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FIFTH INTERNATIONAL WORKSHOP ON COMPUTATIONAL CONDENSED MATTER PHYSICS

16 - 18 January 1991

Adriatico Guest House
I C T P, Trieste, Italy

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Programme
and
Abstracts

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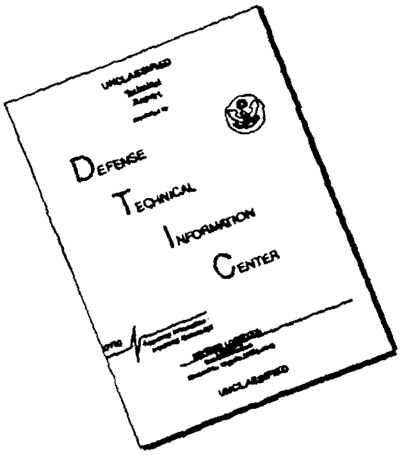

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PREFACE

This workshop will follow the series which began in Oxford (1983) and continued in Braunschweig (1984) and Trieste (1987 and 1989). Following the tradition of the previous meetings, the Workshop will be devoted to recent advances in computational condensed matter physics, based on realistic calculations of the electronic structure of polyatomic systems.

The list of topics to be treated includes: High temperature superconductivity, new materials, alloy phase diagrams, recent developments in density functional theory, new developments in pseudopotential theory, approximate methods, Car-Parrinello appraoch to molecular dynamics, quantum Monte Carlo treatment of correlation effects, time-dependent correlations and excitation properties, quantum dynamics. Emphasis will be put on both theoretical techniques and applications.

As in previous events in this series, the Workshop will consist of invited talks, with ample space devoted to discussion. In addition, there will be one (or more) poster session(s).

This activity is co-sponsored by the Scuola Internazionale di Studi Avanzati (SISSA, Trieste).

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Roberto Car
Raffaele Resta
Michael Schlüter

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INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
I.C.T.P., P.O. BOX 586, 34100 TRIESTE, ITALY, CABLE CENTRATOM TRIESTE

FIFTH INTERNATIONAL WORKSHOP ON COMPUTATIONAL CONDENSED MATTER PHYSICS
(16 - 18 JANUARY 1991)

TENTATIVE PROGRAMME

WEDNESDAY, 16 JANUARY

8.15 - 9.00	**REGISTRATION**

OPENING SESSION (Chairperson: M.P. TOSI)

9.00 - 9.10	YU LU (Acad.Sinica,Beijing/ICTP): **Opening Address**
9.10 - 9.15	General information for Participants
9.15 - 9.45	D.R. HAMANN (AT&T, Murray Hill): "Correlated ground states for real materials"
9.45 - 10.00	Discussion

QUANTUM MONTE CARLO (Chairperson: M.P. TOSI)

10.00 - 10.30	D. CEPERLEY(Univ. Illinois, Urbana): "Calculations of the properties of solids with Green's function MC"
10.30 - 10.45	Discussion
10.45 - 11.00	***COFFEE***
11.00 - 11.30	S.G. LOUIE (Univ.California, Berkeley): "QMC studies of materials: Magnetic structures of BCC hydrogen"
11.30 - 11.45	Discussion

MAXIMUM ENTROPY METHODS (Chairperson: M. GILLAN)

11.45 - 12.15	R.N. SILVER(Los Alamos Nat.Lab.): "Dynamics of the Anderson model from QMC and maximum entropy"
12.15 - 12.30	Discussion
12.30 - 12.50	T.A. ARIAS(MIT) : "Precise and efficient *ab initio* molecular dynamics"
12.50 - 13.00	Discussion
13.00 - 14.30	***LUNCH BREAK***

NEW SCHEMES FOR ELECTRON-ION INTERACTION (Chairperson: A. BALDERESCHI)

14.30 - 14.50	G.B. BACHELET (Univ. Trento) : "Pseudopotentials, pseudohamiltonians and physical ions"
14.50 - 15.00	Discussion
15.00 - 15.20	E.L. SHIRLEY (Univ. Illinois, Urbana): "GW quasiparticle pseudopotentials"
15.20 - 15.30	Discussion
15.30 - 15.45	***BREAK***
15.45 - 16.05	K. LAASONEN (Univ. Helsinki): "Implementation of ultrasoft pseudopotentials in *ab-initio* molecular dynamics"
16.05 - 16.15	Discussion
16.15 - 16.35	J.M. SOLER (Univ. Autonoma, Madrid) "Car-Parrinello-like implementation of the APW method"
16.35 - 16.45	Discussion
16.45 - 17.00	***COFFEE***
17.00 - 19.00	POSTER SESSION
19.00 - 20.30	***DINNER BREAK***
20.30 - 22.00	POSTER SESSION

THURSDAY, 17 JANUARY

HIGH T_c AND HIGHLY CORRELATED ELECTRON SYSTEMS (Chairperson: O.K. ANDERSEN)

8.45 - 9.15	E. TOSATTI (SISSA, Trieste): "Strongly correlated models for high T_c superconductivity"
9.15 - 9.30	Discussion
9.30 - 9.50	W.E. PICKETT (NRL, Washington): "Lattice dynamics and structural instabilities in high T_c superconductors"
9.50 - 10.00	Discussion
10.00 - 10.20	A.I. LIECHTENSTEIN (MPI, Stuttgart): "*Ab-initio* study of zone-boundary phonons and their coupling to electrons in $YBa_2Cu_3O_7$ and $Ba_{1-x}K_xBiO_3$"
10.20 - 10.30	Discussion

10.30 - 10.50	S. MASSIDDA (IRRMA, Lausanne): "Electronic structure and positron annihilation in high T_c superconductors: the problem of the Fermi surface"
10.50 - 11.00	Discussion
11.00 - 11.15	***C O F F E E***
11.15 - 11.45	A. SVANE (Univ. Aarhus): "Localization in the self-interaction corrected density functional formalism"
11.45 - 12.00	Discussion
12.00 - 12.20	C.A. BALSEIRO (Bariloche) : "Static and dynamical properties of quantum many-body systems: Finite cluster calculations"
12.20 - 12.30	Discussion
12.30 - 14.00	***L U N C H B R E A K***

SPECTROSCOPY OF HIGHLY CORRELATED ELECTRON SYSTEMS (Chairperson: K. KUNC)

14.00 - 14.20	H. ESKES (Univ. Groningen): "High energy spectroscopies compared with exact solutions of multiband model hamiltonians"
14.20 - 14.30	Discussion
14.30 - 14.50	M.S. HYBERTSEN (AT&T, Murray Hill): "Model for low energy electronic states probed by X-ray absorption in high T_c cuprates"
14.50 - 15.00	Discussion

QUASIPARTICLE ENERGIES (Chairperson: L. FRITSCHE)

15.00 - 15.30	F. GYGI (IBM, Zürich): "Self-consistent electronic structure of a vortex line in a type-II superconductor"
15.30 - 15.45	Discussion
15.45 - 16.05	F. ARYASETIAWAN (Univ. Lund): " Dielectric response and quasiparticle energies in Ni"
16.05 - 16.15	Discussion
16.15 - 16.30	***C O F F E E***

NEW APPLICATIONS AND DEVELOPMENTS OF DENSITY FUNCTIONAL THEORY (Chairperson: P. ZIESCHE)

16.30 - 16.50	M. POSTERNAK (IRRMA, Lausanne): "Quantum-mechanical calculations of the spontaneous polarization: Pyroelectric BeO"
16.50 - 17.00	Discussion
17.00 - 17.20	M. FOULKES (Imperial College, London): "Alternative total energy functionals in DFT"
17.20 - 17.30	Discussion
17.30 - 17.50	N. CHETTY (TU Denmark, Lyngby): "First principles energy density and its application to GaAs polar surfaces"
17.50 - 18.00	Discussion

FRIDAY, 18 JANUARY

SEMICONDUCTOR AND METAL ALLOYS (Chairperson: S. BARONI)

8.45 - 9.15	A. ZUNGER (SERI, Golden): "First-principle statistical mechanics of semiconductor and metal alloys"
9.15 - 9.30	Discussion
9.30 - 9.50	S. DE GIRONCOLI (IRRMA, Lausanne): "Structure and thermodynamics of Si-Ge alloys from *ab-initio* Monte Carlo simulations"
9.50 - 10.00	Discussion
10.00 - 10.15	K.W. JACOBSEN (TU Denmark, Lyngby): "Alloy formation in the effective medium theory"
10.15 - 10.30	B. CHAKRABORTY (Brandeis Univ., Waltham): "Ordering in Cu-Au alloys: A new approach to alloy phase stability"
10.30 - 10.45	Discussion
10.45 - 11.00	***COFFEE***

SURFACES AND INTERFACES (Chairperson: W. ANDREONI)

11.00 - 11.30	A. SELLONI (SISSA, Trieste): "*Ab-initio* studies of the Si(111) surface"
11.30 - 11.45	Discussion
11.45 - 12.05	M.D. STILES (NIST, Gaithersburg): "Theory of electron transmission through interfaces"
12.05 - 12.15	Discussion

12.15 - 12.25	O.K. ANDERSEN (MPI, Stuttgart): "Comment about density functional calculations of Schottky barrier heights"
12.25 - 12.45	R.W. GODBY (Cavendish Lab., Cambridge): "Exchange and correlation in Schottky barriers and heterojunctions"
12.45 - 13.00	Discussion
13.00 - 14.30	***LUNCH BREAK***
14.30 - 15.00	M. SCHEFFLER (FHI, Berlin): "A self-consistent surface Green-function method; chemical trends, bonding mechanisms and charge transfer of isolated adatoms on Al (100) and Al (111)"
15.00 - 15.15	Discussion

DEFECTS AND DIFFUSION (Chairperson: J. BERNHOLC)

15.15 - 15.35	P. BLOECHL (IBM, Zurich): "*Ab-initio* calculations of self diffusion constants in Si"
15.35 - 15.45	Discussion
15.45 - 16.05	E. SMARGIASSI (SISSA, Trieste): "*Ab-initio* calculation of free energies in real materials: Application to the vacancy formation in Si"
16.05 - 16.15	Discussion
16.15 - 16.30	***COFFEE***

LIQUID AND AMORPHOUS SYSTEMS (Chairperson: R. NEEDS)

16.30 - 17.00	D. HOHL (NCSA, Urbana): "First principles molecular dynamics simulations of amorphous phosphorus and liquid and amorphous selenium"
17.00 - 17.15	Discussion
17.15 - 17.35	G. SEIFERT (TU, Dresden): "*Ab-initio* molecular dynamics simulation of liquid Na-Sn alloy"
17.35 - 17.45	Discussion

CLOSING SESSION (Chairperson: R. NEEDS)

17.45 - 18.00	V. HEINE (Cavendish Lab., Cambridge): **Summary and Outlook**

ABSTRACTS OF

TALKS

Correlated Ground States for Real Materials

D R Hamann
AT&T Bell Laboratories
Murray Hill, New Jersey 07974, USA

With the technical development of electronic structure calculations based on the local density approximation at today's advanced stage, it appropriate to be exploring new paths to greater accuracy. For ground state properties, several strategies based on Monte Carlo methods are being investigated. These include the variational approach, the diffusion or Green's function approach and the auxiliary field approach. I will briefly introduce each of these methods, and summarize its advantages, disadvantages, and present state of development. Recent progress in understanding the auxiliary field method has increased the probability that this least-developed technique may become useful for real materials. Auxiliary field projection of the ground state can be rigorously formulated as the solution of a diffusion equation. A new analysis of the fermion sign problem, which is the major barrier to the application of auxiliary field simulations, can be derived from this formulation. Based on this analysis, we have introduced the "positive projection" method, which does not exhibit the sign problem, and gives excellent results for the energies and correlation functions of small models. As another step towards real materials, we have extended these simulations to Hubbard-style models with long range interactions. Results and directions for further development will be described.

