electronic interactions in the crystal.

The application of this idea to calculate the electronic properties of nanostructures requires a continuous form of $v(G)$ since the few discrete points, v_{111}, v_{220} and v_{311}, fail to address a large structure with a dense mesh of $\mathbf{G}$ vectors. The continuous empirical pseudopotential can be represented, for instance, by a function with 4 parameters a_1, a_2, a_3, a_4 [52] or by a sum of N Gaussians with parameters a_i, c_i, b_i [53]:

$$v^{\text{EPM}}(q) = \frac{a_1(q^2 - a_2)}{a_3 e^{a_4 q^2} - 1} \quad \text{or} \quad v^{\text{EPM}}(q) = \sum_{i=1}^{N} a_i e^{-c_i(q-b_i)^2} \quad . \tag{15}$$

From the empirical atomic pseudopotentials $v(q)$ we construct the *bulk* crystal empirical pseudopotential $V(\mathbf{r})$ from the sum given in Eq. (10). We solve the Schrödinger equation

$$\widehat{\text{H}}\psi_i(\mathbf{r}) = \{-\frac{\nabla^2}{2} + V_{loc}^{\text{EPM}}(\mathbf{r}) + \widehat{\text{V}}_{\text{SO}}\}\psi_i(\mathbf{r}) = \varepsilon_i \, \psi_i(\mathbf{r}) \quad , \tag{16}$$

using a basis set of plane waves with a low energy cut-off (e.g., 4.5 Ry for Si in Ref. [52]). At this point, the parameters from Eqs. (15) are fitted to reproduce known experimental quantities such as the bulk band structure at high symmetry points, the effective masses for different bands at different k-points and along different reciprocal space directions, the deformation potentials, the surface work function [32, 52, 53]. The nonlocal spin-orbit interaction can be written as [54, 55]

$$\widehat{\text{V}}_{SO} = \sum_{i\alpha} \hat{V}_\alpha^{SO}(R_i) = \sum_{i\alpha} \sum_{lm} V_{l,\alpha}^{SO}(r - R_i)|P_{lm}(\mathbf{R}_i)\rangle \mathbf{L} \cdot \mathbf{S} \langle P_{lm}(\mathbf{R}_i)| \quad , \tag{17}$$

where $|P_{lm}(\mathbf{R}_i)\rangle$ is a projector of angular momentum lm centered at the atomic position $\mathbf{R}_i$, $\mathbf{L}$ is the spatial angular momentum operator, $\mathbf{S}$ is the spin operator with components given by Pauli matrices, and $V_{l,\alpha}^{SO}(r)$ is a potential describing the spin-orbit interaction. The functional form of $V_{l,\alpha}^{SO}(r)$ was set to a Gaussian and only the effect of p states (l=1) was included in most recent works [31, 56]. In practice this approach leads to a single spin-orbit parameter for each atom type α.

There have been several modifications to the approach from Eq. (16). The most prominent ones are *(i) The strain dependence of the potential* through the local hydrostatic strain $\text{Tr}(\epsilon)$ [31]:

$$v_\alpha^{\text{EPM}}(r; \epsilon) = v_\alpha^{\text{EPM}}(r)[1 + \gamma_\alpha \text{Tr}(\epsilon)] \quad , \tag{18}$$

where γ_α is a fitting parameter. The explicit strain dependence of the potential helps to capture effects that would enter the picture only through a self-consistent charge rearrangement in response to compression or expansion, which is absent in the conventional EPM framework. More sophisticated strain dependences have been introduced for nitride pseudopotentials [57].

(ii) The rescaling of the kinetic energy. In Eq. (16), the kinetic energy of the electrons has been scaled [31, 56] by a fitting parameter β: $-\beta\nabla^2/2$. This procedure can be seen as the attempt to correct for the lack of non-locality in the potential. The introduction of β enables to fit both the band gap and the effective masses with the same set of few parameters.

(iii) The environment dependence of the potential. If the EPM is used to describe common-anion or common-cation alloys of semiconductors the question of environment dependence needs to
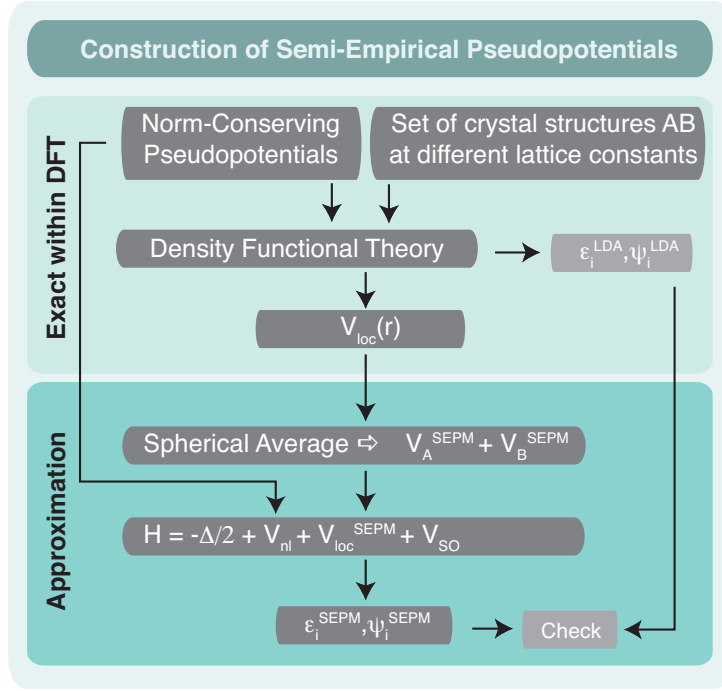
Figure 2: Flowchart describing the steps necessary to generate a semi-empirical pseudopotential (SEPM).

be addressed. For a common anion semiconductor (e.g., $In_xGa_{1-x}As$) each anion is surrounded by n cations of type 1 (e.g., Ga) and $4 - n$ cations of type 2 (e.g. In). The pseudopotentials are always constructed from independent binaries (e.g, InAs and GaAs) so that there are two, likely different, pseudopotentials for the same anion (e.g. As). This is legitimate since the pseudopotential describes not only the bare atom but also the interaction with its neighbors. However, the potentials should remain similar enough to guarantee some degree of transferability. The simplest expression for an As atom surrounded by n Ga and $(4-n)$ In atoms, is a weighted sum of the type:

$$v_{As}(nGa, (4-n)In) = \frac{1}{4}\left(n\, v_{As}^{GaAs} + (4-n)\, v_{As}^{InAs}\right) \quad , \tag{19}$$

where $v_{As}^{InAs(GaAs)}$ represents the As pseudopotentials derived from InAs (GaAs). With this approximation, the parameters in Eqs. (15,17,18) can be slightly modified to correctly reproduce *alloy* properties, such as band gap bowing [53, 58].

2.4   Semi-Empirical Pseudopotentials and their Construction

The EPM framework we described uses a fully local description of the potential, besides the spin-orbit term in Eq. (17). It was soon recognized [59] that this approach can be improved by using non-local potentials. The non-locality is introduced by making the potential dependent on the angular momentum of the electron. It can therefore account for the different behavior of a 2s and a 2p electron in oxygen, for instance. The l-dependent potential v_l can be written as

$$\widehat{V}_{nl}(\mathbf{r}) = \sum_{\mathbf{R}_i}\widehat{v}_{nl}(\mathbf{r} - \mathbf{R}_i) = \sum_{\mathbf{R}_i}\sum_{lm}|P_{lm}(\mathbf{R}_i)\rangle v_l(|\mathbf{r} - \mathbf{R}_i|)\langle P_{lm}(\mathbf{R}_i)| \quad , \tag{20}$$

where $\mathbf{R}_i$ are the atomic positions and $|P_{lm}(\mathbf{R}_i)\rangle$ are projectors of angular momentum lm. In practice $\widehat{v}_{nl}(r)$ is assumed zero outside a cut-off radius r_{cut} typically around the interatomic

distance [53, 60]. This procedure is perfectly equivalent to the one used in the community of *ab-initio* ionic pseudopotentials. There, *l*-dependent ionic pseudopotentials are generated based on all-electron density functional theory (DFT) calculations [40–44]. This similarity in the formalism can be used to connect the total semi-empirical pseudopotentials with the ionic *ab-initio* pseudopotentials.

We will describe the necessary steps to the construction of the ionic semiempirical pseudopotentials following the flowchart of Fig. 2. From DFT in the local density approximation (LDA) the screened local (self-consistent) potential for a set of different crystal structures (zincblende, wurtzite, B2, ...) at different lattice constants is calculated. The norm-conserving *ab initio* ionic pseudopotentials required for the DFT calculations can be obtained from available databases or constructed with ease. The relevant output of the DFT calculation is the screened local effective potential, usually given in real space $V_{\text{loc}}(\mathbf{r})$. Fourier transformed to $\mathbf{G}$ space:

$$V_{\text{loc}}(\mathbf{G}) \;\; = \;\; \frac{1}{\Omega} \int_\Omega V_{\text{loc}}(\mathbf{r}) e^{i\mathbf{r}\mathbf{G}} \; d^3\mathbf{r} \quad . \tag{21}$$

For the local real space potential we make the Ansatz:

$$V_{\text{loc}}(\mathbf{r}) \;\; = \;\; \sum_n v_{\text{anion}}(\mathbf{r} - \mathbf{R}_n + \mathbf{r_0}) + v_{\text{cation}}(\mathbf{r} - \mathbf{R}_n - \mathbf{r_0}) \quad , \tag{22}$$

with the Fourier transform

$$V_{\text{loc}}(\mathbf{G}) \;\; = \;\; \frac{1}{\Omega} \int_\Omega v_{\text{anion}}(\mathbf{r}') e^{i\mathbf{G}(\mathbf{r}'-\mathbf{r}_0)} + v_{\text{cation}}(\mathbf{r}') e^{i\mathbf{G}(\mathbf{r}'+\mathbf{r}_0)} \; d\mathbf{r}' \tag{23}$$

$$= \;\; \frac{\cos(\mathbf{r}_0\mathbf{G})}{\Omega} v_+(\mathbf{G}) - i \frac{\sin(\mathbf{r}_0\mathbf{G})}{\Omega} v_-(\mathbf{G}) \quad , \tag{24}$$

using the short form

$$v_+(\mathbf{G}) = v_{\text{anion}}(\mathbf{G}) + v_{\text{cation}}(\mathbf{G}) \quad , \quad v_-(\mathbf{G}) = v_{\text{anion}}(\mathbf{G}) - v_{\text{cation}}(\mathbf{G}) \quad . \tag{25}$$

In Eq.(22) we separated the real space potential into an anion-centered and a cation-centered contribution, this represents the case of a binary system, e.g. a III-V semiconductor such as GaAs. If $v_{\text{cation/anion}}(\mathbf{r})$ is assumed to have inversion symmetry then $v_+(\mathbf{G})$ and $v_-(\mathbf{G})$ are real and we can write:

$$v_+(\mathbf{G}) = \frac{\Omega}{\cos(\mathbf{r}_0\mathbf{G})} \; \Re\{V_{\text{loc}}(\mathbf{G})\} \quad , \quad v_-(\mathbf{G}) = -\frac{\Omega}{\sin(\mathbf{r}_0\mathbf{G})} \; \Im\{V_{\text{loc}}(\mathbf{G})\} \quad . \tag{26}$$

