Ψ_k Newsletter

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

Number 68 April 2005

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1 Editorial

We start this newsletter with a call for papers for the Psi-k2005 Conference, to be held in Schwäbisch Gmünd in September. In the section of the ESF Psi-k Programme we have an announcement of a hands-on tutorial course on LDA+DMFT. This is followed by a report, including abstracts of presented papers, on a workshop on "Orbital Functionals for Exchange and Correlation: The Optimized Effective Potential and Related Methods", jointly organized by Freie Universität Berlin and Ludwig-Maximilians Universität München, and sponsored by the Nanoquanta Network and Deutsche Forschungsgemeinschaft. More workshop/conference announcements can be found in the **General Workshop/Conference Announcements**' section, followed by announcements of available positions. Abstracts of the recent or newly submitted papers are in their usual section. In the section **Presenting Other Initiatives**, we have information on a European initiative "HPC-Europa" offering funding for collaborative research. The scientific highlight of this newsletter is by Tchavdar Todorov (*Belfast*), Cristián G. Sánchez (*Belfast*), David Bowler (*London and Tsukuba*) and Andrew Horsfield (*London*) on **"Correlated Electron-Ion Dynamics"**. Please consult the table of contents for further details.

The *Networks* have a home page on World Wide Web (WWW). Its *Uniform Resource Locator* (URL) is:

http://psi-k.dl.ac.uk/

The above contains information on the Psi-k 2005 workshops and hands-on courses (subject to funding). In these pages you can also find information on how to apply for funding to make collaborative visits.

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

The following email addresses, which remain in operation, are repeated for your convenience, and are the easiest way to contact us.

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

Dzidka Szotek, Martin Lüders and Walter Temmerman
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2 General News

2.1 Psi-k2005 Conference

2.1.1 CALL FOR PAPERS

”Towards atomistic materials design”

September 17-21, 2005

Schwäbisch Gmünd, Germany

http://www.fyslab.hut.fi/psik2005/

Preparations are well underway for the large Psi-k meeting next September. We can expect a lively and interesting event, covering theoretical and computational research of electronic structure and properties of matter, ranging from nanostructured materials to systems of biological interest.

The scientific programme consists of four plenary sessions with keynote speakers and fourteen topical symposia with invited speakers. Several of the symposia are organised by the Working Groups of the ESF Psi-k Programme, and reflect their specific interests.

The Conference website is at

http://www.fyslab.hut.fi/psik2005.

It contains information of the symposia topics as well as plenary and invited speakers.

This is an invitation to register for participation in the Conference and to submit abstracts of work to be presented in the scientific programme as posters or as contributed oral talks.

The registration and abstract submission will be opened around April 15 and will be available until July 15. Early registration and hotel reservation are strongly encouraged in order to secure accommodation in the area.

There will be a number of stipends available for graduate students and young post-docs as partial support for participation costs. These can be applied for through the website. The stipend recipients will be notified before August 1.

Welcome to Psi-k 2005 at Schwaebisch Gmuend.

Risto Nieminen
Conference Chairman

3 News from the ESF Programme

"Towards Atomistic Materials Design"

3.1 ESF Workshop/Conference Announcements

3.1.1 Hands-on Tutorial Course on LDA+DMFT

May 17-20, 2005

Institute of Theoretical Physics, University of Hamburg

Overview:

A hands-on tutorial workshop introducing the LDA+DMFT method for realistic investigation of correlated materials will be held at the Institute of Theoretical Physics, University of Hamburg.

Scientific scope:

The correlated electronic structure (LDA+DMFT) approach based on the NMTO first-principle tight-binding method (developed by Prof. O. K. Andersen at MPI-Stuttgart) and multi-band cluster QMC-scheme scheme for the realistic Dynamical Mean-Field Calculations (for introduction, see G. Kotliar and D. Vollhardt, Physics Today **57**, 53, (2004)) become a useful tool for investigation of correlated materials:

A. Poteryaev, et. al. Phys. Rev. Lett. **93**, 086401 (2004).

E. Pavarini, et. al. Phys. Rev. Lett. **92**, 176403 (2004).

S. Biermann, et. al. Phys. Rev. Lett. **94**, 026404 (2005).

The purpose of this workshop is to offer an introduction to the LDA+DMFT scheme and practical calculations of correlated systems using multi-band QMC code.

Further information is available at:

http://www.physnet.uni-hamburg.de/hp/alichten/

Deadline for application is 1st of May 2005. Expected number of participants is 25.

A limited financial subsistence is available. Please send application (personal data, scientific interests, arrival, departure and what kinds of financial help is needed) to:

alichten@physnet.uni-hamburg.de

copy to

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4 General Workshop/Conference Reports

4.1 Report on the OEP Workshop in Berlin

Organized by

Stefan Kurth and Eberhard K. U. Gross

Freie Universität Berlin

and

Hubert Ebert

Ludwig-Maximilians Universität München

Financed by

Nanoquanta Network and Deutsche Forschungsgemeinschaft

`http://www.physik.fu-berlin.de/~ag-gross/oep-workshop/organizers.html`

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LMU

Orbital Functionals for Exchange and Correlation

The Optimized Effective Potential and Related Methods

Workshop

11-13 March 2005

Berlin, House Christophorus

The workshop is financed by

nanoquanta

Deutsche Forschungsgemeinschaft DFG

The first workshop on orbital functionals in density-functional theory was held in Berlin, Germany, March 11-13, 2005. The focus of the workshop was on the latest theoretical developments of orbital functionals within density-functional theory. The scientific program covered 30 invited and 4 contributed talks and was attended by 72 participants.

A key feature of the workshop was that it brought together researchers from backgrounds within many-body Green function and density-functional theory which made the workshop mutually stimulating and very lively. It was clear from the many interesting presentations in the workshop that several new developments are going on in the construction of better orbital functionals for electron correlations. Several groups have studied the orbital functionals within second order perturbation theory or based on RPA or GW-type methods or on variational functionals of the many-body Green function. These developments are also stimulated by interest in obtaining optical properties of solids and molecules which require better response functions based on the exchange-correlation kernel of time-dependent density functional theory. Several groups at workshop have presented ways to develop density-functional procedures which are aimed to compete in accuracy with many-body methods based on the Bethe-Salpeter equation while reducing the computational effort considerably. It was also shown that orbital functionals for correlation (based on diagrammatic perturbation theory) have turned out to be very successful is in the first-principles study of superconductors. The first results on these systems, which were presented at the workshop, indicate that such functionals have a promising future. Also various other and related topics were discussed at the workshop such as functionals of the one-particle density matrix based on natural orbitals and occupation numbers, and orbital functionals for relativistic and beyond Born-Oppenheimer systems and systems in strong laser fields.

All in all, this was an intense but scientifically stimulating and rewarding workshop in which the developments of orbital functionals in density-functional theory clearly gave the impression of being a very lively field of research. The development of such functionals and their application is clearly in its early stages but the enthousiastic atmosphere at the workshop clearly gave the impression that there is much more to come in the near future.

Robert van Leeuwen

Program

Time	Friday	Saturday	Sunday
9.00-9.30		**H. Eschrig** Orbital Polarization in the Kohn-Sham-Dirac Theory	**L. Reining** Many-Body Perturbation Theory using the Density-Functional concept: a successful combination!
9.30-10.00		**S. Kurth** Optimized Effective Potentials in Current-Density-Functional Theory	**A. Rubio** Optical and ground state properties of solids within a GW-based OEP scheme
10.00-10.30		**M. Kaupp** The quest for inclusion of nondynamical electron correlation in OEP calculations	**F. Bechstedt** GW approximation: One- and two-particle excitations in solids and molecules
10.30-11.00		**Coffee Break**	**Coffee Break**
11.00-11.30		**R. Godby** Including orbital effects in exchange and correlation through generalized Kohn-Sham and GW approaches*	**E. Engel** Including orbital effects in perturbation theory: Asymptotic properties of correlation potential for finite systems
11.30-12.00		**P. Rinke** Combining quasiparticle energy calculations with exact-exchange density-functional theory	**X. Gonze** Orbital- and energy-dependent exchange-correlation functionals : molecular dissociation and band gap energy
12.00-12.30		**A. Schindlmayr** Surface Contributions to the Self-Energy for Slab and Supercell Geometries	**N. Lathiotakis** Electronic correlation in periodic systems using reduced density matrix functional theory
12.30-13.30		**Lunch**	**Lunch**
13.30-14.00	**A. Görling** Exact-exchange methods as examples of density-functional approaches with orbital-dependent functionals	**Lunch**	**Lunch**

*updated title

Time	Friday	Saturday	Sunday
14.00-14.30	**S. Kümmel** Optimized effective potential and the electrical response of finite systems	**K. Tsemekhman** Self-Consistent implementation of SIC DFT and of the exact exchange functionals in plane-wave DFT*	**U. von Barth** Successively better and conserving response function within time-dependent density-functional theory obtained from variational many-body theory
14.30-15.00	**C. Proetto** Novel properties of the Kohn-Sham exchange potential for open systems*	**M. Lüders** Single-site self-interaction correction in the KKR-CPA*	**N.E. Dahlen** Orbital functionals derived from variational functionals of the Green function
15.00-15.30	**H. Ebert** Relativistic Optimized Potential Method for magnetic solids	**S. Biermann** A dynamical mean field view on the electronic structure of correlated materials: "LDA+DMFT" and beyond	**M. Seidl** An XC-functional with exact exchange, using the ideas of strictly correlated electrons and attractive-electron clusters
15.30-16.00	**H. Akai** OEP method in RPA level and its applications	**A. Lichtenstein** Orbital polarization in correlated electron systems	**N. Gidopoulos** Beyond the Born-Oppenheimer/adiabatic approximation in terms of an OEP*
16.00-16.30	**Coffee Break**	**Coffee Break**	**Departure**
16.30-17.00	**W. Temmerman** SIC-LSD description of rare earths and actinides	**A. Eguiluz** The dynamical density-response function of transition-metal oxides	
17.00-17.30	**Z. Szotek** SIC-LSD description of spintronics materials	**M. van Schilfgaarde** Quasiparticle self-consistent GW approximation*	
17.30-18.00	**A. Floris** Density functional theory for superconductors: Applications to MgB2 and solids under pressure	**A. Ernst** GW approximation in the multiple-scattering theory	
18.00-18.20	**S. Sharma** Exact exchange within the FP-LAPW method*	**G. Kresse** Performance of hybrid density functional methods, screened exchange and EXX-OEP methods in the PAW approach	
18.20-18.40	**J.K. Dewhurst** Exact exchange within the FP-LAPW method*	**I. Grabowski** Orbital dependent correlation potentials in ab initio density functional theory*	

* updated title

Exact-exchange methods as examples of density-functional approaches with orbital-dependent functionals

A. Görling
Institut für Physikalische und Theoretische Chemie, Universität Erlangen-Nürnberg, Erlangen

Density-functional methods using orbital-dependent functionals are introduced. A new view on the Kohn-Sham formalism is given. The optimized effective potential method is briefly reviewed. As examples for the use of orbital-dependent functionals, exact-exchange Kohn-Sham methods and time-dependent density-functional approaches employing exact-exchange kernels are presented. Applications in quantum chemistry and solid state physics are discussed.

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Optimized effective potential and the electrical response of finite systems

S. Kümmel
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Local and semilocal functionals accurately predict the ground-state properties of many electronic systems and, when used in the spirit of adiabatic approximations, can also describe excitations. There are, however, prominent examples where these approximations fail dramatically, e.g., the electrical response of molecular chains is overestimated by orders of magnitude and the strong-field double ionization of the helium atom is not described correctly. These paradigm cases for the failures of (semi)local functionals will be discussed. It will be shown that orbital functionals and the Optimized Effective Potential can lead to much improved results since they incorporate the derivative discontinuity which is missing in the (semi)local approximations.

Novel properties of the Kohn-Sham exchange potential for open systems application to the two-dimensional electron gas

C.R. Proetto
Centro Atómico Bariloche, Rio Negro, Argentina

The properties of the Kohn-Sham (KS) exchange potential for open systems in thermodynamical equilibrium, where the number of particles is non-conserved, are analyzed with the OEP method of DFT at zero temperature. The 2DEG is used as an illustrative example. The main findings are that the KS exchange potential builds a significant barrier-like structure under slight population of the second subband, and that both the asymptotic value of the KS exchange potential and the inter-subband energy jump discontinuously at the one subband → two subband transition. The results obtained in this system offer new insights on open problems of semiconductors, such as the band-gap underestimation and the band-gap renormalization by photo-excited carriers.

Relativistic Optimized Potential Method for magnetic solids

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[b] *University of Nijmegen, Netherlands,*
[c] *Institut für Theoretische Physik, Universität Hamburg*

We present a charge and self-energy self-consistent computational scheme for correlated systems based on the Korringa-Kohn-Rostoker (KKR) multiple scattering theory with the many-body effects described by the means of dynamical mean field theory (DMFT). The corresponding local multi-orbital and energy dependent self-energy is included into the set of radial differential equations for the single-site wave functions. The Green's function is written in terms of the multiple scattering path operator, the later one being evaluated using the single-site solution for the t-matrix that in turn is determined by the wave functions. An appealing feature of this approach is that it allows to consider local quantum and disorder fluctuations on the same footing. Within the Coherent Potential Approximation (CPA) the correlated atoms are placed into a combined effective medium determined by the dynamical mean field theory (DMFT) self-consistency condition. Results of corresponding calculations for pure Fe, Ni and $\mathrm{Fe}_x\mathrm{Ni}_{1-x}$ alloys are presented.

OEP in RPA level and its applications

H. Akai
Department of Physics, Osaka University, Japan

The OEP in the RPA level was shown to be able to give rise to reasonable description of both moderately correlated (e.g. transition metal oxides) and rather weakly correlated systems (e.g. alkaline metals). Only the problem of the OEP within RPA is that the procedure is rather time consuming, which prevents us from applying the method to the daily job of electronic structure

calculations. One possibility to overcome such a situation is to take only account of the short range correlation effects. The results of such attempts will be presented together with general review of the OEP within RPA.

SIC-LSD description of rare earths and actinides

W. Temmerman
Computational Science and Engineering Department, Daresbury Laboratory, UK

We present applications of the self-interaction corrected local spin density approximation (SIC-LSDA) to 4f and 5f systems. It will be shown that the SIC-LSDA describes (i) localization/delocalization transitions in the 4f systems and (ii) a more complex character of the localized 5f electrons in the actinides. It will also be shown that the metal/insulator transition in some of these systems can be described as a localization/delocalization transition.

SIC-LSD description of spintronics materials

Z. Szotek
Computational Science and Engineering Department, Daresbury Laboratory, UK

The self-interaction corrected local spin density approximation is applied to study electronic structure and magnetic properties of Mn- and Co-doped III-V and II-VI diluted magnetic semiconductors, magnetite, such spinel ferromagnetic insulators as $NiFe_2O_4$ and $CoFe_2O_4$, and some f-electron compounds of possible interest to spintronics. In the diluted magnetic semiconductors we concentrate on the understanding and realization of the carrier mediated ferromagnetism. The electronic structure of $NiFe_2O_4$ and $CoFe_2O_4$ is discussed in comparison with the insulating charge ordered Verwey phase of magnetite. We speculate on the implications for possible technological applications.

Density functional theory for superconductors: Applications to MgB2 and solids under pressure

A. Floris
Institut für Theoretische Physik, Freie Universität Berlin

Understanding and predicting the properties of superconductors is of both fundamental and technological importance. The discovery of superconductivity in MgB_2, of its rather high critical temperature ($T_c = 39.5$K), and the appearance of multiple gaps, has renewed the interest in conventional, phonon driven superconductivity. Here we present several applications of a novel approach to superconductivity that allows one to calculate material-specific properties, such as the gap and the T_c, in a truly ab-initio fashion without using any adjustable parameters. Within this approach, we obtained the T_c and the two gaps of MgB_2 in good agreement with experiment, taking into account the strong anisotropy of both the electron-phonon and the Coulomb interactions. As a further application, we studied the behavior of T_c in Li and Al as a function of pressure. Despite their common simple metal structure, these materials show different behavior upon pressure. While Li undergoes several transitions favoring superconductivity, in Al the electron-phonon coupling decreases with pressure leading to a complete suppression of Tc around 8GPa.

Magnetism in FeAl, Ni_3Al and Ni_3Ga Within Density Functional Theory: Importance of Asymmetry in the Exact Exchange Potential

S. Sharma, J. K. Dewhurst, C. Ambrosch-Draxl
Institut für Physik, Karl–Franzens–Universität Graz, Austria

We have calculated the magnetic properties of FeAl, Ni_3Al and Ni_3Ga with exact exchange DFT within the all-electron full-potential linearized augmented-plane-wave method, including core-valence interactions [1]. The correct ground state for these materials is obtained in all cases: non-magnetic for FeAl and Ni_3Ga and ferromagnetic in Ni_3Al with a magnetic moment of 0.20 μ_B per formula unit, which is in excellent agreement with experiments. Both LDA and GGA fail to produce the correct magnetic ground state of all three compounds. This failure has been the subject of several investigations in the past [2, 3, 4]. *Ad hoc* corrections to the LDA have been used to obtain the correct ground state for these materials, but are either not parameter free (LDA+U) or include dynamical variables (spin fluctuations) which are closer in spirit to the quasi-particle picture.

We attribute the success of exact exchange to the strong asymmetry in the exchange potential. This should be a desirable feature for next generation approximate functionals.

References

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All-electron Exact Exchange Treatment of Semiconductors: Effect of Core-valence Interaction on Band-gap and d-band Position

J. K. Dewhurst,S. Sharma, C. Ambrosch-Draxl
Institut für Physik, Karl–Franzens–Universität Graz, Austria

Exact exchange (EXX) Kohn-Sham calculations within an all-electron full-potential method are performed on a range of semiconductors and insulators (Ge, GaAs, CdS, Si, ZnS, C, BN, Ne and Ar). We find that the band-gaps are not as close to experiment as those obtained from previous pseudopotential EXX calculations. Full-potential band-gaps are also not significantly better for *sp* semiconductors than for insulators, as had been found for pseudopotentials. The locations of d-band states, determined using the full-potential EXX method, are in excellent agreement with experiment, irrespective of whether these states are core, semi-core or valence. We conclude that the inclusion of the core-valence interaction is necessary for accurate determination of EXX Kohn-Sham band structures, indicating a possible deficiency in pseudopotential calculations.

Orbital Polarization in the Kohn-Sham-Dirac Theory

H. Eschrig
Institut für Theoretische Festkörperphysik, Leibniz-Institut für Festkörper- und Werkstoffforschung Dresden

The consequent relativistic form of density functional theory is the 4-current density functional theory (CDFT). With Gordon's decomposition of the 4-current, the spin density enters, and is used to obtain the spin density functional theory (SDFT). The orbital current and orbital polarization effects are usually neglected in SDFT. This orbital current density of unfilled inner shells can be used to define a kind of an orbital angular momentum density, which may be treated in a local density approximation of the correlation energy leading to orbital polarization correction terms to the ordinary Kohn-Sham or Kohn-Sham-Dirac equation. Preliminary results for transition metal and rare earth atoms are presented.

Optimized Effective Potentials in Current-Density-Functional Theory

S. Kurth
Institut für Theoretische Physik, Freie Universität Berlin

The proper description of many-electron systems in the presence of magnetic fields within a density-functional framework requires the current density to be used as basic variable besides the electron density. Unlike in ordinary spin-density functional theory, where only the coupling of the magnetic field to the spin degrees of freedom is taken into account, in current-density-functional theory (CDFT) one also allows for the coupling to the orbital currents. Electron-gas-based (LDA-type) approximations of CDFT exhibit derivative discontinuities as a function of the magnetic field whenever a new Landau level is occupied. The corresponding exchange-correlation potentials then become singular which makes these functionals difficult to use in practice. As an alternative we present an optimized effective potential (OEP) method within a CDFT framework which allows for the use of explicitly orbital-dependent functionals. The derivation of these equations and a numerically tractable scheme for their solution within a KLI-type approximation will be discussed. We present first results at the exchange-only level for open shell atoms and quantum dots in external magnetic fields.