Calculations of the Properties of Solids with Green's Function Monte Carlo

David Ceperley
University of Illinois at Urbana-Champaign, USA

We have recently calculated the equation of state of solid Si with Green's Function Monte Carlo. Pseudo-hamiltonians were used to eliminate the core degrees of freedom. The cohesive energy is found to be 4.66(3) ev in excellent agreement with experiment 4.62(8) ev. This demonstrates the feasibility of this approach in calculating realistic systems and the order of accuracy obtainable.

The pseudo-Hamiltonian approach runs into difficulty with systems containing transition metals. Recently we have performed Green's Function calculation of Si , Sc and Cu atoms with a non-local pseudopotential with the non-locality projected out on a highly optimized atomic wavefunction achieving reasonable results. However the assumed pseudopotential needs improvement to obtain accurate results.

Quantum Monte Carlo Studies of Materials: Magnetic Structures of BCC Hydrogen

Steven G. Louie
Department of Physics, University of California
Materials Sciences Division, Lawrence Berkeley Laboratory
Berkeley, California 94720

Abstract

The variational quantum Monte Carlo approach to materials properties is discussed using a recent application to solid hydrogen as example. Solid **hydrogen in the atomic bcc structure is studied as a prototype single-band correlated electron system with long-range Coulomb interactions.** Several **magnetic phases are investigated at densities between Wigner-Seitz radius** of $r_s = 1.0$ and $r_s = 3.0$ a.u. Correlated wavefunction of the Jastrow-Slater form with both extended and localized single-paritcle orbitals are employed. A transition from paramagnetic to antiferromagnetic phase at lower density is found at near $r_s = 2.4$. However, over the density range studied, there is no evidence for a metastable partial ferromagnetic structure. If time permits, results from applications to other systems such as D^- centers in semiconductor quantum wells and in strong magnetic fields will also be presented.

DYNAMICAL PROPERTIES FROM QUANTUM MONTE CARLO AND MAXIMUM ENTROPY

R. N. Silver[1], J. Gubernatis[1], M. Jarrell[2], D. Sivia[1]

[1] Theoretical Division and Manuel Lujan Jr. Neutron Scattering Center, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

[2] Dept. of Physics, University of Cincinatti, Cincinatti, Ohio 45221, USA

We present a new method[1] for calculating the dynamical properties of condensed matter systems by computer simulations. It has been successfully applied to the Anderson model for dilute magnetic alloys. We have obtained results for spectral functions[2], transport coeffecients[3] and dynamical magnetic susceptibility which obey Kondo universality and agree with experiment. The method combines a quantum Monte Carlo method to generate Matsubara Greens' functions in imaginary times, maximum entropy and Bayesian methods for data analysis to analytically continue to real times, and perturbation theory to provide informative default models needed as a starting point for the data analysis procedure. The method is generally applicable to obtaining dynamical information from a wide range of quantum simulations.

[1] R. N. Silver, *et al.*, Phys. Rev. B41, 2380 (1990).

[2] R. N. Silver, *et al.*, Phys. Rev. Lett. 65, 496 (1990).

[3] M. Jarrell, *et al.*, Phys. Rev. B Brief Reports, January 1991.

Precise and Efficient *Ab-initio* Molecular Dynamics. T.A. ARIAS **M.I.T.**, M.C. PAYNE Univ. Cambridge, UK and J.D. Joannopoulos **M.I.T.** - The Born-Oppenheimer approximation divides the problem of quantum molecular dynamics into two familiar problems: (1) solution for the electronic wave functions for a given *instantaneous* arrangement of ions and (2) the motion of the atomic cores under the influence of those wave functions. Combination of conjugate-gradient methods to solve (1), standard molecular dynamics to solve (2) and an efficient method for producing trial wavefunctions results in a scheme that is capable, with the same computational effort of traditional schemes, of solving (1) three to four orders of magnitude more accurately. The resulting ionic dynamics not only conserves energy over picosecond time scales without the need for external thermostat controls, it also exhibits well defined phonon spectra, as determined from the Maximum Entropy Method (MEM), in excellent agreement with experiment. Finally, this method may be applied to systems with large length scales without complications involving convergence rates or stability.

Pseudopotentials, pseudohamiltonians, and physical ions

G. B. Bachelet, A. Bosin, P. Focher and A. Lastri

Dipartimento di Fisica and Laboratorio di Fisica Computazionale
Università degli Studi di Trento, I-38050 Povo Trento, Italy

The increasing interest in the use of effective core-valence hamiltonians outside the traditional context of single-particle schemes (like the Local Density Approximation or the Hartree-Fock theory) has raised a number of new questions in pseudopotential theory. A general question is to which extent available pseudoions, constructed within single-particle schemes, can reliably represent the physical electron-ion interaction in the context of e.g. variational Monte Carlo, quantum Monte Carlo or auxiliary-field quantum simulations of realistic valence-only systems. A second question, of special interest for Quantum Monte Carlo studies of condensed-matter systems, is how far one can go in the attempt of recasting contemporary nonlocal ionic pseudopotentials into equivalent, local pseudo-hamiltonians. Theoretical developments and numerical results for the Periodic Table will be reviewed.

GW Quasiparticle Pseudopotentials. ERIC L. SHIRLEY,[1] L. MITAS, RICHARD M. MARTIN, *Univ. of Illinois*.— We use a generalized version of Hedin's *GW*[2] to determine the binding energy of one electron outside an atomic core for angular momenta of interest. We next represent our self-energies by semi-local potentials from which we generate pseudopotentials. Unlike traditional single-body pseudopotentials, our potentials systematically include core relaxation and core polarization effects, as well as "real" core-valence exchange and correlation effects. Tests of our potentials include configuration interaction and diffusion Monte Carlo valence calculations on the Na_2 molecule and transition metal atoms. We also discuss using "pseudointeractions" to improve pseudopotential transferability.

[1] Supported by the Fannie and John Hertz Foundation.

[2] L. Hedin and S. Lundquist, *Solid State Physics* 23, 1 (1969), ed. F. Seitz, D. Turnbull, and H. Ehrenreich.

Eric Shirley

Eric L. Shirley
Department of Physics
University of Illinois
1110 W. Green St.
Urbana, IL 61801

Implementation of Ultrasoft Pseudopotentials in Ab-initio Molecular Dynamics

Kari Laasonen and Roberto Car
International School for Advanced Studies, 34014 Trieste, Italy

Changyol Lee and David Vanderbilt
Department of Physics, Harvard University, Cambridge, Massachusetts 02138

A scheme for the construction of ultra-soft separable pseudopotentials recently proposed by Vanderbilt is tested in the context of Car-Parrinello *ab-initio* molecular dynamics calculations on atoms and molecules. For the case of oxygen, the transferability of the pseudopotential is demonstrated by comparing the calculated properties of molecular O_2 and O_3 with those obtained from conventional approaches. Converged results are obtained using plane-wave basis cutoffs of only $\sim$ 25 Ry dramatically lower than that required for conventional pseudopotentials. Forces can be calculated efficiently, and a molecular-dynamics simulation of molecular vibration is demonstrated.

Support for this work was provided by the Italian Consiglio Nazionale delle Ricerche (CNR) Grant No. 89.00006.69, by the European Research Office of the U.S. Army Grant No. DAJA45-89-C-0025, and by NSF Grant No. DMR-88-17291. One of us (D.V.) also wishes to acknowledge support from the Alfred P. Sloan Foundation.

Car-Parrinello-like implementation of the Augmented-Plane-Wave method

José M. Soler[1] and Arthur R. Williams[2]

[1]Dep. de Física de la Materia Condensada, Univ. Autónoma, E-28049 Madrid, Spain
[2]IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

An exciting convergence of ideas is taking place in the context of effective-single-particle electronic-structure theory. The concepts of Car and Parrinello are being synthesized with those of Kleinman and Bylander and those of Slater to produce methods capable of describing the equilibrium geometries and dynamics of "difficult" systems, such as those with first-row and transition-metal atoms. We have implemented one such synthesis capable of very accurate description of chemically general systems. Molecules and surfaces can be treated efficiently without any adaptation and the atomic forces are obtained directly, allowing for structure optimization. Our work combines the nonlinear Augmented-Plane-Wave method with that of Car and Parrinello, but is interestingly similar to that of Kleinman and Bylander and to recent proposals by Vanderbilt and Blöchl, which bring the pseudopotential method to a closely related form. These relationships will be discussed and we will also present results for several systems: small molecules, Cu phonons, Al stacking faults, etc.

STRONGLY CORRELATED ELECTRON MODELS FOR HIGH-TEMPERATURE SUPERCONDUCTORS

E. Tosatti

SISSA/ICTP, Trieste, Italy

I have been asked to provide a brief review of the model Hamiltonians which are currently being considered in connection with high-T_c superconductivity.

Starting from the basic fact that high-T_c seems to arise by doping one kind or another of unconventional insulator, I shall specialize to models which embody this feature.

Issues of current debate, such as absence or presence of in-plane hole-hole attractive correlations, Fermi liquid versus non-Fermi liquid behaviour, and phase separation will be addressed.

Lattice Dynamics and Structural Instabilities in High T_c Superconductors*

Warren E. Pickett,[1] Ronald E. Cohen,[2] and Henry Krakauer[3]
[1]Cavendish Laboratory, Cambridge, U.K., and Complex Systems Theory Branch, Naval Research Laboratory, Washington, DC 20375-5000, USA
[2]Geophysical Laboratory, Washington, DC 20015-1305, USA
[3]Physics Department, College of William and Mary, Williamsburg VA 23185

A variety of experimental results indicate a close relationship between the dynamics of the lattice and the charge carriers, or of strong electron-phonon coupling, in the high temperature cuprate superconductors: Raman spectra, phonon dispersion curves, a low T structural instability that kill T_c, phonon shifts at T_c, changes in atomic structure at T_c, femtosecond laser spectroscopy, and unusual (in some cases large) oxygen isotope shifts, among others. In an attempt to understand the implications of electron-phonon interaction in the cuprates, we have carried out extensive first principles, local density functional calculations of phonon frequencies, lattice instabilities, and preliminary estimates of the strength and character of electron-phonon coupling in $La_{2-x}M_xCuO_4$ and $YBa_2Cu_3O_7$. The picture that arises is one of strong Madelung-like shifts of potential due to sublattice displacements which lead to strong ionic forces and can produce strong electron-phonon coupling. We will also present preliminary results on studies of the low temperature tetragonal (LTT) structural transition in $La_{1.88}Ba_{0.12}CuO_4$ which kills superconductivity and produces a large isotope shift .

**Supported* by the Office of Naval Research and by National Science Foundation DMR-87-19535.

Ab–initio study of zone–boundary phonons and their coupling to electrons in $YBa_2Cu_3O_7$ and $Ba_{1-x}K_xBiO_3$.

A.I.Liechtenstein, C.O.Rodriguez, O.Jepsen, O.K.Andersen and M.Methfessel
Max-Planck-Institut für Festkörperforschung, D–7000 Stuttgart 80, F.R.G.