It is possible to obtain $v_{\text{anion}}(\mathbf{G})$ and $v_{\text{cation}}(\mathbf{G})$ exactly. However, v_{anion} and v_{cation} are very well represented by their spherically averaged counterparts: $v_{\text{anion}}(|\mathbf{G}|)$ and $v_{\text{cation}}(|\mathbf{G}|)$ and we make use of this simplification, which represents a pivotal approximation. The DFT results for $v_+(|\mathbf{G}|)$ in GaAs calculated for the crystal structures zincblende and B2, each of them at the two lattice constants 10.658 a.u. and 11.452 a.u. are given as black dots in Figure 3. The inset (Fig 3(b)) is a magnification of the area indicated by black arrows. It can be seen that the discrete points mostly lie on a smooth curve. The fit through the points in Fig. 3 was done using cubic splines with an exponential truncation but any other function such as in Eq. (15) can be used. It can be seen that around $G = 2.5$ a.u. some points scatter above and below the fitted curve. Indeed, there is no guarantee that the points lie on a smooth curve and the amount of scatter will depend
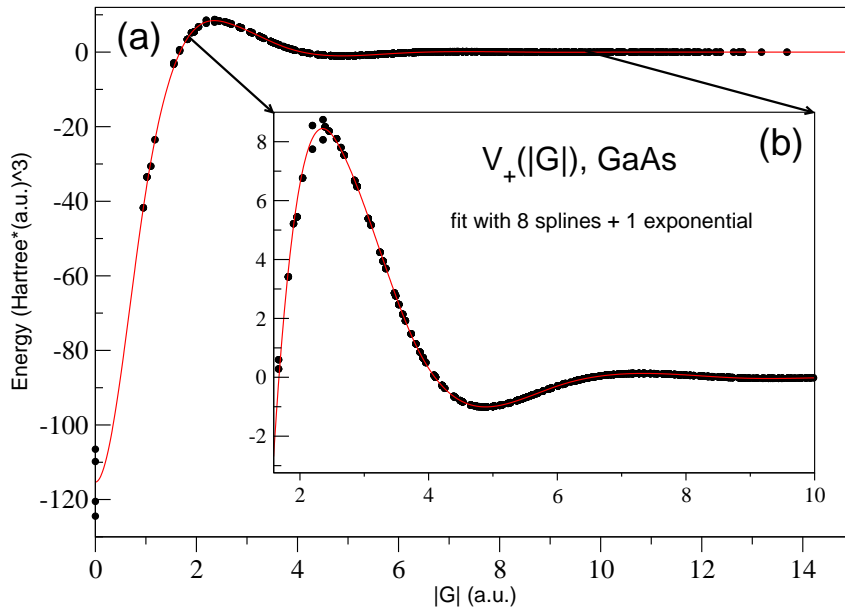
Figure 3: This figure shows one of the steps in the construction of a semiempirical pseudopotential. The points are the DFT results for the screened effective potential for GaAs at discrete **G**-vectors. The line is the fit of our semiempirical pseudopotential through these points.

on the material, the crystal structures and the range of different lattice constants used in the fit. It is also representative of the degree of transferability of the potential. Up to this point, two approximations have been made: (1) The spherical approximation, by going from **G** to $|\mathbf{G}|$ and (2) the average over different crystal structures, by fitting a single curve that passes through several points at a single $|\mathbf{G}|$ value. This procedure turns out to be very accurate for several semiconductors [60, 61] and the overlap of the semi-empirical wave functions, indexed SEPM, and the LDA wave functions, $\langle \psi_i^{\mathrm{LDA}} | \psi_i^{\mathrm{SEPM}} \rangle$, is larger than 99.9% [60, 61].

From the smooth curves fitted through the $v_+(|\mathbf{G}|)$ and $v_-(|\mathbf{G}|)$ points, we obtain the continuous atomic semi-empirical pseudopotentials through Eq. (25). Once this potential is known for each atom type α, we can reconstruct the crystal potential (*Calculate the Crystal Potential* in Fig. 1) by the superposition (as in Eq. (10)),

$$V_{loc}^{\mathrm{SEPM}}(\mathbf{r}) \;\; = \;\; \sum_{\alpha,j,n} v_\alpha(\mathbf{r} - \mathbf{R}_n - \mathbf{r}_{\alpha,j}) = \frac{1}{\Omega} \sum_{\alpha,j,n} \int_\Omega v_\alpha(|\mathbf{G}|) e^{-i(\mathbf{r} - \mathbf{R}_n - \mathbf{r}_{\alpha,j})\mathbf{G}} \, d^3\mathbf{G} \;\; . \quad (27)$$

To reconstruct the full crystal potential we need to include the non-local part of the *ab-initio* ionic pseudopotential $\widehat{V}_{nl}(\mathbf{r})$ (Eq. (20)) . This operator is simply added to the local potential $V_{loc}^{\mathrm{SEPM}}(\mathbf{r})$ (long arrow in Fig. 2) in a fashion very much analogous to the way non-local potentials are treated in DFT [62].

Before the potential can be used to quantitatively predict the properties of nanostructures, two modifications are necessary. One is to reduce the energy cut-off used in the DFT calculation to a value where the quality of the potential/wave functions is not significantly deteriorated but which allows to numerically handle several hundred thousand atoms. Typically energy cut-off values of 5 - 8 Ry have been used [60, 61] in conjunction with an empirical "Gaussian correction" [61]. The second modification is to refit to potential slightly to correct for the known errors of LDA with respect to the bulk band gap and the effective masses. Since these values

are crucial for quantum dots, we need to make sure they agree well with experiment. These last two steps probably give the most part of the empirical "flavor" to the overall methodology. While the first step is of technical nature and for smaller systems (up to ten thousands of atoms at present computational capabilities) the cut-off could be unchanged, the second step might be avoidable by using a quasiparticle approach such as GW, instead of LDA, which gives in some cases very accurate band gaps and effective masses.

2.5   Solving the Schrödinger Equation for the Nanostructure

After having obtained the crystal potential we move on to *solve the Schrödinger equation* in Fig. 1. The Schrödinger equation is given by

$$\widehat{H}\psi_i(\mathbf{r}) = \{-\frac{\nabla^2}{2} + V_{loc}^{\text{SEPM}}(\mathbf{r}) + \widehat{V}_{\text{nl}} + \widehat{V}_{\text{SO}}\}\psi_i(\mathbf{r}) = \varepsilon_i\,\psi_i(\mathbf{r}) \quad. \tag{28}$$

We know that the spectrum of $\widehat{H}$ has an energy gap and we know approximately from the pseudopotential construction at which spectral energy this gap develops. Our aim is to find a dozen of the interior eigenvalues on either side of the gap which determines most of the properties related to excitations. Our aim is therefore not to calculate all the occupied bands, as is customary in DFT approaches, but only a few relevant ones. We therefore have no access to the total energy of the system which requires a sum over all the occupied bands. Since our approach is to represent the total potential by a pseudopotential there is no self-consistent loop to undergo and the Hamiltonian is diagonalized only once. This is another difference to the *ab-initio* ionic pseudopotentials where a self-consistent treatment of the valence electrons is required.

To solve this *interior eigenstate* problem we use [63] a conjugate gradient (CG) type algorithm applied with the Folded Spectrum Method (FSM) [64] or other strategies using state-of-the-art algorithms for the eigenvalue problems at hand, in particular variations of the CG, the locally optimal block preconditioned CG (LOBPCG) [65], and Jacobi-Davidson methods [66].

Depending on the size of the problem we use two different basis sets for ψ_i. For small enough structures, up to a few hundred thousand atoms, we use a simple but large plane wave basis set

$$\psi_i(\mathbf{r}) = \sum_{\mathbf{G}} c_i(\mathbf{G})e^{i\mathbf{G}\cdot\mathbf{r}} \quad, \tag{29}$$

where $\mathbf{G}$ is a reciprocal lattice vector and $c_i(\mathbf{G})$ are the expansion coefficients to be determined variationally. The advantage of the plane wave basis set is that it can be increased systematically and $\widehat{H}\psi$ can be evaluated easily on the fly. The Hamilton matrix is large (dimension can be several millions) and very sparse. Due to its large size the matrix H is never explicitly computed and the solver is matrix free with $\widehat{H}$ acting on each vector ψ. As usual, we calculate the kinetic energy part in Fourier space, where it is diagonal, and the potential energy part in real space where the number of operations required for the matrix-vector product scales as $n\log n$ where n is the dimension of H. We move between Fourier and real space by three dimensional FFTs.

Another basis set is used for larger nanostructures, such as self-assembled quantum dots, and is constructed from a linear combination of strained bulk Bloch states (SLCBB [67]), ϕ_{nk}, from

bands, n, and k-points, k,

$$\psi_i(\mathbf{r}, \epsilon) = \sum_{n,k} c_{n,k}^{(i)} \, \phi_{nk}(\mathbf{r}, \epsilon) \quad, \tag{30}$$

taken at a few strain values ϵ. With this basis set, the Hamilton matrix is rather small, typically $n=40{,}000$, but dense and expensive to compute. H is locally stored and solved for a few eigenvectors and eigenvalues using ARPACK [68].

The plane wave code is parallel and can handle hundred thousands of atoms while the SLCBB code is serial but can handle up to millions of atoms due to the underlying assumption in the small basis set used. When it is affordable, the plane wave code is superior because of the possibility to include the non-local potential $\widehat{V}_{\mathrm{nl}}$ (while SLCBB can presently only handle local pseudopotentials except for spin-orbit) and because the basis set can be converged systematically by increasing the cut-off energy (while the basis set in SLCBB requires a non-trivial choice from the user for the basis and must be carefully checked for convergence).

2.6   External Constraints and Piezoelectric Field

At this point, a longitudinal external electric fields $\mathbf{E}$ can be added to Eq. (28) [69] through the external potential

$$V_{\mathrm{ext}}(\mathbf{r}) = -\int_{\mathcal{C}} \mathbf{E} \cdot d\mathbf{l} \quad, \tag{31}$$

where $\mathcal{C}$ is an arbitrary path connecting the point with zero potential to the point $\mathbf{r}$.

Constrains such as pressure effects can be naturally investigated [70] since we use an atomistic description and the potentials are constructed to reproduce deformation potentials. The use of a multi-band approach that is not limited to expansion around certain points of the Brillouin zone allows us to investigate transitions that are indirect in k-space [70], such as Γ to L transitions in the conduction band with pressure.

Since our method is non-self-consistent and hence does not allow for long ranged charge redistributions, it neglects effects such as piezoelectricity where charge is moved due to strain. In this case, the piezoelectric potential must be calculated independently [71, 72] and added as an external potential, just like in the case of "truly" external fields. This is *a priori* difficult for large structures but through a combination of strain calculations that can be done with empirical force fields and DFT calculations for the piezoelectric response we can obtain the necessary potential [71]. It turns out that second order effects in strain need to be taken into account [71] to obtain reliable results.

2.7   Solution of the many-body problem

2.7.1   Correlations in the Ground State

The word *correlation* in the context of quantum dots can lead to some confusions that we intend to prevent by this short section. Correlations are usually defined as the difference between the Hartree-Fock ground state and the exact many-body solution. In this context, correlations are purely a ground state property. The conventional quantum chemical methods start from the Hartree-Fock (HF) single-determinant ground state and use configuration interaction (CI),

Møller Plesset, coupled cluster (CC), among other methods, to add correlations to the ground state. We, however, do not attempt to solve the many-body problem for the ground state, since it consists of thousands of electrons. Our approach is purely empirical at this stage: we assume that the solutions of our Schrödinger equation (Eq. (28)) with the effective empirical pseudopotential are already fully correlated quasiparticle eigenfunctions and quasiparticle eigenvalues. The fact, that our pseudopotential is local or semi-local while the true quasiparticle equation is fully non-local points to the underlying approximation.

2.7.2 Correlations in the excitation: Configuration Interaction

Once the quasiparticle eigenfunctions have been calculated we follow the configuration interaction (CI) method (see Fig. 1) to obtain the excitations (such as an exciton) of the system. At this point, the correlations of the ground state are assumed to be decoupled from the correlations of the excitation. This is justified by the Brillouin theorem which states that there is no coupling between the Hartree-Fock (HF) ground state and the single-exciton ("singles") excitation $|\Phi_{h_i,e_j}\rangle$. Note that we are not starting from the HF ground state, as in the Brillouin theorem, but from the solution of the quasiparticle equation. It can still be shown [27] that $|\Phi_{h_i,e_j}\rangle$ and $|\Phi_0\rangle$ are decoupled. There is, however, coupling between the higher excitations such as double-exciton excitation ("doubles") and the ground state. These are neglected in our approach, which can be justified by the fact that doubles are energetically remote from the ground state.

The correlations in the excitation are treated at the level of "singles" only, i.e., only single-exciton excitation where one hole in the valence band and one electron in the conduction band are created, are allowed to interact. Formally, the correlated exciton wave function can be constructed from a set of Slater determinants [73, 74]:

$$|\Phi_{h_i,e_j}\rangle = b_{h_i}^\dagger c_{e_j}^\dagger |\Phi_0\rangle \tag{32}$$

where $b_{h_i}^\dagger$ is the creation operator for holes and $c_{e_j}^\dagger$ the creation operator for electrons. The Slater determinants $|\Phi_{h_i,e_j}\rangle$ can be calculated from anti-symmetrized products of single-particle wave functions ψ_i from equation (28).