The quest for inclusion of nondynamical electron correlation in OEP calculations

M. Kaupp
Institut für anorganische Chemie, Universität Würzburg

The full and adequate description of nondynamical correlation (NDC) presents one of the main challenges for modern density functional theory. The available correlation functionals usually take into account only dynamical correlation. On the other hand, even the simplest LDA exchange functional is known to model implicitly a significant part of NDC, simply because of the essential locality of the corresponding exchange hole. Unfortunately, LDA or GGA functionals include spurious self-interactions. Exact exchange (EXX) has the great advantage of being free of self interaction. But it misses NDC completely and thus lacks the "useful" error cancellation of, e.g., GGA functionals. The success of traditional hybrid functionals (with a constant amount of EXX admixture) in quantum chemistry can therefore be explained by a reasonable balance between reduction of self-interaction and partial inclusion of NDC. Recently, more flexible local hybrid functionals have been proposed [1] with the amount of the EXX admixture being a function of the position vector (local mixing function, LMF). In our presentation, we will focus on our own more or less pragmatic approaches towards an efficient inclusion of NDC in OEP-based calculations. This involves the use of "localized hybrid potentials" in calculations of magnetic resonance parameters [2, 3], as well as first steps in the development of coordinate-space models [4] for the treatment of NDC and position-dependent exact-exchange admixture into localized hybrid potentials. Our implementations into the ReSpect quantum chemistry code make use of the LHF approximation [5] to the OEP.

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Including orbital effects in exchange and correlation through generalized Kohn-Sham and GW approaches

R. Godby
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The GW approximation is the first-order term in an expansion of the self-energy operator Σ in powers of the dynamically screened electron-electron interaction, W. It may be thought of as exact exchange (the Hartree-Fock exchange operator), together with an partial inclusion of correlation diagrams through dynamical screening of the Coulomb interaction. From Σ, the one-electron Green's function G may be calculated, from which various spectral and ground-state properties are available. For transport properties (as well as certain other excited-state properties), the two-electron Green's function is required, which may also be formulated at the same level of approximation as GW.

In applying GW to the ground-state total energy, the choice of whether G and/or W are made to be consistent with the Green's function that arises *from* Σ is particularly important: G_0W_0, GW_0 and fully self-consistent GW, where G_0 generally indicates the LDA Green's function. I shall present results for finite and infinite systems at all three levels of self-consistency. These include converged results resulting from the incorporation of self-consistency and GW total-energy techniques into our general-purpose GWST "space-time" supercell code suite [1], which interfaces with pseudopotential plane-wave DFT calculations as its input. This allows the extension of the GW total-energy approach from high-symmetry test systems [2] to general systems, and opens the possibility of applications to systems whose energetics is not described sufficiently reliably within the usual DFT-based approaches.

Generalized Kohn-Sham (GKS) schemes [3] minimize the Hohenberg-Kohn energy starting from an explicit orbital functional for the major part of exchange and correlation, and conveniently yield a self-energy-like GKS Schrödinger equation. This leads to a family of GKS schemes based on the self-energy operator [4, 5].

I shall also describe our recent formulation [6] of the conductance of a junction between two nanowires in a form which permits the inclusion of electronic correlation effects in a GW-like framework.

Further details at http://www-users.york.ac.uk/~rwg3/.

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Combining quasiparticle energy calculations with exact-exchange density-functional theory

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We present a systematic *ab initio* study of the electronic structure for selected II-VI compounds and group III nitrides in the zinc-blende structure with special emphasis on analyzing the role played by the semicore *d*-electrons. We show that applying density-functional theory (DFT) in the exact-exchange (EXX) approach [1] leads to an improved description of the *d*-electron hybridisation compared to the local-density approximation (LDA). Moreover we find that it is essential to use the newly developed EXX pseudopotentials [2] in order to treat core-valence exchange consistently.

In combination with quasiparticle energy calculations in the *GW* approximation we achieve very good agreement with available photoemission data. Since the DFT energies and wavefunctions serve as input for the *GW* calculation we conclude that for these materials EXX constitutes the better starting point.

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Combining quasiparticle energy calculations with exact-exchange density-functional theory

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The combination of density-functional theory and many-body perturbation theory is a powerful method to determine the electronic structure of solids with high accuracy. While self-energy calculations within the GW approximation were long confined to simple bulk materials, it has now become possible to treat fairly complex systems, such as surfaces and even surface defects.

For computational convenience, a periodic supercell geometry is usually adopted in these cases. Electric multipoles may lead to an artificial long-range interaction between the repeated slabs, however. Even if no static low-order multipoles are present in the ground state, the mutual polarization induces dynamic dipoles and leads to a slow convergence of the self-energy with respect to the supercell size. Based on numerical results, we demonstrate the effect of the supercell geometry on the band structure of semiconductors. The behavior is in agreement with a model for the induced polarization that can be used to correct the band structure a posteriori. Furthermore, we discuss the prospects for GW surface calculations without systematic errors due to the simplified slab geometry.

Self-Consistent SIC method and its extension to the exact exchange functionals for extended systems

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We extend the technique previously developed for self-consistent implementation of the self-interaction corrected DFT (SIC-DFT) to the exact exchange functionals (EXX). By making use of the Wannier functions we show that the exact exchange interaction in semiconductors and insulators is short-ranged, and utilize this property to construct a relatively simple and scalable implementation of EXX to periodic systems. Various applications of the PBE0 functional are discussed: we show its reliability in predicting the band gaps in a number of crystals, compare its ability to overcome the tendency of standard functionals to delocalize the charge and spin densities and compare PBE0 with SIC-DFT. With the method not falling into Kohn-Sham scheme, we discuss its extension to the OEP domain. Finally, we address the applicability of the proposed technique to metallic systems.

Self-interaction correction in multiple scattering theory

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We propose a simplified version of self-interaction corrected local spin-density (SIC-LSD) approximation, based on multiple scattering theory, which implements self-interaction correction locally, within the KKR method. The multiple scattering aspect of this new SIC-LSD method allows for the description of crystal potentials which vary from site to site in a random fashion and the calculation of physical quantities averaged over ensembles of such potentials using the coherent potential approximation (CPA). This facilitates applications of the SIC to alloys and pseudoalloys which could describe disordered local moment systems, as well as intermediate valences. As a demonstration of the method, we study the well-known α-γ phase transition in Ce, where we also explain how SIC operates in terms of multiple scattering theory.

A dynamical mean field view on the electronic structure of correlated materials: "LDA+DMFT" and beyond

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Materials with strong Coulomb correlations are challenges for electronic structure calculations. During the last years new methods for their description have been developed. The combination of dynamical mean field techniques with density functional theory allows for the calculation of electronic properties of materials from first principles, taking into account the effect of arbitrarily strong Coulomb interactions.

We will give a brief introduction to dynamical mean field theory and its use within electronic structure calculations. Then, we will describe some recent advances on transition metal compounds, in particular on VO2 [1]. This material presents a metal insulator transition at 340 K, accompanied by a structural transition involving a dimerisation of the vanadium atoms. The origin – Peierls or Mott – of this metal insulator transition has been debated in a very controversial manner. On the basis of our cluster dynamical mean field calculations we argue that Coulomb correlations are indeed crucial for opening the gap which, however, retains a strong Peierls character.

Finally, we will also give a critical account of the "LDA+DMFT" technique and its shortcomings and discuss perspectives of how to go beyond [2].

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Orbital polarization in correlated electron systems

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We analyzed different ways to go beyond the LDA approximation and includes the effects of local Coulomb interactions in d and f-electron systems. Realistic dynamical mean field theory (LDA+DMFT) which takes into account spin and orbital polarization as well as a frequency dependence of the self energy have been combined with the first-principle LDA method. A numerically exact Quantum Monte-Carlo scheme can describe the effects of orbital fluctuations in spin-polarized multi-orbital systems. The different orbital ordering and orbital liquid states of perovskite compounds will be discussed.

The dynamical density-response function of transition-metal oxides

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The density-response function (electron-hole excitations) in prototype transition-metal oxides is investigated via dynamical density-response calculations framed in the spirit of time-dependent density-functional theory. The ground state is described within the LDA+U ”correlated band-structure” method. The electron dynamics is handled within the random-phase approximation (RPA). The loss spectra of a wide class of materials, including half-metals, late transition-metal monoxides, prototype manganites, and sodium cobaltates, feature a striking collective excitation; the same is directly related to the underlying electronic structure, as its energy is a signature of the relative location of the upper and lower Hubbard bands. The physics of the dynamical screening is controlled by d-d transitions and the microscopic crystal local fields. Our predictions can be readily verified via measurements of the dynamical structure factor with (non-resonant) inelastic scattering of hard x-rays -providing a direct test of the quality of the LDA+U ground state and the RPA dynamics. The available experimental data is supportive of key aspects of the calculated spectra. At the same time, there are clear indications that the theory, in its present state of development, is incomplete. Prospects for improvements are hinted at. These include the introduction of dynamical electron-hole interactions, and the implementation of schemes developed strictly within the TDDFT framework (e.g., within the optimized-potential method).

Quasiparticle Self-Consistent GW Theory

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We present a new version of self-consistent GW approximation, which we call the quasiparticle self-consistent GW (QPscGW) approximation. In this Landau-Silin picture the GW approximation is based on the ansatz of the existence of bare quasiparticles generated from a noninteracting Hamiltonian H_0 and corresponding Green's function G_0. In this picture electrons and holes should have real meaning; W is computed from the time-dependent Hartree approximation; $\Sigma = iG_0W$ means “exchange effect” + electrons and holes interacting. A key issue is how to construct the optimum H_0. The true Green's function G should have corresponding one-particle excitations, and H_0 should approximate the corresponding energies and eigenfunctions as well as possible. We present a prescription for H_0 that approximately minimizes the difference between G^{-1} and G_0^{-1}.

Another key aspect of this work is that essentially no important approximation beyond GW itself is made, enabling reliable calculation of compounds with any element in the periodic table. It adopts and all-electron approach where all states are treated at least at the Hartree-Fock level.

The theory is applied to sp bonded materials, simple and transition metals, transition-metal oxides, some magnetic compounds such as MnAs and some f systems (e.g. CeO_2, and Gd). We compare to a variety of experimental data for these different materials classes. The errors are quite small and highly systematic in *sp* systems, they are somewhat larger but still systematic in transition-metal oxides, and are largest for Gd. Some analysis of the origin of the errors will be presented. Self-consistency dramatically improves agreement with experiment, and is sometimes essential for even a qualitatively reliable description of the electronic structure.

GW approximation in the multiple-scattering formalism

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We present a non-self-consistent realization of the GW approximation, which avoids many numerical problems and can be used for a wide range of systems such as bulk, surfaces and clusters. The zeroth-oder Green function is represented in terms of the multiple-scattering theory and can be calculated self-consistently by the Korringa-Kohn-Rostoker (KKR) method. The Hedin's equations in the random phase approximation are solved in imaginary-energy presentation. This schema enables accurate calculations of $sp-$ as well as $d-$ and $f-$ electron systems. We illustrate our approach by the examples of electronic structure study of some $sp-$ and $3d-$ materials.

Performance of hybrid density functional methods, screened exchange and EXX-OEP methods in the PAW approach

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The exact exchange operator has been implemented in the Vienna ab initio program within the framework of the projector augmented wave (PAW) method [1]. Details of the implementation will be briefly described, and the performance for molecular systems and periodic systems is discussed. In particular for screened exchange functionals, the method is only roughly one order of magnitude slower than purely local density functionals. This opens a wide field of applicability, with periodic systems containing 100 atoms per unit cell now within reach.

On top of this approach a variety of methods relying on the exact exchange operator have been added. This includes hybrid functionals (PBE0), screened exchange methods (SEX) [2], model-GW (COH-SEX), local Hartree Fock (LHF) methods, and the exact-exchange optimized-effective-potential (EXX OEP) method [3]. The last one was implemented using an approach recently suggested by Kümmel and Perdew [4]. The performance of the methods is critically examined for a number of simple systems, including simple metals, semiconductors and ionic materials. Particular attention is devoted to the simple itinerant magnetic systems, Fe, Co, and Ni. When correlation is treated using current state of the art semi-local density functionals, the hybrid functionals overestimate the magnetic moment slightly for Fe. The LHF and EXX-OEP methods, however, yield much too large magnetic moments close to Hund's first rule. This result is discussed, paying particular attention to the present limitations of the implementation, which is a valence only method. Future development, which might include core relaxation, are briefly discussed.

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New orbital dependent exchange-correlation potentials from correlated OEP method in ab initio Density Functional Theory

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From many-body theory and coupled-cluster theory we derive the local exchange-correlation potential of density functional theory in an orbital dependent form. Starting from a general theoretical framework based on the density condition in Kohn-Sham (KS) theory and combining them with Coupled Cluster methodology, we define a rigorous exchange-correlation functional, potential and orbitals.

Specifying initially to second-order terms, which defines correlated OEP procedure, we show that our ab initio correlation potential provides the correct shape compared to those from reference quantum Monte Carlo calculations, and we demonstrate the superiority of using Fock matrix elements in defining the unperturbed Hamiltonian. This enables us to introduce ab initio Density Functional Theory as a method that is guaranteed to converge to the right answer in the correlation and basis set limit, just as does ab initio wavefunction theory. We also demonstrate that the energies obtained from this generalized second-order method [OEP-MBPT(2)-f] are often of coupled cluster accuracy and substantially better than ordinary Hartree-Fock based second-order MBPT=MP2.

Also, a new approximate noniterative procedure to obtain accurate correlation and exchange-correlation potentials of KS DFT is presented. By carrying out only one step of the correlated OEP, following the standard iterative exchange-only OEP or Hartree-Fock calculations, we can recover accurate correlation potentials that are hardly discernible from those obtained by the more expensive, fully iterative procedure.

Many-Body Perturbation Theory using the Density-Functional concept: a successful combination!

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Today, in the framework of solid state physics two main approaches are used to describe ground- and excited state properties of condensed matter: on one side, static ground state density functional theory (DFT) and its time-dependent extension (TDDFT) for the description of excited states; on the other side, Many-Body Perturbation Theory (MBPT), most often used in Hedin's GW approximation for the electron self-energy, or the Bethe-Salpeter equation for the calculation of response functions.

Both approaches have lead to breakthroughs, but suffer from different shortcomings: MBPT has a relative conceptual clarity, but calculations are in general numerically very demanding; in particular, it is prohibitive to go beyond the GW approximation. DFT-based approaches are in principle computationally more efficient, but, despite recent progress a generally reliable and at the same time very efficient description of exchange-correlation effects has still to be developed for TDDFT.

We propose a way to overcome this dilemma, by introducing the density-functional concept into the MBPT equations. This combination leads to a new set of equations for response functions and self-energies that allows one to easily go beyond the standard approximations (namely GW for the self-energy and RPA or TDLDA for the density-density response). We show that other recent work on response functions, like exact-exchange or screened-exchange like kernels, are obtained as a particular approximation to our scheme. One aspect of this approach is therefore the derivation of orbital-dependent exchange-correlation functionals. We give several illustrations, both for the high precision that can be obtained and for approximations that lead to computationally very efficient methods.

Optical and ground state properties of solids within a GW-based OEP scheme

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In this talk we will show two alternative (and equivalent ways) of treating correlation effects within a density-functional-based approach. On one side, the adiabatic-connection fluctuation-dissipation theorem (ACFDT) in the framework of Time Dependent Density Functional Theory (TD-DFT) has emerged as a promising alternative to standard implementations of Kohn-Sham (KS) theory to calculate correlation energies. In this approach, the correlation energy is calculated from the knowledge of the interacting density response. On the other, the linearize Sham-Schlüter equation that determines the exchange-correlation potential with the electron self-energy of many-body perturbation theory. Both approaches are equivalent, however the numerical implementation is different. In this context we have calculated the RPA energies as well as the structural properties of simple solids (Si, NaCl), where the KS-LDA performs quite well. As expected, there are minor differences between the KS-LDA and the RPA results. However, in model layered systems, where layer-layer interactions are very weak, there are evident discrepancies between the KS and the TD-DFT binding energies. This is due to the presence of long-ranged correlations that cannot be described at all by mean-field approximations. All this effects are illustrated taking as example hexagonal boron-nitride, where all the structural properties including phonon frequencies are very good described by this approach.

We will also discuss preliminary results for the optical properties of Si and LiF based on a common energy denominator approximation to the Sham-Schlüter equation. In this way a static and spatially-non-local exchange correlation kernel is obtained from which the spectra is computed using the standard TDDFT machinery.

GW approximation: One- and two-particle excitations in solids and molecules

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The many-body perturbation theory is able to describe electronic single- and two-particle excitations for systems of arbitrary dimension. Thereby, the standard approach to exchange and correlation effects is based on the linear expansion of the self-energy in terms of the screened potential W, the so-called GW approximation. We demonstrate the power of the method for bulk crystals, surfaces, noncrystals, and molecules. In addition, we illustrate the influence of non-diagonal elements of the self-energy, the dynamics of the screening and the $\delta W/\delta G$ term in the kernel of the Bethe-Salpeter equation.

Second order Kohn-Sham perturbation theory: Asymptotic properties of correlation potential for finite systems

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It has been shown that the application of the standard form of the OPM integral equation to the second order correlation functional resulting from Kohn-Sham perturbation theory leads to a divergent potential in the large-r regime of atoms [PRL 86, 2241 (2001)]. In the talk these findings will be reviewed and complemented by some new results. In particular,the role of continuum states and the representation of the OPM Green's function will be considered in detail.

Orbital- and energy-dependent exchange-correlation functionals : molecular dissociation and band gap energy

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Orbital- and energy- dependent functional have raised considerable interest recently, because they are potentially able to overcome limitations of commonly used approximations like the local-density approximation, the generalized-gradient approximation, or hybrid methods (B3LYP), especially in the description of Van der Waals forces, and dissociation of molecules.

We show that Density Functional theory within the random-phase approximation (RPA) for the exchange-correlation energy provides a correct description of bond dissociation in H_2 in a spin-restricted Kohn-Sham formalism, i.e. without artificial symmetry breaking. However the RPA dissociation curve displays unphysical repulsion at larger but finite bond lengths. We also calculate the bandgap energy of a solid using the RPA, and find that it is similar to the one obtained from non-renormalized GW calculations, non-self-consistently, i.e. the G_0W_0 approximation. This provides a well-defined and meaningful interpretation to G_0W_0 quasiparticle bandgap calculations, but questions the physics behind the renormalization factors in the expression of the bandgap energy.

Electronic correlation in periodic systems using reduced density matrix functional theory

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Reduced Density Matrix Functional Theory is based on Gilbert's theorem [1] according to which every observable is a functional of the one-body-reduced density matrix (1-RDM). Implicit functionals of the 1-RDM have been introduced [2]. They depend explicitly on the natural orbitals and occupation numbers, i.e. the eigenfunctions and eigenvalues of 1-RDM.

In the present work, we generalize these functionals (a) to the case of periodic systems and (b) to the case of open shell systems.

In the case of periodic systems, our functional formulation is based on a Wannier-states description of the system [3]. We apply this formalism to the calculation of correlation energy of prototype 1-dimensional periodic systems like LiH chain. Furthermore in a similar fashion to DFT we explore the possibility of using the discontinuity of the chemical potential as a function of the number of electrons in the calculation of the electronic gap.