The phonon frequencies and eigenvectors for five S_1–modes in $YBa_2Cu_3O_7$ and two R–mode (breathing and tilting) in $Ba_{1-x}K_xBiO_3$ (x=0, 0.5) together with structural related properties were calculated from first–principles within the local density functional formalism and using the full–potential linear muffin–tin orbital method. For $YBa_2Cu_3O_7$ the full S_1–dynamical matrix was calculated using 63–**k** points in 1/8 Brillouin zone for the double cell and by evaluating the total energy for 30 displacement pattern. We found a large coupling between the O_2/O_3 breathing mode in CuO_2–planes and the O_4 mode in c–direction. Normal state phonon linewidths, electron–phonon coupling constants, and softening of phonon frequencies due to metallic screening were calculated including electron–phonon matrix elements. Furthermore, comparisson of theoretical and experimental resonant Raman scattering spectra of the 5 A_{1g} modes will be presented. For $Ba_{1-x}K_xBiO_3$ at x=0.5 the cubic perovskite phase is stable while for x=0 an instability was found for a combination of breathing and tilting mode for . The mechanism for this behaviour is explained in terms of the competition between the electrostatic and band energies.

Electronic Structure and Positron Annihilation in High T_c Superconductors: The Problem of the Fermi Surface

S. Massidda
Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA)
PHB-Ecublens 1015 Lausanne, (Switzerland)

The electronic structure of high T_c superconducting oxides in their normal state and in particular the existence of a Fermi surface (FS) is a crucial issue in these materials. While however the agreement between band theory and angle-resolved photemission spectroscopy seems to be good for some of these systems, still positron annihilation experiments do not show the agreement necessary to clearly define a Fermi surface structure in $YBa_2Cu_3O_{7-\delta}$. We present here theoretical calculations of the electron-positron momentum density for some high T_c superconductors, based on first-principle LDA electronic structure calculations. Our results for $YBa_2Cu_3O_7$ and for the insulating parent compound $YBa_2Cu_3O_6$ indicate a small overlap of the positron wave function with the CuO_2 plane electrons, and consequently small signals due to the related Fermi surfaces. By contrast we find, after the folding of *Umklapp* terms according to Lock, Crisp, and West clear Fermi surface breaks arising from the $Cu - O$ chain bands. A comparison of the present results with the (unfolded) experimental two-dimensional angular correlation of annihilation radiation (2D-ACAR) recently measured in Geneva shows an overall agreement for $YBa_2Cu_3O_7$ and a good agreement for the insulating compound, despite the spurious LDA metallic state. Our results possibly suggest the importance of O vacancies in experiments performed on non-stoichiometric $YBa_2Cu_3O_{7-\delta}$ samples. Predictions will be given for materials where experimental data are still lacking.

Localization in the Self-Interaction Corrected Density Functional Formalism

Axel Svane
Institute of Physics, Aarhus University, Denmark
and
Olle Gunnarsson
Max-Planck-Institut FKF, Stuttgart, Germany

A method for performing fully self-consistent, ab-initio electronic structure calculations in the self-interaction corrected (SIC) local spin density (LSD) approximation is presented. The linear-muffin-tin orbitals method is used in the tight-binding representation and with the atomic spheres approximation. The minimization of the SIC energy functional is achieved by the steepest descent method with special care taken to secure stability with respect to unitarian mixing of electron states. The method is applied to the 3d monoxides and predicts correctly that MnO, FeO, CoO, NiO and CuO are antiferromagnetic insulators and that VO is a nonmagnetic metal. The band gaps and moments are significantly improved compared with the LSD approximation. The main effect of the SIC is to pull down the metal d states below the oxygen p-band. As a result, the transition metal monoxides emerge as charge-transfer (rather than Mott-Hubbard) insulators with the highest hole-state having O p character, however with the symmetry of a metal d state. This picture is in accordance with the most recent interpretation of these materials and at variance with predictions of LSD. Preliminary results for La2CuO4 are also presented.

STATIC AND DYNAMICAL PROPERTIES OF QUANTUM MANY BODY SYSTEMS; FINITE CLUSTER CALCULATIONS

C.A. Balseiro
Centro Atomico Bariloche
8400 Bariloche, Argentina

We review a method to calculate the ground state and the frequency dependent correlation functions in finite many-body systems based on a modified Lanczos Method.

As examples of the method we present some results for the electronic structure of the CuO_2 planes of high T_c superconductors and Green functions of the polarized t-J model which can be used to study the pairing bags of strong coupling superconductors.

High Energy Spectroscopies Compared With Exact Solutions of Multiband Model Hamiltonians

Henk Eskes and George Sawatzky
Materials Science Centre, Department of Solid State and
Applied Physics, University of Groningen,
Nijenborgh 18, 9747 AG Groningen, The Netherlands

ABSTRACT

In order to extract information from peak positions and intensities of high energy spectroscopic measurements of strongly correlated mixed valence compounds, it is important to take explicitly into account the Coulomb interactions as well as the effects of hybridization. This is the motive for studying spectra calculated by means of an exact solution (exact diagonalization of small clusters or an impurity calculation) of multiband model Hamiltonians. We will present calculations of the photo- and inverse photoemission spectra, as well as O 1s core level spectra for the high T_c cuprates. The spectra are obtained for small clusters containing two Cu atoms (Cu_2O_7 and Cu_2O_8). We discuss the sensitivity of the spectra to cluster size by comparing them with results for an ($\vec{K}$ dependent) impurity approach and results from a CuO_4 cluster. Special attention is paid to the redistribution of spectral weights upon doping.

Model for Low Energy Electronic States Probed by X-ray Absorption in High T_c Cuprates

Mark S. Hybertsen, W.M.C. Foulkes, and Michael Schluter
AT&T Bell Laboratories
Murray Hill, NJ, 07974

E.B. Stechel
Condensed Matter Theory Division 1151
Sandia National Laboratories
Albuquerque, NM 87185

X-ray absorption near the O K-edge reveals important, chemically specific, information on the electronic states near the fermi level. Recent bulk sensative measurements by Chen and Sette[1] for $La_{2-x}Sr_xCuO_4$ show the systematic evolution of the spectra from x=0, through the insulator-metal transition and well into the superconducting regime (x=0.15). We provide a theory for these spectra starting from a three band Hubbard model for the electronic states. The parameters for this model have been previously derived from Local Density Functional calculations[2]. Direct diagonalization studies show that the model quantitatively accounts for the charge transfer gap and the antiferromagnetic interactions in the parent insulator[3]. The three-band Hamiltonian, including core-hole interactions, is mapped into an effective one-band model[3]. This allows calculation of the X-ray spectra, as a function of carrier concentration, using exact diagonalization techniques for clusters of adequate size. Including the role of local fluctuations in carrier concentration (e.g. due to fluctuations in Sr concentration) a detailed comparison is made to the experimental spectra. The resulting picture shows that the two pre-edge peaks observed are precisely the O p-like states separated from the Cu d-like states by the charge transfer gap renormalized by the core-hole excitonic effect. The combined results of theory and experiment support the model of the electronic states based on a doped charge transfer insulator.

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Self-Consistent Electronic Structure of a Vortex Line in a Type-II Superconductor

Francois Gygi* and Michael Schluter

AT&T Bell Laboratories
600 Mountain Avenue
Murray Hill, NJ 07974

The electronic structure of a vortex line in a type-II superconductor is calculated self-consistently in the framework of the Bogoliubov-de Gennes theory. The Debye frequency, the Fermi velocity and the coupling constant of the electron-electron attractive interaction are used as microscopic input parameters. The resulting quasiparticle excitation spectrum, the pair potential and the current distribution are studied as function of temperature, and can be used to define a coherence length and to determine the magnetic penetration depth. The local density of one-particle excitations, calculated from the quasiparticle amplitudes explains the results of Scanning Tunneling Microscopy (STM) experiments by Hess *et al.* [Phys. Rev. Lett. 62, 214 (1989)] on $NbSe_2$. The main spectroscopic features in the experimental results are caused by bound states in the vortex cores. Spatial distortions of the bound state wavefunctions caused by neighbouring vortices and by the crystallline lattice are discussed in terms of a simplified two-band model. In the case of $NbSe_2$, the resulting local density of states has a characteristic "star" shape in real space, whose orientation is energy-dependent, in agreement with recent STM experiments [Phys. Rev. Lett. 64, 2711 (1990)].

*Present address: IBM Research Division, CH-8803 Ruschlikon, Switzerland

Dielectric response and quasiparticle energies in Nickel

Ferdi Aryasetiawan and Ulf von Barth
Lund University, Solvegatan 14A, S-22362 Lund, Sweden

Field-theoretic methods in the many-body theory of solids was an important area of research in the early sixties. Unfortunately, neither the computational facilities nor the numerical techniques of those days were adequate for working out, in real systems, the predictions of even the simpler approximations proposed at the time. Over the past fifteen years the situation has improved considerably. The dielectric response and the connected optical absorption spectrum of elemental semiconductors has been worked out, at least approximately, in the well known RPA meaning free particles responding to the applied plus the induced fields [1,2,3]. Simple attempts to go beyond the RPA and include also the particle-hole interaction have also been made [3,4]. The results are quite encouraging compared to those obtained from the standard methods based on one-particle band theory and a Golden-Rule expression for non-interacting particles. Recently, several people [5,6,7] have used the RPA response of silicon in order to calculate the one-electron excitation spectrum, i.e. the quasiparticle band structure, of the system in an approximation proposed by Hedin [8] in the mid sixties and often referred to as the GW approximation. Again the results are superior to those of standard band theory methods. For one thing, the calculated band gaps are close to experiment.

In the present work we have concentrated our efforts on transition metals using nickel as the prototype case. As our starting point for the many-body perturbation expansion we have chosen a zero:th-order Green's function obtained from a self-consistent band-structure calculation based on the local-density approximation (LDA). This Green's function is known to give accurate charge and spin densities although the quality of the one-electron energies are relatively poor. The d-band width is, e.g., almost 30a factor two too large. We proceeded to calculate the dielectric matrix and the closely related screened Coulomb interaction within the RPA. Due to consistency requirements, as discussed by Kadanoff and Baym [9,10], we have so far made no attempts to include the effects of particle-hole interaction either in the response function or in the self-energy. From the response function (essentially the dielectric matrix) we obtain the energy-loss spectrum, the optical absorption spectrum and the closely related optical conductivity spectrum. Contrary to some suggestions we find that the local-field effects are small - especially at small frequencies and small momentum transfers. Therefore, our optical conductivity spectrum closely reflect structure in the one-electron spectrum of the starting Green's function and, consequently, the conductivity peaks occur at different energies compared to their experimental counterparts [11]. The discrepancies are of the order of 1.5 eV . Starting from a Green's function constructed from LD wave functions but instead using either experimental one-electron excitation energies or our calculated quasi-particle energies (see below) would result in an optical absorption spectrum in much closer agreement with experiment. Such a procedure would , however, require further theoretical justification.

From the calculated screened interaction and the LDA Green's we computed the GW approximation for the electronic self-energy. From this we can, e.g., obtain the spectral function of the interacting one-electron Green's function, the quasi particle energies i.e. the positions of well defined peaks in the spectral function as well as extensive quantities like the charge density and the total energy per atom of the solid. The resulting quasi particle energies are in general closer to the Fermi level as compared to the eigen energies of the LDA. The deeper d-states move upwards by 0.5 to 1.0 eV resulting in an approx. 25are within a few tenths of an eV from the experimental results [12.13.14].