The exciton wave functions $|\Psi\rangle$ are expanded in terms of this determinental basis set:

$$|\Psi\rangle = \sum_{h_i,e_j} A(h_i,e_j)|\Phi_{h_i,e_j}\rangle \quad , \tag{33}$$

where A are the expansion coefficients and we use i to index hole states and j to index electron states. The Slater rules [73] allow us to express the matrix elements between Slater determinants in terms of one– and two–center integrals:

$$\langle \Phi_{h_i,e_j}|H|\Phi_{h_{i'},e_{j'}}\rangle = (\varepsilon_{e_j} - \varepsilon_{h_i})\delta_{h_i h_{i'}}\delta_{e_j e_{j'}} + \langle e_j h_{i'}|v|h_i e_{j'}\rangle - \langle e_j h_{i'}|v|e_{j'} h_i\rangle \quad , \tag{34}$$

with the two center integrals

$$\langle e_j h_i|v|h_{i'} e_{j'}\rangle = \iint \psi_j^\star(\mathbf{r}_e)\psi_i^\star(\mathbf{r}_h)v(\mathbf{r}_e,\mathbf{r}_h)\psi_{i'}(\mathbf{r}_e)\psi_{j'}(\mathbf{r}_h)\,\mathrm{d}\mathbf{r}_e\,\mathrm{d}\mathbf{r}_h \quad , \tag{35}$$

using $v(\mathbf{r}_e, \mathbf{r}_h)$ for the screened Coulomb interaction described in the next section. The last term in Eq. (34) describes the direct Coulomb integrals and the one before last the exchange integrals. The formalism described from Eq. (32) to Eq. (35) can be generalized to the case of an arbitrary number of electrons and holes and is not limited to the case of excitons. For the case of multiexcitons or charged excitons, the subspace of Slater determinants included in Eq. (32) has been restricted to excitations that conserve the number of electrons and the number of holes. For instance, a biexciton state has been constructed from Slater determinants with two electrons and two holes (double excitation), neglecting the coupling to Slater determinants with one electron and one hole (singles). This coupling is non zero, but rather small since the energy difference between the single and the double excitations is approximately given by the band gap. This generalization from the exciton case to an arbitrary number of electrons and holes, represents one of the advantages of this approach. In our numerical treatment, equations such as (34) are not directly implemented but rather the action of creation and annihilation operators in a general second quantization form.

2.7.3 Screening

In quantum chemistry, configuration interaction is often treated at the level of triples, quadruples, all the way to *full* CI which exactly solves the electronic Schrödinger equation within the space spanned by the one-particle basis set. In these calculations, the integrals (35) are the bare unscreened ($v(\mathbf{r}_e, \mathbf{r}_h) = 1/(|\mathbf{r}_e - \mathbf{r}_h|)$) Coulomb integrals. For excitations in a nanostructure, such an approach is computationally not feasible using an atomistic description and we have to limit ourselves in the one-particle basis set to only few states close to the band gap and to single excitations only. To neglect the coupling of singles to higher excitations is a poor approximation. However, it can be shown that the effect of higher order excitations can be folded back onto the considered subspace of single excitations [27, 75]. The effect of this procedure is to renormalize (screen) the Coulomb interactions, as we already indicated in Eq. (35) by $v(\mathbf{r}_e, \mathbf{r}_h)$. There was, and partly still is, some debate about the screening of the electron-hole exchange terms that was recently addressed via field theory arguments [75]. It was argued [75] that in the limiting case where transitions are considered over a wide energy range the electron-hole exchange term should be unscreened while in the limiting case where only the few lowest energy transitions are considered (usually our case) the interaction should be screened by the full dielectric function.

Besides this rather fundamental issue of whether to screen or not screen the interactions, the choice of the dielectric function is another important and developing theme. The screened Coulomb potential from Eq. (35) can be generally written as

$$v(\mathbf{r}_e, \mathbf{r}_h) = e^2 \int \epsilon^{-1}(\mathbf{r}_e, \mathbf{r}) |\mathbf{r} - \mathbf{r}_h|^{-1} \, d\mathbf{r} \quad , \tag{36}$$

with the inverse dielectric function $\epsilon^{-1}(\mathbf{r}_e, \mathbf{r})$. For large nanostructures, the screening function used has been directly taken from the literature for bulk systems. We used [76] the phenomenological isotropic and uniform ($\epsilon(\mathbf{r}_e, \mathbf{r}_h) \simeq \epsilon(|\mathbf{r}_e - \mathbf{r}_h|)$) model proposed by Resta [77] for the electronic screening and by Haken [78] (for the case of the exciton) for the ionic part: $\epsilon^{-1} = \epsilon_{el}^{-1} + \epsilon_{ion}^{-1}$ with

$$\epsilon_{el}^{-1}(k) = \frac{k^2 + q^2 \sin(k\rho_\infty)/(\epsilon_\infty k \rho_\infty)}{k^2 + q^2}, \quad \epsilon_{ion}^{-1}(k) = \left(\frac{1}{\epsilon_0} - \frac{1}{\epsilon_\infty} \right) \left(\frac{1/2}{1 + \rho_h^2 k^2} + \frac{1/2}{1 + \rho_e^2 k^2} \right), \tag{37}$$

with q the Thomas-Fermi wave vector, ρ_∞ is the solution of $\sinh(q\rho_\infty)/(q\rho_\infty) = \epsilon_\infty$ and $\rho_{h,e} = (\hbar/2m_{h,e}^*\omega_{\rm LO})^{1/2}$, with $m_{h,e}^*$ the hole and electron effective masses and $\omega_{\rm LO}$ the bulk LO-phonon frequency.

For small nanostructures the approximation of bulk screening is not appropriate since the effect of the interface plays an increasing role. A screening function depending on the radius of a spherical nanostructure was used for colloidal quantum dots [74]. The high frequency bulk dielectric constant ϵ_∞ from Eq. (37) was replaced [74] by a constant $\epsilon_\infty^{\rm dot}$ obtained from a modified Penn model where the size dependence enters the equation through the value of the optical band gap of the dot [74]. The low frequency dielectric constant of the dot $\epsilon_0^{\rm dot}$ was obtained simply by keeping $\epsilon_0^{\rm dot} - \epsilon_\infty^{\rm dot} = \epsilon_0 - \epsilon_\infty$. In this approach, the dielectric function remains dependent on the distance $|\mathbf{r} - \mathbf{r}'|$ but is independent of the position $\mathbf{r}$, i.e., screening is modified (typically reduced) throughout the nanostructure.

More recently, truly position dependent dielectric functions have been derived from tight binding calculations [79] and from density functional theory [80] for nanostructures. The screening function is obtained from the induced response of the system to an external perturbation, such as a delta-function or Coulomb-like perturbation of the potential. These calculations suggest that the screening function remains "bulk-like" inside the core of the structure and changes only in the close proximity of the interface.

2.7.4 Dielectric Mismatch and Polarization Charges

In the discussion of the screening function and the single-particle Schrödinger equation we did not mention the fact that the nanostructures are usually surrounded by a material with different dielectric properties. In this case, polarization charges appear on the surface of the nanostructure which have effects on the self-energy [81] and on the two particle binding energy [82]. Indeed, the dielectric mismatch leads to a surface polarization potential which corresponds to the classic electrostatic potential caused by a point charge inside an object, similarly to the image potential created by a point charge close to a dielectric medium. Quantum mechanically, the effect can be treated as an additional on-site potential $P(\mathbf{r})$ in the Schrödinger equation Eq. (28) [81]:

$$\widehat{\rm H}\psi_i(\mathbf{r}) = \{-\frac{\nabla^2}{2} + V_{loc}^{\rm SEPM}(\mathbf{r}) + \widehat{\rm V}_{\rm nl} + \widehat{\rm V}_{\rm SO} + P(\mathbf{r})\}\psi_i(\mathbf{r}) = \varepsilon_i\,\psi_i(\mathbf{r}) \quad . \tag{38}$$

This additional potential leads to a modification of the quasiparticle eigenvalues that we label as $\Sigma_c^{\rm surf}$ for the conduction band and $\Sigma_v^{\rm surf}$ for the valence band. The terms $\Sigma_{c,v}^{\rm surf}$ vanish for $\epsilon_{\rm in} = \epsilon_{\rm out}$ and are positive for the conduction band and negative for the valence band in case $\epsilon_{\rm in} > \epsilon_{\rm out}$, i.e. both contribute to an increase of the quasiparticle gap.

The dielectric mismatch and the ensuing surface polarization has an effect on the screened Coulomb interaction between the two quasi-particles. In addition to the direct Coulomb interaction we discussed previously, there is an additional interaction between one of the quasi-particles and the image surface charge of the other. This effect results in a modification of the direct Coulomb interaction $J^{\rm dir}$ by a surface polarization term $J^{\rm pol}$. It can be shown [27, 83] that for spherical nanocrystals the contributions from the surface self-energy terms to the exciton $\Sigma_e^{\rm surf} + \Sigma_h^{\rm surf}$ mostly cancel the surface polarization contribution to the Coulomb term $J^{\rm pol}$. It is therefore a common approximation [23, 74], when dealing with excitons in nearly

spherical colloidal quantum dots, to neglect the effects of polarization charges altogether, i.e., in the quasiparticle picture by using a simplified Schrödinger equation such as Eq. (28) and in the exciton problem, by neglecting the surface polarization term. On the other hand, for non-spherical nanostructures but with small dielectric mismatch, such as in self-assembled embedded quantum dots, the polarization terms $\Sigma_{e,h}^{\mathrm{surf}}$, $\Sigma_{e,h}^{\mathrm{surf}}$ and J^{pol} are often assumed to be small [76]. For non-spherical colloidal nanostructures such as tetrapods [84] or dumbbells [85], where dielectric mismatch is usually large, the polarization terms must be explicitly taken into account [27, 84]. Also in the calculation of charging energies or charged excitons, where the cancellation of self-energy and surface polarization is not given, effects of dielectric mismatch must be included [83].

2.7.5 Discussion

Before we move on to the next step where the many-body wave functions will be used to calculate observables, we will summarize in a qualitative and rather schematic manner the computational scheme used so far. In Fig. 4 we give an overview of the different energetic contributions to the band gap of a semiconductor or insulator. The left side of the Figure [a) LDA] corresponds to the band gap obtained with a single-particle description of the ground state such as density functional theory in the local density approximation (LDA). The band gap $\varepsilon_c^0 - \varepsilon_v^0$ is typically underestimated. The error in the band gap is mainly due to a missing or incorrect description of the self-energy $\Sigma_{\mathrm{bulk}}^{e,h}$. In Hedin's GW approximation [86], at the quasiparticle level, this contribution is properly accounted for and the band-gap opens up [b) GW]. The next column [c) LDA] describes the situation in a nanostructure where in the single-particle case, the band gap opens up by $E_{\mathrm{conf}}^{e,h}$ because of confinement. $E_{\mathrm{conf}}^{e,h}$ depends on the size of the nanostructure, the band structure (effective mass) of the material, the strain and deformation potentials. In the next column [d) GW], at the GW level, the contributions of $\Sigma_{\mathrm{bulk}}^{e,h}$ add up but also the contributions due to surface polarization effects $\Sigma_{\mathrm{surf}}^{e,h}$ described in the previous section 2.7.4. Our empirical pseudopotential method enters the picture at the level given in "e) EPM" where the self-energy contributions to the bulk $\Sigma_{\mathrm{bulk}}^{e,h}$ are taken into account but not the ones of surface polarization $\Sigma_{\mathrm{surf}}^{e,h}$. In the right column [f) Exciton], the optical band gap is given, where the Coulomb interaction, J_{pol}^{eh}, and J_{direct}^{eh}, contribute to reduce the band gap. J_{pol}^{eh}, and J_{direct}^{eh} have been artificially split into two parts $J_{\mathrm{pol}}^{eh,1,2}$, and $J_{\mathrm{direct}}^{eh,1,2}$ to be able to visually include the two-particle excitonic description of the right column within the single-particle and quasiparticle description of columns a)-e). As discussed in section 2.7.4 the terms $\Sigma_e^{\mathrm{surf}} + \Sigma_h^{\mathrm{surf}}$ tend to cancel $J_{\mathrm{pol}}^{eh} = J_{\mathrm{pol}}^{eh,1} + J_{\mathrm{pol}}^{eh,2}$ for spherical nanostructures. In the case of no dielectric mismatch between the nanostructure and the environment, the terms Σ_e^{surf}, Σ_h^{surf} and J_{pol}^{eh} vanish.