In the case of open-shell atomic and molecular systems, we based our formulation of 1-RDM functional [2] on the Restricted Open-Shell Hartree-Fock theory (ROHF). The first application is the Li atom and we investigate the effect spin resolved constraints in the variation of occupation numbers.

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Successively better and conserving response function within time-dependent density-functional theory obtained from variational many-body theory

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The traditional approach to the optical response of electronic systems is the computationally demanding Bethe-Salpeter theory. Time-dependent density-functional theory (TDDFT) offers an alternative route toward the same goal but involving much less computational effort. A description within TDDFT requires some knowledge of the so called exchange-correlation kernel for which approximations can be constructed from many-body perturbation theory. A particularly well behaved set of successively better approximations for the kernel is obtained from the variational approach to many-body perturbation theory. The resulting kernels give rise to response functions which obey several experimentally important conservation laws and consistency requirements like, e.g., the f-sum rule or momentum conservation.

Of particular interest to extended Coulombic systems is the version of variational many-body theory referred to as the PSI formalism. This version allows for the use of approximate screening functions leading to a strong reduction of the computational effort in low-symmetry systems. Alternatively, the PSI formalism lends itself to the use of approximate model vertices or particle-hole interactions thereby enabling a more realistic description many-body effects without causing an undue increase of the computational labour.

Orbital functionals derived from variational energy functionals of the Green function

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Diagrammatic techniques in many-body perturbation theory are useful for deriving orbital functionals in (TD)DFT such as OEP. The exchange-correlation potential then corresponds to a certain diagrammatic approximation that one can select based on which physical process is believed to be important in the system being considered. For a given self-energy approximation there are, however, many possible ways to define orbital functionals. While the total energy calculated from the self-consistent Green function depends only on the chosen self-energy, the orbital functionals will depend both on the diagrammatic self-energy approximation and on the particular choice of orbital functional scheme. The main topic of this talk will be to compare the conventional OEP method to an orbital functional derived from the Luttinger-Ward functional. We have calculated the total energy of atoms and diatomic molecules from both these functionals, and compared the results to results from self-consistent solutions of the Dyson equation.

An XC-functional with exact exchange, using the ideas of strictly correlated electrons and attractive-electron clusters

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The interaction-strength interpolation model (ISI) for the exchange-correlation energy $E_{xc}[\rho]$ in DFT uses the exact exchange energy $E_x[\rho]$ as starting point for an extrapolation to the strong-interaction limit. The latter can be described rather accurately by two simple functionals $W_\infty[\rho]$ and $W'_\infty[\rho]$. The most expensive ingredient to ISI is the second-order correlation energy of the Görling-Levy perturbation expansion, $E_c^{GL(2)}[\rho]$. Instead of evaluating this orbital-dependent functional directly (using, e.g., OEP methods for the exchange potential), it is estimated here by a generalization of the adiabatic connection to negative coupling-strengths α (corresponding to "attractive" electrons). This approach is illustrated for a model system where the adiabatic connection can be constructed virtually exactly for all (positive and negative) values of α.

Optimized effective potential beyond the Born-Oppenheimer approximation

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A novel treatment of non-adiabatic couplings is proposed. The derivation starts from the long-known, but not well-known, fact that the wave function of the complete system of electrons and nuclei can be written, without approximation, as a Born-Oppenheimer-type product of a nuclear wavefunction, $X(R)$, and an electronic one, $\Phi_R(r)$, which depends parametrically on the nuclear configuration R. From the variational principle we deduce formally exact equations for $\Phi_R(r)$ and $X(R)$. The algebraic structure of the exact nuclear equation coincides with the corresponding one in the adiabatic approximation. The electronic equation, however, contains terms not appearing in the adiabatic case, which couple the electronic and the nuclear wavefunctions and account for the electron-nuclear correlation beyond the Born-Oppenheimer level. It is proposed that these terms can be incorporated using an optimized local effective potential.

Poster Abstracts

Kohn-Sham approximation scheme for interacting bosons

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The density functional for a non-relativistic system of interacting bosons is obtained as the effective action for composite operator. The effective action functional depends both on the particle density and on the order parameter, and determines the equilibrium values of these parameters by a minimum principle. A systematic approximation scheme is formulated by expanding the effective action in powers of the Planck constant. The given order approximation reduces to the problem of non-interacting bosons in a self-consistently determined external potential, which appears a practical implementation of the Kohn-Sham idea.

Further investigation of the asymptotic divergence of the correlation potential in Kohn-Sham perturbation theory

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The second-order perturbation theory based on Kohn-Sham (KS) Hamiltonian leads an implicit density functional for the correlation energy, E_c, which is explicitly dependent on KS orbitals and energies. The corresponding correlation potential, $v_c(\mathbf{r})$, calculated by optimized potential method (OPM), was found to be divergent in the asymptotic region [See Bonetti, et.al., Phys. Rev. Lett. **86**, 2241 (2001)] due to the presence of unoccupied states. In this work, we study the issue systematically in an atomic system with a hard-wall boundary condition to further reveal the nature of this divergence behavior.

Multiple scattering formalism for correlated systems: A KKR+DMFT approach

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We present a charge and self-energy self-consistent computational scheme for correlated systems based on the Korringa-Kohn-Rostoker (KKR) multiple scattering theory with the many-body effects described by the means of dynamical mean field theory (DMFT). The corresponding local multi-orbital and energy dependent self-energy is included into the set of radial differential equations for the single-site wave functions. The Green's function is written in terms of the multiple scattering path operator, the later one being evaluated using the single-site solution for the t-matrix that in turn is determined by the wave functions. An appealing feature of this approach is that it allows to consider local quantum and disorder fluctuations on the same footing. Within the Coherent Potential Approximation (CPA) the correlated atoms are placed into a combined effective medium determined by the dynamical mean field theory (DMFT) self-consistency condition. Results of corresponding calculations for pure Fe, Ni and $\mathrm{Fe}_x\mathrm{Ni}_{1-x}$ alloys are presented.

The Kimball-Overhauser approach to the pair density of the 3D electron gas and Friedel-like phase-shift sum rules

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MPI für Physik komplexer Systeme Dresden

Kimball-Overhauser geminals follow from a 2-body Schrödinger equation with an appropriately screened Coulomb repulsion [1, 2, 3]. They parametrize the pair density together with geminal occupancies, which follow from the non-idempotent momentum distribution [4]. The neutrality sum rule for the pair density leads to sum rules for the geminal phase-shifts, which resemble the Friedel sum rule of solid-state physics [5, 6, 7, 8]. Friedel-like oscillations orig- inate from the singularities of the geminal weights [9].

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Study of the phase transitions in titanium with ab initio calculations and molecular-dynamics

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We have studied the crystal structures of titanium metal and dioxides by means of *ab initio* total-energy calculations. The phases of interest for titanium metal are the α phase (hcp), the high-temperature phase β (bcc), and the high-pressure phase ω (hex), for TiO_2 the rutile phase (stable) and the anatase phase (metastable). For rutile the electron energy loss spectra have already been studied in our Laboratory [1].

We have used Density Functional Theory (DFT) with a plane-wave basis set and the pseudopotential method (PWSCF and FHIPP codes). We have calculated the relaxed lattice parameter for each structure and the energy differences between the phases. Different pseudopotentials were used, where semicore states were or were not explicitly treated. The stabilization between the different phases changes a lot depending on whether or not we include the semicore states. In order to understand this effect, we have performed DOS calculations and we have taken into account the Self-Interaction Correction (SIC) for the semicore states.

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Understanding the dissociation of diatomic molecules in the DFT-ACFD formalism

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There is a growing need for exchange-correlation (XC) functionals going beyond the Local-Density and Generalized-Gradient Approximations (LDA and GGA), in particular in systems where van der Waals (vdW) interactions play a crucial role. These can only be taken into account by means of fully non-local XC functionals, which often depend on the Kohn-Sham orbitals and their energies. One way to build such a functional is to resort to the Adiabatic-Connection Fluctuation-Dissipation (ACFD) theorem [1, 2] in conjunction with the Random-Phase Approximation (RPA).

We are currently using the ACFD scheme implemented in ABINIT to study the dissociation of diatomic molecules. This scheme behaves correctly both near the equilibrium distance and asymptotically for the systems considered so far. However, a spurious maximum in the dissociation curve was evidenced for the N_2 [3] and H_2 [4] molecules. It may result from either (a) H_2 and N_2 being pathological cases, or (b) the lack of self-consistency, as well as (c) the RPA being insufficient to describe the dissociation regime.

In order to tackle point (a), we are examining the dissociation of several diatomic molecules, such as LiH, Be_2, Mg_2 and Ca_2, both within the LDA/GGA and the ACFD frameworks. While the first system is of interest because it is heteroatomic and contains one hydrogen atom, the three others are known to be weakly-bonded vdW molecules for which LDA and GGA perform quite badly. The calculations we have already carried out on Be_2 using ABINIT default pseudopotentials show a huge bump at intermediate range too. We are now exploring thoroughly the influence of several parameters, such as cell size, number of bands, and pseudopotential on both the quality of the final results and the characteristics of the bump.

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A Novel Generelised Kohn Sham Scheme

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Generalised Kohn-Sham (GKS) theory [1], [2], provides a variety of possible generalisations of the well-known Kohn Sham implementation of density functional theory for the calculation of total energies of systems of interacting electrons such as molecules and solids. We present an assessment of various GKS schemes for a one-dimensional model semiconductor. Comparison is made with previous quantum Monte Carlo calculations [3] and with previous GW calculations within many-body perturbation theory for this system. Further GW calculations suggests a new GKS approach based on a GW formulation of the total energy, which will lead to a new version of density functional theory for efficient practical calculations which circumvents the problem of approximating the usual Kohn Sham exchange correlation energy functional.

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Exchange-correlation potentials and kernels from many-body perturbation theory for optical response properties of insulators and semiconductors

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The calculated optical absorption spectra of semiconductors and insulators with the (adiabatic) local density approximation (ALDA) (or any other local or gradient approximation) for the exchange-correlation (xc) potential and kernel present two main shortcomings: the spectra are shifted towards lower energies and excitonic effects are not taken into account. In this study we want first, to determine in which measure the LDA for the xc potential is responsible for the downward-shift in the optical absorption spectra; second, to find approximations for the kernel that can reproduce excitonic effects.

To achieve the first objective we calculated self-consistently the KS band structure with a new xc potential that corresponds to the optimized effective potential equation for the GW (G, Green's function; W screened Coulomb interaction) approximation to the many-body self-energy operator (i.e. solving the Kohn-Sham DFT equations for the Klein functional within the GW approximation that leads to the so-called linearized Sham-Schlüter equation). This orbital dependent potential is expected to be very accurate and provides benchmark results that can be compared with the LDA band structure. In particular we can asses how different the DFT and GW-quasiparticle gaps are and their impact in the "consistent" calculation of the response function (optical absorption spectra). As a particular case of this scheme we get the exact-exchange (EXX) equations (using the bare Coulomb potential instead of the screened one).

The EXX kernel takes into account excitonic effects [1], but it is computationally very expensive. To achieve the second objective we approximated the EXX kernel using the common energy denominator approximation for the KS Green function. With this approximation we avoided the summation on the conduction bands that makes the calculations expensive. This provides a consistent and efficient numerical implementation of the EXX functional for both ground state and response function calculations. We have extended this scheme to the potential derived from a GW-self-energy and preliminary results will be shown.

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GW+T approach for the calculations of excited electron lifetimes in metals.
1. Description of the approach.

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We expose a first-principle method for the calculations of excited electron lifetimes in metals that includes the evaluation of the lowest self-energy term of the many-body perturbation theory the GW approximation and the highest terms in the T-matrix approximation. For GW we employ the nonlocal dynamic screened interaction potential calulated within RPA approximation, whereas for T-matrix we use the static screened potential. We evaluate the T-matrix terms with electron-hole and electron-electron multiple scattering, both with and without spin flips. Two double-counting terms are also evaluated. We implement the method employing the linear muffin-tin orbital (LMTO) method of the band-structure calculations and products of LMTO's as a basis of many-body calculations. The lifetimes of excited electrons are calcuated from the imaginary part of quasi-particle self-energy corrections to the LDA band energies.

GW+T approach for the calculations of excited electron lifetimes in metals.
2. Applications: lifetimes in Fe, Ni, Pd, Ta, Al

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We discuss the results of the GW+T calculations for the excited electron lifetimes in ferromagnetic Fe, Ni and paramagnetic Pd, Ta, Al. We analize transverse magnetic susseptibility connected with the T-matrix electron-hole term. In Fe and Ni at the excitation energy below 0.5 eV we find essential contributions of the T-matrix spin-flip terms in the scattering rates (inverse lifetimes) of the spin-minority electrons that are connected with the generation of spin waves; at higher energy dominates GW term. The T-matrix electron-hole contribution term is relatively small in Pd, but it is unexpectedely high in Ta and Al. We explain this basing on the value of the static screened potential. The T-matrix terms in Al well agree with those calculated within the theory of interacting free electron gas. In Al alsoessential is the electron-electron T-matrix term. The inclusion of T-matrix merkedly improves the agreement with experimental data on lifetimes in Ta and Al. We find that the double-counting terms are small in all the cases.

Time-dependent OEP: ideas, attempts and problems

M. Mundt, S. Kümmel

We present an approach towards the exact solution of the time-dependent OEP equation based on time-dependent orbital shifts. Analogous to the static case equations for the orbitals and the orbital shifts are derived. Different numerical schemes are tested to solve these equations. First results show that the highly non-linear character of the equations complicates the solution considerably.

Non-local vertex corrections in Hedin's equations

M. Stankovski, R. Godby
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Many-body perturbation theory provides a potentially powerful class of orbital-functional methods, which may be implemented within Kohn-Sham theory, generalized Kohn-Sham theory, or other frameworks. For their successful implementation it is essential to have adequate and tractable models for the self-energy.A non-local operator, like the self energy, can be consistently calculated through many-body perturbation theory. We have implemented a non-local model vertex correction in Hedin's equations and are investigating various quantities which have to be adequately described if such a model is going to be successful in fully self-consistent calculations. So far these quantities have been the static structure factor, the pair-correlation function and the various sum rules for the dielectric function of a homogenous electron gas. The pair-correlation function, in particular, is a powerful benchmark in this model, since it can be directly compared with quantum Monte Carlo calculations for jellium. We are studying the effect of including this truly non-local vertex correction on the total energies and quasiparticle structure of several popular test cases.

Recent progress in OEP-based calculations of magnetic resonance parameters

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DFT predictions for magnetic resonance parameters are known to be very sensitive to the exchange-correlation functional applied. Another crucial point is the way of deriving the potential from a given functional. Hybrid functionals containing certain admixture of the exact exchange as well as meta-GGA functionals including terms depending on the local kinetic energy density (e.g., PKZB functional [1]) are traditionally treated in the "Hartree-Fock spirit", i.e. by evaluating functional derivatives with respect to the orbitals. The resulting potentials turn out to be different for different orbitals, non-multiplicative and (for hybrid functionals) non-local. For the abovementioned cases, we construct local and multiplicative Kohn-Sham potentials, using the OEP method (LHF approximation [2]). The potentials are evaluated in calculations of nuclear shielding constants for main-group molecules [3, 4] and electronic g-tensors of transition metal complexes [5]. For hybrid functionals, there is a significant progress over their traditional implementation. We also make first steps in applying the OEP method for the treatment of exact exchange admixtures in more flexible and promising local hybrid functionals [6].

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5 General Workshop/Conference Announcements

5.1 IPAM-2005-W3 Hands-on Computer Course

October 30 - November 5, 2005

Los Angeles, Institute for Pure and Applied Mathematics (IPAM)

As part of the long program "Bridging Time and Length Scales in Materials Science and Bio-Physics" at the

Institute for Pure and Applied Mathematics (IPAM) in Los Angeles

http://www.ipam.ucla.edu/programs/ma2005/

we are organizing a hands-on computer course

"Density-Functional Theory Calculations for Modeling Materials and Bio-Molecular Properties and Functions"

October 30 - November 5, 2005.

http://www.fhi-berlin.mpg.de/th/Meetings/IPAM-2005-W3/

Some financial support is available for highly qualified Ph.D. students and postdocs.

It is strongly recommended that applications are submitted ASAP, because only 40 participants can be accepted, and the first selection will be made in mid/end March.

With best wishes – the organizers:

Peter Blaha, Karsten Reuter, Matthias Scheffler, Karlheinz Schwarz

5.2 CECAM: Carl Moser Symposium

First Announcement

CECAM Symposium

27th May 2005, Lyon, France

Dr. Carl Moser, founder of CECAM and first director, has passed away last December. The past and present directors of CECAM felt it appropriate to organize a symposium on Friday 27th May 2005 in Lyon dedicated to the memory of Carl Moser.

The theme of the symposium is

"Molecular simulations and computer experiments: do they change the future?"

Speakers for the scientific part of the symposium include:

Michael Klein, University of Pennsylvania, Philadelphia, USA
Daan Frenkel, FOM Institute, Amsterdam, The Netherlands,
Matthias Scheffler, Fritz Haber Institute, Berlin, Germany,
Jean Pierre Hansen, Cambridge University, United Kingdom,
Rafaele Resta, University of Trieste, Italy,
David Ceperley, University of Illinois at Urbana Champain, USA.

At the end of the symposium a special session will be dedicated to highlight the importance of Dr. Carl Moser for CECAM. All information can be find at

http://www.new.cecam.fr/index.php?content=symposium

Financial support for travel and lodging will be available. In order to estimate it, we would appreciate very much that people wishing to participate to this symposium register as participants through the above web site.

A more detailed program will follow.

On behalf of the organisers,

Emmanuelle Crespeau-Foltzer and Berend Smit

5.3 ICDS-23 Conference in Japan

The 23rd International Conference on Defects in Semiconductors (ICDS-23)

July 24 - July29, 2005, Awaji Island, Hyogo, Japan

Note that submissions are still accepted for poster presentations.

http://www.sanken.osaka-u.ac.jp/icds23/

We invite you to submit abstracts for oral and poster presentations to ICDS-23. The abstract deadline was March 11. PLEASE NOTE that March 11 was the final opportunity if you preferred oral presentations. However, the late papers, whose abstracts we continue to receive till June 1, will be given poster presentation opportunities only upon acceptance.

We would like to encourage young researchers (35 and under) to apply for the Corbett Prize. Nomination letters by candidates' colleagues should be sent separately by May 1, which has been extended from March 11.

Please visit our web page

http://www.sanken.osaka-u.ac.jp/icds23/

for details.

Your sincerely,

ICDS-23 Secretary

WORKSHOP ANNOUNCEMENT

5.4 Workshop on ”Quantum Monte Carlo in the Apuan Alps”

Sun 24th July - Sun 31st July 2005

The Towler Institute, 22 via del Collegio, Vallico Sotto, Tuscany, Italy

http://www.tcm.phy.cam.ac.uk/ mdt26/tti/tti.html

This small informal workshop has the aim of gathering together in Tuscan tranquility some of the world's most promising young quantum Monte Carlo researchers (it says here), allowing them to get out of the office and to enjoy some fresh mountain air and the cuisine of the Garfagnana in order that they stop looking so pale and stressed. Mornings and early evenings will be spent with short presentations and discussions about quantum Monte Carlo and related topics in the Institute Church. Long walks in the mountains will be organized.

Preliminary list of invited speakers:

Richard Needs, Matthew Foulkes, Mike Towler, Alexander Badinski, Andrea Ma, Idoia Garcia de Gurtubay, John Trail, Matthew Brown, Neil Drummond, Pablo Lopez Rios, Zoltan Radnai, Nick Hine (and various other international speakers yet to confirm).

There are a few places remaining. If you would like to participate contact Mike Towler (mdt26@cam.ac.uk) for further details.