The differences between corresponding quasi particle energies of the spin-up and the spin-down channels are reduced (10-30LDA but we are still far from the 50experiment. Neither do our spectral function show a satellite peak corresponding to the famous two-hole state [15.16 6 eV below the Fermi level as indicated by experiment or by theoretical calculations on model systems. We believe we understand these shortcomings and our results demonstrate the necessity to go beyond the GW approximation for certain properties in the narrow band systems.

physically inspired approximation schemes. We believe this knowledge to be instrumental in attacking more complicated but also more rewarding systems such as e.g. nickel oxide.

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Quantum-mechanical Calculation of the Spontaneous Polarization: Pyroelectric BeO

M. Posternak, R. Resta[†], and A. Baldereschi
Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA),
PHB-Ecublens, CH-1015 Lausanne, Switzerland

Crystals which can carry a spontaneous macroscopic polarization constitute a special class of useful solid-state materials. Their electrical polarization **P** can be modified by changing the temperature, as in pyroelectrics, or by applying external electric fields, as in ferroelectrics where even the direction of the polarization may be altered. Only variations of **P** are experimentally detectable, through measurements of pyroelectricity or ferroelectricity. The key idea of our approach, in order to calculate **P**, is to make use of the differential concept also in the theoretical treatment [1]. Two steps are necessary, which constitute in fact an alternative definition of spontaneous polarization: *(i)* the calculation of the difference $\Delta\mathbf{P}$ between two phases of the same material, and *(ii)* a suitable symmetry argument. The simplest material where bulk polarization is allowed by symmetry is *BeO*: it has the hexagonal wurtzite structure and its constituents are first-row elements. The crystal has a preferred axis, which is the direction of spontaneous polarization. This latter quantity is obtained, using all-electron local-density FLAPW calculations and the two steps outlined above. Resulting values of **P** are discussed, and compared to existing experimental data.

[†] *Permanent address:* Scuola Internazionale Superiore di Studi Avanzati, Trieste, Italy.

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ALTERNATIVE TOTAL ENERGY FUNCTIONALS IN DENSITY FUNCTIONAL THEORY

W.Matthew C. Foulkes

Blackett Laboratory,
Imperial College of Science, Technology and Medicine
Prince Consort Road, London SW7 2BZ, England

It has recently been realized that the Hohenberg-Kohn energy functional, which gives the total energy of the interacting electrons in an atom, solid or molecule, as a functional of the electron density, is only one of several possible alternatives. In self-consistent calculations, it may sometimes be computationally convenient to use one of these alternative functionals in place of the original; and in non-selfconsistent calculations (when one is trying to obtain quick but reliable results based on some input guess at the potential or electron density) it may also be more accurate. This talk examines the freedom available in choosing alternative energy functionals, describes some of the ways in which they have been used up until now, and makes some suggestions as to how they may be used in future.

First Principles Energy Density and its Applications to GaAs Polar Surfaces, N. Chetty* and Richard M. Martin, University of Illinois at Urbana-Champaign, Department of Physics and Materials Research Laboratory, 1110 W.Green Street, Urbana, Illinois 61801

Density Functional Theory has been successfully applied in solid state calculations where is has been customary to extract a single number, the total energy. Within this formalism, we show that one can in addition define a local energy density $\mathcal{E}(\mathbf{r})$ which is a sum of kinetic, Maxwell, exchange-correlation and other contributions that depend on the external potential. Despite the nonuniqueness of $\mathcal{E}(\mathbf{r})$, we show that it can be used to calculate well-defined energies from integrals over regions, e.g. surfaces. We present explicit calculations for GaAs (100) surfaces where we demonstrate the efficiency of using $\mathcal{E}(\mathbf{r})$ to determine the energies of the two inequivalent surfaces from a single calculation. We also calculate the formation enthalpy of single isolated GaAs (111) and $(\bar{1}\bar{1}\bar{1})$ surface which is not possible using conventional total energy methods. We are able to address, for the first time, questions related to the stability of GaAs surfaces.

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* present address, Laboratory of Applied Physics, Technical University of Denmark, Building 307, DK-2800 Lyngby, Denmark

First-principle statistical mechanics of semiconductor and metal alloys

A. ZUNGER

Solar Energy Research Institute
1617 Cole Boulevard 16/3, Golden CO 80401, U.S.A.

Ordering in Cu-Au Alloys: A New Approach to Alloy Phase Stability

Bulbul Chakraborty, Physics Department, Brandeis University, Waltham, MA 02254-9110

Abstract

New results concerning ordering in Cu-Au alloys will be presented. The ordering has been studied using a formalism based on the effective medium theory (EMT) of chemical binding. The EMT is an approximate method based on density functional theory. It is a variational approach to calculating total energies of arbitrary atomic configurations and because of its simplicity it can be used efficiently in numerical simulations. It will be shown that both ground state properties and order-disorder transition temperatures of the Cu-Au alloys come out in very good agreement with experiment. Results of Monte Carlo simulations of the phase diagram will be presented and the origins of the ordering transitions will be discussed. Finally the virtues and drawbacks of EMT will be discussed in the context of existing *ab-initio* density functional calculation of alloys.

Ab-initio studies of the Si(111) surface

A. Selloni
International School for Advanced Studies, I-34014 Trieste, Italy

A number of applications of the *ab-initio* molecular dynamics scheme to semiconductor surfaces are presented. We shall focus in particular on some properties of the defect-free and defective clean Si(111) surface, including:
(i) The 2×1 reconstruction of Si(111), and in particular the transformation process from the bulk-terminated 1×1 to the reconstructed 2×1 surface, and the details of the resulting structure.
(ii) The influence of surface point-defects, namely surface vacancies, on this transformation process.
(iii) Surface vacancies and their connection to the recently discovered $\sqrt{3} \times \sqrt{3}$ reconstruction of the clean Si(111) surface.
(iv) The structural and electronic properties of an isolated surface vacancy on Si(111)2×1.

Our studies, besides demonstrating the feasibility of *ab-initio* calculations for rather complex systems, such as surface defects, bring out several interesting specific features which will be discussed in detail in this talk.

This work was done in collaboration with F. Ancilotto, W. Andreoni, R. Car, M. Parrinello and E. Tosatti. It was supported in part by the Italian Ministry of the University and Scientific Research under the SISSA-CINECA collaborative project, by the Italian CNR under grant no 89.00006.69, by the National Institute for the Physics of Matter (INFM), and by the European Research Office of the US Army.

Theory of Electron Transmission through Interfaces. M. D. Stiles, National Institute of Standards and Technology and D. R. Hamann, AT&T Bell Laboratories - As material growth techniques improve, the detailed scattering properties of atomically abrupt interfaces become more and more important. For many of these interfaces simple methods to calculate scattering properties, like the effective mass approximation, can not give reliable results. We have developed[1] a method of calculating electron transmission and reflection probabilities of such interfaces based on a layer-by-layer construction of the interfacial electronic states. The method is based on a linearized-augmented-plane-wave implementation of the local-density approximation. The electronic potentials for the layers are taken from separate self-consistent calculations assuming that each layer is either bulk-like or is similar to a section of a supercell. Using these potentials, variational electronic states are constructed in each layer, and joined by matching the values and slopes at the boundaries between adjacent layers. The scattering states, and hence the transmission and reflection probabilities, are found by expanding the states in the bulk-like layers in terms of the appropriate generalized Bloch states. The transmission properties of $NiSi_2/Si(111)$ interfaces are of particular interest because not only can good interfaces be grown, but interfaces with two different relative orientations can be grown. Our prediction,[2] of substantial differences in transmission for the two interfaces has motivated several groups to look for them.

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Comment about density functional calculations of Schottky barrier heights

O.K. ANDERSEN

Max-Planck-Institut für Festkorperforschung
Heisenbergstrasse 1, D-7000 Stüttgart, Germany

EXCHANGE AND CORRELATION IN SCHOTTKY BARRIERS AND HETEROJUNCTIONS[1]

R.W. Godby, Cavendish Laboratory, University of Cambridge
Madingley Road, Cambridge CB3 0HE, U.K.

Exchange and correlation at semiconductor interfaces is discussed, with particular reference to the contrast between the local quasiparticle energies and local density-functional theory (and LDA) eigenvalues. This includes

- Consideration of the exchange-correlation potential in the neighbourhood of such an interface. Slow variation of the potential within the depletion layer can give rise to bending of the DFT bands relative to the quasiparticle bands[2].
- A computational study of many-body effects in a Al-GaAs(110) Schottky barrier. The GW calculation shows significant effects on the semiconductor's excitation energies in the vicinity of the metal which are absent from conventional local-density approximation (LDA) calculations[3].

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A self-consistent surface Green-function method; chemical trends, bonding mechanisms and charge transfer of isolated adatoms on Al (100) and Al (111)

M. Scheffler

Fritz-Haber-Institut der MPG, Berlin, Germany

We describe the basic aspects of a new, self-consistent Green-function method which allows to calculate the density of states, electron density, and related quantities for a *localized* perturbation (e.g. an isolated adsorbate or an intrinsic surface defect) at a crystal surface. The atomistic nature and the macroscopic extension of the substrate are fully taken into account. The method is based on the density-functional theory and combines several ideas from recent theoretical developments, as for example from the layer-KKR Green-function method, from *ab-initio* pseudopotential theory, and from the self-consistent defect Green-function method.

In particular we discuss applications of the method, namely the adsorption of group III adatoms (Na → Cl) on Al (111) and Al (100). We address a recent controversial discussion of the nature of bonding of adsorbates at very low coverage ($\Theta \rightarrow 0$): ionic, covalent or metallic.

Ab-Initio Calculations of Self Diffusion Constants in Silicon

P. E. Bloechl
IBM T. J. Watson Research Laboratory, Yorktown Heights, USA
and
IBM Research Laboratory, Zurich, Switzerland

Theoretical discussion of diffusion mechanisms has so far focussed on activation energies. Here, we report first-principles calculations of diffusion constants, which allow a direct and unambiguous comparison of the relative contributions of two defect mediated mechanisms for self-diffusion, the vacancy mechanism and the interstitial mechanism. Each diffusion constant is the product of the concentration of the native defect species and its diffusivity: we have calculated the diffusivity via Car-Parrinello simulations[1] and the concentration within the local harmonic approximation, that has been suggested by LeSar et al.[2]. The electronic contribution to the entropy of formation will be discussed. Our results suggest that both defect-mediated mechanisms contribute importantly to self-diffusion.

This work was done in collaboration with W. Andreoni, R. Car, D. Laks, S.T. Pantelides, M. Parrinello and E. Smargiassi. It was supported in part by ONR Contract N00014-84-0396, USARDSG grant DAJA 45-89-C0025 and CNR grant 89.00006.69.

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Ab-initio calculation of free energies in real materials: application to the vacancy formation in silicon.

E. Smargiassi and R. Car

International School for Advanced Studies, 34014 Trieste, Italy

Only few *ab-initio* calculations of free-energies of materials exist to date. Moreover these calculations have been often based on harmonic or quasi-harmonic approximations. A full inclusion of anharmonic effects can be achieved by using appropriate statistical mechanical simulation techniques. A popular method consists in the construction of a reversible path to a state of known free energy. Such approach has been applied so far only to classical many-body systems with empirical interatomic potentials.