2.8 Post-Processor Tools

After we have calculated the many-body wave function we have access to observables through the use of post-processor tools as shown in the last step of the flowchart in Fig. 1 .
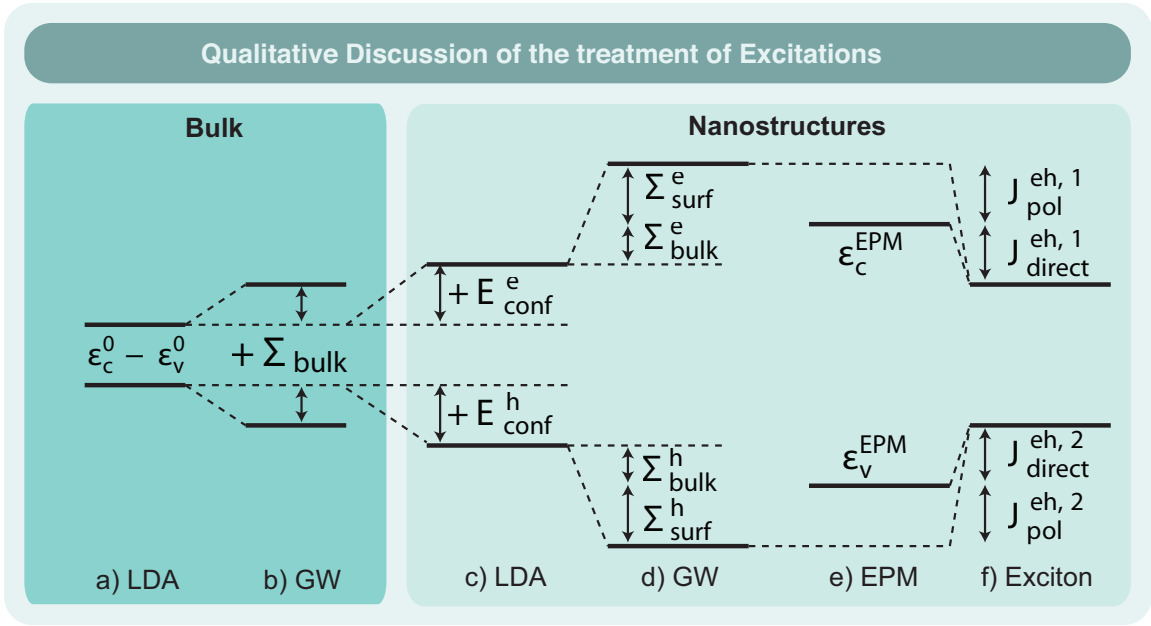
Figure 4: Qualitative description of the position of the conduction band minimum (or LUMO) and valence band maximum (or HOMO) in different theoretical approaches. See section 2.7.5.

2.8.1 Optics

The optical properties of semiconductor nanostructures are among the most relevant observables. The optical transition of an excitonic complex χ to the excitonic complex $(\chi - 1)$, where one electron-hole pair has been annihilated, is characterized by both the transition energy between the initial state i and the final state f, $\omega_{if}(\chi)$, and the optical transition dipole matrix element

$$M_{if}^{(\hat{\mathbf{e}})}(\chi) = \langle \Psi^{(f)}(\chi - 1) | \hat{\mathbf{e}} \cdot \mathbf{p} | \Psi^{(i)}(\chi) \rangle \quad , \tag{39}$$

with the momentum operator $\mathbf{p}$ and the polarization vector of the electromagnetic field $\hat{\mathbf{e}}$ [87,88]. The oscillator strength for the exciton complex χ and for polarization $\hat{\mathbf{e}}$ is given by

$$\alpha^{(\hat{\mathbf{e}})}(\omega, T; \chi) \propto \sum_{i,f} \left| M_{if}^{(\hat{\mathbf{e}})}(\chi) \right|^2 P_i(T; \chi) \, \delta(\omega - \omega_{if}(\chi)) \quad , \tag{40}$$

where

$$P_i(T; \chi) = \mathcal{N} \exp\{-[E^{(i)}(\chi) - E^{(0)}(\chi)]/k_B \, T\} \tag{41}$$

is the occupation probability of the initial state $|\Psi^{(i)}(\chi)\rangle$ at temperature T and $\mathcal{N}$ is a normalization constant. The delta function can be replaced by a Gaussian to account for size distribution (inhomogeneous broadening) or by a Lorentzian to account for intrinsic sources of broadening (homogeneous broadening). We can define a radiative lifetime, $\tau_{if}(\chi)$, that is specific to the transition between states i and j as:

$$\frac{1}{\tau_{if}(\chi)} \propto n \, \omega_{if}(\chi) \sum_{\hat{\mathbf{e}} = \hat{x}, \hat{y}, \hat{z}} \left| \mathbf{M}_{if}^{(\hat{\mathbf{e}})}(\chi) \right|^2 \quad , \tag{42}$$

where, e and m_0 are the charge and mass of the electron, respectively, c is the velocity of light in vacuum and n is the refractive index of the dot material. The underlying assumption in Eq. (42) that guarantees a simple linear dependence of $1/\tau_{if}(\chi)$ on refractive index is a similar dielectric

constant inside and outside the nanostructure, as is the case of many embedded self-assembled quantum dots. In a more general case, more complicated dependences have been proposed [89].

Note that the "specific" radiative lifetime defined in Eq. (42) does not depend on temperature nor on the occupation probabilities of the states while the actual (measured) radiative lifetime $\tau(\chi)$ depends non-trivially on occupation probabilities. To obtain the actual lifetime, the time dependent Schrödinger equation has to be solved. This can be done by reducing the problem to a few level system and by solving a set of master equations [88, 90].

2.8.2 Quantum Entanglement

With our CI results we have access to quantum mechanical quantities related to correlations, such as quantum entanglement. Entanglement is one of the most important quantities for successful quantum gate operations and it is interesting to quantify the amount of entanglement present, or achievable, given a certain system. The degree of entanglement of *distinguishable* particles can be calculated from the von Neumann-entropy formulation [91,92]. For example for a two component system (A, B), it is defined as, [91–93]

$$\mathcal{S} = -\text{Tr}\,\rho_A \log_2 \rho_A = -\text{Tr}\,\rho_B \log_2 \rho_B \ , \tag{43}$$

where, ρ_A and ρ_B are the reduced single-particle density matrices of the subsystems A and B. However, there are some subtleties for defining the degree of entanglement for *indistinguishable* particles, since it is impossible to separate the subsystems A and B. Recently, we have derived a generalization of the von Neumann definition [94, 95] for *identical* particles through a Slater decomposition [96,97] where the maximum entanglement of a two-electron system is $\mathcal{S} = \log_2 N$, where N is the number of available single-particle states. Our definition reduces to Eq. (43) when the two-electrons are far from each other [94,95].

2.8.3 Tunneling Experiments

From the many-body wave functions we can obtain informations relevant to tunneling and optical experiments such as scanning tunneling microscopy (STM), magnetotunneling spectroscopy (MTS) or near-field scanning optical microscopy (NSOM or SNOM). For the case of STM and MTS, we calculate [20] the transition probability of an electron or hole from an emitter in state κ to a quantum dot containing N particles from the expression $\frac{2\pi}{\hbar}|\mathcal{M}_{\kappa,N}|^2 n(\varepsilon_{\text{F}})$ [98] where $n(\varepsilon_{\text{F}})$ is the enegy of the final quantum dot states. The transition matrix elements $\mathcal{M}_{\kappa,N}$ for the transfer of one particle from the emitter in state κ to the quantum dot state $|N\rangle$, filled by N electrons, can be factorized [99] as $\mathcal{M}_{\kappa,N} \propto T_\kappa M_{\kappa,N}$ where T does not depend on N, nor on the coordinates in-plane, x,y (if z is the tunneling direction). The relevant matrix element is therefore $M_{\kappa,N}$ and is given by:

$$M_{\kappa,N} = \int \phi_\kappa^*(\mathbf{x})\Psi_{\text{QD}}(\mathbf{x})d\mathbf{x} \quad . \tag{44}$$

Here, $\phi_\kappa^*(\mathbf{r})$ is the probing or emitter wave function and $\Psi_{\text{QD}}(\mathbf{x})$ is the quasi-particle excitation between the $N-1$ particle states $|N-1\rangle$ and the N particle states $|N\rangle$, i.e.,

$$\Psi_{\text{QD}}(\mathbf{x}) = \sum_i \langle N-1|\hat{c}_i|N\rangle\,\psi_i(\mathbf{x}) \quad . \tag{45}$$

$\psi_i(\mathbf{x})$ is the atomistic ith single-particle wave function and $\hat{c}_i$ is an electron (hole) annihilation operator. The correlated many-body states are obtained, as described in section 2.7, by configuration interaction:

$$|N\rangle = \sum_\beta C_\beta^{(N)} \Phi_\beta(\mathbf{x}_1, \cdots, \mathbf{x}_{N-1}, \mathbf{x}_N) \quad , \tag{46}$$

and

$$M_{\kappa,N} = \sum_i \langle N-1|\hat{c}_i|N\rangle\langle\phi_\kappa|\psi_i\rangle = \sum_i \sum_{\alpha,\beta} C_\alpha^{*(N-1)} C_\beta^{(N)} \langle \Phi_\alpha^{(N-1)}|\hat{c}_i|\Phi_\beta^{(N)}\rangle \langle\phi_\kappa|\psi_i\rangle \tag{47}$$

with

$$\langle \Phi_\alpha^{(N-1)}|\hat{c}_i|\Phi_\beta^{(N)}\rangle = \begin{cases} 1 & \text{if } |\Phi_\alpha^{(N-1)}\rangle = \hat{c}_i|\Phi_\beta^{(N)}\rangle, \\ -1 & \text{if } |\Phi_\alpha^{(N-1)}\rangle = -\hat{c}_i|\Phi_\beta^{(N)}\rangle, \\ 0 & \text{otherwise.} \end{cases}$$

where i indexes the single particle states obtained from the solution of Eq. (28).

There are different techniques to probe the quasi-particle excitations. For example, in scanning tunneling microscopy experiments, the probing wave function $\phi_\kappa(\mathbf{x})$ can be represented by a δ-function at a given real space point, $\phi(\mathbf{x}) \sim \delta(\mathbf{x})$, in which case the transition rate is given by $\sim |\psi_{\mathrm{QD}}(\mathbf{x})|^2$ and maps out the square of the quasi-particle excitations in real space.

An alternative approach is taken in MTS where the quasiparticle excitations are mapped out in reciprocal space. Using an atomistic description, the probing wave functions can be written as a Bloch function $\bar{u}_\mathbf{k}$ modulated by a plane wave:

$$\phi_\mathbf{k}(\mathbf{x}) = \bar{u}_\mathbf{k}(\mathbf{x})e^{i\,\mathbf{k}\cdot\mathbf{x}} \quad . \tag{48}$$

The atomistic wave functions for the quantum dot states can be written as:

$$\psi(\mathbf{x}) = \sum_n^{N_B} \sum_\mathbf{k}^{N_k} c_{n,\mathbf{k}}\, u_{n,\mathbf{k}}(\mathbf{x})\, e^{i\mathbf{k}\cdot\mathbf{x}} \tag{49}$$

where $u_{n,\mathbf{k}}(\mathbf{x})$ are Bloch wave functions with band index n and k-points $\mathbf{k}$ [20, 100] so that the product $\langle\phi_\kappa|\psi_i\rangle$ in Eq. (47) is given by:

$$\langle\phi_\mathbf{k}|\psi_i\rangle = \sum_n^{N_B} \langle\bar{u}_\mathbf{k}|u_{n,\mathbf{k}}\rangle c_{n,\mathbf{k}} \quad . \tag{50}$$

The overlap $\langle\bar{u}_\mathbf{k}|u_{n,\mathbf{k}}\rangle$ is largest at the interface and since we do not know the exact form of the Bloch part of the probing wave function, we have to resort to certain approximations. We assumed [20, 100] a constant $\langle\bar{u}_\mathbf{k}|u_{n,\mathbf{k}}\rangle$ in which case $M_{\kappa,N}$ in Eq. (47) is a function of $\mathbf{k}$ and N that can be directly calculated.

2.9   Charging Energies

The charging energy $\mu(N)$ is the energy necessary to add one more carrier to the dot already charged by $N-1$ carriers:

$$\mu(N) = E(N) - E(N-1) \quad , \tag{51}$$

where $E(N)$ are the correlated many-body total energies of the ground states of the N-particle dot. The addition energy $\Delta(N-1,N)$ indicates how much more energy is needed to add the Nth carrier compared to the energy needed to add the $(N-1)$th carrier:

$$
\begin{aligned}
\Delta(N-1,N) &= \mu(N) - \mu(N-1) \\
&= E(N) - 2E(N-1) + E(N-2) \quad .
\end{aligned}
\tag{52}
$$

The charging and addition energies are therefore directly obtained from the many-body energy calculated using the configuration interaction approach described in section 2.7 and can directly be compared to experiment.

3 Applications

Extensive work has been done recently using the empirical pseudopotential methodology on the material system InAs and GaAs [20, 26, 56, 69–72, 76, 88, 93–95, 100–104] and CdSe [74, 104–110]. Beyond these materials —in the focus of attention because of the wide availability of experimental results— potentials for InAs/InSb [111], PbSe [112, 113], InP/GaP [74, 114], nitrides [58, 115], among others, have been developed for embedded structures and for colloidal nanocrystals with adequate surface passivations. We will not attempt to review these many results but will rather select a few examples that should emphasize the generality of the method and its accuracy, able to predict new and unexpected physics.