5.5 Conference on "Plutonium Futures-The Science 2006"

Asilomar Conference Grounds, Pacific Grove, California

July 9-13, 2006

The organizers, Lawrence Livermore and Los Alamos National Laboratories, of "Plutonium Futures-The Science 2006" wish to notify you of this valuable conference and invite you to participate.

The Plutonium Futures-The Science 2006 conference, fourth in a series of conferences, will be held at the famous Asilomar Conference Grounds, Pacific Grove, California, July 9-13, 2006. Asilomar is nestled along the shoreline of California's famed Monterey Peninsula. Forests and white sand beaches cradle this tranquil ocean front retreat. This is an extraordinary scenic venue for our gathering. For more detailed information, please view the Conference WEB site:

http://www-cms.llnl.gov/pu2006/index.html

We strongly recommend that you pre-register to indicate your interest in the conference and join our mailing list to receive news, updates, and announcements for this upcoming conference, please fill out the pre-registration form at:

http://www-cms.llnl.gov/pu2006/pre-reg-form.html

The conference will provide an international forum for presentation and discussion of current research on physical and chemical properties and environmental interactions of plutonium and other actinide elements. U.S. and international scientists, engineers, faculty, and students from universities, national laboratories, and DOE's nuclear complex are encouraged to participate and make technical contributions.

Conference Scope

The conference will cover scientific topics in plutonium and actinide sciences including actinides in the environment and the science underlying plutonium disposition. Anticipated conference subtopics include:

Plutonium Properties
Materials Science
Condensed Matter Physics
Nuclear Fuels/Isotopes
Separations and Process Chemistry
Detection and Analysis
Plutonium Chemistry and Compounds

Actinide Compounds and Complexes
Actinides in the Environment
Life Sciences

Special Tutorial: Plutonium Futures-The Science 2006 conference was established to increase awareness of the importance of the scientific underpinnings of plutonium research, and facilitate communication among its international practitioners. Most importantly, we hope that this conference will stimulate the next generation of scientists and students to study the fundamental properties of plutonium and other actinides. To help prepare students, non-specialists, and other interested parties, we have organized, in a special session preceding the conference, a half-day tutorial session, staffed by experts in plutonium science and technology, and based on current topics of this conference.

We look forward to welcoming you to Plutonium Futures-The Science 2006.

On behalf of the Organizers,

Michael Fluss, Chair, LLNL, pufutures06@llnl.gov
David Hobart, Co-Chair, LANL

6 General Job Announcements

Project Manager position (Ph.D. required) in DFT program development at CSC, the Finnish IT Center for Science

MIKA is a real-space, multigrid-based density-functional theory program package. For the next three years it will be developed in an open-source project led by CSC, the Finnish IT Center for Science. In addition to the Project Manager at CSC, the project team developing MIKA will consist of three graduate students and a post-doc working half-time. These other team members will be located in different research groups in Finland, led by Professors Risto Nieminen and Martti Puska (Helsinki Univ. of Technology), Tapio Rantala (Tampere Univ. of Technology), and Timo Eirola (Helsinki Univ. of Technology), and Dr. Hannu Häkkinen (Univ. of Jyväskylä).

We are looking for the project an

Application Scientist (Project Manager).

The position will be filled for a three-year period, starting as early as possible (preferably early Summer 2005).

As the Project Manager, your main duty is to lead program development in the project team and coordinate program development done elsewhere. (Whereas home universities have the primary responsibility for the scientific progress of team members.) You should also contribute to the program development yourself, and have a positive influence on the spreading of the code within the scientific community. Additionally, you can contribute to MIKA-based scientific publications.

You have a Ph.D. in condensed matter physics or in another relevant discipline. You have excellent skills in project management. You have strong experience in density-functional theory and scientific program development. In addition, knowledge of real-space DFT and/or time-dependent DFT is an asset.

For further information see www.csc.fi/physics/mika/ . In addition, a description of the MIKA package can be found as the Scientific Highlight of the October 2004 issue of the Psi-k Newsletter.

Applications with CV and salary requests should arrive at the latest on 22nd of April 2005 to rekry@csc.fi, or to CSC - Scientific Computing Ltd, Human Resources, P.O. Box 405, FIN-02101 Espoo, Finland. Please mark the application or envelope with the position in question.

The Independent Junior Research Group “First-Principles Statistical Mechanics” at the Fritz Haber Institute of the Max Planck Society invites applications for several

Research Studentships (Ph.D. and Diploma Students) and Postdoctoral Researcher Positions

Our research aims at achieving a predictive materials science modeling, particularly in the area of heterogeneous catalysis at metal and oxide surfaces. Emphasis is put on capturing the role of realistic environments in such applications. We therefore develop and employ approaches that combine modern many-body quantum mechanics (density-functional theory), with concepts from thermodynamics and statistical mechanics (kinetic Monte Carlo).

The group offers a lively atmosphere for theoretical research projects at the forefront of science. Projects involve collaboration with colleagues in the Fritz Haber Institute and groups from all over the world. With English as our working language, we combine excellent research and working conditions with a unique intercultural atmosphere in one of Europe’s most vibrant capitals. Classes at the Berlin International Max Planck Research School provide an advanced training on all facets of surface and materials science. Post-docs and Ph.D.s may perform part of their project at one of our partner institutions in European Union networks.

We are looking for highly qualified candidates from physics, chemistry, and materials science. Ph.D. students must hold a Masters Degree (diploma) with a thesis or equivalent. Post-docs must hold a Ph.D. degree and are offered a position for 1 up to 3 years, dependent on qualification.

We consider applications until the positions are filled. Please send your application (either by e-mail or postal mail) as soon as possible to

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Postdoctoral Fellowship
Département de physique, Université de Montréal

Applications are invited for a postdoctoral position in computational condensed matter/materials physics. The successful candidate should have significant experience in one or more of the following topics: semiconductor structure, dynamics and relaxation; glass structure and glass transition; diffusion and growth; radiation-matter interactions; clusters; superlattices; surface physics; algorithmic development; etc. She/he should also have extensive experience with various computational methods, in particular first-principles electronic structure calculations, ab-initio (Car-Parrinello), tight-binding, and semi-empirical (e.g., EAM, EMT) molecular dynamics, atomistic and kinetic Monte-Carlo simulations, etc. The activities of our group can be found on site

http://www.esi.umontreal.ca/grofnum//perso/lewisl.html.

Requirements are a Ph.D. in physics or equivalent. Note that in conformity with the university's policy, this position is open to recent Ph.D.'s, no more than two or three years after graduation. Individuals who expect to receive their Ph.D. within the next few months are encouraged to apply. Only suitable candidates will receive a reply and will be invited to provide letters of reference; there is no need to provide such letters at this time. The appointment is for two years: an initial one-year appointment, renewable for a second year upon mutual agreement. The position will remain open until filled.

Interested individuals should send their curriculum vitae as soon as possible, preferably by e-mail, to Prof. Laurent J. Lewis, Département de physique, Université de Montréal, P.O. Box 6128, Station centre-ville, Montréal, Québec, Canada H3C 3J7; laurent.lewis@umontreal.ca.

In accordance with Canadian immigration requirements, priority will be given to Canadian citizens and permanent residents of Canada. The Université de Montréal is committed to equal employment opportunity for women and to employment equity.

Postdoctoral Position
RMIT University, Melbourne, Australia

Applications are invited for a postdoctoral position in the area of computational condensed matter simulation with Professor Ian Snook and Associate Professor Salvy Russo, Applied Physics, School of Applied Sciences, RMIT University, Australia. This position is funded by the Australian Research Council Discovery Grant, "Accurate quantum modeling of the van der Waals interaction and its application to molecular physisorption onto surfaces" awarded to Professor Ian Snook and Associate Professor Salvy Russo, Applied Physics, School of Applied Sciences, RMIT University, Australia, Professor Richard Needs and Dr. Mike Towler, TCM Group, Cavendish Lab., Cambridge University, UK. The major aims of this project are to develop a methodology using Quantum Monte Carlo(QMC)methods to calculate exact molecule-surface interaction energies where the van der Waals(vdW) interaction dominates and to use this to develop methods to accurately incorporate vdW interactions into Density Functional Theory (DFT). This will enable the accurate modeling of molecular physisorption onto surfaces due to van der Waals forces. The role of the postdoctoral fellow is to use QMC to calculate the exact

exchange-correlation energy density and exchange-correlation hole functions about a molecule-surface absorption site and develop methods to accurately incorporate vdW interactions into Density Functional Theory (DFT). The successful applicant must hold a PhD in Physics, Chemistry, or Materials Science, and have good knowledge of electronic structure theory, and experience in first-principles calculations. A knowledge of QMC methods would be an advantage.

The position is full-time fixed term for three years, subject to the completion of a satisfactory probation period for new appointees. The remuneration level is the Academic Level B2, $(AU)59,389 pa.

For further information on this position or to apply please contact

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The application, which should be sent by email, should address the selection criteria, and include a CV, the names, addresses, e-mail, fax and phone number of two referees, and a cover letter outlining current research interests.

The deadline for application is April 15, 2005.

Postdoctorial Position

Institute for Materials Chemistry

Technical University of Vienna, Austria

A post-doctorial position funded by the EU-STREP project ”Nanomesh” is available in the area

”Electronic structure and formation of the h-BN/Rh(111) nanomesh”.

The investigations will be carried out in close collaboration with our experimental partners within this EU project. We will employ our full-potential LAPW bandstructure package WIEN2k (developed in our group over many years). For the investigation of the dynamics and self-organisation tight-binding molecular dynamics and Kinetic Monte-Carlo simulations are planned using parameters from the ab initio calculations.

The position is available starting with April 2005.

She/he should have some experience in Computational Condensed Matter Theory, Unix and Fortran programming. Knowledge of molecular dynamics simulations and in particular Kinetic Monte-Carlo would be very beneficial.

Further information on our group can be found on:

http://www.tuwien.ac.at/theochem/

and

http://www.wien2k.at

Applications with resumes, list of publications, and name (address) of referees should be sent to (preferable by email):

Dr. P.Blaha
Institute for Material Chemistry
TU Wien
Getreidemarkt 9/165-TC
A-1060 Vienna
Austria

E-mail: pblaha@theochem.tuwien.ac.at

PhD Studentship: Materials Science and Nanotechnology Center for Theoretical Chemistry, University of Bochum, Germany

Applications are invited for a PhD position embedded in our international doctorate study program which gives individual support to our foreign graduate students. The preferred starting date would be spring or summer 2005.

You will learn about state–of–the–art electronic structure and ab initio simulation techniques (e.g. advanced Car–Parrinello molecular dynamics) and apply them to challenging problems at the nanoscale in order to understand complex materials and processes. Candiates should have, or be about to receive, an honors degree in Physics or Chemistry with a solid background in theory.

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

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

The Center for Theoretical Chemistry at RUB offers an exciting interdisciplinary environment with excellent working conditions (e.g. about 1 TFlop/s for parallel computing in house),
see http://www.theochem.rub.de/go/jobs.html.

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

`Professor Dominik Marx`
`Lehrstuhl fuer Theoretische Chemie`
`Ruhr-Universitaet Bochum`
`44780 Bochum, Germany`
`Email: office@theochem.rub.de`
`Fax: ++49 234 32 14045`
`URL: http://www.theochem.rub.de/`

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

POSTDOC IN LINEAR SCALING ELECTRONIC STRUCTURE THEORY

Los Alamos National Laboratory, USA

Applications are invited for a postdoctoral position at the interface of quantum chemistry, materials science, applied math and high performance computing. Research will involve the development and application of MondoSCF, a suite of parallel, linear scaling electronic structure programs, which are GPL and written in F9X/MPI using modern data structures.

Several areas of research are open, including

(1) The further development and application of linear scaling response theory. See [PRL, 92 p.193002-1 and -2 (2004)] and also [physics/0501038, cond-mat/0406094].

(2) The large scale application of hybrid HF/DF theories to chemical problems in the condensed phase. See [cond-mat/0406094, cond-mat/0405500]. This might include some development of advanced sampling methods, transition state theory, and ab initio molecular dynamics.

(3) Continued development of parallel algorithms. Topics include: (a) dynamic load balance and the general, parallel sparse matrix-matrix multiply. See [CPC, 128, p.93 (2000)]. (b) parallel multipole tree construction for a data parallel Quantum Chemical Tree Code. See [JCP, 121, p.6608 (2004)].

A background in quantum chemistry, applied mathematics, materials chemistry, computer science, as well as programming experience in MPI and FORTRAN9x are highly desirable. This is a two year position and is available immediately.

A Ph.D. in Computer Science, Computational Physics or Chemistry completed within the last five years (or soon to be completed) is required. Candidates are encouraged to compete for a Director's Fellowship and outstanding candidates may be considered for the prestigious J. Robert Oppenheimer, Richard P. Feynman or Frederick Reines Fellowships. Further details about the Postdoctoral Program may be found at:

http://www.lanl.gov/science/postdocs

For consideration, submit a cv including references and publications, along with a cover letter outlining current research interests to Matt Challacombe (MChalla@LANL.Gov).

Los Alamos National Laboratory is an Affirmative Action/Equal Opportunity Employer. Individuals with disabilities needing reasonable accommodation should call (505) 667-8622. A Teletype Device for the Deaf (TDD) is available by calling (505) 665-5357. Los Alamos National Laboratory is operated by the University of California for the US Department of Energy.

Postdoc Position in Theoretical Surface Science
School of Physics at the University of Sydney, Australia

Applications are invited for a Postdoctoral position in the area of computational theoretical surface science in the group of Professor Stampfl in the School of Physics at the University of Sydney, Australia. The research involves development and application of ab initio based thermodynamic and statistical mechanical schemes for the study of processes and reactions at surfaces eg. Kinetic Monte Carlo, including adparticle interactions via the lattice-gas approach, for calculation of reaction rates in heterogeneous catalysis, or stable and metastable phases in crystal growth.

The successful applicant must hold a PhD in Physics, Chemistry, or Material Science, and have good knowledge of electronic structure theory, and experience in first-principles calculations.

The position offers a good opportunity for international collaborations, and the campus is located near the heart of Sydney. The position is full-time fixed term for two years, subject to the completion of a satisfactory probation period for new appointees. For further information, contact Professor Catherine Stampfl on (+61 2) 9351 5901 or email: stampfl@physics.usyd.edu.au. Remuneration: Level A Academic.

To apply, please email C.Stampfl at the above email address. The application should address the selection criteria, and include a CV, the names, addresses, e-mail, fax and phone number of two referees, and a cover letter outlining current research interests.

Professor Catherine Stampfl
School of Physics
The University of Sydney
Sydney 2006, Australia

Phone: +61 2 9351 5901
Fax: +61 2 9351 7726

`http://www.physics.usyd.edu.au/~stampfl/`

Ph. D. Position

"Study of heat transfer in nanoscale multilayered interphases"

Center of Thermal Sciences in Lyon, France

This position will start in October 2005. It will be financed by the French government.

The student will be hosted in Center of Thermal Sciences in Lyon, France. The supervisors are Patrice Chantrenne (CETHIL) and Pascal Thibaudeau (CEA-le Ripault).

Description of the subject :

The nanoscale multilayered interphases are made by deposition of successive layers which thicknesses are of the order of a few nanometers. Due to their special mechanical and chemical properties, these materials are used to protect fibers in composite materials, thus increasing their life time. They are used in many applications such as high performance brakes, materials for new nuclear power-plants, materials to protect spatial shuttles during the atmospheric reentry, turbines, etc.To optimise these materials, their thermal properties must be known. This PhD study concerns the modeling of the heat transfer properties at the scale of the layer thickness scale i.e. the nanometer. The aim is to understand heat transfer phenomena from their analysis and simulation at the atomic scale and then to predict the thermal conductivity. So, Molecular Dynamics and ab-initio calculations will be used.

First stage : literature research and compilation of the experimental results on the structural characterisation of the nanoscale multilayered interphases. This study should lead to a structural model of the material at the atomic scale. This work will be done in narrow collaboration with people dealing with elaboration and structural characterisation.

Second stage : literature research on the interatomic potential used for the elements and the structures considered in this study.

Third stage : validation of the interatomic potential by comparison of the properties obtained with Molecular Dynamics to those obtained by ab initio calculations and to experimental determinations. As these potentials will be used for heat transfer studies, the vibrational properties will be particularly considered.

Fourth stage : prediction of the thermal conductivity of nanoscale multilayered interphases using atomic scale heat transfer simulation by Molecular dynamics and an analytical model of phonon propagation. The results will be compared to experimental determinations.

The candidate should have a serious background in the various domains cited below :

- heat transfer
- solid state physics

- statistical physics
- numerical simulation
- FORTRAN languages, and shell languages for various OSs.

Applications, with a covering letter, a detailed CV and the names and addresses of two referees, should be posted to

Patrice Chantrenne
CETHIL INSA bt. Sadi Carnot
20, Av. A. Einstein
69621 Villeurbanne Cedex
email : patrice.chantrenne@insa-lyon.fr

Postdoctoral Research Fellowship

”Condensed matter theory applied to technologically important oxides”

Tyndall National Institute, Cork, Ireland

Applications are invited for a postdoctoral research fellowship at Tyndall National Institute investigating the atomic and electronic structure of semiconducting oxide materials. The work will involve proposing novel materials and evaluating their optical and electrical characteristics, by using first principles calculations. This is part of an EU-funded project to develop new transparent conductive oxides and the research will be carried out in collaboration with experimental groups in Tyndall and across Europe.

The ideal candidate will have experience in first principles or quantum chemical methods, preferably density functional theory of condensed phases. A background in the derivation of optical or electrical properties would be beneficial. Candidates must hold a doctoral degree or equivalent in physics, chemistry, computational or materials science, or a related discipline.

Tyndall National Institute (http://www.tyndall.ie) is the centre for research in Information and Communications Technology in Ireland, having being formed recently from NMRC and other research centres in Cork. Cork is Ireland’s second city and holds the title of European Capital of Culture in 2005.

To apply, please send a curriculum vitae and cover letter to
mailto:careers@tyndall.ie
mentioning the reference number SE01.
For technical information please contact Dr Simon Elliott at:
mailto:simon.elliott@tyndall.ie
Tel: +353-21-4904392
Tyndall National Institute, Lee Maltings, Cork, Ireland.

For further information on the Computational Modelling Group at Tyndall please see

http://www.tyndall.ie/research/computational-modelling-group/

This advert is available online at

http://www.tyndall.ie/careers/research.html

Postdoctoral Research Associate

Computational Materials Theory

California State University Northridge, USA

A postdoctoral position is available immediately in the Computational Materials Theory Center at California State University Northridge in the area of multi-scale modeling of mechanical properties of materials, electronic structure and atomistic simulations.

The candidate must have a strong background in computational materials physics, first-principles electronic structure and/or molecular dynamics. The candidate will work on dislocation core properties in metals and intermetallics and the effect of solutes on dislocation motion in metallic alloys.

Initial appointment is for one year, renewable for a second and/or third year (based on satisfactory performance). Interested applicant should submit a curriculum vita, list of publications to:

Prof. Nicholas Kioussis, Department of Physics, California State University Northridge,
18111 Nordhoff Street, Northridge, CA 91330-8268

or via email to:

nick.kioussis@csun.edu.

California State University Northridge is an Affirmative Action Equal Opportunity Employer.

The research group ”Atomistic Modelling in Interface Science” at the Max-Planck-Institute for Iron Research invites applications for

PhD Studentships

and

Postdoctoral Positions

Max-Planck-Institute for Iron Research, Düsseldorf, Germany

Our newly established group is integrated into the Department of Interface Chemistry and Surface Engineering. Initially research will focus on ab initio and density functional theory (DFT) based atomistic modelling of surfaces (in particular oxide films), their interaction with organic molecules, and on the chemical and electronic structure of metal/oxide/polymer interfaces. After testing the limitations of various ab initio and DFT based approaches for the problems mentioned above, the modelling of adhesion and de-adhesion processes is planned.