In this paper, we show that this method can be generalized to first-principles molecular dynamics simulations, in which the atomic potential energy surface is derived quantum mechanically from the electronic ground-state. We apply our scheme to compute the free energy of formation of a lattice vacancy in silicon at finite temperature. This is a basic quantity to evaluate the equilibrium vacancy concentration and the diffusion constants of vacancy mediated processes. In both cases our results are in good agreement with the available experimental data. Our approach is not limited to applications involving defective solids but can also be used in a wider context, such as the study of phase transitions in materials.

Support for this work was provided by the Italian Consiglio Nazionale delle Ricerche (CNR) Grant No. 89.00006.69, by the European Research Office of the U.S. Army Grant No. DAJA45-89-C-0025, and by the Italian Ministry of the University and Scientific Research under the SISSA-CINECA collaborative project.

First Principles Molecular Dynamics Simulations of Amorphous Phosphorus and Liquid and Amorphous Selenium

D. Hohl
NCSA, University of Illinois at Urbana-Champaign
R.O. Jones
IFF, Forschungszentrum Jülich (KFA)

Parameter-free, first principles molecular dynamics studies[1] (MD/DF) of amorphous phosphorus and semiconducting liquid and amorphous selenium are presented, focussing primarily on the atomic microstructure in these materials.

Although easy to prepare in various chemical and thermal ways and important as industrial material, amorphous phosphorus is poorly characterized experimentally and theoratically. A simple cubic unit cell of constant volume comprising 124 P atoms was chosen to represent the system under consideration, making it the largest system investigated with the MD/DF method to date. Starting from a hypothetical sixfold coordinated P, the system is melted and annealed to room temperature in two cycles. Trajectories several ps long serve to calculate pair correlation functions $g(r)$, scattering functions $S(Q)$, phonon densities of states and other static and dynamic quantities. The results serve to guide the interpretation of recent detailed neutron scattering experiments and are put into perspective with our MD/DF study on isolated P_n clusters in the vacuum.[2]

The MD/DF simulation of liquid and amorphous selenium[3] in the temperature range 350–720 K used 64 atoms in a constant volume simple cubic cell. Ring statistics, pair correlation functions $g(r)$, structure factors $S(Q)$, bond angle and dihedral angle distribution functions, phonon densities of states and diffusion constants D were computed and compared with experimental and theoretical data where available. Several structural models proposed previously for Se are evaluated and their predictions compared with the results of the present simulation. Special emphasis is given to the concentration, structure and stability of the dominant defects, and a new structure and defect model is presented.

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Ab initio Molecular Dynamics Simulation of liquid Sodium - Tin alloy

by

G. Seifert
Institute for Theoretical Physics, TU Dresden, Dresden, Germany

and

G. Pastore, R. Car
SISSA - International School for Advanced Studies, Trieste, Italy

Abstract

A first principle molecular-dynamics study of liquid NaSn alloy is presented. The structural properties (static structure factor, pair correlation, bond angle distribution) are discussed. The calculated static structure factor is in good agreement with that from neutron diffraction experiments. A prepeak in the structure factor can be attributed to the existence of tetrahedral Sn_4 units in the liquid phase. The Sn_4 complexes - Zintl anions $[Sn_4^{4-}]$- are typical structural units in solid NaSn. However, the calculations show also a tendency of network formation of three- and fourfold coordinated tin atoms in the liquid. As a consequence of this network formation there is an indication of a "bimodal" bond angle distribution for the tin atoms.

Alloy Formation in the Effective Medium Theory

Karsten W. Jacobsen

Laboratory of Applied Physics
Technical University of Denmark
DK-2800 Lyngby
Denmark

The formation of alloys are discussed within the framework of the effective medium theory for interatomic interactions. The total energy of simple metal or noble metal alloys are shown to consist of an electron density dependent term which determines the volume of the alloys and an electrostatic correction to the atomic sphere approximation. Structural energy changes are to a large extend determined by the latter term. The stabilities of the three binary alloys formed by Cu, Ag, and Au are discussed.

For transition metal alloys in the center of the periodic table an additional contribution to the heat of formation comes from the formation of an alloy d-band. This contribution is modelled using a moment method.

The effective medium approach is shown to be simple enough to allow for analytic calculation of cluster interactions from properties of the constituents alone. Furthermore, the method can be used for Monte Carlo simulations of thermal properties of alloys.

Structure and thermodynamics of Si_xGe_{1-x} alloys from ab-initio Monte Carlo simulations

Stefano de Gironcoli,[1] Paolo Giannozzi,[1] and Stefano Baroni[2]

[1]*IRRMA - Institut Romand de Recherche Numérique en Physique des Matériaux*
PHB - Ecublens, CH-1015, Lausanne - Switzerland

[2]*SISSA - Scuola Internazionale Superiore di Studi Avanzati*
Strada Costiera 11, I-34014 Trieste - Italy

We present a new method for studying from first principles the finite-temperature properties of semiconductor alloys. The alloy is considered as a perturbation with respect to periodic virtual crystal, and the relevant energies calculated by density-functional perturbation theory. We first show that—up to second order in the perturbation—the energy of the alloy is equivalent to that of a *lattice gas* with only two body interactions. The interaction constants of this lattice gas are particular linear response functions of the virtual crystal, which can be determined from first principles. As an application, we consider the case of Si_xGe_{1-x}. Ignoring lattice relaxation, the range of the interactions is very short. Atomic relaxation renormalizes the interactions and makes them rather long range, propagating mainly along the bond chains. A comparison with traditional self-consistent calculations for small supercells demonstrates that the acccuracy of the perturbative approach is in this case of the same order as that state-of-the-art density-functional calculations. Once the interaction constants have been calculated, the finite-temperature properties of the alloy can be studied rather inexpensively by MonteCarlo simulations on the lattice gas. Our results show that Si_xGe_{1-x} is a model random alloy with a miscibility gap below $\approx$ 170 K. The bond length distribution displays three well defined peaks whose positions depend on composition, but not on temperature. The resulting lattice parameter follows very closely Vegard's law.

ABSTRACTS OF

POSTERS

Ab-Initio Lattice-Dynamics in Semiconductors

P. Pavone[a], S. Baroni[a], S. de Gironcoli[b], and P. Giannozzi[b]
[a] *Scuola Internazionale Superiore di Studi Avanzati (SISSA)*
Strada Costiera 11, I-34014 Trieste, Italy
[b] *Institut Romand de Récherche Numérique en Physique des Matériaux (IRRMA)*
PHB-Ecublens, CH-1015 Lausanne,Switzerland

We present some calculations of the lattice-dynamical properties of semiconductors, based on density-functional linear-response theory. As a first application, we compute complete phonon dispersions for the elemental semiconductors Si and Ge, and for the III-V semiconductor compounds GaAs, AlAs, GaSb, and AlSb. Our results are in excellent agreement with experiments, where available, and provide predictions where they are not.

As a byproduct, we obtain real-space *interatomic* force constants for these materials, which are useful both for interpolating the dynamical matrices throughout the Brillouin zone, and as ingredients of approximate calculations for mixed systems such as alloys and microstructures. We study the transferability of force constants among isoelectronic compounds. We find that force constants of III-V compounds differing only by their cation are quite similar, whereas this is not true when only the anion is different. The situation is intermediate in the case of elemental semiconductors.

As a further application we calculate the thermal expansion of Si, Ge, AlAs, and GaAs in the quasiharmonic approximation. As intermediate results we obtain the Grüneisen parameters of these systems troughout the Brillouin zone. Also in this case, the agreement with available experiments is good.

Phonons and effective charges in Boron Phosphide

H. W. L. Alves and K. Kunc
Laboratoire de Physique des Solides associé au CNRS
Université P. et M. Curie 4, Pl. Jussieu Tour 13 75005 Paris France

Static and dynamical properties of Boron Phosphide are studied within the local density approximation, using the norm-conserving pseudopotentials and plane-waves expansions. Calculated lattice constant, bulk modulus, selected phonon frequencies and Gruneisen parameters agree with experiment to within 1% ,5% for a_0, B_0 respectively, and within 5-7% for the phonon frequencies, whenever experiment is available.

Real space distribution of electronic charge density shows that the valence charge is nearly equally divided between the cation and anion. Previous estimations of this partition led, in the past, to speculations that the effective charges might have the signs reversed, compared to other III-V compounds. Our calculations on the quadrupled supercells with the longitudinal displacements did not confirm the above conjecture-at the zero pressure, at least. Results corresponding to higher compressions will be discussed.

SOFT PHONONS IN CUBIC $BaBiO_3$

R. Zeyher and K. Kunc

Max-Planck-Institut für Festkörperforschung, 7000 Stuttgart, Germany,
C.N.R.S. and Université P. et M. Curie, 75230 Paris, France

The occurence of superconductivity in $BaPb_{1-x}Bi_xO_3$ and $Ba_{1-x}K_xBiO_3$ has attracted lot of interest: These systems share many characteristic features of the Cu-based, high-T_c superconductors, but they are considerably simpler. The crystal structure of the undoped $BaBiO_3$ derives from the cubic perovskite structure where the charge density at the lattice sites has been modulated, leading to a doubling of the primitive cell along one axis. It has been widely believed that the distortion of the cubic perovskite cell is due to a local electronic instability leading to a charge disproportion $2Bi^{4+} \rightarrow Bi^{3+} + Bi^{5+}$ with two inequivalent Bi sites. The aim of this work was to investigate possible electronic and lattice instabilities of a hypothetical cubic perovskite structure of $BaBiO_3$ and to determine resulting distortions by means of total energy calculations.

We have carried out the calculations by applying the LDF theory in plane-wave basis and using the norm-conserving pseudopotentials. We verified that our energy eigenvalues $\varepsilon_i(k)$ correctly reproduce the "band structures" obtained previously by other methods (LAPW), and checked that our prediction for the lattice constant a_0 agrees with experiment (1 % error). Keeping the ions at their ideal lattice positions we did not find any evidence for a local electronic instability in cubic $BaBiO_3$ towards a modulated charge density which was observed experimentally. Performing calculations with frozen phonons at the R-point of the B.Z. we found the breathing mode Γ_2' to be stable. On the contrary, the [1,-1,0]-component of the rotational mode Γ_{25} is unstable in the cubic structure and drives the transition.

α-Gallium: A metallic molecular crystal

X. G. Gong[a,b], Guido L. Chiarotti[a,c], M. Parrinello[a,d], E. Tosatti[a,b]

a) International School for Advanced Studies (SISSA), Strada Costiera 11, I-34014 Trieste, Italy

b) International Centre for Theoretical Physics (ICTP), P.O. Box 586, I-34014 Trieste, Italy

c) Laboratorio Tecnologie Avanzate Superfici e Catalisi(TASC), del Consorzio Interuniversitario Nazionale per la Fisica della Materia (INFN), Padriciano 99, I-34012 Trieste, Italy

d) IBM Research Division, Zurich Forschunglaboratorium, CH-8803 Rüschlikon, Switzerland

Abstract

We present a first principle theoretical study of the atomic and electronic structures, and of the zero temperature phases of gallium. The picture of α-Ga which emerges is that of a metallic molecular crystal, with a strong Ga_2 covalent bond, and weaker intermolecular forces. It is supported in detail by the charge density, the electronic structure, and differential bonds stretching under pressure. Anomalous features of α-Ga, such as Knight shift, anisotropic Fermi Surface effects, and optical absorption find a consistent explanation. Accurate X-ray measurements should reveal the Ga_2 covalent bonds.