3.1 Optics and Fine Structure

The term *fine structure* has been used in the realm of nanostructure physics to describe the small splittings due to the electron-hole exchange interaction. In the simplest case when the electron and hole states are derived from a single Kramers doublet, four possible electron-hole state combinations emerge due to the particle's pseudospins (indicated with arrows): $|e\uparrow\, h\uparrow\rangle$, $|e\uparrow\, h\downarrow\rangle$, $|e\downarrow\, h\uparrow\rangle$, $|e\downarrow\, h\downarrow\rangle$. The electron-hole exchange integrals are special cases of the integrals given in Eq. (35) and can be rewritten as:

$$
K_{ij',ji'} = \iint \psi_i^\star(\mathbf{r}_e)\psi_{j'}^\star(\mathbf{r}_h)v(\mathbf{r}_e,\mathbf{r}_h)\psi_j(\mathbf{r}_e)\psi_{i'}(\mathbf{r}_h)\,\mathrm{d}\mathbf{r}_e\,\mathrm{d}\mathbf{r}_h \quad ,
\tag{53}
$$

where we have kept the notation that i, i' indexes hole states and j, j' indexes electron states. The "exchange" of particle can be seen from Eq. (53) through the fact that at position $\mathbf{r}_e$ a hole wave function is on the left of v but an electron wave function on the right. These integrals lead to the splitting of the four electron-hole pairs and to the appearance of the fine structure. The integrals given in Eq. (53) require knowledge about the details of the Bloch part of the wave function which is naturally given by an atomistic description [76] but not readily available in envelope function theories. The integrals from Eq. (53) are sensitive to the effects of spin-orbit interaction, the atomistic symmetry, band mixing and to the full range of screening (long- and short-range) [76].

The atomistic calculation of fine structure splittings [72, 76, 88, 116, 117] and the comparison of the results with experiments [116] is an excellent benchmark for the theory and leads to

an understanding of the experimental results otherwise difficult or impossible to obtain. To illustrate the physical insight that can be obtained, we choose the example of the fine structure of the X^{2-} charged exciton shown in Fig. 5. On the left side (Fig. 5 a)) we show the initial configuration that consists of three electrons and one hole and the final configuration, after the recombination of one electro-hole pair, which consists of two electrons. Four many-body levels can be constructed from the limited set of one hole state h_0 and two electron states e_0 and e_1. Since the electrons in state e_0 must be paired, only the configurations $|(e_0{\uparrow}\ e_0{\downarrow})e_1{\uparrow}\ h_0{\uparrow}\rangle$, $|(e_0{\uparrow}\ e_0{\downarrow})e_1{\uparrow}\ h_0{\downarrow}\rangle$, $|(e_0{\uparrow}\ e_0{\downarrow})e_1{\downarrow}\ h_0{\uparrow}\rangle$, $|(e_0{\uparrow}\ e_0{\downarrow})e_1{\downarrow}\ h_0{\downarrow}\rangle$, are possible, much like in the case of a single electron-hole pair mentioned previously. Note that this is only a simplifying model that helps us to understand the results which do take many more configurations into account. Indeed, the number of configurations included in the CI treatment (section 2.7.2) is given by

$$N_{\mathrm{conf}} = \frac{b_c!}{n_e!(b_c - n_e)!} \frac{b_v!}{n_h!(b_v - n_h)!} \quad , \tag{54}$$

where n_h and n_e are the number of holes and electrons, respectively, distributed among b_v and b_c valence and conduction band states, counting spin. For the initial state of Fig. 5 a) with a configuration space of 10 electron and 10 hole states (i.e., counting spin, $b_c = b_v = 20$) we have 22800 mixing configurations. However, an analysis such as the one in Fig. 5 a) describes most of the physics properly in this case. Some striking deviations of the simple model have been addressed in Ref. [117]. The electron-hole exchange interaction splits the four levels of X^{2-} into a doublet and two singlets in the initial state and the electron-electron exchange interaction splits the final state into a singlet and a triplet state. The magnitude of the electron-electron and the electron-hole interaction is significantly different, the latter being more than an order of magnitude smaller than the former, with splittings in the order of tens of μeV. From the initial to the final many-body states we can anticipate six transitions as marked in Fig. 5 a), 1-3 are split from 4-6 by electron-electron exchange, while 1-3 and 4-6 are themselves split by the small electron-hole exchange interaction. The optical transitions that connect initial and final states can be calculated using the formalism described in section 2.8.1. The theoretical results for the oscillator strength for a lens shaped InAs self-assembled quantum dot embedded in GaAs are given in Fig. 5 b) and the corresponding experimental results in Fig. 5 c). The transition "1" from Fig. 5 a) has vanishing oscillator strength and therefore dark. The transitions are also polarized along certain crystallographic directions giving us a useful tool to clearly identify transitions and their origin [116, 117].

3.2 Entanglement

The field of nanostructure science is increasingly driven by efforts aimed at using the electrons in confined geometries to realize different schemes of quantum information science, where the physical information is held in the *state* of the quantum system. This represents an area of science where quantitative theories able to predict many-body properties of realistic systems are important. Some prominent examples are the proposal to use two vertically [118, 119] or laterally [120] coupled quantum dots containing two electrons [17], or an exciton [121] to perform some basic gate operations. The carrier of quantum informations, the qubits, can be realized by either the spin of the electron [17] or by the location of an electron or hole [121]. Our methodology
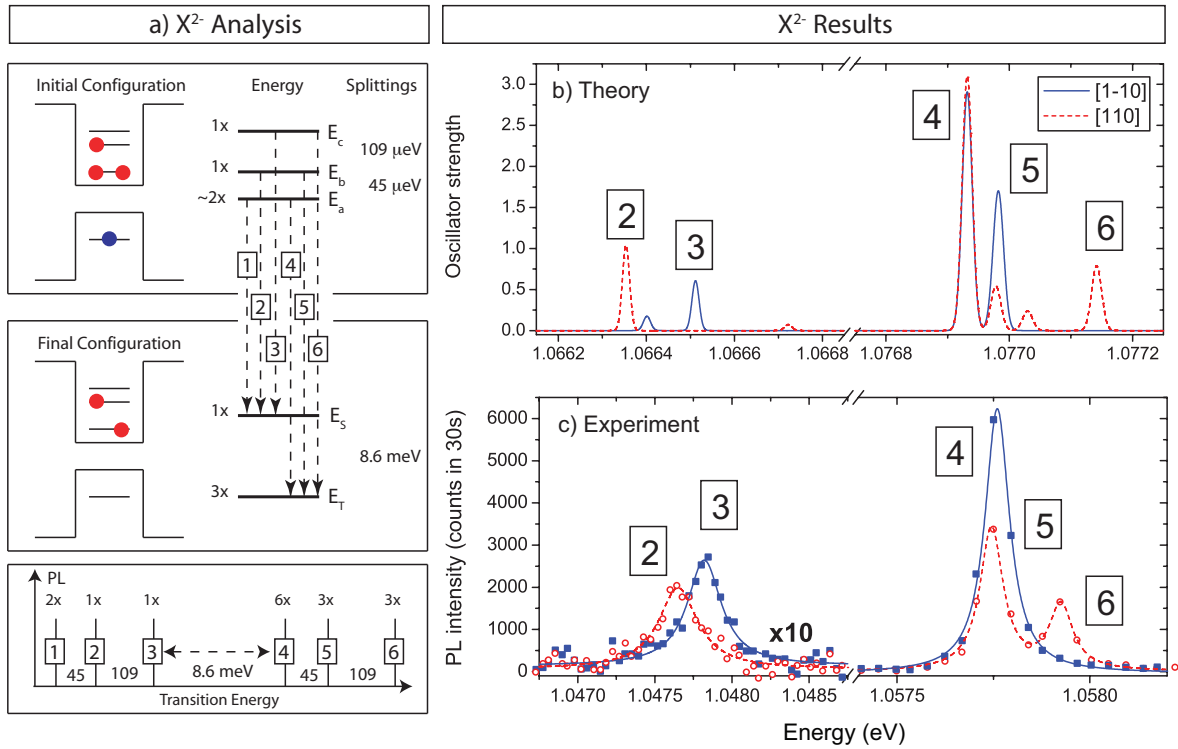
Figure 5: Fine structure of the X^{2-} charged exciton in a self-assembled InAs quantum dot. a) Analysis of the results in a simplified picture where only few many-body states for the initial and final states are considered. Note that the splitting of the initial states is given in μeV while the splitting of the final states in meV. b) Theoretical results for the oscillator strength in arbitrary units. c) Experimental results. Figure adapted from Ref. [116].

gives us access to some of the relevant quantities such as the degree of entanglement between the two electrons [94, 95] or between the electron and the hole [69, 93, 101], or the singlet-triplet splitting [95]. These quantities are sensitive to the geometry of the system, spin-orbit interaction, the amount of strain, and only a methodology that takes these effects into account can give a quantitative prediction.

In Figure 6 we present the results obtained for an InGaAs quantum dot molecule with dimensions and composition taken from experiment [121] as 12 nm in diameter and 2 nm height with a graded In-composition profile [69]. The two dots are vertically stacked, around 8 nm apart. A fully entangled electron-hole pair can be represented by the the maximally entangled Bell state $|e_T h_T\rangle + |e_B h_B\rangle$, where e and h stand for the electron and the hole (the two qubits) and T and B for their localizations in top or bottom dot (the state of the qubits). The entropy of entanglement is calculated according to Eq. (43) where A is the reduced density matrix for qubit A (the electron) and B is the reduced density matrix for qubit B (the hole). The density matrices are calculated from the correlated CI exciton density which requires a projection of the exciton wave functions on the dot localized basis set [69]. From the right side of Fig. 6 we can see that the degree of entanglement as a function of electric field is peaked at a certain electric field achievable experimentally [122–126] (5.4 kV/cm in our specific case) and can reach 80%. The left side of Fig. 6 shows that at this specific electric field the peaks in oscillator strength originating from the exciton states $|1\rangle$ and $|2\rangle$ anticross and $|1\rangle$ becomes dark. This optical signature may be used by experimentalists in the future to identify the electric field needed to achieve maximum entanglement in specific dot molecules. The theoretical results can be further

analyzed to understand, in terms of electron and hole localization on either one of the two dots, the way the particles conspire to create entangled states and what are the limiting and driving factors [69, 101] such as the effect of geometry, composition, dot-separation and the ensuing strain on tunneling and Coulomb interactions. From this understanding we could construct a simplified model hamiltonian with few and well defined parameters [93].
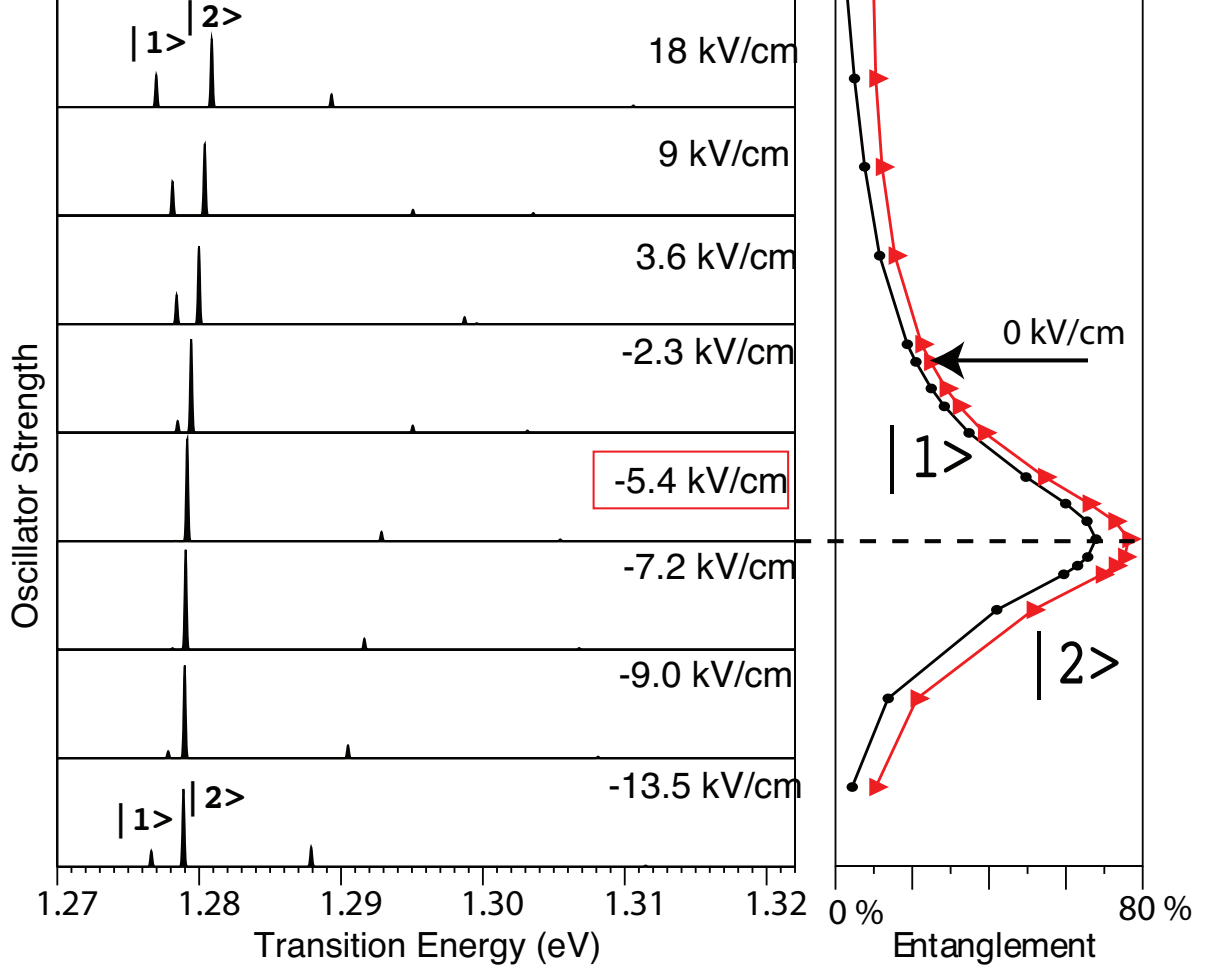