The complexity of the problems to be tackled will require the multiscale combination of different theoretical methods and the collaboration with the department's experimental groups. The latter will perform new experiments on well defined model systems and structures, which are feasible for computational modelling. This will in particular be supported by the preparation of well defined substrate surfaces in the UHV system of the department.

Research projects will, although focused on basic research, include the collaboration with major industrial companies.

We expect applicants to be motivated and to be highly qualified with a physics, chemistry or materials science background. Good communication skills (English or German) and the willingness to collaborate interdisciplinary are required.

Applicants for a PhD Studentship must hold a Masters Degree with thesis or equivalent.

For enquiries or to send your complete application, please contact:

Dr. Alexander T. Blumenau
Max-Planck-Institut für Eisenforschung GmbH
Department of Interface Chemistry and Surface Engineering
Max-Planck-Str. 1
D-40237 Duesseldorf
Germany

Email: blumenau@mpie.de

7 Abstracts

Ferromagnetic Moment and Antiferromagnetic Coupling in (Ga,Mn)As Thin Films

K.W. Edmonds and N.R.S. Farley
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T.K. Johal and G. van der Laan
Daresbury Laboratory, Warrington WA4 4AD, United Kingdom
R.P. Campion, B.L. Gallagher, and C.T. Foxon
School of Physics and Astronomy, University of Nottingham, United Kingdom

Abstract

We demonstrate that carefully prepared (Ga,Mn)As films can show large magnetic moments per atom across a wide range of Mn concentrations, indicating almost full participation of the Mn in the ferromagnetism. Applying sum rules to Mn $L_{2,3}$ x-ray magnetic circular dichroism (XMCD) spectra yields a magnetic moment per Mn of around 4.5 μ_B, including a small positive orbital moment. We also present direct evidence for antiferromagnetic coupling between interstitial and substitutional Mn in unannealed (Ga,Mn)As. The Mn $L_{2,3}$ x-ray absorption lineshapes display no significant site or concentration dependence, but in unannealed (Ga,Mn)As the XMCD signal is significantly smaller, and increases linearly under high magnetic fields.

Accepted for publication in Physical Review B. **71**, 064418 (2005)
Manuscript available from g.van_der_laan@dl.ac.uk

Random-phase approximation for T_C of collinear magnets with multiple sublattices: GdX compounds (X=Mg, Rh, Ni, Pd)

Ján Rusz[1,2], Ilja Turek[1,3], Martin Diviš[1]
[1] *Dept. of Electronic Structures, Charles University, Prague*
[2] *Institute of Physics, ASCR, Prague*
[3] *Institute of Physics of Materials, ASCR, Brno*

Abstract

An efficient scheme for evaluating the critical temperatures of ferro-, antiferro- and ferrimagnetic crystals with multiple sublattices is presented. The approach is based on a pairwise Heisenberg Hamiltonian and a random-phase approximation (Tyablikov's decoupling) for magnon Green's functions. The pair exchange interactions are derived from self-consistent electronic structure calculations using a magnetic force theorem. The developed technique is applied to hexagonal gadolinium and its selected intermetallic compounds GdX (X = Mg, Rh, Ni, Pd) with CsCl and CrB structures. The calculated critical temperatures are quite sensitive to a neglect of the non-magnetic (X) element; their values are in a fair agreement with experiment.

(Accepted to Physical Review B)
Contact person: Ján Rusz, rusz@mag.mff.cuni.cz

Effects of (multi)branching of dipolar chromophores on photophysical properties and two-photon absorption

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F-75231 Paris Cedex 05, France
[§]*Los Alamos National Laboratory*
Theoretical Division, Los Alamos, New Mexico 87545

Abstract

To investigate the effect of branching on linear and nonlinear optical properties, a specific series of chromophores, epitome of (multi)branched dipoles, has been thoroughly explored by a combined theoretical and experimental approach. Excited state structure calculations based on quantum-chemical techniques (time-dependent density functional theory) as well as a Frenkel exciton model nicely complement experimental photoluminescence, one- and two-photon absorption findings and contribute to their interpretation. This allowed getting a deep insight into the nature of fundamental excited state dynamics and nonlinear optical response involved. Both experiment and theory reveal that a multidimensional intramolecular charge transfer takes place from the donating moiety to the periphery of the branched molecules upon excitation, while fluorescence stems from an excited state localized on one of the dipolar branches. Branching is also observed to lead to cooperative enhancement of TPA while maintaining high fluorescence quantum yield, thanks to localization of the emitting state. Comparison between results obtained in the Frenkel exciton scheme and ab initio results suggests coherent coupling between branches as one of the possible mechanisms for the observed enhancement. New strategies for rational design of NLO molecular assemblies are thus inferred on basis of the acquired insights.

J. Phys. Chem. A, Web Release Date: 15-Mar-2005; (Article) DOI: 10.1021/jp044193e
Contact person: Claudine.Katan@univ-rennes1.fr

Structural stability of silica at high pressures and temperatures

Artem R. Oganov[1], Michael J. Gillan[2], G. David Price[2]
[1]*ETH Hönggerberg, Zürich, Switzerland*
[2]*University College London, UK*

Abstract

The high-pressure phase diagram of SiO2 has been calculated using density-functional perturbation theory. We find that phase transitions of silica do not correspond to any observed seismic discontinuities within the Earth. We analyse the breakdown of close packing occurring in SiO_2 above 200 GPa and conclude that it is due to asphericity and deformability of ions, which can generally lead to the formation on non-close-packed structures at high pressure. Our calculations indicate that pyrite-structured SiO_2, stable above 200 GPa, has no soft modes down to ambient pressure and could, therefore, be quenchable. Above 750 GPa a cotunnite-type phase is stable.

(Published in: Phys. Rev. B71, art. 064104)
Contact person: A.R. Oganov (a.oganov@mat.ethz.ch)

Interface stabilization of Fe/Al(001) films by Ti interlayers - an ab-initio DFT study

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Institut für Materialphysik and Center for Computational Materials Science,
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Abstract

The stabilization of the growth of near-perfect Fe layers on Al(001) by the deposition of a Ti interface layer has been investigated using ab-initio density-functional method. We find that Ti deposition on Al(001) leads to the formation of an Al_3Ti surface alloy with strong Al-Ti and Ti-Ti bonds and hence an increased stiffness of the surface. As a consequence, a barrier against diffusion of Fe atoms into the Al substrate is formed. At a complete monolayer coverage of the Al_3Ti/Al(001) surface, however, a subsurface position of the Fe layer is again energetically preferred. This demonstrates that the stabilizing effects of the Ti interfactant is of kinetic origin and vanishes at elevated temperatures.

(Accepted, Surf. Science)
Contact person: D. Spišák (Daniel.Spisakqunivie.ac.at)

Density of Configurational States from First-principles: The Phase Diagram of Al-Na Surface Alloys

Mikael Borg[a,b], Catherine Stampfl[c,b], Anders Mikkelsen[b],
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[c] *School of Physics, The University of Sydney,*
Sydney 2006, Australia

Abstract

The structural phases of $\mathrm{Al}_x\mathrm{Na}_{1-x}$ surface alloys have been investigated theoretically and experimentally. We describe the system using a Lattice-gas Hamiltonian, determined from density-functional theory, together with Monte Carlo (MC) calculations. The obtained phase diagram reproduces the experiment on a quantitative level. From calculation of the (configurational) density of states by the recently introduced Wang-Landau MC algorithm, we derive thermodynamic quantities such as the free energy and entropy, which are not directly accessible from conventional MC simulations. We accurately reproduce the stoichiometry, as well as the temperature at which an order-disorder phase transition occurs, and demonstrate the crucial role, and magnitude, of the configurational entropy.

(submitted to: ChemPhysChem)
Contact person: Mickeal Borg (mikael.borg@utoronto.ca)

Strain effects on the Electronic and Optical Properties of InAs/GaAs Quantum Dots: Tight-binding Study

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21941-972 Rio de Janeiro, Brazil

P. Kratzer, M. Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6,
D-14195 Berlin-Dahlem, Germany

Abstract

We present an atomistic investigation of strain effects on the electronic and optical properties of capped pyramidal InAs/GaAs quantum dots (QDs) within an empirical sp3s* tight-binding model with interactions up to 2nd nearest neighbors and spin-orbit coupling. The strain is incorporated through the atomistic valence-force field model. We demonstrate that the strain: (i) significantly increases the QD gap, (ii) induces a macroscopic spatial asymmetry in the ground state wave functions, (iii) strongly enhances the oscillator strength of the fundamental optical transition and (iv) introduces a spatial anisotropy of the optical absorption coefficient of this transition.

(submitted to: Proceedings of the 27th International Conference on the Physics of Semiconductors)

Contact person: Peter Kratzer (kratzer@fhi-berlin.mpg.de)

First principles study of rare-earth oxides

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[2] *Department of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark*
[3] *Daresbury Laboratory, Daresbury, Warrington WA4 4AD, UK*

Abstract

The self-interaction-corrected local-spin-density approximation is used to describe the electronic structure of dioxides, REO_2, and sesquioxides, RE_2O_3, for the rare earths, RE=Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy and Ho. The valencies of the rare earth ions are determined from total energy minimization. We find Ce, Pr, Tb in their dioxides to have the tetravalent configuration, while for all the sesquioxides the trivalent groundstate configuration is found to be the most favourable. The calculated lattice constants for these valency configurations are in good agreement with experiment. Total energy considerations are exploited to show the link between oxidation and f-electron delocalization, and explain why, among the dioxides, only CeO_2, PrO_2, and TbO_2 exist in nature. Tetravalent NdO_2 is predicted to exist as a metastable phase - unstable towards the formation of hexagonal Nd_2O_3.

(Submitted to Phys. Rev. B; cond-mat/0503667)

Contact person: petitl@ornl.gov

8 Presenting Other Initiatives

8.1 HPC-Europa: EC funding available for collaborative research

JC Desplat
EPCC, University of Edinburgh

We would like to bring to the attention of Psi-k network members some new funding opportunities available to computational scientists based in Europe. The programme is particularly targeted at researchers who can benefit from gaining access to high-performance computers for their research.

The HPC-Europa consortium operates a visitor programme open to researchers of postgraduate level upwards, to conduct short (2 to 13 weeks) collaborative visits to universities in the UK, Spain, Italy, Germany, France, and the Netherlands, that are associated with one of the participating supercomputing sites: CEPBA (Barcelona), CINECA (Bologna), EPCC (Edinburgh), HLRS (Stuttgart), IDRIS (Paris), and SARA (Amsterdam). A list of associated institutions can be obtained from HPC-Europa website at:

`http://www.hpc-europa.org/host_departments.html`.

The researchers are provided with computing power to carry out their project and technical support and consultancy from experienced and friendly staff. HPC-Europa covers all expenses, including accommodation and travel, and all logistics is taken care of.

Applicants are requested to apply using an on-line form at

http://www.hpc-europa.org/ta.html,

and attach a well-defined project proposal, a workplan and a CV. Applicants are also asked to name a scientific collaborator in the research group they would like to visit.

Guidelines for applicants are available online at

http://www.hpc-europa.org/guideline.html.

Please note that researchers cannot visit research groups based in their own country, the visit has to be transnational.

All applications go through a selection process and review by an international panel of experts. Currently, the acceptance rate stands at about 69%. The programme runs until end 2007, and there are four deadlines a year for review meetings. The next deadline is 31 May 2005.

Further information, including guidelines for applicants, can be found at the HPC-Europa web site:

http://www.hpc-europa.org/ta.html

9 SCIENTIFIC HIGHLIGHT OF THE MONTH

Correlated Electron-Ion Dynamics

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Abstract

Correlated Electron-Ion Dynamics (CEID) is an extension of molecular dynamics that allows us to introduce in a correct manner the exchange of energy between electrons and ions. The formalism is based on a systematic approximation (Small Amplitude Moment Expansion - SAME). This formalism is introduced, including modifications to account for open boundaries, its structure analysed, and some results given (the heating of an ion by current carrying electrons, and inelastic I-V spectroscopy). The computer code that implements the closed system version of the formalism (Dinamo) is described. We close with some thoughts about the future prospects of this approach.

1 Introduction

Molecular dynamics is a well-established computational method for studying the dynamical properties of materials[1]. The central idea is to allow a collection of atoms to move under the influence of forces according to Newton's second law of motion ($\ddot{R}_\nu = F_\nu/M_\nu$), where $R_\nu(t)$ is an atomic coordinate at time t, F_ν is the force on the coordinate and M_ν is an atomic mass. Different materials are accommodated through the choice of the expression for the force (which ranges from simple force fields[2] to high-level electronic structure calculations[3]) and the mass of the atoms. The immense utility of this approach stems from two things: its great generality and its obvious connection to the material world. The generality of force expression allows a huge array of materials to be considered (common examples include biological molecules[4] and metals subjected to high energy radiation[5]), while the generality of the dynamical equations allows a wide range of conditions to be considered (notably both equilibrium and non-equilibrium systems) through the choice of initial and boundary conditions[1, 6]. This is a remarkable achievement for one modelling technique.

Underlying conventional molecular dynamics is a pair of well-defined assumptions: the atoms can be treated as classical (that is, not-quantum) particles that follow precise trajectories; there exists a well-defined set of forces which are a function of atomic position (and possibly velocity). The latter assumption can be interpreted to mean that the electrons remain on one Born-Oppenheimer surface (in the absence of velocity dependent forces). This will be true provided the energy separation between the surfaces is greater than $\hbar\omega$, where ω is a characteristic atomic vibrational frequency. This clearly eliminates all metals. But even then the effects are small because the atomic forces from each of the Born-Oppenheimer surfaces sampled are rather similar to one another. The lowest order corrections can the approximately included by means of a velocity dependent force that introduces the loss of energy of fast atoms to the electrons[7], but this is negligible except for highly energetic atoms.

The above represents a state of affairs that applies to many materials problems. However, there are particular problems in which transitions between Born-Oppenheimer surfaces control the phenomena being investigated. Two problems of this type with which we are familiar are: irreversible exchange of energy between ions and current carrying electrons (leading to Joule heating and inelastic I-V spectroscopy); non-radiative relaxation of excited electrons (or polarons or electron-hole pairs) in polymers. Conventional molecular dynamics cannot handle these problems, so we need to introduce some modifications to accommodate them.

An approach used by a number of researchers when faced with these phenomena is the Ehrenfest approximation[8]. At the back of this is an exact set of results, namely the Ehrenfest *equations*[9] which are $\dot{\bar{R}}_\nu = \bar{P}_\nu/M_\nu$ and $\dot{\bar{P}}_\nu = \bar{F}_\nu$ where P_ν is a component of momentum. While these look like the ordinary equations of Newtonian mechanics, they of course involve quantum expectation values ($\bar{R}_\nu = \langle\Psi|\hat{R}|\Psi\rangle$, $\bar{P}_\nu = \langle\Psi|\hat{P}|\Psi\rangle$, $\bar{F}_\nu =$

$\langle\Psi| - \partial\hat{H}(\hat{R})/\partial\hat{R}_\nu|\Psi\rangle$ where $\hat{H}(\hat{R})$ and $|\Psi\rangle$ are the Hamiltonian and wavefunction for the whole system (electrons and ions)). The Ehrenfest *approximation* then makes an anzatz for $\bar{F}_\nu$ namely $\bar{F}_\nu = \langle\Phi| - \partial\hat{H}_e(\bar{R})/\partial\bar{R}_\nu|\Phi\rangle$. Thus the full Hamiltonian $\hat{H}(\hat{R})$ which depends on the ionic position *operator* $\hat{R}$ is replaced by the mean field Hamiltonian $\hat{H}(\bar{R}) = \hat{T}_I + \hat{H}_e(\bar{R})$ ($\hat{T}_I$ is the ionic kinetic energy operator) produced by substituting the ionic position operator by its expectation value, and the full wavefunction $|\Psi\rangle$ is replaced by the electronic wavefunction $|\Phi\rangle$ which obeys $\hat{H}_e(\bar{R})|\Phi\rangle = \mathrm{i}\hbar\partial|\Phi\rangle/\partial t$. This approximation describes some phenomena correctly (such as the excitation of electrons by fast ions), but others incorrectly (such as the heating of ions by current carrying electrons[10]).

The Ehrenfest approximation is attractive because it retains the good features of molecular dynamics (generality of systems and properties), while adding the new feature of being able to model some non-adiabatic processes. But it clearly needs further extensions to reproduce many other non-adiabatic processes, notably the excitation of ionic motion by energetic electrons.

In the next section we describe the basic mathematical structure of our method which allows us to model more general non-adiabatic processes[11], discuss a way of thinking about quantum mechanics that is particularly well suited to this problem, and then explain the behaviour of our method from this perspective. In the subsequent section this molecular dynamics approach is compared with established perturbative calculations[12, 13, 14]. We then look at an extension of the method to accomodate open boundaries[8], and describe the program used to implement the algorithm (DINAMO). Finally we report results obtained with our method, and then conclude with some thoughts about the future of this approach.

2 Moment expansion approach to CEID

2.1 Small Amplitude Moment Expansion (SAME)

2.1.1 Main equations

As we have described above, the Ehrenfest approximation is achieved by replacing the ionic position operator $\hat{R}_\nu$ by its expectation value $\bar{R}_\nu$. We now introduce fluctuations about this mean value through the quantity $\Delta\hat{R}_\nu = \hat{R}_\nu - \bar{R}_\nu$[11]. Instead of using wavefunctions it is much easier to work with the density matrix of the system $\hat{\rho}$, in terms of which we can immediately define an electronic density matrix $\hat{\rho}_e = \mathrm{Tr}_I\{\hat{\rho}\}$ where $\mathrm{Tr}_I\{\star\}$ means the trace over ionic coordinates. In a real space representation this would be $\hat{\rho}_e = \int \mathrm{d}\vec{R}\langle\vec{R}|\hat{\rho}|\vec{R}\rangle$. The equation of motion is the quantum Liouville equation

$$\mathrm{i}\hbar\frac{\partial\hat{\rho}}{\partial t} = \left[\hat{H}, \hat{\rho}\right] \tag{1}$$

where the square brackets signify a commutator: $\left[\hat{H},\hat{\rho}\right] = \hat{H}\hat{\rho} - \hat{\rho}\hat{H}$. This equation of motion is the foundation of our approach. If we write the Hamiltonian as $\hat{H} = \hat{T}_I + \hat{H}_e(\hat{R})$, then the Ehrenfest approximation can be written as

$$\dot{\bar{R}}_\nu = \frac{\bar{P}_\nu}{M_\nu}, \qquad \dot{\bar{P}}_\nu = \bar{F}_\nu$$
$$\bar{F}_\nu = \mathrm{Tr}_e\left\{\hat{\rho}_e\left(-\frac{\partial \hat{H}_e(\bar{R})}{\partial \bar{R}_\nu}\right)\right\}, \qquad \mathrm{i}\hbar\frac{\partial\hat{\rho}_e}{\partial t} = \left[\hat{H}_e(\bar{R}),\hat{\rho}_e\right] \tag{2}$$

where $\mathrm{Tr}_e\left\{\star\right\}$ means a trace over electronic degrees of freedom. Note that if we define the Ehrenfest energy by $E_{Ehrenfest} = \sum_\nu \bar{P}_\nu^2/2M_\nu + \mathrm{Tr}_e\left\{\hat{\rho}_e\hat{H}_e(\bar{R})\right\}$ the above equations of motion have the great virtue of conserving this energy.