Structural and Electronic Properties of $\alpha-$Sn, CdTe and Their Monolayer Superlattices[+].

A. Continenza[*] and A.J. Freeman
Department of Physics and Materials Research Center
Northwestern University, Evanston, Il 60208

November 8, 1990

Interest in small direct gap semiconductors is driving the attention on compounds based on group IV materials. In particular, recent experiments have demonstrated that the $\alpha-$Sn zero band gap can be opened by quantum confinement effects in ultra-thin layers of $\alpha-$Sn deposited on suitable substrates (such as CdTe). Moreover, the successful growth of superlattices of $\alpha-$Sn/CdTe along different growth directions, has been reported by several groups.

In view of all this interest, we performed a systematic study of the structural and electronic properties of $\alpha-$Sn, CdTe and their [001] monolayer superlattices (namely: $SnTeCd_2$, $SnCdTe_2$, and Sn_2CdTe) using the total energy local density all-electron full potential linearized augmented plane wave (FLAPW) method.

Our calculations reproduce with good accuracy the ground state properties of the pure constituents and give some insights regarding the properties of the ultra-thin superlattices. In particular, we found that (i) the "compensated" structure (i.e. Sn_2CdTe) is unstable with respect to phase separation, (ii) that the structure in which Sn substitutes for Cd is the most unstable and (iii) that large tetragonal distortions are caused by this same substitution. In addition, in all the structures studied the direct band gap is favored over the indirect $\Gamma - L$ gap and that this direct band gap is higher (within LDA) than in pure $\alpha-$Sn.

[+] Work supported by the NSF (through the NU MRC).

[*] Present Address: Università degli Studi di L'Aquila - Coppito, I-67010 (Italy).

LCAO Band Calculation for the Hexagonal Y_2Fe_{17} and $Y_2Fe_{17}N$

Y. P. Li, D. L. Weaire, Hong-Shuo Li and J. M. D. Coey

Department of Pure and Applied Physics, Trinity College, Dublin 2.
Ireland

Abstract

First principle band calculation, by using Orthogonal Linear Conbination of Atomic Orbitals (OLCAO) approximation, have been carried out on Y_2Fe_{17} and the newly discovered $Y_2Fe_{17}N$ compounds. This iron-rich rare-earth nitride phase is expected to be the main phase for high-performance magnets with Curie temperature and the saturation magnetization higher than those of $Nd_2Fe_{14}B$ magnets. The atomiclike valence basis was adjusted according to the local environment of each crystallographic site. It is found that the average iron moment are $2.40\mu_B$ for Y_2Fe_{17} and $2.50\mu_B$ for $Y_2Fe_{17}N$, which is in good agreement with Mössbauer results.

All the correspondences should be addressed to

Prof. Y. P. Li
Department of Pure and Applied Physics,
Trinity College, Dublin 2, Ireland.
Fax: +353-1-711759
Tel: +353-1-772941

Relativistic Atomic Evaluation for the Exchange Interactions in the Rare Earth - Iron Intermetallics

Hong-Shuo Li, Y. P. Li and J. M. D. Coey

Department of Pure and Applied Physics, Trinity College, Dublin 2, Ireland

Abstract

Intra-atomic exchange integrals $\mathbf{J}_{4f\text{-}5d}$, $\mathbf{J}_{4f\text{-}6s}$ and $\mathbf{J}_{4f\text{-}6p}$, for rare-earth trivalent ions were obtained from relativistic self-consistent field atomic calculations, using the local-density approximation for exchange and correlation potential. The resulting effective (molecular field) exchange coefficients n_{RT} and n_{RT} show a decrease in magnitude across the rare-earth series, which agree well with those observed in many rera-earth transition-metal intermetallic series. It is shown that the *4f-5d* exchange interaction is far more important than the *4f-6s* and *4f-6p* interactions, as expected from Campbell model for the exchange interactions occuring in rare-earth transition-metal intermetallics.

All the correspondences should be addressed to

Prof. Y. P. Li
Department of Pure and Applied Physics,
Trinity College, Dublin 2, Ireland.
Fax: +353-1-711759
Tel: +353-1-772941

Change of sign of orbital moment in bcc Fe

L. Severin, L. Nordström and B. Johansson

Condensed Matter Theory Group, Institute of Physics, University of Uppsala
BOX 530 S-751 21 Uppsala, Sweden

We report on electronic bandstructure calculations, including spin-orbit coupling, for the magnetic transition metals Fe, Co and Ni where the spin moment is constrained to a given value. For bcc Fe a change of sign of the orbital moment with decreasing spin moment is predicted, in contradiction with intuitive thinking. This effect is not present in hcp Co and fcc Ni. This is explained in terms of the detailed structure of the m_l - projected density of states for the bcc structure.

Real-Space Iterative Methods in Electronic Structure Calculations*

D. J. Sullivan and J. Bernholc
Department of Physics, NC State University, Raleigh, NC 27695-8202

Iterative methods such as the Car-Parrinello method have very successfully used plane wave bases in the study of bulk crystals, surfaces, liquids, and clusters. However, since plane waves provide uniform representation of physical quantities throughout the unit cell, the addition of a strong impurity requires an improvement of the basis everywhere. Consequently, the number of plane waves and the cost of the calculation increase dramatically with the addition of, *e.g.*, a transition-metal impurity. In surface and cluster calculations, much of the supercell's volume is outside the ionic core and bonding regions; nonetheless, the plane wave basis covers the vacuum region as accurately as the interior region. Non-uniform real space grids allow for a local improvement of the representation of wavefunctions, *i.e.*, in the ionic core and bonding regions, while using fewer basis states in the regions where the wavefunction is small or slowly varying. We illustrate a real-space iterative method with applications to atoms and diatomics without the use of periodic boundary conditions, and discuss the tailoring of the basis and the smoothness of the representation. Our results indicate that the procedure is similar in efficiency to the Car-Parrinello method.

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An LAPW Approach to Separable First-Principles Pseudopotentials

S. Goedecker, K. Maschke
IPA, Ecole Polytechnique Féderale de Lausanne
CH-1015 Lausanne, Switzerland

Electronic structure calculations based on separable pseudopotentials require much less computer time than calculations based on non-separable forms. Unfortunately the most reliable pseudopotentials are non-separable and it is not always possible to make them separable without loosing precision. Following ideas borrowed from the LAPW method, we derive a First-Principles pseudopotential which is separable by construction. We show that for sufficiently small muffin-tin spheres it is not necessary to recalculate the selfconsistent potential in the muffin-tin sphere at each step of the selfconsistency cycle as it is done in the LAPW method. This means, that one reference potential in the muffin-tin sphere is enough to ensure good transferability.

A fast full-potential LCAO-method for total-energy minimizations

P. M. Oppeneer, W. Hierse and J. Kübler

Institut für Festkörperphysik, Technische Hochschule Darmstadt, D-6100 Darmstadt,
Federal Republic Germany

A new bandstructure method has been developed, specifically for the purpose of fast total-energy minimizations of large systems. Most characteristic of this Linear-Combination-of-Atomic-Orbitals-method is that nowhere position dependent meshes for numerical integrations in real space are needed. All appearing integrations are done analytically, which makes the setting-up of the secular matrix fast. Furthermore, with this LCAO-method a number of new computational techniques are introduced, namely: (a) an efficient and simple solution of Poisson's and Schrödinger's equation for full-potentials, (b) a new treatment of the non-linearity of the LDA exchange-correlation energy, and (c) an approximation technique for 3-centre integrals. The method described here is particularly suited for molecular dynamics simulations and we also developed a scheme for this LCAO-method, in which a minimum of the total-energy is found by iterating the electronic and/or ionic degrees of freedom.

Spurious pressure effects on LDA band structure of semiconductors

Vincenzo Fiorentini

Dipartimento di Fisica Teorica, Università di Trieste, Italy

A consistent description of the band structure of semiconductors in the LDA by the pseudopotential method (indeed by any scheme not reproducing exactly the experimental equilibrium volume) can only be obtained by calculations done at the theoretical equilibrium volume, $\Omega = \Omega_{th}$. The choice of different cell volumes (such as the experimental volume Ω_{ex}) is equivalent to a spurious pressure applied to the crystal.

These statements are substantiated by converged total energy studies, and calculations of electronic states, pressure derivatives, and effective masses of Si, Ge, GaAs, AlAs (using Bachelet-Hamann-Schlüter *ab initio* norm-conserving pseudopotentials, Ceperley-Alder LDA, and a plane wave basis) : at Ω_{th}, the discrepancies in Γ and L energy gaps are definitely smaller than usually believed; in particular, the correct ordering of conduction band is obtained in Ge. This is easily understood in terms of pressure derivatives, whose calculated values agree well with existing experimental data. Effective masses are also very sensitive to variations of Ω, and, contrary to common wisdom, the calculated conduction effective masses in GaAs and AlAs are found to be in remarkably good agreement with experiment.

HARTREE-FOCK PLUS DENSITY FUNCTIONAL CALCULATION OF GROUND STATE PROPERTIES OF SEMICONDUCTOR AND IONIC COMPOUNDS.

Mauro Causa'
Department of Inorganic, Physical and Material Chemistry,
University of Torino, via Giuria 5, I-10125 Torino, Italy.

The binding energy (B.E.), the equilibrium lattice parameter (a_0), the bulk modulus (B) and the central-zone transverse optical phonon frequency (ν_{TO}) of seventeen diamond and zinc-blend type structure semiconductors and of lithium, sodium and potassium oxides have been evaluated. The periodic *ab initio* Hartree-Fock LCAO program CRYSTAL has been used. Core pseudopotentials have been adopted in order to limit the calculation to valence electrons. Two gaussian type function per each atomic orbital plus polarization d function have been adopted as basis set. The quality of the pseudopotential results has been checked by comparison with all electron calculations performed on six light-atom systems (diamond, silicon, BN, BP, AℓP, SiC). The mean error of the pseudopotential calculations with respect to experimental data is -38%, +1.2%, +6.5%, +7.8% for A.E., a_0, B and ν_{TO}, respectively. A correlation-only density-functional a posteriori correction to the Hartree-Fock total energy is performed, which reduces the absolute B.E. mean error to 2.6%.

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ON THE ELASTIC PROPERTIES OF LITHIUM, SODIUM AND POTASSIUM OXIDE. AN AB-INITIO STUDY
submitted to Int. J. of Quantum Chem.

The effect of spin-orbit coupling on ground-state properties of materials.

X. Gonze, P.C.P.M., U.C.L., Place Croix du Sud, 1, B-1348 Louvain-la-Neuve, Belgium, and (present address) LASSP, Cornell University, Ithaca, N.Y. 14853 USA.

Using perturbed density functional theory (PDFT), we show that the modifications of ground state total energy and charge density of a non-magnetic crystal, due to the spin-orbit term, are only second-order effects in the spin-orbit coupling constant, while this is not true for atoms or molecules.
Then, we adress the magnitude of these effects in As, Sb, and Bi (mainly same chemical properties, but increasing atomic number, and increasing spin-orbit coupling constant). We also try to answer more generally the following practical question : given a ground state property to be calculated, what is the magnitude of the error caused by ignoring the spin-orbit coupling terms in the calculation ?

First-principles study of graphite electronic properties

J.-C. Charlier, X. Gonze, J.-P. Michenaud.
Université Catholique de Louvain.
Unité de Physico-Chimie et de Physique des Matériaux (PCPM).
Batiment Boltzmann, Place Croix du Sud, 1
B - 1348 Louvain-La-Neuve (Belgium).