Figure 6: Electric field dependence of the oscillator strength (left) and the entropy of entanglement (right) of the two exciton states $|1\rangle$ and $|2\rangle$ in an InGaAs self assembled quantum dot embedded in GaAs. At the critical field of 5.4 kV/cm, applied in growth direction, the entanglement is maximized and the two peaks in the oscillator strength originating from $|1\rangle$ and $|2\rangle$ anticross and $|1\rangle$ becomes dark. Figure adapted from Ref. [69].

3.3 Wave Function Imaging

In section 2.8.3 we described the formalism used to calculate tunneling amplitudes from correlated many-body wave functions. We will illustrate it by an application to magnetotunneling spectroscopy (MTS) of self-assembled InAs quantum dots grown by the Stranskii-Krastanov method [127, 128]. We choose this system because of recent measurements on this system [20]. The experimental method is based on capacitance-voltage (C-V) spectroscopy [15, 99, 129–132] where the energy of the quantum dot states can be shifted by an applied out of plane voltage to allow electron (or hole) to tunnel into the dots controllably. Additionally, a magnetic field B is applied in-plane. The tunneling rate can be measured and compared to the theoretical

calculations [20]. Figure 7 a) shows the theoretical results for the tunneling amplitude of holes mapped out in **k**-space for an InAs lens-shaped quantum dot with an elliptical base of 26 nm in $[1\bar{1}0]$ and 25 nm in [110] direction and 3.5 nm height. The labels $nh \rightarrow mh$ describes the process of tunneling the mth hole into the dot already filled with n holes. The arrows with labels [110] and $[1\bar{1}0]$ describe the crystallographic directions in real-space. From the Figure it is clear that tunneling of the first and second hole occurs into an S-like state. We can quantitatively analyze the orbital momentum character of the final state and it is indeed to more than 95% $l = 0$. The tunneling of the third and fourth holes occurs into P-like states. For the fifth hole, **4h $\rightarrow$ 5h** the situation is interesting since it is the signature of the tunneling into the D state. Indeed 82% of the final state, in which the hole tunnels, is given by a configuration with dominant D character. In Figure 7 b) we show that the filling sequence expected from the Aufbau principle would lead to a tunneling into a second P state (labelled P2 in Figure 7 b)) and not into a D-state, as given by the many-body calculation. The holes 5 and 6 therefore entirely skip the P2 shell to tunnel directly into the D-shell, in contrast to the expectation from the Aufbau principle. This result is confirmed by a side-by-side comparison of experiment and theory [20]. In Figure 7 c) we show a contour plot for the experimental MTS result for the tunneling of the first hole along with theoretical results for a dot with circular base of 25 nm diameter and for a dot with ellipsoidal base of 24x26 nm^2. The comparison of theory and experiment shows a better fit for the elongated dot. These results should illustrate the capability to draw conclusions on dot morphology, difficult to get by other means, and on unexpected many-body effects.
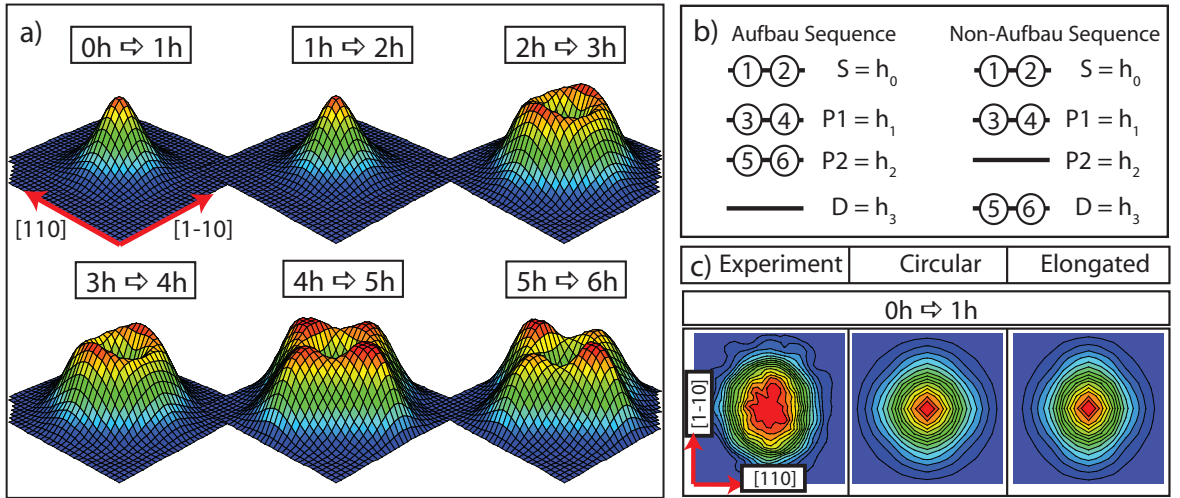

Figure 7: a) Calculated quasi-particle tunneling probability densities for 1 to 6 holes in reciprocal space [20] b) Two possible charging scenarios for holes. c) Quasi-particle tunneling probability density for the first hole from experiment (left), a calculation for a dot with circular base (middle), and a calculation for an elliptical base (right).

4   Summary and Outlook

We have described an approach to obtain accurate properties, including excitations, of semi-conductor nanostructures of realistic and relevant sizes. The approach is based on empirical or semi-empirical pseudopotentials and configuration interaction. The critical steps that allow us

to treat million atom systems are (i) we forgo the calculation of total energies and solve an inner eigenvalue problem around the band gap for a few states only, (ii) the constructed empirical potentials are total effective potentials that include the effect of valence electrons. There is no self-consistent procedure and the Hamilton matrix is solved for few eigenvalues only once. (iii) For the largest structures we use a basis set made of Bloch functions of the underlying strained bulk matrix, leading to a dense but manageable eigenvalue problem. The ensuing quasiparticle eigenfunctions can be directly used to calculate correlated few-particle states, with N electrons and M holes, by a configuration interaction treatment. This give access to observables that can be calculated using post-processor tools. The accuracy and applicability of the method was illustrated by three different applications in the area of optics, quantum entanglement and wave function imaging.

One of the appeals of the method, besides the fact that it can address a large number of atoms, may come from the fact that, for the *semi* empirical potentials, the construction is directly tied to *ab initio* methods. The results from density functional theory (DFT) are fed into the semi-empirical pseudopotentials in a controllable fashion during construction. Applications of the method are, however, seamless in the sense that no more interface between SEPM and DFT exists, unlike multi-scale approaches where this interface represents the crux of the methods. The most fundamental limitation of the method originates from one of its strength and is the lack of self-consistency. Indeed, effects related to long range charge transfer, well captured by self-consistent methods such as DFT, are absent in the SEPM framework. These effects can be sometimes included *a posteriori* as external fields, as in the case of piezoelectricity, but this represents a complication.

The solid foundation of the framework presented here, allows us to envision some interesting extensions for the coming years. A natural and useful development would be the inclusion of *dynamical processes* where electron-phonon coupling could be treated perturbatively or non-perturbatively. This would enable us to predict the effect of temperature on the observables described previously and give us access to processes forbidden in the absence of phonons, such as spin-relaxation times. These are fundamentally interesting effects, relevant to the world of technology. Another interesting avenue is the effect of magnetic fields on nanoscopic systems treated almost exclusively at continuum level until now. An accurate prediction of magnetic properties, such as g-factors, would be useful, e.g., to the area of spintronics. Yet another valuable developments would be the creation of a link between the potential construction and the modern theories beyond LDA, such as GW. Such a link could help removing some of the empirical steps in the construction and may lead to a more automatic way of pseudopotential generation, ideally close to the ones used commonly in DFT. Finally, improving the numerics and algorithms is a never ending and often surprising task that can open the way to applications and developments not easy to foresee.

References

[1] A.D. Yoffe. Semiconductor quantum dots and related systems: electronic, optical, luminescence and related properties of low dimensional systems. *Adv. Phys.*, 50:1–208, 2001.

[2] C. Celebi, P.M. Koenraad, A. Y. Silov, W. Van Roy, A. M. Monakhov, J. M. Tang, and M.E. Flatté. Anisotropic spatial structure of deep acceptor states in GaAs and gap. *Phys. Rev. B*, 77:075328, 2008.

[3] A. M. Yakunin, A. Y. Silov, P. M. Koenraad, J. M. Tang, M. E. Flatte, J. L. Primus, W. Van Roy, J. De Boeck, A. M. Monakhov, K. S. Romanov, I. E. Panaiotti, and N. S. Averkiev. Warping single Mn acceptor wavefunction by straining the GaAs host. *Nature Materials*, 6(7):512–515, Jul 2007.

[4] A. Kudelski, A. Lemaitre, A. Miard, P. Voisin, T. C. M. Graham, R. J. Warburton, and O. Krebs. Optically probing the fine structure of a single Mn atom in an InAs quantum dot. *Phys. Rev. Lett.*, 99(24):247209, Dec 2007.

[5] J. Fernandez-Rossier and L. Brey. Ferromagnetism mediated by few electrons in a semi-magnetic quantum dot. *Phys. Rev. Lett.*, 93(11):117201, Sep 2004.

[6] Y. Leger, L. Besombes, L. Maingault, D. Ferrand, and H. Mariette. Geometrical effects on the optical properties of quantum dots doped with a single magnetic atom. *Phys. Rev. Lett.*, 95(4):047403, Jul 2005.

[7] L. Besombes, Y. Leger, L. Maingault, D. Ferrand, H. Mariette, and J. Cibert. Probing the spin state of a single magnetic ion in an individual quantum dot. *Phys. Rev. Lett.*, 93(20):207403, Nov 2004.

[8] Y. Leger, L. Besombes, J. Fernandez-Rossier, L. Maingault, and H. Mariette. Electrical control of a single Mn atom in a quantum dot. *Phys. Rev. Lett.*, 97(10):107401, 2006.

[9] S. C. Erwin, L. J. Zu, M. I. Haftel, A. L. Efros, T. A. Kennedy, and D. J. Norris. Doping semiconductor nanocrystals. *Nature*, 436(7047):91–94, 2005.

[10] R. J. Warburton, C. Schaflein, D. Haft, F. Bickel, A. Lorke, K. Karrai, J. M. Garcia, W. Schoenfeld, and P. M. Petroff. Optical emission from a charge-tunable quantum ring. *Nature*, 405:926, 2000.

[11] B. Urbaszek, R J Warburton, K. Karrai, B.D. Gerardot, P.M. Petroff, and J.M. Garcia. Fine structure of higly charged excitons in semiconductor quantum dots. *Phys. Rev. Lett.*, 90:247403, 2003.

[12] E Dekel, D Gershoni, E Ehrenfreund, D Spektor, J M Garcia, and P M Petroff. Multi-exciton spectroscopy of a single self-assembled quantum dot. *Phys. Rev. Lett.*, 80:4991, 1998.

[13] M Bayer, A Kuther, A Forchel, A Gorbunov, V B Timofeev, F Schäfer, J P Reithmaier, T L Reinecke, and S N Walck. Electron and hole g factors and exchange interaction from

studies of the exciton fine structure in $In_{0.60}Ga_{0.40}As$ quantum dots. *Phys. Rev. Lett.*, 82:1748, 1999.