Keeping the above in mind, we now derive a more general set of equations for which the Ehrenfest method is the lowest order approximation. The key physical idea is that atoms are well defined by classical trajectories ($\bar{R}_\nu$) but that these are slightly broadened (characterised by $\overline{\Delta R_\nu^2}$) because of the quantum nature of the ions. Thus we have:

$$\begin{aligned}
\mathrm{i}\hbar\frac{\partial\hat{\rho}_e}{\partial t} &= \mathrm{Tr}_I\left\{\left[\hat{T}_I + \hat{H}_e(\hat{R}),\hat{\rho}\right]\right\}\\
&= \mathrm{Tr}_I\left\{\left[\hat{H}_e(\bar{R}) + \sum_\nu \Delta\hat{R}_\nu\frac{\partial\hat{H}_e(\bar{R})}{\partial\bar{R}_\nu} + \cdots,\hat{\rho}\right]\right\}\\
&= \left[\hat{H}_e(\bar{R}),\hat{\rho}_e\right] - \sum_\nu\left[\hat{F}_\nu,\hat{\mu}_{1,\nu}\right] + \ldots
\end{aligned}$$

where we have introduced the force operator $\hat{F}_\nu = -\partial\hat{H}_e(\bar{R})/\partial\bar{R}_\nu$, and the first moment $\hat{\mu}_{1,\nu} = \mathrm{Tr}_I\left\{\Delta\hat{R}_\nu\hat{\rho}\right\}$. In general the moments measure the ionic distribution[15, 16, 17] as a function of electronic state. We will provide a more intuitive explanation for this later on. Note that we will only keep terms in expansions that produce the effects we are interested in.

To evaluate the equation of motion for $\hat{\rho}_e$, we need to find $\hat{\mu}_{1,\nu}$. We do this by using its equation motion:

$$\begin{aligned}
\frac{\partial\hat{\mu}_{1,\nu}}{\partial t} &= \frac{1}{\mathrm{i}\hbar}\mathrm{Tr}_I\left\{\Delta\hat{R}_\nu\left[\hat{T}_I + \hat{H}_e(\hat{R}),\hat{\rho}\right]\right\} - \dot{\bar{R}}_\nu\hat{\rho}_e\\
&= \frac{1}{\mathrm{i}\hbar}\mathrm{Tr}_I\left\{\Delta\hat{R}_\nu\left[\hat{T}_I + \hat{H}_e(\bar{R}) + \sum_{\nu'}\Delta\hat{R}_{\nu'}\frac{\partial\hat{H}_e(\bar{R})}{\partial\bar{R}_{\nu'}} + \cdots,\hat{\rho}\right]\right\} - \dot{\bar{R}}_\nu\hat{\rho}_e\\
&= \frac{\hat{\lambda}_{1,\nu}}{M_\nu} + \frac{1}{\mathrm{i}\hbar}\left[\hat{H}_e(\bar{R}),\hat{\mu}_{1,\nu}\right] - \sum_{\nu'}\frac{1}{\mathrm{i}\hbar}\left[\hat{F}_{\nu'},\hat{\mu}_{2,\nu\nu'}\right] + \ldots
\end{aligned}$$

We have introduced two further moments: $\hat{\lambda}_{1,\nu} = \mathrm{Tr}_I\left\{\Delta\hat{P}_\nu\hat{\rho}\right\}$ and $\hat{\mu}_{2,\nu\nu'} = \mathrm{Tr}_I\left\{\Delta\hat{R}_\nu\Delta\hat{R}_{\nu'}\hat{\rho}\right\}$, where $\Delta\hat{P}_\nu = \hat{P}_\nu - \bar{P}_\nu$. We only need to keep electron-ion correlations in the first moments, but we need the width of the ions to appear somewhere, so we write

$$\hat{\mu}_{2,\nu\nu'} \approx C_{\nu\nu'}^{RR}\hat{\rho}_e$$

where $C^{RR}_{\nu\nu'} = \mathrm{Tr}\left\{\Delta\hat{R}_\nu \Delta\hat{R}_{\nu'}\hat{\rho}\right\}$. The equation of motion for $\hat{\lambda}_{1,\nu}$ is

$$\begin{aligned}\frac{\partial\hat{\lambda}_{1,\nu}}{\partial t} &= \frac{1}{\mathrm{i}\hbar}\left[\hat{H}_e(\bar{R}), \hat{\lambda}_{1,\nu}\right] - \sum_{\nu'}\frac{1}{\mathrm{i}\hbar}\left[\hat{F}_{\nu'}, \hat{\chi}_{2,\nu\nu'}\right] + \\ &\quad \frac{1}{2}\left(\Delta\hat{F}_\nu\hat{\rho}_e + \hat{\rho}_e\Delta\hat{F}_\nu\right) - \frac{1}{2}\sum_{\nu'}\left(\hat{K}_{2,\nu\nu'}\hat{\mu}_{1,\nu'} + \hat{\mu}_{1,\nu'}\hat{K}_{2,\nu\nu'}\right) + \ldots\end{aligned}$$

where $\hat{\chi}_{2,\nu\nu'} = \frac{1}{2}\mathrm{Tr}_I\left\{\left(\Delta\hat{P}_\nu\Delta\hat{R}_{\nu'} + \Delta\hat{R}_{\nu'}\Delta\hat{P}_\nu\right)\hat{\rho}\right\} \approx C^{PR}_{\nu\nu'}\hat{\rho}_e$, and we have defined $C^{PR}_{\nu\nu'} = \frac{1}{2}\mathrm{Tr}\left\{\left(\Delta\hat{P}_\nu\Delta\hat{R}_{\nu'} + \Delta\hat{R}_{\nu'}\Delta\hat{P}_\nu\right)\hat{\rho}\right\}$, $\hat{K}_{2,\nu\nu'} = \partial^2\hat{H}_e(\bar{R})/\partial\bar{R}_\nu\partial\bar{R}_{\nu'}$ (a sort of spring constant), $\Delta\hat{F}_\nu = \hat{F}_\nu - \bar{F}_\nu$, and $\bar{F}_\nu = \mathrm{Tr}_e\left\{\hat{\rho}_e\hat{F}_\nu\right\} - \sum_{\nu'}\mathrm{Tr}_e\left\{\hat{\mu}_{\nu'}\hat{K}_{\nu'\nu}\right\}$. To obtain closure we need equations of motion for $C^{RR}_{\nu\nu'}$ and $C^{PR}_{\nu\nu'}$. This involves introducing $C^{PP}_{\nu\nu'} = \mathrm{Tr}\left\{\Delta\hat{P}_\nu\Delta\hat{P}_{\nu'}\hat{\rho}\right\}$, and hence we have

$$\begin{aligned}\frac{\partial C^{RR}_{\nu\nu'}}{\partial t} &= \frac{C^{PR}_{\nu\nu'}}{M_\nu} + \frac{C^{PR}_{\nu'\nu}}{M_{\nu'}} \\ \frac{\partial C^{PR}_{\nu\nu'}}{\partial t} &= \frac{C^{PP}_{\nu\nu'}}{M_{\nu'}} + \mathrm{Tr}_e\left\{\hat{F}_\nu\hat{\mu}_{1,\nu'}\right\} - \sum_{\nu''}\bar{K}_{2,\nu\nu''}C^{RR}_{\nu''\nu'} \\ \frac{\partial C^{PP}_{\nu\nu'}}{\partial t} &= \mathrm{Tr}_e\left\{\hat{F}_\nu\hat{\lambda}_{1,\nu'} + \hat{\lambda}_{1,\nu}\hat{F}_{\nu'}\right\} - \sum_{\nu''}\left(C^{PR}_{\nu\nu''}\bar{K}_{2,\nu''\nu'} + \bar{K}_{2,\nu''\nu}C^{PR}_{\nu'\nu''}\right)\end{aligned}$$

where $\bar{K}_{2,\nu\nu'} = \mathrm{Tr}_e\left\{\hat{K}_{2,\nu\nu'}\hat{\rho}_e\right\}$. We now have a closed set of equations. However, these involve many-electron density matrices which are computationally intractable. Thus we have to reduce the many-electron density matrices to single-electron matrices by tracing out all but one electron[11]. To produce closure we have to make a Hartree-Fock approximation for two-electron density matrices. But note that since the single particle density matrix is not in general idempotent we need to augment the usual result $\hat{\rho}^{(2)}_e(12, 1'2') = \hat{\rho}^{(1)}_e(1, 1')\hat{\rho}^{(1)}_e(2, 2') - \hat{\rho}^{(1)}_e(1, 2')\hat{\rho}^{(1)}_e(2, 1')$[18]. The formal procedure (taken only to first moment) is explained elsewhere[11], and the new result will be given in an upcoming paper. From now on, the equations will be for single-electron matrices.

2.1.2 A model of quantum mechanics

Having written down a set of opaque equations we need some way to understand them intuitively. This first requires us to have some way of thinking about quantum mechanical density matrices. In this context they are most naturally thought of as distribution functions corresponding to collections of trajectories (or Feynman paths: they do not need to correspond to solutions of an equation of motion). Thus the quantum width of an atom refers to the range of allowed trajectories available to it. Immediately we see that the average kinetic energy of an atom is not determined by the average momentum, but also by the spread of momentum

$$\bar{T}_I = \sum_\nu \frac{\overline{P^2_\nu}}{2M_\nu} = \sum_\nu \frac{1}{2M_\nu}\left(\bar{P}^2_\nu + \overline{\Delta P^2_\nu}\right)$$

Thus atomic heating (increase in kinetic energy) has two components: the "classical" component from the average momentum, and the "quantum" component from the spread in momentum.

The force from the atoms felt by the electrons depends on the positions of the atoms, and hence their trajectories. Thus a spread of atomic trajectories will produce a spread of forces on the electrons, and hence the spread of electronic trajectories. Likewise, a spread of electronic trajectories will produce a spread of forces on the atoms, and hence of atomic trajectories. We are now in a position to understand the SAME equations.

2.1.3 An interpretation of SAME

We begin with the simplest case, the Ehrenfest approximation. The atoms are clearly represented by just one trajectory ($\bar{R}_\nu(t)$), and so the quantum width is zero. This is reflected in the dynamics of the electrons which experience only $\hat{H}_e(\bar{R})$. Because there is no dispersion of atomic trajectories there is similarly no dispersion of the electronic trajectories.

This latter point can be seen most clearly by assuming that the electrons can be represented by a single Slater determinant. In this case the equation of motion for the electrons (in terms of the single particle density matrix) becomes

$$\mathrm{i}\hbar\frac{\partial\hat{\rho}_e^{(1)}}{\partial t} = \left[\hat{H}_e^{(HF)}, \hat{\rho}_e^{(1)}\right]$$

where $\hat{H}_e^{(HF)}$ is the Fock matrix. If $\hat{H}_e^{(HF)}|\psi_n^{(1)}(t)\rangle = \mathrm{i}\hbar\frac{\partial}{\partial t}|\psi_n^{(1)}(t)\rangle$ where $|\psi_n^{(1)}(t)\rangle$ is a single-particle state, and $\hat{\rho}_e^{(1)} = \sum_n |\psi_n^{(1)}(t)\rangle f_n \langle\psi_n^{(1)}(t)|$, then we find that $\partial f_n/\partial t = 0$. Thus the eigenspectrum of the density matrix remains unchanged, and if the electronic system starts as a single Slater determinant, it remains so for evermore. This is what we mean by a single electron trajectory. Thus the Ehrenfest approximation corresponds to representing the electrons and ions individually as single trajectories that interact with one another.

Another way of phrasing this is that the Ehrenfest approximation is a mean field approximation in which all fluctuations have been suppressed. It is this feature that prevents it from properly describing the flow of energy from electrons to the ions[10]: the ions see the electrons as a cold gas regardless of the state of excitation (defined by the occupancies f_n), and so heat flows predominantly from ions to electrons. There can be a small flow the other way if the mean electron density becomes sufficiently rough, but this still provides quantitatively wrong results[8].

Thus we see that the correct energy transfer requires the electron gas to have its fluctuations restored, which by our earlier arguments means that the ions must also be allowed to fluctuate about their mean trajectory. Quantitative results can be obtained at the level of the first moment (see later in this article for results). The explanation is as follows.

Consider first the equation motion for the electrons

$$\mathrm{i}\hbar\frac{\partial\hat{\rho}_e^{(1)}}{\partial t} = \left[\hat{H}_e^{(HF)}, \hat{\rho}_e^{(1)}\right] - \sum_\nu \mathrm{Tr}_I\left\{\left[\Delta\hat{R}_\nu\hat{F}_\nu^{(1)}, \hat{\rho}^{(1)}\right]\right\}$$

where we have unpacked $\hat{\mu}_{1,\nu}^{(1)}$. The first term is just the Ehrenfest term, so we focus on the second one. The quantity $\Delta\hat{R}_\nu\hat{F}_\nu^{(1)}$ gives the linear variation of the force felt by the electrons due to the ions with displacement of the ionic trajectory from the mean trajectory. Thus, dispersion in the ionic trajectory will now produce dispersion in the electronic trajectories.

To see explicitly what is meant by dispersion of electron trajectories let us write $\mathrm{i}\hbar\hat{\Gamma}^{(1)} = -\sum_\nu\left[\hat{F}_\nu^{(1)}, \hat{\mu}_{1,\nu}^{(1)}\right]$ so that

$$\mathrm{i}\hbar\frac{\partial\hat{\rho}_e^{(1)}}{\partial t} = \left[\hat{H}_e^{(HF)}, \hat{\rho}_e^{(1)}\right] + \mathrm{i}\hbar\hat{\Gamma}^{(1)} \tag{3}$$

As above, we now write $\hat{\rho}_e^{(1)} = \sum_n |\psi_n^{(1)}(t)\rangle f_n\langle\psi_n^{(1)}(t)|$, which after inserting into equation (3) gives

$$\frac{\partial f_n}{\partial t} = \langle\psi_n^{(1)}(t)|\hat{\Gamma}^{(1)}|\psi_n^{(1)}(t)\rangle$$

Thus the occupancies can now change. This means that if we started from a single Slater determinant, this must evolve into an incoherent sum of determinants corresponding to evolving fluctuations in the electron gas. That is, we now must write:

$$\hat{\rho}_e^{(1)} = \sum_m \wp_m\hat{\rho}_{e,m}^{(1)}$$

where $\hat{\rho}_{e,m}^{(1)}$ is produced from a single Slater determinant and evolves as $\mathrm{i}\hbar\partial\hat{\rho}_{e,m}^{(1)}/\partial t = \left[\hat{H}_e^{(HF)}, \hat{\rho}_{e,m}^{(1)}\right]$ and $\wp_m$ is the probability of being in that state, and itself evolves in response to ionic fluctuations.

So far we have not considered the explicit width of the ionic bundle of trajectories. This information is present in $\hat{\mu}_{1,\nu}^{(1)}$, but has to get there from somewhere, and that somewhere is the equation of motion which we can write as

$$\frac{\partial\hat{\mu}_{1,\nu}^{(1)}}{\partial t} = \frac{\hat{\lambda}_{1,\nu}^{(1)}}{M_\nu} + \frac{1}{\mathrm{i}\hbar}\left[\hat{H}_e^{(HF)}, \hat{\mu}_{1,\nu}^{(1)}\right] - \frac{1}{\mathrm{i}\hbar}\sum_{\nu'} C_{\nu\nu'}^{RR}\left[\hat{F}_{\nu'}^{(1)}, \hat{\rho}_e^{(1)}\right]$$

Information about the ionic width is provided explicitly by $C_{\nu\nu'}^{RR}$. It also propagates through from $\hat{\lambda}_{1,\nu}^{(1)}$ which depends on $C_{\nu\nu'}^{PR}$.

Thus, by keeping electron-ion correlations up to the first moment ($\hat{\mu}_{1,\nu}^{(1)}$ and $\hat{\lambda}_{1,\nu}^{(1)}$) and using the mean field expressions for the second moments ($\hat{\mu}_{2,\nu\nu'} \approx C_{\nu\nu'}^{RR}\hat{\rho}_e$ *etc.*) we are able to capture many important features (see below for results) deriving from the interaction of time-evolving fluctuating electrons and ions.

2.2 Analytical features of the method

We will now discuss several analytical properties of the method. We have continually found these properties helpful both as a reality check and, in a broader sense, as an additional source of insight into CEID and into the dynamical processes that the SAME algebra represents.

2.2.1 Detailed balance and statistical properties

Let us return to the question of electronic transitions driven by the electron-ion correlations, viewed this time at the many-electron level. Let $|\alpha\rangle = |\alpha(t)\rangle$ and $P_\alpha = P_\alpha(t)$ be the eigenvectors and eigenvalues of the many-electron density matrix $\hat{\rho}_e$ so that

$$\hat{\rho}_e = \sum_\alpha |\alpha\rangle \, P_\alpha \, \langle\alpha|$$

Then SAME enables us to write the equation of motion for $\hat{\rho}_e$ in the form

$$\mathrm{i}\hbar\dot{\hat{\rho}}_e = [\hat{H}_e, \hat{\rho}_e] + \hat{\Sigma}\hat{\rho}_e - \hat{\rho}_e\hat{\Sigma}^\dagger + G[\hat{\rho}_e] \tag{4}$$

and to obtain explicit forms for the self-energy-like operator $\hat{\Sigma}$ and for the superoperator $G[\hat{\rho}_e]$, which remain valid for restricted, but finite, lengths of time after the combined electron-ion system has been allowed to evolve. Leaving these forms to a future paper, let us here concentrate on the following results.

The hermitian part of $\hat{\Sigma}$ constitutes an effective correction to $\hat{H}_e$. The resultant new effective Hamiltonian for the electrons would, by itself, produce unitary temporal evolution with constant P_α. As was indicated earlier, this is the type of evolution that would be obeyed by an isolated system of electrons, or by electrons that interact with their surroundings through at most mean field interactions.

The antihermitian part of $\hat{\Sigma}$, together with $G[\hat{\rho}_e]$, on the other hand, drives transitions in the density matrix, which manifest themselves as time-variation in its eigenvalues. This means that even if the combined electron-ion system is described by a pure state (a single state-vector that could itself of course be a coherent superposition of other state-vectors), the electron subsystem itself cannot be described in that way. Instead, after tracing out the ionic degrees of freedom, we are left with an effective description of the electrons given by an incoherent mix of many-electron state-vectors (the eigenvectors of $\hat{\rho}_e$), with time-dependent weights. The propagation of this incoherent mix of states furthermore cannot be described by a single effective hermitian electronic Hamiltonian, for if it could, then an initially pure electronic state would not split into an incoherent shower in the first place.

Notionally, we could think of this incoherent shower of electronic states as a collection of independent quantum electronic evolutions, corresponding to different possible evolutions of the original correlated electron-ion system. It is a strength of SAME, however, that we do not have to make this interpretation. We do not, furthermore, have to in any way prejudge the nature of the evolution of the shower. We do not, in particular, have to attempt to impose *ad hoc* forms on the above transitions, such as hops – instantaneous or not, random or not – between different states. These processes are allowed to take place naturally, in whatever way the quantum Liouville equation dictates. Indeed, SAME is as accurate – within a given level of the moment expansion – as the many-body electron-ion time-dependent Schrödinger equation (TDSE). A strength of SAME though is that by breaking down the TDSE into interpretable terms, it helps us understand the processes described by this equation.

The forms of $\hat{\Sigma}$ and $G[\hat{\rho}_e]$, furthermore, are such that the time-varying eigenvalues of $\hat{\rho}_e$ obey a rate equation of the form

$$\dot{P}_\alpha = \sum_\beta \left(-P_\alpha\, W_{\alpha\beta} + P_\beta\, W_{\beta\alpha}\right) \tag{5}$$

where the coefficients $W_{\alpha\beta}$ are set by $\hat{\Sigma}$. Since $\hat{\Sigma}$ depends on $\hat{\mu}_1$ and since the propagation of the latter is driven by $\hat{\rho}_e$, the coefficients $W_{\alpha\beta}$ can themselves be viewed as functions of the density matrix. Equation (5) therefore relates the rate of change of every P_α to the microscopic content of $\hat{\rho}_e$, and for this reason, at least for the purposes of the present discussion, we regard equation (5) as a statement of detailed balance. Equation (5) comes about as a consequence of SAME. It is not an *a priori* stipulation.