The electronic properties of hexagonal graphite have been studied in the framework of the density functional technique, using non-local ionic pseudopotentials and a large number of plane waves. The band structure, at the Fermi level, is compared with the Slonczewski-Weiss-McClure model for a three dimensional graphite. The valence charge density, the density of states and the Fermi surface are also presented.

DFT Band Gap problem and crystallographic structure

X. Gonze, P.C.P.M., U.C.L., Place Croix du Sud, 1, B-1348 Louvain-la-Neuve, Belgium
and (present address) LASSP, Cornell University, Ithaca, N.Y. 14853 USA.

The origin of the DFT band-gap problem is well understood : the exchange-correlation potential can change abruptly if one conduction electron is added to the solid. But, until now, the actual size of this effect has been examined mainly in the restricted class of diamond and zinc-blende semiconductors, or on model semiconductors.
In the present communication, it is shown that the magnitude of the band-gap problem is strongly structure-dependent. From simple theoretical arguments, we explain why the IV-VI semiconductors band gap problem is weaker, and we relate this fact to the good agreement observed for the elemental semimetal overlaps, especially Bismuth. In the same framework, we show that diamond and Zinc-blende structures are expected to generate large DFT band gap discrepancies, but small discrepancies for deformation potentials.

Calculation of Gap Corrections in a Generalized Density Functional Theory

L. Fritsche and Y. M. Gu

Institut für Theoretische Physik, TU Clausthal, D-3392 Clausthal-Zellerfeld

As has been shown by one of the authors (L.F.), the Kohn Sham-equations can be rederived by requiring the expectation value of the N-electron Hamiltonian to be only stationary against variation of the wave function, i.e. it must not necessarily attain a global minimum. Consequently, the entire KS-scheme is valid not only for the ground state but applies to excited N-electron eigenstates as well. Total energy differences for excitations across the gap of insulators and semiconductors prove to be expressible by the respective band energy differences and a correction term which may be of the same order of magnitude. This correction term can be approximated by a simple expression which gives surprisingly good results for the true band gaps in solid rare gases which have been chosen as a first test case.

The 2-D Hubbard-Peierls model in the self-interaction corrected density functional formalism

J. A. Majewski and P. Vogl, Physics Department, Technical University of Munich, FRG

We present results for correlation functions, the energy gap, and the phonon-induced electronic energy gain in the 2-D Hubbard-Peierls model near half-filling. Noticeably, we find that lattice distortions destabilize the antiferromagnetic ground state in 2D and cause the electronic energy gap to decrease. Contrary to the 1D case, the 2D Hubbard-Peierls model thus exhibits a negative U-type behavior. We have employed both exact diagonalizations and the self-interaction-corrected local spin-density functional theory (SIC-LSD). In the latter case, the off-diagonal Langrange multipliers are taken into account self-consistently. SIC-LSD gives excellent agreement with exact results on small lattices; detailed comparisons of the exact and SIC-LSD exchange-correlation energy are presented.

We discuss an efficient method for minimizing the SIC total energy for a given band filling and spin configuration. Various numerical minimization techniques are compared to one another.

OVERVIEW OF THE DEGENERACY-DEPENDENT SELF-INTERACTION CORRECTION (D-SIC)

P. Cortona, Dipartimento di Fisica, Università di Genova, I-16146 Genova, Italy.

D-SIC is a method of correcting the local-density approximation to the density-functional theory for the self-interaction effects which is strictly based on the homogeneous gas theory. In this communication we review the theoretical foundations of the method as well as his more relevant results. Particular attention will be devoted to the comparison with a variety of other approximations in use in the density-functional theory.

Optical Matrix Elements for Non-local Pseudopotential Calculations

A. J. READ and R. J. NEEDS
Cavendish Lab., Cambridge Univ., U.K.

Calculated absorption and emission spectra are important tools for understanding the electronic structure of materials. The optical matrix element required (in the dipole approximation) is usually calculated using the momentum operator $\underline{p}$, but the position operator $\underline{r}$ can also be used. These two operators give the same answer only if the potential in the Hamiltonian commutes with $\underline{r}$, which is not true for non-local potentials. We consider the construction of standard non-local pseudopotentials and show that the $\underline{r}$ operator is the correct one. If a gauge transformation is used to change the $\underline{r}$ perturbation into a $\underline{p}$ perturbation we find the pseudopotential must also be changed, and this change included in the perturbation. Numerical results for free atoms are given which confirm this interpretation, and show that the errors caused by using the $\underline{p}$ operator incorrectly can be comparable to the matrix element itself. Many bulk pseudopotential calculations involve wavefunctions and potentials expanded on a plane wave basis set with repeating boundary conditions. We present a direct method for calculating the $\underline{r}$ matrix element for these systems, allowing the correct optical matrix element to be calculated using standard density functional theory wavefunctions.

A SEPARABLE FINITE GAP POTENTIAL METHOD AS NEW METHOD FOR CALCULATION OF ELECTRON ENERGY SPECTRUM OF SOLIDS

Bar'yaktar V.G., Belokolos E.D., Korostil A.M.
Institute for Physics of Metals of the Ukrainian Academy of
Sciences, Kiev State University, Kiev, USSR

A new method for calculation of the electron energy spectrum of solids that based on using of exact expression for separable potential and wave functions of electron system with finite set gaps in spectrum is suggested. The method gives a possibility to describe with simple formula and analyze in details all properties of energy electron spectrum. In particular methods of free electrons and strongly bound electrons are shown to be limit cases of the proposed method.

Within the framework of separable one gap potential we have calculated an electron energy spectrum, an isoenergetical surfaces, an electron-phonon interaction constant, etc. and have applied these results for explanation different properties of conductors and superconductors.

HAMILTONIAN CHAOS IN THE ENERGY TRANSFER OF A NONLINEAR DIMER MODE

D. HENNIG and B. ESSER

Fachbereich Physik der Humboldt-Universitat zu Berlin, Institut fur Theoretische Physik

Invalidenstr. 42, O-1040, Berlin, FRG

Abstract

Energy transfer in a nonlinear dimer model is represented as a Hamiltonian flow on the Bloch sphere. Using this representation the possibility of chaotic transfer regimes induced by a harmonic time dependent perturbation is established.

Electronic Structure of Conducting Copolymers

Nagendra N. Beladakere, R. S. Rao and B. D. Malhotra
National Physical Laboratory
Dr. K. S. Krishnan Road
New Delhi. 110012. INDIA

Abstract

There is a quest for electrically conducting copolymers and blends as it is possible to synthesize a single polymeric material possessing both electrical conductivity and desired mechanical properties. It is both useful and important to study the electronic structure, moieties and disorder of these materials. The valence effective Hamiltonian technique has been used by us to calculate the elecctronic structure of poly α naphthalene oxide pyrrole and polyanisidine aniline copolymers. Our calculated results are compared with the experimental results. Attempts are being made to study these materials as disordered systems.

Some improvements for EMT, Application to O in $YBa_2Cu_3O_7$

André Zwartkruis, Institute of Theoretical Physics,
Chalmers University of Technology, S-41296 Göteborg, Sweden

We have calculated diffusion paths for interstitial O in $YBa_2Cu_3O_7$ by using the Effective-Medium Theory for chemical binding (the version described in J.K. Norskov, Phys. Rev. B26 (1982) 2875). We have found that for internal consistency of the theory. one needs to include an extra kinetic repulsion term which can be derived in a systematic way from Density Functional Theory. For larger impurities, as e.g. oxygen atoms, the contribution from the extra term is large, and unphysical, deep wells in the potential energy surface are removed. Inclusion yields two further advantages. Firstly, one can now easily establish the equivalence of EMT and another embedding scheme, CEM, recently proposed by Kress and DePristo (J. Chem. Phys. 87 (1987) 4700). Secondly, one can justify to much larger extent the splitup of the first-order corrections in either the EMT or the CEM scheme as a sum of pairpotentials.

Relaxation was included in the computations. For O diffusion paths along the c-direction we find barriers of about 1.5 [eV] and for paths in the b-direction, parallel to the Cu-O chains, we find barriers of typically 0.5 [eV].

Light lanthanide impurities in iridium: from non-magnetic 4*f* states to large local magnetic moments with both a spin and an orbital part.

Lars Nordström and Börje Johansson
Phys. Dept., Uppsala Univ., Box 530, Uppsala,Sweden.

The electronic structure of light lanthanide impurities in the small volume host iridium is calculated by the LMTO Green's function method. In the calculation both spin- and orbital polarization are allowed to occur. Ce and Pr are found to not form local magnetic moments while Nd and Pm form local magnetic moments with both the spin and the orbital part almost saturated.The hybridization between the iridium 5*d* states and the impurity 4*f* states with t_{2u} symmetry is shown to be the mechanism for the unstable magnetic moments in Ce and Pr. The results are compared with and are found to be in agreement with data from experiment.

"Ab initio total-energy calculations on hydrogen in aluminium"

A. De Vita and M.J. Gillan
Physics Department, Universtiy of Keele,
Keele, Staffordshire, ST5 5BG, U.K.

We have performed pseudopotential total-energy calculations on hydrogen in aluminium using the Kleinman-Bylander form of the Bachelet-Hamann-Schluter pseudopotential for aluminium and the bare Coulombic potential for the proton. The physical quantities studied are the hydrogen heat of solution, the relative energies of different interstitial sites, the diffusional migration energy and the hydrogen-vacancy binding energy. In all cases, the calculations fully include the relaxation of the aluminium ions. We shall present a comparison of the calculated energies with available experimental results, and maps of the electron density distribution surrounding the hydrogen.

Quantum Behaviour of Muons in Crystalline Silicon

C. Pennetta
Dipartimento di Fisica, Università di Lecce, Via Arnesano, I-73100 Lecce

A. Baldereschi
Dipartimento di Fisica Teorica, Università di Trieste, Strada Costiera, I-34100 Trieste
IRRMA, PHB - Ecublens, CH-1015 Lausanne

We report the results of a fully quantum-mechanical calculation of the states of an isolated positive muon in crystalline Si. The interaction of the muon with the host is described with an effective potential derived within the Born-Oppenheimer approximation. The one-particle Schrödinger equation of the muon is solved using a localized orbital basis set. We find that muons do not behave like protons, as commonly assumed. In particular, even in the ground state the muon wave function is significantly delocalized. Furthermore, the general features of the energy spectrum and of the excited state wave functions indicate that quantum effects strongly affect the behaviour of muons inside the crystal.

EXCITONS BOUND TO AN IONIZED DONOR IMPURITY IN SEMICONDUCTORS

J.J.De Groote, C.D. Caldwell*, O. Hipólito, M.H. Degani and J.E.M. Hornos
Departamento de Física e Ciência dos Materiais
Instituto de Física e Química de São Carlos
Universidade de São Paulo, C.P. 369
13560 - São Carlos - São Paulo - Brasil

* University of Central Florida
Orlando, Florida 32816 - U.S.A.

Abstract

Hyperspherical coordinates are used to investigate the three-particle complex corresponding to an exciton bound to a Coulomb center in a semiconductor. The ground and excited-state potential curves and binding energies are calculated as function of the mass ratio of the hole and electron. The results we have obtained are in very good agreement with experimental data for several semiconductor materials. The technology is extend to more complex systems as biexcitons and clusters of excitons. The solution of the partial equations in this case is impossible by tradicional methods and a procedure based in the simulated annealing is sugested.