[14] A Zrenner, F Findeis, M Baier, M Bichler, G Abstreiter, U Hohenester, and E Molinari. Optically detected single-electron charging in a quantum dot. *Physica E*, 13:95, 2002.

[15] D. Reuter, P. Kailuweit, A. D. Wieck, U. Zeitler, O. Wibbelhoff, C. Meier, A. Lorke, and J. C. Maan. Coulomb-interaction-induced incomplete shell filling in the hole system of InAs quantum dots. *Phys. Rev. Lett.*, 94:026808, 2005.

[16] L. P. Kouwenhoven, D. G. Austing, and S. Tarucha. Few-electron quantum dots. *Reports on Progress in Physics*, 64(6):701–736, 2001.

[17] D. Loss and D. P. DiVincenzo. Quantum computation with quantum dots. *Phys. Rev. A*, 57:120–126, 1998.

[18] U. Woggon. *Optical Properties of Semiconductor Quantum Dots.* Springer-Verlag, Berlin, 1997.

[19] R. D. Schaller and V. I. Klimov. High efficiency carrier multiplication in PbSe nanocrystals: Implications for solar energy conversion. *Phys. Rev. Lett.*, 92:186601, 2004.

[20] G. Bester, D. Reuter, L. He, A. Zunger, P. Kailuweit, A. D. Wieck, U. Zeitler, J. C. Maan, O. Wibbelhoff, and A. Lorke. Experimental imaging and atomistic modeling of electron and hole quasiparticle wave functions in InAs/GaAs quantum dots. *Phys. Rev. B*, 76(7):075338, Aug 2007.

[21] A. M. Yakunin, A. Y. Silov, P. M. Koenraad, J. M. Tang, M. E. Flatte, W. Van Roy, J. De Boeck, and J. H. Wolter. Spatial structure of Mn-Mn acceptor pairs in GaAs. *Phys. Rev. Lett.*, 95(25):256402, Dec 2005.

[22] D. Kitchen, A. Richardella, J. M. Tang, M. E. Flatte, and A. Yazdani. Atom-by-atom substitution of Mn in GaAs and visualization of their hole-mediated interactions. *Nature*, 442(7101):436–439, Jul 2006.

[23] G. Bastard. *Wave Mechanics Applied to Semiconductor Heterostructures.* Halstead, New York, 1988.

[24] H.X. Fu, L.-W. Wang, and A. Zunger. Applicability of the k · p method to the electronic structure of quantum dots. *Phys. Rev. B*, 57:9971, 1998.

[25] L.-W. Wang, A. J. Williamson, A. Zunger, H. Jiang, and J. Singh. Comparison of the k.p and direct diagonalization approaches to the electronic structure of InAs/GaAs quantum dots. *Appl. Phys. Lett.*, 76:339, 2000.

[26] G. Bester and A. Zunger. Cylindrically shaped zinc-blende semiconductor quantum dots do not have cylindrical symmetry: Atomistic symmetry, atomic relaxation, and piezoelectric effects. *Phys. Rev. B*, 71:045318, 2005.

[27] C. Delerue and M. Lannoo. *Nanostructures: theory and modelling.* Springer Verlag, Berlin and Heidelberg, 2004.

[28] G. Klimeck, F. Oyafuso, T. B. Boykin, R.C. Bowen, and P. von Allmen. Development of a nanoelectronic 3-D (NEMO 3-D) simulator for multimillion atom simulations and its application to alloyed quantum dots. *CMES-computer modeling in engineering and sciences*, 3:601, 2002.

[29] P. N. Keating. Effect of invarience requirements on the elastic strain energy of crystals with application to the diamond structure. *Phys. Rev*, 145:637–645, 1966.

[30] C Pryor, J Kim, L.-W Wang, A J.Williamson, and A. Zunger. Comparison of two methods for describing the strain profiles in quantum dots. *J. Appl. Phys.*, 83:2548, 1998.

[31] A. J. Williamson, L.-W Wang, and A. Zunger. Theoretical interpretation of the experimental electronic structure of lens-shaped self-assembled InAs/GaAs quantum dots. *Phys. Rev. B*, 62:12963, 2000.

[32] A J Williamson and A. Zunger. InAs quantum dots: Predicted electronic structure of free-standing versus GaAs-embedded structures. *Phys. Rev. B*, 59:15819, 1999.

[33] U. von Barth and C. D. Gelatt. Validity of the frozen-core approximation and pseudopotential theory for cohesive energy calculations. *Phys. Rev. B*, 21:2222, 1980.

[34] W. M. C. Foulkes and R. Haydock. Tight-binding models and density-functional theory. *Phys. Rev. B*, 39(17):12520, 1989.

[35] J. C. Phillips and L. Kleinman. New method for calculating wave functions in crystals and molecules. *Phys. Rev.*, 116:287, 1959.

[36] M. L. Cohen, M. L. and V. Heine. Cancellation of kinetic and potential energy in atoms, molecules, and solids. *Phys. Rev.*, 122:1821, 1961.

[37] W. C. Topp and J. J. Hopfield. Chemically motivated pseudopotential for sodium. *Phys. Rev. B*, 7:1295, 1973.

[38] M. T. Yin and M. L. Cohen. Theory of lattice-dynamical properties of solids - application to Si and Ge. *Phys. Rev. B*, 26:3259, 1982.

[39] E. L. Shirley, D. C. Allan, R. M. Martin, and J. D. Joannopoulos. Extended norm-conserving pseudopotentials. *Phys. Rev. B*, 40:3652, 1989.

[40] D. R. Hamann, M. Schlüter, and L. Chiang. Norm-conserving pseudopotentials. *Phys. Rev. Lett.*, 43:1494, 1979.

[41] D. Vanderbilt. Optimally smooth norm-conserving pseudopotentials. *Phys. Rev. B*, 32:8412, 1985.

[42] G. B. Bachelet, D. R. Hamann, and M. Schlüter. Pseudopotentials that work: From H to Pu. *Phys. Rev. B*, 26:4199, 1982.

[43] N. Troullier and J. L. Martins. A straightforward method for generating soft transferable pseudopotentials. *Solid State Comm.*, 74:613, 1990.

[44] G. P. Kerker. Non-singular atomic pseudopotentials for solid-state applications. *J. Phys. C: Solid St. Phys.*, 13:L189, 1980.

[45] D. Vanderbilt. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Phys. Rev. B*, 41:7892, 1990.

[46] P. E. Blöchl. Generalized separable potentials for electronic-structure calculations. *Phys. Rev. B*, 41:5414, 1990.

[47] P. E. Blöchl. Projector augmented-wave method. *Phys. Rev. B*, 50:17953, 1994.

[48] M. L. Cohen and V. Heine. *The fitting of pseudopotentials to experimental data and their subsequent application*, volume 24 of *Solid State Physics*. Academic Press, New York, 1970.

[49] D. Brust, J. C.. Phillips, and M. L. Cohen. Reflectance and photoemission from Si. *Phys. Rev. Lett.*, 9:389, 1962.

[50] D. Brust, F. Bassani, and J. C. Phillips. Critical points and ultraviolet reflectivity of semiconductors. *Phys. Rev. Lett.*, 9(3):94, 1962.

[51] M. L. Cohen and T. K. Bergstresser. Band structures and pseudopotential form factors for 14 semiconductors of diamond and zinc-blende structures. *Phys. Rev.*, 141(2):789, 1966.

[52] L.-W. Wang and A. Zunger. Electronic-structure pseudopotential calculations of large (approximate-to-1000 atoms) Si quantum dots. *J. Phys. Chem.*, 98(8):2158, 1994.

[53] K. A. Mäder and A. Zunger. Empirical atomic pseudopotentials for AlAs/GaAs superlattices, alloys, and nanostructures. *Phys. Rev. B*, 50:17393, 1994.

[54] Weisz G. Band structure and Fermi surface of white tin. *Phys. Rev.*, 149:504, 1966.

[55] M.S. Hybertsen and S. G. Louie. Spin-orbit splitting in semiconductors and insulators from the ab initio pseudopotential. *Phys. Rev. B*, 34:2920, 1096.

[56] G. Bester and A. Zunger. Compositional and size-dependent spectroscopic shifts in charged self-assembled $In_xGa_{1-x}As$/GaAs quantum dots. *Phys. Rev. B*, 68:073309, 2003.

[57] L. Bellaiche. *Progress in Semiconductor Materials for Optoelectronic Applications*, volume 692, pages 9–20. Mater. Res. Soc. Proc., Pittsburgh, 2002.

[58] L. Bellaiche, S.H. Wei, and A. Zunger. Localization and percolation in semiconductor alloys: GaAsN vs GaAsP. *Phys. Rev. B*, 54:17568, 1996.

[59] J. R. Chelikovsky and M. L. Cohen. Nonlocal pseudopotential calculations for the electronic structure of eleven diamond and zinc-blende semiconductors. *Phys. Rev. B*, 14:556, 1976.

[60] L.-W. Wang and A. Zunger. Local-density-derived semiempirical pseudopotentials. *Phys. Rev. B*, 51:17398, 1995.

[61] H.X. Fu, L.-W. Wang, and A. Zunger. Comparison of the k.p and the direct diagonalization approaches for describing the electronic structure of quantum dots. *Appl. Phys. Lett.*, 71:3433, 1997.

[62] L. Kleinman and D. M. Bylander. Efficacious form for model pseudopotentials. *Phys. Rev. Lett.*, 48:1425, 1982.

[63] A. Zunger, A. Franceschetti, G. Bester, W.B. Jones, K. Kim, P.A. Graf, A. Canning L-W Wang, O. Marques, C. Voemel, J. Dongarra, J. Langou, and S. Tomov. Predicting the electronic properties of 3D, million-atom semiconductor nanostructure architectures. *J. Phys.: Conf. Ser.*, 46:292, 2006.

[64] L.-W. Wang and A. Zunger. Solving Schrödingers equation around a desired energy - application to silicon quantum dots. *J. Chem. Phys.*, 100:2394, 1994.

[65] A. V. Knyazev. Toward the optimal preconditioned eigensolver: Locally optimal block preconditioned conjugate gradient method for tight-binding parametrization: Application to silicon nanostructures. *SIAM J. Sci. Comput*, 23:517, 2001.

[66] A. Stathopoulos and J.R. McCombs. A parallel, block, Jacobi-Davidson implementation for solving large eigenproblems on coarse grain environments. *Proceedings of the International Conference on Parallel and Distributed Processing, Techniques and Applications*, page 2920, 1999.

[67] L.-W Wang and A. Zunger. Linear combination of bulk bands method for large-scale electronic structure calculations on strained nanostructures. *Phys. Rev. B*, 59:15806, 1999.

[68] D.C. Sorensen, R.B. Lehoucq, C. Yang, and K. Maschhoff. ARPACK software package. Rice University, 2001.

[69] G. Bester and A. Zunger. Electric field control and optical signature of entanglement in quantum dot molecules. *Phys. Rev B*, 72(16):165334, 2005.

[70] G. A. Narvaez, G. Bester, and A. Zunger. Pressure effects on neutral and charged excitons in self-assembled (In,Ga)As/GaAs quantum dots. *Phys. Rev. B*, 72(4):041307, 2005.

[71] G. Bester, X. Wu, D. Vanderbilt, and A. Zunger. Importance of second-order piezoelectric effects in zinc-blende semiconductors. *Phys. Rev. Lett.*, 96:187602, 2006.

[72] G. Bester, A. Zunger, X. Wu, and D. Vanderbilt. Effects of linear and nonlinear piezo-electricity on the electronic properties of InAs/GaAs quantum dots. *Phys. Rev. B*, 74:081305(R), 2006.

[73] A. Szabo and N. S. Ostlund. *Modern Quantum Chemistry*. McGraw-Hill, New York, 1989.

[74] A. Franceschetti, H Fu, L.-W Wang, and A. Zunger. Many-body pseudopotential theory of excitons in InP and CdSe quantum dots. *Phys. Rev. B*, 60:1819, 1999.

[75] L. X. Benedict. Screening in the exchange term of the electron-hole interaction of the Bethe-Salpeter equation. *Phys. Rev. B*, 66:193105, 2002.

[76] G. Bester, S. Nair, and A. Zunger. Pseudopotential calculation of the excitonic fine structure of million-atom self-assembled $In_{1-x}Ga_xAs$/GaAs quantum dots. *Phys. Rev. B*, 67:R161306, 2003.

[77] R. Resta. Thomas-Fermi dielectric screening in semiconductors. *Phys. Rev. B*, 16:2717, 1977.