Let us now briefly turn to another question. Let us go back to the world of classical mechanics and ask, how would one go about writing down an analogue of SAME for a system of classical interacting electrons and ions. The first question we would have to resolve is what quantity, if any, is to take up the role of moment operators such as $\hat{\mu}_{1,\nu}$. There is but one possible answer. We would first and foremost have to consider a statistical ensemble of copies of our correlated electron-ion system, described by a classical phase-space distribution function $f(\vec{r},\vec{p},\vec{R},\vec{P},t)$, where lower- and upper-case symbols represent classical electron and ion canonical variables respectively. *Then* we can define the classical analogue of $\hat{\mu}_{1,\nu}$ (now a scalar function of $\vec{r},\vec{p}$)

$$\mu_{1,\nu} = \int \Delta R_\nu\, f(\vec{r},\vec{p},\vec{R},\vec{P},t)\, \mathrm{d}\vec{R}\mathrm{d}\vec{P}$$

where $\Delta R_\nu = R_\nu - \bar{R}_\nu$, $\bar{R}_\nu = \int R_\nu\, f(\vec{r},\vec{p},\vec{R},\vec{P},t)\, \mathrm{d}\vec{r}\mathrm{d}\vec{p}\mathrm{d}\vec{R}\mathrm{d}\vec{P}$. For the actual development of the classical moment expansion (based on the classical Liouville equation), we would expect an algebraically analogous route to above, with certain replacements: electronic operators become scalar functions in the classical phase space; traces become phase-space integrals; $[\,,\,]/\mathrm{i}\hbar$ turns into a corresponding Poisson bracket.

While this mapping from quantum to classical SAME may seem trivial, it has the following implication. Suppose that quantum mechanics, and, in particular, the quantum state-vector $|\Psi\rangle$ (e.g. that for the combined electron-ion system, but also more generally) and the TDSE, described a single system (as opposed to an ensemble). Then, since as we have seen the TDSE leads to SAME in the quantum case, we would expect Hamilton's equations of motion to lead to a classical form of SAME for the corresponding classical system.

But we have just argued that we may write down a classical form of SAME only for a classical ensemble, not for a single system. Therefore, we have to conclude that quantum mechanics, and $|\Psi\rangle$ and the TDSE in particular, describe an appropriate (quantum) ensemble of copies of a given system, and not a single system. Of course, this statistical view of quantum mechanics is known. But we have found that the SAME description of interacting many-particle systems makes it especially compelling and intuitive (and the other way round).

2.2.2 Connection with electron-phonon perturbation theory

A widely used tool in the theory of electron-phonon interactions is a model electron-phonon Hamiltonian, based on an expansion of the true electron-ion Hamiltonian to second order in the ionic displacements on some reference Born-Oppenheimer surface. We could make this expansion in two ways. If we expand about the equilibrium classical ionic positions, R_0, on that surface, then we obtain the Hamiltonian [10]

$$\hat{H}_0 = \hat{H}_e(R_0) - \sum_{\nu} \hat{F}_\nu(R_0)\hat{X}_\nu + \hat{T}_I + \frac{1}{2}\sum_{\nu,\nu'} \hat{X}_\nu K_{\nu\nu'}\hat{X}_{\nu'} \tag{6}$$

where $\hat{X}_\nu = \hat{R}_\nu - (R_0)_\nu$ and K is the Born-Oppenheimer dynamical response matrix. The first term describes unperturbed electrons, in a phonon-free environment, with relaxed frozen classical ions. The second term is the electron-phonon interaction. The last two terms describe unperturbed Born-Oppenheimer phonons. This is the standard electron-phonon Hamiltonian in solid state theory.

Making the expansion about $\bar{R}$ instead, in the spirit of SAME, yields the closely related Hamiltonian [10]

$$\bar{H} = \hat{H}_e(\bar{R}) - \sum_{\nu} \hat{F}_\nu(\bar{R})\Delta\hat{R}_\nu + \hat{T}_I + \frac{1}{2}\sum_{\nu,\nu'} \Delta\hat{R}_\nu K_{\nu\nu'}\Delta\hat{R}_{\nu'} \tag{7}$$

For small variations in $\bar{R}$ about R_0, the two Hamitonians are equivalent.

Our task now is to show that SAME, applied to $\bar{H}$, yields the same lowest-order electron-phonon transition rates, as standard electron-phonon perturbation theory, applied to $\hat{H}_0$. The purpose of the exercise is to demonstrate that despite its different algebraic appearance, SAME incorporates the selection rules that control inelastic transitions.

For simplicity, we consider non-interacting electrons and just one dynamical ionic degree of freedom, so that the index ν can be dispensed with. All electronic operators below are one-electron operators and we dispense with superscript 1 for simplicity. We ignore variations in $\bar{R}$, with $\bar{R} \approx R_0$, so that the two Hamiltonians above are now the same and we can dispense with the arguments of $\hat{H}_e$ and $\hat{F}$. Consider first the equations of motion for the ionic moments. They now read

$$\dot{C}^{RR} = \frac{2}{M}C^{PR}$$

$$
\begin{aligned}
\dot{C}^{PR} &= \frac{C^{PP}}{M} - KC^{RR} + \mathrm{Tr}_e \left\{ \hat{F}\hat{\mu} \right\} \\
\dot{C}^{PP} &= -2KC^{PR} + 2\mathrm{Tr}_e \left\{ \hat{F}\hat{\lambda} \right\}
\end{aligned}
\tag{8}
$$

where, for short, we have written $\hat{\mu}$ ($\hat{\lambda}$) for $\hat{\mu}_1$ ($\hat{\lambda}_1$). The physics described by these equations is the following. The quantity

$$
w = \frac{1}{M} \mathrm{Tr}_e \left\{ \hat{F}\hat{\lambda} \right\}
\tag{9}
$$

is the power dissipated into the ion by the electrons [10]. This power comes in as kinetic energy. It is then repartitioned, between kinetic and potential energy, via the quantity C^{PR}, which effectively mediates the communication between the two ionic canonical variables (momentum and position). This conduction of heat around ionic phase space, however, is modulated by the electrons, via the last term in the second one of equations (8). Indeed, we know that lattice heat conduction in metals is heavily suppressed by phonon-electron scattering.

Let us now turn to the equations of motion for the electronic density matrix and moment operators. Making use of the Hartree-Fock relation for the two-electron density matrix, given earlier, we obtain

$$
\dot{\hat{\rho}}_e = \frac{1}{\mathrm{i}\hbar} [\hat{H}_e, \hat{\rho}_e] - \frac{1}{\mathrm{i}\hbar} [\hat{F}, \hat{\mu}]
\tag{10}
$$

$$
\dot{\hat{\mu}} = \frac{1}{\mathrm{i}\hbar} [\hat{H}_e, \hat{\mu}] - \frac{1}{\mathrm{i}\hbar} C^{RR} [\hat{F}, \hat{\rho}_e] + \frac{\hat{\lambda}}{M}
\tag{11}
$$

$$
\dot{\hat{\lambda}} = \frac{1}{\mathrm{i}\hbar} [\hat{H}_e, \hat{\lambda}] + \frac{1}{2} (\hat{F}\hat{\rho}_e + \hat{\rho}_e\hat{F}) - \hat{\rho}_e\hat{F}\hat{\rho}_e - \frac{1}{\mathrm{i}\hbar} C^{PR} [\hat{F}, \hat{\rho}_e] - K\hat{\mu}
\tag{12}
$$

We imagine releasing the electron-ion system from an initial product state, in which $\hat{\rho}_e$ commutes with $\hat{H}_e$, while the vibrations are in a harmonic-oscillator eigenstate with N phonons and with $C^{PR} = 0$. In the absence of electron-phonon interactions, the two subsystems would remain in that state forever.

The electron-phonon interaction is realised by the quantity $\hat{F}$. To do a lowest-order perturbative calculation we therefore now have to linearise the above equations in $\hat{F}$. Thus, we set $C^{PR} = 0$, $C^{RR} = C^{RR}(0) = n\hbar\omega/K$, $n = N + 1/2$, $\omega^2 = K/M$, and drop the last term in equation (10). This leaves us with two coupled equations for $\hat{\mu}$ and $\hat{\lambda}$. Taking matrix elements of these two equations in two eigenstates of $\hat{\rho}_e$ (and of $\hat{H}_e$), with occupations f_α, f_β and energies E_α, E_β, and defining $\hat{z} = K\hat{\mu}$ we get

$$
\begin{aligned}
\dot{z}_{\alpha\beta} &= -\mathrm{i}\omega_{\alpha\beta} z_{\alpha\beta} + \omega^2 \lambda_{\alpha\beta} + \mathrm{i}n\omega (f_\beta - f_\alpha) F_{\alpha\beta} \\
\dot{\lambda}_{\alpha\beta} &= -\mathrm{i}\omega_{\alpha\beta}\lambda_{\alpha\beta} - z_{\alpha\beta} + \left(\frac{f_\alpha + f_\beta}{2} - f_\alpha f_\beta \right) F_{\alpha\beta}
\end{aligned}
$$

where $\hbar\omega_{\alpha\beta} = E_\alpha - E_\beta$. The solution for $\lambda_{\alpha\beta}$ is

$$
\lambda_{\alpha\beta} = \frac{1}{2} \frac{F_{\alpha\beta}}{\omega^2 - \omega_{\alpha\beta}^2} \{ \exp[\mathrm{i}(\omega_{\beta\alpha} + \omega)t] \, (P/\mathrm{i}\omega - Q) - \exp[\mathrm{i}(\omega_{\beta\alpha} - \omega)t] \, (P/\mathrm{i}\omega + Q) + 2Q \}
$$

where

$$P = -n\omega\omega_{\alpha\beta}(f_\beta - f_\alpha) + \omega^2 \left(\frac{f_\alpha + f_\beta}{2} - f_\alpha f_\beta \right)$$
$$Q = -\mathrm{i}n\omega(f_\beta - f_\alpha) + \mathrm{i}\omega_{\alpha\beta} \left(\frac{f_\alpha + f_\beta}{2} - f_\alpha f_\beta \right)$$

Substituting this into equation (9) and taking the long-time limit (when $(\sin \omega t)/\omega \to \pi\delta(\omega)$), gives (with a factor of 2 added for spin degeneracy)

$$\begin{aligned} w \quad &= \frac{\pi}{M} \sum_{\alpha,\beta} |F_{\alpha\beta}|^2 \{ \delta(\omega_{\beta\alpha} + \omega)[-(N + 1/2)(f_\beta - f_\alpha) + (f_\beta + f_\alpha)/2 - f_\alpha f_\beta] \\ &+ \delta(\omega_{\beta\alpha} - \omega)[(N + 1/2)(f_\beta - f_\alpha) + (f_\beta + f_\alpha)/2 - f_\alpha f_\beta] \} \end{aligned}$$

This expression is algebraically identical (after some rearrangement) to the corresponding result for the power dissipated into phonons by excited electrons obtained by first-order scattering theory based on the standard electron-phonon Hamiltonian $\hat{H}_0$ given earlier [13].

We have demonstrated in a previous paper [11] that SAME, already at the level of the first moment, indeed reproduces the above analytical result in actual numerical simulations of ionic heating in a current carrying atomic wire. This agreement is highly significant because, unlike the argument above, the SAME equations on which the simulations are based do not make use of any reference Born-Oppenheimer surfaces, nor are these simulations perturbative.

Let us now consider the transition rates directly in $\hat{\rho}_e$. The solution for $z_{\alpha\beta} = K\mu_{\alpha\beta}$ is

$$z_{\alpha\beta} = \frac{1}{2} \frac{F_{\alpha\beta}}{\omega^2 - \omega_{\alpha\beta}^2} \{ \exp[\mathrm{i}(\omega_{\beta\alpha} + \omega)t] \, (-P + \mathrm{i}\omega Q) - \exp[\mathrm{i}(\omega_{\beta\alpha} - \omega)t] \, (P + \mathrm{i}\omega Q) + 2P \}$$

From equation (10) we have

$$\dot{\rho}_{\alpha\alpha} = \frac{2}{\hbar} \, \mathrm{Im} \sum_\beta F_{\beta\alpha}\mu_{\alpha\beta}$$

Substituting in and taking the long-time limit gives

$$\begin{aligned} \dot{\rho}_{\alpha\alpha} \quad &= \frac{2\pi}{\hbar} \frac{\hbar}{2M\omega} \sum_\beta |F_{\alpha\beta}|^2 \{ \delta(E_{\beta\alpha} + \hbar\omega)[(N + 1/2)(f_\beta - f_\alpha) - (f_\beta + f_\alpha)/2 + f_\alpha f_\beta] \\ &+ \delta(E_{\beta\alpha} - \hbar\omega)[(N + 1/2)(f_\beta - f_\alpha) + (f_\beta + f_\alpha)/2 - f_\alpha f_\beta] \} \end{aligned}$$

This is algebraically identical to

$$\begin{aligned} \dot{\rho}_{\alpha\alpha} \quad &= \frac{2\pi}{\hbar} \frac{\hbar}{2M\omega} \sum_\beta |F_{\alpha\beta}|^2 \{ -(N + 1)f_\alpha(1 - f_\beta)\delta(E_{\beta\alpha} + \hbar\omega) - N f_\alpha(1 - f_\beta)\delta(E_{\beta\alpha} - \hbar\omega) \\ &+ (N + 1)f_\beta(1 - f_\alpha)\delta(E_{\beta\alpha} - \hbar\omega) + N f_\beta(1 - f_\alpha)\delta(E_{\beta\alpha} + \hbar\omega) \} \end{aligned}$$

The latter is the known quantum correlated electron-phonon scattering-rate expression, which incorporates the selection rules for inelastic current-voltage spectroscopy [14]. Therefore, we expect SAME, at the level of the second moment, to capture inelastic transport spectral features. We will demonstrate by direct numerical simulations later on that this is indeed the case. The above analytical results incorporate also the ingredients needed for making the crossover from ionic heating, via thermal equilibrium, to ionic cooling, in the presence of an excited electron gas, as a function of the effective phonon energy [12]. We therefore assert that SAME enables us to monitor directly the flow of heat back and forth between the two subsystems, with the added advantages that SAME is not a perturbative scheme, that it makes no use of any Born-Oppenheimer reference surfaces, that it implicitly accounts for anharmonicity and that it is, above all, a form of MD that portrays these processes in real time.

2.3 Infinite lead current formalism

One area where the interaction between electrons and ions (and the transfer of energy between the different subsystems) is important is in the area of conduction of nanostructures, e.g. atomic-scale wires[19]. To examine problems of this nature, we need to be able to consider a device (where the physics which we are concerned with is localised) connected to an environment, which might typically be a pair of leads (allowing exchange of electrons and energy with the surroundings). In the description below we explicitly consider two leads, working at the Ehrenfest level, though the formalism extends in principle to a much broader environment model, and to the higher moment expansions (details will be presented in a paper under preparation).

We start from the quantum Liouville equation, Eq. (1), and divide the system into two regions: a device, labelled D, and the environment, labelled E. Then we can write:

$$\begin{aligned}
\mathrm{i}\hbar\frac{\partial\hat{\rho}_D}{\partial t} &= [\hat{H}_D,\hat{\rho}_D] + (\hat{H}_{DE}\hat{\rho}_{ED} - \hat{\rho}_{DE}\hat{H}_{ED}) && (13)\\
\mathrm{i}\hbar\frac{\partial\hat{\rho}_{DE}}{\partial t} &= \hat{H}_D\hat{\rho}_{DE} - \hat{\rho}_D\hat{H}_{DE} + \hat{H}_{DE}\hat{\rho}_E - \hat{\rho}_{DE}\hat{H}_E && (14)\\
\mathrm{i}\hbar\frac{\partial\hat{\rho}_E}{\partial t} &= [\hat{H}_E,\hat{\rho}_E] + (\hat{H}_{ED}\hat{\rho}_{DE} - \hat{\rho}_{ED}\hat{H}_{DE})\\
&- 2\mathrm{i}\hbar\Gamma_E(\hat{\rho}_E - \hat{\rho}_{ref}), && (15)
\end{aligned}$$

where a damping term, $2\mathrm{i}\hbar\Gamma_E(\hat{\rho}_E - \hat{\rho}_{ref})$, has been introduced to the environment and will be descibed below.

Now we can apply different time evolution schemes to the environment (which we want to act as a bath of energy and electrons) and the device. For the environment, we seek a closed, integral form. We assume that the Hamiltonian is static. If we define a driving term $\mathrm{i}\hbar\hat{G}_E = (\hat{H}_{ED}\hat{\rho}_{DE} - \hat{\rho}_{ED}\hat{H}_{DE})$ and define the value of the reference driving term by $0 = [\hat{H}_E,\hat{\rho}_E(0)] + \mathrm{i}\hbar\hat{G}_E^{(0)} - 2\mathrm{i}\hbar\Gamma(\hat{\rho}_E(0) - \hat{\rho}_{ref})$, then we can write:

$$\hat{\rho}_E(t) = \hat{\rho}_E(0) + \int_0^t \mathrm{d}x\ \hat{O}(x)\left(\hat{G}_E(t-x) - \hat{G}_E^{(0)}\right)\hat{O}^\dagger(x), \qquad (16)$$

where $\hat{O}(t) = \mathrm{e}^{-\Gamma_E t}\mathrm{e}^{\hat{H}_E t/\mathrm{i}\hbar}$ is a time evolution operator which arises from the commutator of $\hat{\rho}_E$ and $\hat{H}_E$, and includes the damping introduced in Eq. (15). The effect of this scattering-like Γ_E term will be to localise $\hat{\rho}_E(t)$ in time, enhancing the natural time localisation of the time evolution operators[8].

The time evolution operators are most easily evaluated from the electronic Green's functions for the environment region, $\hat{g}(z)$:

$$\hat{O}(t) = e^{-\Gamma_E t} \int \mathrm{d}E e^{Et/\mathrm{i}\hbar} \lim_{\eta \to 0^+} \mathrm{Im} \left(-\frac{1}{\pi} \right) \hat{g}(E + \mathrm{i}\eta). \tag{17}$$

These operators implicitly include the semi-infinite environment given by the Green's functions; when coupled with the reference density matrix, $\hat{\rho}_{ref}$, for a similar environment they give a restoring force towards the chosen semi-infinite system whatever the size of the explicit environment chosen.

For the device and device-environment terms, we use the leapfrog method to evolve the equations forward in time; this is also used by the DINAMO code.

2.4 Implementation of DINAMO

The computational implementation of the SAME has been named DINAMO, which stands for Dynamics in Non-Adiabatic Molecular Orbitals. This is a code written from scratch in Fortran 90, which at present roughly consists of 10k lines of code, and is an implementation of the SAME equations for orthogonal tight binding Hamiltonians. The following methodologies have been implemented:

- Geometry optimization, using an efficient quasi-Newton algorithm [20, 21].
- Born-Oppenheimer molecular dynamics.
- Ehrenfest dynamics.
- First moment SAME.
- Second moment SAME.

Self consistency is implemented at the BO and Ehrenfest levels via point charge inter-site Coulomb interactions and an onsite Hubbard "U" like term[22].

All input is handled using the FDF package written by Alberto Garcia and Jose Soler (used in the SIESTA code) which makes input files easy to read and edit and provides great flexibility. All parameters are read from a single input file (which may be separated in different files using FDF's "include" capabilities). Most input parameters will acquire sensible default values when not explicitly defined.