[78] H. Haken. Kopplung nichtrelativistischer Teilchen mit einem quantisierten Feld .1. das Exziton im schwingenden, polaren Kristall. *Nuovo Cimento*, 3:1230, 1956.

[79] C. Delerue, M. Lannoo, and G. Allan. Concept of dielectric constant for nanosized systems. *Phys. Rev. B*, 68(11):115411, 2003.

[80] X. Cartoixa and L.-W. Wang. Microscopic dielectric response functions in semiconductor quantum dots. *Phys. Rev. Lett.*, 94(23):236804, 2005.

[81] L.E. Brus. A simple-model for the ionization-potential, electron-affinity, and aqueous redox potentials of small semiconductor crystallites. *J. Chem. Phys.*, 79(11):5566, 1983.

[82] L.E. Brus. Electron electron and electron-hole interactions in small semiconductor crystallites - the size dependence of the lowest excited electronic state. *J. Chem. Phys.*, 80(9):4403, 1984.

[83] A. Franceschetti and A. Zunger. Hund's rule, spin blockade, and the aufbau principle in strongly confined semiconductor quantum dots. *Europhys. Lett.*, 50:243, 2000.

[84] L.-W. Wang. Charging effects in a CdSe nanotetrapod. *J. Phys. Chem. B*, 109(49):23330, 2005.

[85] A. Franceschetti, L.-W. Wang, G. Bester, and A. Zunger. Confinement-induced versus correlation-induced electron localization and wave function entanglement in semiconductor nano dumbbells. *Nano Lett.*, 6:1069, 2006.

[86] L. Hedin. New method for calculating 1-particle greens function with application to electron-gas problem. *Phys. Rev.*, 139(3A):A796–+, 1965.

[87] P.Y. Yu and M. Cardona. *Fundamentals of Semiconductors*. Springer, Berlin, 2001.

[88] G. A. Narvaez, G. Bester, and A. Zunger. Excitons, biexcitons, and trions in self-assembled (In,Ga)As/GaAs quantum dots: Recombination energies, polarization, and radiative lifetimes versus dot height. *Phys. Rev. B*, 72(24):245318, 2005.

[89] A. Thranhardt, C. Ell, G. Khitrova, and H. M. Gibbs. Relation between dipole moment and radiative lifetime in interface fluctuation quantum dots. *Phys. Rev. B*, 65(3):035327, 2002.

[90] E. Dekel, D. V. Regelman, D. Gershoni, E. Ehrenfreund, W. V. Schoenfeld, and P. M. Petroff. Cascade evolution and radiative recombination of quantum dot multiexcitons studied by time-resolved spectroscopy. *Phys. Rev. B*, 62:11038, 2000.

[91] M. A. Nielsen and I. L. Chuang. *Quantum Computation and Quantum Information*. Cambridge University Press, Cambridge, 2000.

[92] C. H. Bennett, H. J. Bernstein, S. Popescu, and B. Schumacher. Concentrating partial entanglement by local operations. *Phys. Rev. A*, 53:2046, 1996.

[93] G. Bester, J. Shumway, and A. Zunger. Theory of excitonic spectra and entanglement engineering in dot molecules. *Phys. Rev. Lett.*, 93:47401, 2004.

[94] L. X. He, G. Bester, and A. Zunger. Electronic asymmetry in self-assembled quantum dot molecules made of identical InAs/GaAs quantum dots. *Phys. Rev. B*, 72(8):081311, 2005.

[95] L. X. He, G. Bester, and A. Zunger. Singlet-triplet splitting, correlation, and entanglement of two electrons in quantum dot molecules. *Phys. Rev. B*, 72(19):195307, 2005.

[96] C.N. Yang. Concept of off-diagonal long-range order and quantum phases of liquid He and of superconductors. *Rev. Mod. Phys.*, 34:694, 1962.

[97] J. Schliemann, J. I. Cirac, M. Kus, M. Lewenstein, and D. Loss. Quantum correlations in two-fermion systems. *Phys. Rev. A*, 64:022303, 2001.

[98] J. Bardeen. Tunnelling from a many-particle point of view. *Phys. Rev. Lett.*, 6:57, 1961.

[99] M. Rontani and E. Molinari. Imaging quasiparticle wave functions in quantum dots via tunneling spectroscopy. *Phys. Rev. B*, 71(23):233106, 2005.

[100] L. X. He, G. Bester, Z. Q. Su, and A. Zunger. Calculation of near-field scanning optical images of exciton, charged-exciton, and multiexciton wave functions in self-assembled InAs/GaAs quantum dots. *Phys. Rev. B*, 76(3):035313, Jul 2007.

[101] G. Bester, A. Zunger, and J. Shumway. Broken-symmetry and quantum entanglement of an exciton in InGaAs/GaAs quantum dot molecules. *Phys. Rev. B*, 71:075325, 2005.

[102] L. He, G. Bester, and A. Zunger. Strain-induced interfacial hole localization in self-assembled quantum dots: Compressive InAs/GaAs versus tensile InAs/InSb. *Phys. Rev. B*, 70:235316, 2004.

[103] G. A. Narvaez, G. Bester, and A. Zunger. Dependence of the electronic structure of self-assembled (In,Ga)As/GaAs quantum dots on height and composition. *J. Appl. Phys.*, 98(4):043708, 2005.

[104] G. A. Narvaez, L He, G. Bester, and A. Zunger. Theoretical predictions of the electronic and optical properties of single and coupled (In,Ga)As/GaAs quantum dots. *Phys. E*, 32:93, 2006.

[105] L.-W. Wang and A. Zunger. Pseudopotential calculations of nanoscale CdSe quantum dots. *Phys. Rev. B*, 53(15):9579–9582, 1996.

[106] L.-W. Wang and A. Zunger. High-energy excitonic transitions in CdSe quantum dots. *J. Phys. Chem. B*, 102(34):6449–6454, 1998.

[107] L.-W. Wang, M. Califano, A. Zunger, and A Franceschetti. Pseudopotential theory of Auger processes in CdSe quantum dots. *Phys. Rev. Lett.*, 91(5), 2003.

[108] A Franceschetti and A. Zunger. Addition energies and quasiparticle gap of CdSe nanocrystals. *Appl. Phys. Lett.*, 76(13):1731–1733, 2000.

[109] M. Califano, A. Zunger, and A. Franceschetti. Direct carrier multiplication due to inverse auger scattering in CdSe quantum dots. *Appl. Phys. Lett.*, 84:2409, 2004.

[110] M. Califano, A. Franceschetti, and A. Zunger. Lifetime and polarization of the radiative decay of excitons, biexcitons, and trions in CdSe nanocrystal quantum dots. *Phys. Rev. B*, 75(11), 2007.

[111] L. He, G. Bester, and A. Zunger. Prediction of an excitonic ground state in InAs/InSb quantum dots. *Phys. Rev. Lett.*, 94:016801, 2005.

[112] J. M. An, A. Franceschetti, S. V. Dudiy, and A. Zunger. The peculiar electronic structure of PbSe quantum dots. *Nano Lett.*, 6(12):2728–2735, 2006.

[113] A. Franceschetti, J. M. An, and A. Zunger. Impact ionization can explain carrier multiplication in PbSe quantum dots quantum dots. *Nano Lett.*, 6:2191, 2006.

[114] M. Gong, K. D., C.-F. Li, R. Magri, G. A. Narvaez, and L. He. Electronic structure of self-assembled InAs/InP quantum dots: Comparison with self-assembled InAs/GaAs quantum dots. *Phys. Rev. B*, 77:045326, 2008.

[115] P. R. C. Kent and A. Zunger. Theory of electronic structure evolution in GaAsN and GaPN alloys. *Phys. Rev. B*, 6411(11), 2001. 115208.

[116] M. Ediger, G. Bester, B. D. Gerardot, A. Badolato, P. M. Petroff, K. Karrai, A. Zunger, and R. J. Warburton. Fine structure of negatively and positively charged excitons in semiconductor quantum dots: Electron-hole asymmetry. *Phys. Rev. Lett.*, 98:036808, 2007.

[117] M. Ediger, G. Bester, A. Badolato, P. M. Petroff, K. Karrai, A. Zunger, and R. J. Warburton. Peculiar many-body effects revealed in the spectroscopy of highly charged quantum dots. *Nature Physics*, 3(11):774–779, Nov 2007.

[118] M. Pi, A. Emperador, M. Barranco, F. Garcias, K. Muraki, S. Tarucha, and D. G. Austing. Dissociation of vertical semiconductor diatomic artificial molecules. *Phys. Rev. Lett.*, 87:066801, 2001.

[119] M. Rontani, S. Amaha, K. Muraki, F. Manghi, E. Molinari, S. Tarucha, and D. G. Austing. Molecular phases in coupled quantum dots. *Phys. Rev. B*, 69:085327, 2004.

[120] F. R. Waugh, M. J. Berry, D. J. Mar, R. M. Westervelt, K. L. Campman, and A. C. Gossard. Single-electron charging in double and triple quantum dots with tunable coupling. *Phys. Rev. Lett.*, 75:705, 1995.

[121] M. Bayer, P. Hawrylak, K. Hinzer, S. Fafard, M. Korkusinski, Z. R. Wasilewski, O. Stern, and A. Forchel. Coupling and entangling of quantum states in quantum dot molecules. *Science*, 291:451–453, 2001.

[122] P. W. Fry, I. E. Itskevich, D. J. Mowbray, M. S. Skolnick, J. J. Finley, J. A. Barker, E. P. O'Reilly, L. R. Wilson, I. A. Larkin, P. A. Maksym, M. Hopkinson, Al.-M. Khafaji, J. P. R. David, A. G. Cullis, G. Hill, and J. C. Clark. Inverted electron-hole alignment in InAs-GaAs self-assembled quantum dots. *Phys. Rev. Lett.*, 84:733, 2000.

[123] M. Sugisaki, H. W. Ren, S. V. Nair, K. Nishi, and Y. Masumoto. External-field effects on the optical spectra of self-assembled InP quantum dots. *Phys. Rev. B*, 66(23):235309, 2002.

[124] B. Alen, F. Bickel, K. Karrai, R.J. Warburton, and P.M. Petroff. Stark-shift modulation absorption spectroscopy of single quantum dots. *Appl. Phys. Lett.*, 83(11):2235, 2003.

[125] H. J. Krenner, M. Sabathil, E. C. Clark, A. Kress, D. Schuh, M. Bichler, G. Abstreiter, and J. J. Finley. Direct observation of controlled coupling in an individual quantum dot molecule. *Phys. Rev. Lett.*, 94:057402, 2005.

[126] G. Ortner, M. Bayer, Y. Lyanda-Geller, T. L. Reinecke, A. Kress, J. P. Reithmaier, and A. Forchel. Control of vertically coupled InGaAs/GaAs quantum dots with electric fields. *Phys. Rev. Lett.*, 94:157401, 2005.

[127] S. Guha, A. Madhukar, and K. C. Rajkumar. Onset of incoherency and defect introduction in the initial-stages of molecular-beam epitaxial-growth of highly strained $In_xGa_{1-x}As$ on GaAs(100). *Appl. Phys. Lett.*, 57:2110, 1990.

[128] D. Bimberg, M. Grundmann, and N. N. Ledentsov. *Quantum Dot Heterostructures*. John Wiley & Sons, New York, 1999.

[129] H. Drexler, D. Leonard, W. Hansen, J. P. Kotthaus, and P. M. Petroff. Spectroscopy of quantum levels in charge-tunable InGaAs quantum dots. *Phys. Rev. Lett.*, 73:2252, 1994.

[130] M. Fricke, A. Lorke, J. P. Kotthaus, G. MedeirosRibeiro, and P. M. Petroff. Shell structure and electron-electron interaction in self-assembled InAs quantum dots. *Europhys. Lett.*, 36(3):197–202, 1996.

[131] A. Patane, R. J. A. Hill, L. Eaves, P. C. Main, M. Henini, M. L. Zambrano, A. Levin, N. Mori, C. Hamaguchi, Y. V. Dubrovskii, E. E. Vdovin, D. G. Austing, S. Tarucha, and G. Hill. Probing the quantum states of self-assembled InAs dots by magnetotunneling spectroscopy. *Phys. Rev. B*, 65(16):165308, 2002.

[132] E. E. Vdovin, A. Levin, A. Patane, L. Eaves, P. C. Main, Y. N. Khanin, Y. V. Dubrovskii, M. Henini, and G. Hill. Imaging the electron wave function in self-assembled quantum dots. *Science*, 290(5489):122–124, 2000.

[133] A. M. Stoneham and J. L. Gavartin. Dynamics at the nanoscale. *Materials Science & Engineering C*, 27(5-8):972–980, 2007.