In a tight binding basis set, all SAME equations of motion are equations between matrices. Operations like commutators and matrix products are required to calculate the derivatives of the different operators in their equations of motion and they represent the bottleneck of the calculation. These operations must be optimized to achieve maximum performance. At the core of the code is a purpose built linear algebra module which implements all matrix operations, including additions and multiplications by scalars. Although some of these operations could be dealt with by using Fortran 90 array features, we have chosen to encapsulate them in the linear algebra module. In this way, parallelization, vectorization or changes in the storage structures can be restricted to the internal workings of the module and no modification of the rest of the code is needed. A new Fortran type `matrix` is defined, the structure of which is hidden from the user. Using the abstract matrix operations, the implementation of the SAME equations is a matter of translating the algebra into these operations. This made the task of implementing and debugging the SAME equations relatively straightforward since never in the code is an actual element of any of the operators explicitly modified or referenced.

The Hamiltonian matrix and its derivatives are inherently sparse, and taking this sparsity into account is crucial to make the SAME equations computationally manageable. The matrix structure can contain both sparse and dense matrices. Subroutines that implement the abstract matrix operations can choose internally the most appropriate algorithm according to the nature of the operands. For sparse matrix operations we have implemented our own algorithms that operate only on non-zero elements based on a simple coordinate storage format. This is not the most efficient approach, both in terms of the required storage and cache efficiency, but has the advantage of being simple. More sophisticated methods should be easy to implement. For all dense matrix operations, BLAS routines are used. Routines within the linear algebra module and other time consuming routines such as the construction of the Hamiltonian matrix have been parallelized using OpenMP directives.

The implementation of new tight binding models is a straightforward task, and only requires to add calls to particular subroutines to calculate the model-dependent radial hopping matrix elements, their derivatives and pair repulsion functions. These routines are easily plugged into a single interface module, and there is no need to modify any of the higher level routines. General routines for the calculation of the Slater-Koster factors and their derivatives have been implemented.

Equations of motion for the operators, such as $\hat{\rho}_e$ or the various $\hat{\mu}_\nu$, are integrated using the following "leapfrog" like method:

$$\hat{q}(t+\Delta t) = \hat{q}(t-\Delta t) + 2\Delta t\, \left.\frac{d\hat{q}}{dt}\right|_t$$

which is time reversible and unitary and therefore unconditionally stable. This simple integration scheme is extremely powerful. As an example, we have successfully performed Ehrenfest calculations (including self-consistency, which makes the Liouville equation non-linear) for systems of thousands of atoms for many tens of femtoseconds using a time step of 0.01 femtoseconds. Particle numbers are conserved within numerical precision, and energy is conserved to a part in 10^9.

For an Ehrenfest calculation, the bottleneck is the calculation of the commutator $[\hat{H}, \hat{\rho}]$ which for a sparse Hamiltonian scales as M^2, where M is the number of basis functions. This makes Ehrenfest dynamics very competitive with Born-Oppenheimer dynamics. For large numbers of atoms, the better scaling compensates the fact that a hundred times smaller time step is needed, in a similar way to the Car-Parrinello method. Both the first-moment and second-moment dynamics have similar computational costs. The bottleneck in these cases is the calculation of products of the form $\hat{q}\hat{A}\hat{q}$, where $\hat{q}$ is $\hat{\rho}$ or $\hat{\mu}_{1,\nu}$ and $\hat{A}$ is a sparse operator. These terms appear in the equations of motion for the one-particle density matrices after the Hartree-Fock approximation is applied. In the present implementation, these are treated as dense-dense products, but in principle their scaling can be reduced to M^2. There are about N^2 of these products where N is the number of "quantum" ions.

3 Results

3.1 Joule heating

We present results for Joule heating of a single atom within a linear chain, using a first moment extension of the open boundary formalism described above. The tight binding model used was extremely simple: a chain of 1s atoms, with a hopping integral of -1eV between nearest neighbours only, and an atomic spacing of 1.0 Å. A repulsive potential was fitted to give the correct equilibrium spacing, with a value of 0.648 eV. The variation with distance was a simple power law, with an exponent of 2 for the hopping integral and 4 for the repulsive potential. The device consists of nine atoms, the central atom of which is allowed to move (and whose quantum evolution is followed). The leads are 16 atoms long, and the integral for the environment covers only the most recent 7.5 fs. The initial electronic density matrix (which is also the reference density matrix for the environment) is found by diagonalising a wire 1001 atoms long, and using the central 41×41 site portion of the resulting density matrix. A timestep of 0.008 fs was used throughout (after tests to establish the largest practical value). We have considered two slightly different systems: the first, with ordinary coupling between the central atom and the surrounding atoms; the second, with a weaker coupling (hopping integral of -0.5eV) for this atom only.

Before considering heating, we examine the current that results from application of a bias to this system. In Fig. 1(a) we see that a steady current is easily achieved after application of a bias (in all cases, the bias is applied to the left-hand lead and the left-hand side of the device by shifting the on-site terms in the Hamiltonian). There are two further important effects shown in Fig. 1(b): the effect of changing the coupling of the central atom to its neighbours and the effect of introducing classical kinetic energy to the central ion. The effect of weakening the coupling is, as expected, to reduce the current (though other effects will be explored below). The classical kinetic energy causes the ion to oscillate about its mean position: for the ordinary coupling at the ionic equilibrium position, current is a maximum as hopping into and out of the ion is equal, while at each extremum, current is a minimum as one of the two bonds to the nearest neighbours is significantly weakened. For the weak coupling, we see two further effects: first, the magnitude of the oscillations of the ionic position is smaller, resulting in smaller oscillations in the current; second, the

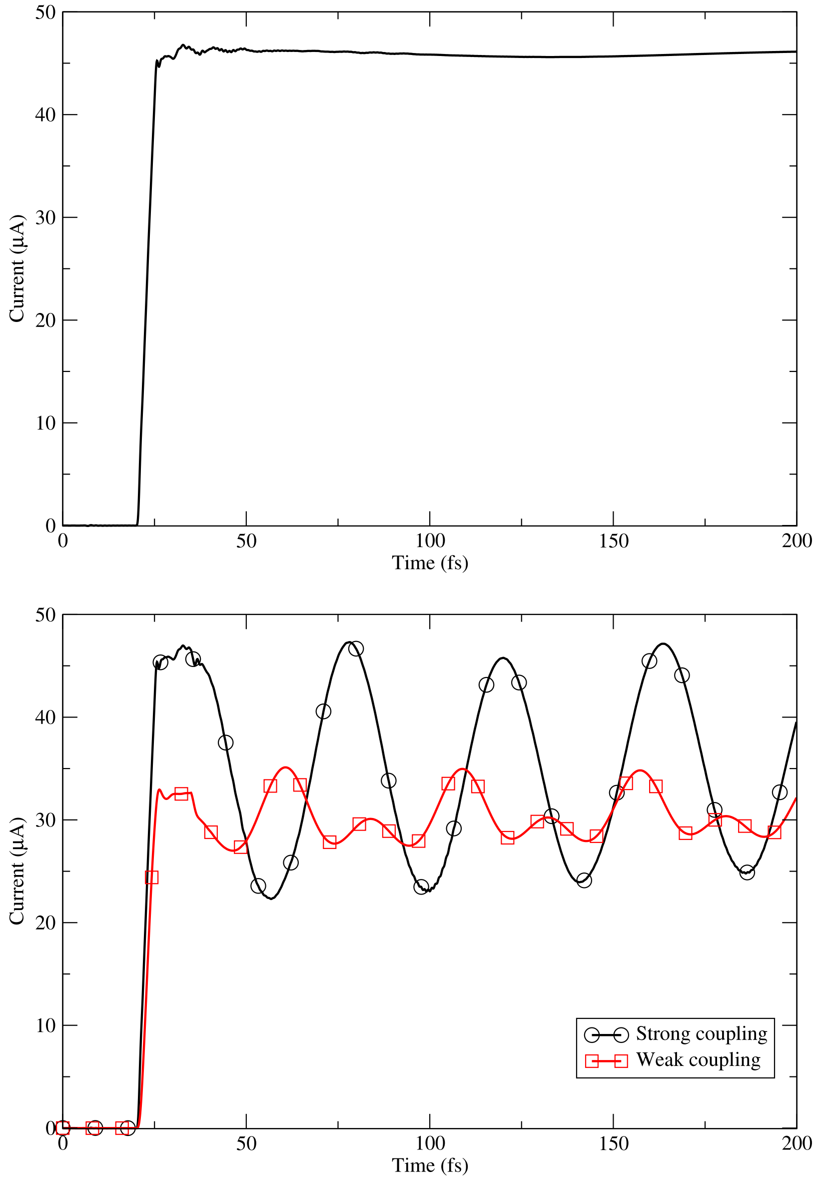

Figure 1: Current into central atom of chain when a bias of -0.6 V is applied at t =2 0 fs (linearly increased over 5 fs). (a) Ordinary coupling, no classical KE given to atom. (b) Ordinary and weak coupling with small classical KE given to the atom at 35 fs.

oscillations in the current show a doubling of the period and two separate height maxima relative to the ordinary coupling oscillations. This behaviour relates to the charging of the central ion at different extrema: when it is at the left-hand extremum (near the biased electrode) it loses charge to that electrode, so that when it reaches the mid-point, it has less charge than at equilibrium (i.e. zero bias) and the current is (relatively) large. When it is at the right-hand extremum it gains charge from the right-hand electrode, so that when it returns to the mid-point it has more charge than at equilibrium and the current is (relatively) small.

We now turn to heating, within the first moment approximation (i.e. retaining only $\hat{\mu}_{1,\nu}$ and $\hat{\lambda}_{1,\nu}$). The average kinetic energy now includes two terms, one arising from the average momentum of the ion, and the other from the qantum spread of momentum (we label these as "classical" and "quantum" contributions). These are plotted against time for the weak and ordinary coupling cases in Fig. 2, with classical KE in the top graph in each case, and quantum KE in the bottom graph. We see a number of important features: first, the classical kinetic energy decreases, as expected (electrons are being excited by the ions and removed from the open boundaries, leading to cooling); second, the quantum kinetic energy increases with bias and with time; third, the frequency of the classical kinetic energy oscillation increases with bias, due to a population of anti-bonding states as well as bonding states. The weakly coupled system exhibits higher frequency oscillations due to the weaker coupling; it also exhibits less heating *in the central ion* due to the lower current and weaker electronic correlations (in the limit of zero coupling, the heating goes to zero as expected).

3.2 Inelastic current-voltage spectroscopy

We will now show a direct calculation of inelastic current-voltage spectroscopy from second-moment CEID. The calculation is based on direct numerical integration of the full second-moment SAME equations of motion, with no approximation. Thus, this numerical calculation is inherently different, and superior, to the earlier analysis, based on the standard electron-phonon harmonic Hamiltonian expanded on a reference Born-Oppenheimer surface. We have a 131-atom metallic chain described by a tight binding-model with all parameters as in reference [11] except the ionic mass which is now 1 a.m.u. A single atom in the middle of the chain is allowed to move. A bias is applied, and a current flows, as in reference [11]. The current, for a given bias, is averaged over about one thermal vibration period. The current, differential conductance and its derivative with voltage are plotted against bias in figure 3.

The characteristic inelastic spectral feature (in the bottom panel) is clearly visible. The shoulder (bottom plot) beyond the voltage where the spectral feature occurs is the signature of the quantum heating of the ion that becomes activated at that critical voltage. This critical voltage, on the plot, is in excellent agreement with the value of $\hbar\omega = 0.26$ eV (where ω is the Born-Oppenheimer frequency of the ion), which may be expected on the basis of electron-phonon perturbation theory [14], and on the basis of the earlier

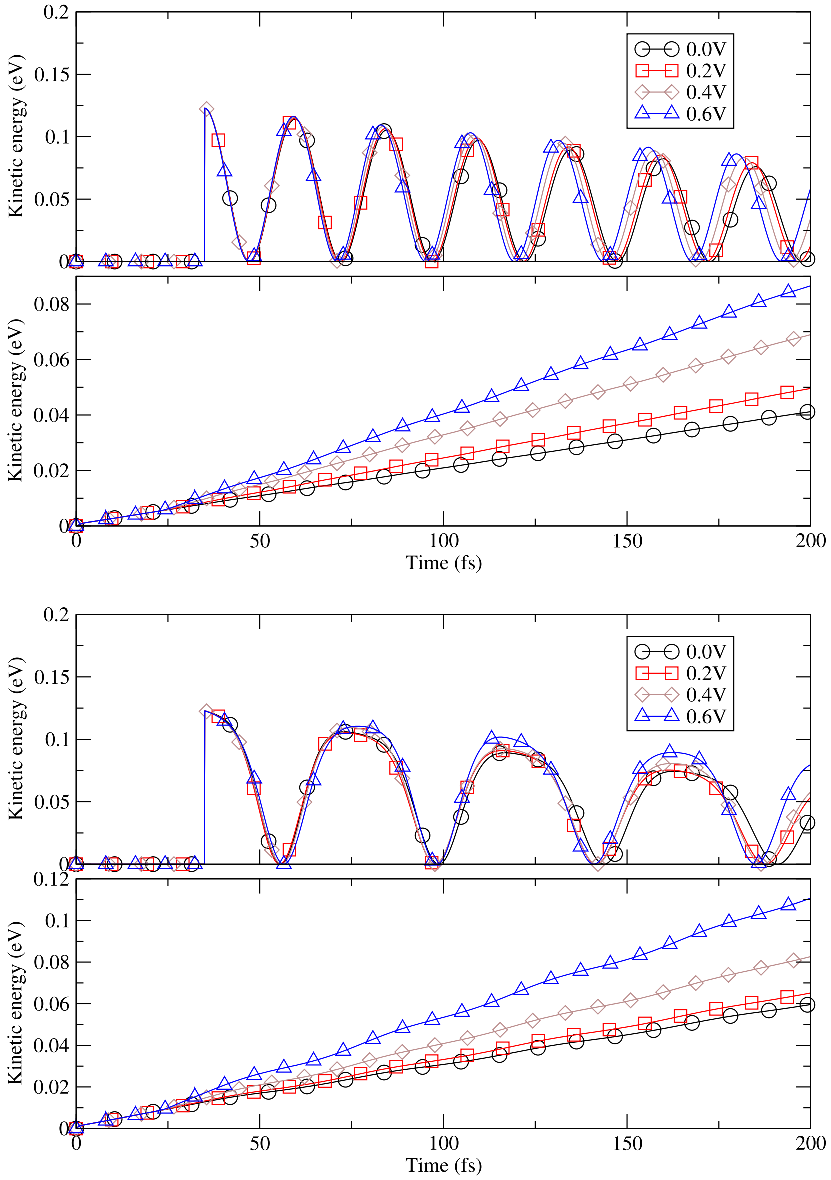

Figure 2: Classical (upper panels) and quantum (lower panels) KE for four biases: 0V, -0.2V, -0.4V and -0.6V. Bias applied at t=20fs (linearly increased over 5fs). A small classical KE was given to the atom at 35fs. Top graphs: Weak coupling. Bottom graphs: Ordinary coupling. Note the different energy scales for the quantum KE plots.

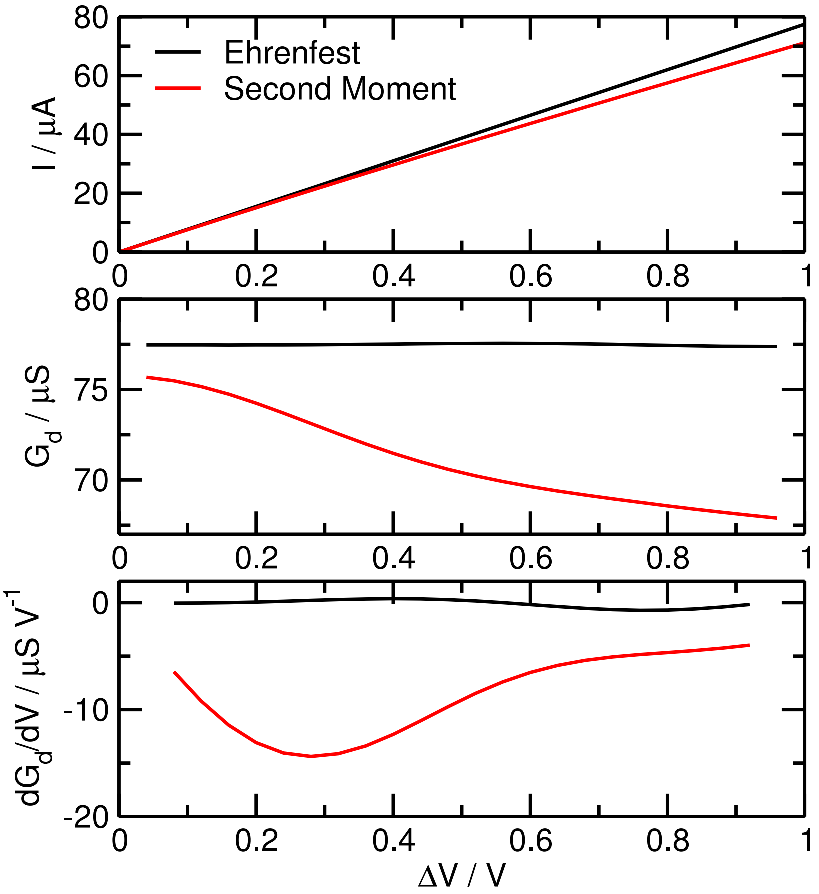

Figure 3: Current, differential conductance and its derivative with voltage, versus bias, for a single dynamical atom in a metallic chain.

analytical derivations. The physical origin of this feature is that for current carrying electrons to be able to excite vibrations, the excess electronic energy, set by the bias, has to exceed a phonon quantum. There is no other way to satisfy the selection rules for inelastic scattering, derived earlier. Hence, we expect inelastic scattering, the onset of dissipation and ionic heating, and a drop in conductance (due to the newly opened scattering mechanism) to occur at a bias that matches this phonon energy. And indeed it does. But, once again, the present simulations start from scratch and know nothing about any Born-Oppenheimer surfaces. Nor are the simulations constrained by the assumption of harmonicity, not are they perturbative. They furthermore allow phonons and electrons to be perturbed by each other in a consistent manner, both ways. In principle (though this is not done here) the method allows also the inclusion of electron-electron interactions and dynamical screening, at least in a Hartree-Fock, or in an adiabatic-LDA, spirit.

4 Conclusion and future directions

The range of problems to which this modelling technique can be applied is already large (ranging from low-energy I-V spectra to high-energy radiation damage) and we expect new and exciting insights to emerge as a result of this. However, the development of the formalism is not yet complete. The one qualitative feature left to work out is electron-electron correlation. We will begin at the mean-field level (Hartree-Fock or density functional theory). This is essential for describing (for example) the discharge of a capacitor. At the level of the Ehrenfest approximation this is straightforward and has already been implemented. Of course, if we could consider explicit two-electron correlation we should be able to model the onset of superconductivity in very small devices. This project, though, is for the more distant future.

A major area for which this approach is particularly well-suited is the transport of charge in biological systems. Biological systems have three important features that make conventional perturbative approaches difficult, but make a molecular dynamics based approach attractive:

1. They have very low symmetry in general, so many degrees of freedom need to be treated explicitly.
2. They are made from soft matter, so it is hard to define lattice sites about which oscillations occur. Indeed, diffusion can take place.
3. Calculations at zero temperature to define a reference state for the perturbation calculations could be qualitatively wrong, as biological systems make use of water, and water at low temperatures solidifies and behaves quite differently from the liquid at higher temperatures.

The presence of an environment that can contain charges clearly makes it important to introduce electrostatics into our equations of motion.

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