THEORETICAL INVESTIGATION OF THE MOTIONAL STATES OF THE NITRITE ION IN ALKALI HALIDE CRYSTALS

G. K. Pandey, M. Massey and K. L. Pandey
Physics Department, Allahabad University, Allahabad, India

A microscopic model for the subsitutional NO_2^- impurity ion in NaCl-structure alkali halide crystals is developed on the basis of a specific theoretical potential. Coulomb, induction, and short- range interactions are included to obtain expressions for the barriers hindering the rotational motion of the impurity in the matrix cage. Preferred orientations, off-center displacements, and barrier parameters for this impurity are calculated in KCl, KBr, and KI host crystals. The results are used to explain most of the features of the infrared spectra in these impurity systems.

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The total energy pseudopotential method used on stacking faults in Aluminium

B. HAMMER

Laboratory of Applied Phyiscs, Technical University of Denmark
Building 307, DK-2800 Lyngby, Denmark

MANY-BODY EFFECTS IN A SCHOTTKY BARRIER

J. Charlesworth, R.W. Godby and R.J. Needs
Cavendish Laboratory, University of Cambridge, Madingley Rd., Cambridge CB3 0HE, UK

Research into the rectifying action of the Schottky barrier has been going on since the 1930's but there still exists no accurate theory to explain the Schottky barrier height or the relative importance of different effects. Recently, calculations have been done on a range of interfaces using the LDA in DFT, but these greatly underestimate the band gap in the semiconductor. In addition, the LDA calculations omit important correlation effects, such as the image-like band-gap narrowing described below.

We investigate many body effects in the Al-GaAs(110) Schottky barrier using *ab-initio* computational many body theory in the form of the *GW* self energy where the Greens function, *G*, and the screened Coulomb interaction, *W*, may both be gained from LDA approximation calculations. This method is known to give accurate band gaps for a number of materials and so allows an accurate evaluation of the barrier heights.

We have extended the usual treatment to allow us to examine the variation in the self energy contribution to the many body "Hamiltonian" as a function of distance from the Al-GaAs interface which we may consider to be a state dependent local potential which gives the effective exchange and correlation potential. Because the self energy is integrated over all space, this effective potential in the semiconductor includes the correlation of an electron with those in the metal. In particular, it includes an image-type potential term, which being a measure of the electron correlation, is absent in local density calculations.

By evaluating this effective potential for various states over equivalent regions (i.e. over slabs whose length is commensurate with that of the semiconductor cell parameter), we can evaluate the importance of the image-type terms as a function of the distance to the interface. We thus observe the variation of the effective potential and so measure the resultant band bending and band gap narrowing for both valence and conduction bands.

Pseudopotential calculations of the valence band offsets at the ZnSe/Ge, ZnSe/GaAs and GaAs/Ge (110) interfaces: effects of the Ga and Zn 3d-electrons

A. Qteish and R. J. Needs

Cavendish Laboratory, Madingley Road, Cambridge CB3 OHE, U.K.

Valence band offsets at semiconductor interfaces involving Zn and Ga atoms are calculated using a first-principles pseudopotential technique. We show that accurate results can be obtained, with the 3d-electrons treated as core states, *provided* that nonlinear core exchange-correlation corrections are included. In this work the ZnSe/Ge, ZnSe/GaAs and GaAs/Ge (110) interfaces have been considered. The calculated valence band offsets are in excellent agreement with the experimental data and with linear-muffin-tin-orbital calculations (in which the 3d-electrons are treated as valence states). Furthermore, we show that such effects can be incorporated within the model-solid theory of Van de Walle and Martin.

INTERFACE-LIMITED ORDERED COMPOUND FORMATION: APPLICATION TO SI/GE

K.A. Mäder[1,2], *H. von Känel*[1], *and A. Baldereschi*[2,3]
[1]*Lab. für Festkörperphysik, ETH, CH-8093 Zürich, Switzerland*
[2]*Inst. de Physique Appliquée, EPF, CH-1015 Lausanne, Switzerland*
[3]*IRRMA, PH Ecublens, CH-1015 Lausanne, Switzerland*

A static model for the atomic structure of semiconductor interfaces which takes into account both strain and chemical energies is presented. It is shown that space-confined ordered intermixing, limited by enthalpy rather than diffusion, can occur at the interface in spite of bulk-instability of the new phase. We apply the model to Si/Ge heterojunctions and strained-layer superlattices, where strain and chemical energies are of the same order of magnitude. The qualitative trends of our results agree with experimental data, but the occurrence of ordered SiGe phases at high temperature remains still unexplained.

VALENCE BAND OFFSET AT Si/Ge INTERFACES

L.Colombo(1), R.Resta(2) and S.Baroni(2)
(1) *Dipartimento di Fisica, Università di Milano, via Celoria 16, 20133 Milano*
(2) *SISSA - Strada Costiera 11, 34014 Trieste*

The *Si/Ge* superlattices (SL's) are the paradigmatic case of *isovalent*, *non − polar*, *lattice − mismatched* system. In this work we consider thick (but still pseudomorphic) SL's such that each of the *Si/Ge* interfaces can be considered as isolated, and the main issue is whether the valence band offset (VBO) is tunable by means of either chemistry (i.e. altering the abruptness of the interface) or strain. The present **theoretical study is performed within the state-of-the-art DFT-LDA framework.**

As far as chemistry is concerned, our finding is that the VBO is independent of chemical composition **and abruptness of the interface. Detailed calculations for (001)-oriented heterojunctions show** that the **difference in VBO between a sharp *Si/Ge* interface and a mixed one is smaller** than our present computational noise (0.01 eV). Similar results are expected for different orientations as well, being the *Si/Ge* interface isovalent.

As far as strain is concerned, our main finding is that the VBO at strained *Si/Ge* junctions is *not* affected by interface features (neither strain nor buckling), while it *does* depend upon the macroscopic strain conditions, governed by both substrate and orientation. The nontrivial orientation dependence of the strain-induced VBO is a general qualitative features of the *Absolute Deformation Potentials* (ADP)[1]. The VBO for (001) interfaces, when expressed in terms of the alloy concentration of the Si_xGe_{1-x} substrate, takes the form (in eV):

$$\mathrm{VBO}(x) = 0.42x + 0.46(1 - x),$$

and displays perfect linearity. The tunability feature of the VBO is therefore present, although in a very *limited range* (0.04 eV), due to the very close values of the ADP's for pure *Si* and *Ge*.

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TUNING BAND OFFSETS AT SEMICONDUCTOR HETEROJUNCTIONS BY INTRALAYER DEPOSITION

M. Peressi,[a,b] S. Baroni,[b] R. Resta,[b] and A. Baldereschi[a,c]

(a) *DFT, Università di Trieste, Strada Costiera 11, I-34014 Trieste - Italy*
(b) *SISSA, Strada Costiera 11, I-34014 Trieste - Italy*
(c) *IRRMA, PHB - Ecublens, CH-1015, Lausanne - Switzerland*

Band offsets can be modified at semiconductor heterojunctions or created at homojunctions by depositing thin intralayers of atoms with different chemical valence. Only very recently this has been realized in the case of Ge/GaAs/Ge (111),[1] and GaAs/Si/AlAs (001)[2], and the corresponding modifications of the band offsets have been measured.

We present here a theoretical study (based on density-functional self-consistent and linear response techniques) of Si and Ge intralayers deposited at GaAs/AlAs (001) heterojunctions, and at GaAs and AlAs (001) homojunctions. Our results show that the band offset can be tuned in a wide range (about 1 eV), being very sensitive to the nominal thickness and the abruptness of the intralayer. A comparison with recent experiments for GaAs/Si/AlAs suggests that in the real samples Si atoms are confined over two atomic planes for coverages lower than about 0.5 monolayers, whereas for higher coverages Si diffusion occurs.

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TUNING BAND BAND DISCONTINUITIES IN SEMICONDUCTOR HETEROJUNCTIONS.

A. Muñoz

Departamento de Física Fundamental y Experimental, Fac. Física Universidad
de La Laguna, E38204 LA LAGUNA, TENERIFE. SPAIN

The possibility of tuning heterojunctions band offsets has been recently theoretically proposed[1], and has been made experimentally possible[2]. he idea in this studies is to generate a local dipole at the interface region, this dipole can be different depending on the interface composition and geometry, so that provide a mechanism for the possibility of band offsets engineering by using thin layers at interface, that support strongly the idea that in some cases the extrinsic charge neutrality level. In this work we will present different results for the case of thin Si layers embedded in Ge/GaAs (100) and GaAs/AlAs (100) heterojunctions using state of the art calculations based on local density functional theory, using nonlocal normconserving pseudopotentials. in this case we can extract not only the band offsets , we also provide the formation enthalpy for this interfaces.

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OPTICAL PROPERTIES OF SUPERLATTICES

C.Tserbak, H.M.Polatoglou, G.Theodorou

Aristotle University of Thessaloniki, Physics Department
54006 Thessaloniki, GREECE

In recent years, the optical properties of the superlattices (SLs) have received a great deal of attention. In this work we show that the dielectric function, for thick SLs, becomes the average of the dielectric functions of the materials that it consists of. In order to show this, we decompose the SL wavefunction in two parts, one part which has amplitude in the first constituent and another one which has amplitude in the second constituent. By using this decomposition, the dielectric function becomes a sum of different terms. It is shown that most of them are generally small and only two terms are important for thick SLs. These terms correspond to the dielectric function of the bulk constituents. This decomposition is also useful for thin superlattices. In this case it is possible to find the origin of the different structures which appear in the dielectric function. As a numerical example, we apply the above decomposition to the GaAs/AlAs SLs.

FIRST-PRINCIPLES CALCULATION OF THE MAGNETOCRYSTALLINE ANISOTROPY ENERGY OF Co_nX_m METALLIC MULTILAYERS.

G.H.O. Daalderop, P.J. Kelly and M.F.H. Schuurmans.

Philips Research Laboratories, 5600 JA Eindhoven, The Netherlands

The results of first principles calculations of the magnetocrystalline anisotropy energy (MAE) of (111) metallic multilayers Co_nX_m (X = Cu, Pd and Ag; $n + m = 3$ or 6) are presented. The MAE calculations were carried out within the local-spin density approximation using the LMTO method. For Co_nPd_m the easy axis is found to be perpendicular to the superlattice plane, in agreement with experiment. The anisotropy energy decreases with increasing n and is not strongly dependent on m; in our calculations Co_1Pd_2 and Co_1Pd_5 have approximately the same anisotropy energy. The easy axis is found to be perpendicular to the superlattice plane in the series Co_1X_2 with the maximum anisotropy energy occuring for X = Pd. By neglecting the Pd on-site spin-orbit coupling, the anisotropy energy is reduced by a factor ~2. This underlines the importance of having not only low symmetry but also large spin-orbit coupling. By calculating the MAE for bulk trigonal Co for a large range of c/a ratios we can show that the large MAE found above results from the presence of the Co/Pd interface.

Electronic structure of metallic superlattices: Mo/V

S. Papadia
Institute of Theoretical Physics,
Chalmers University of Technology, S-412 96 Göteborg, Sweden

K. Karlsson and P. O. Nilsson
Department of Physics,
Chalmers University of Technology, S-412 96 Göteborg, Sweden

Abstract

Electronic structure calculations have been performed for a metallic superlattice system (Mo/V) using the linear muffin-tin orbital method (LMTO) in the atomic sphere approximation (ASA). Total energies have been calculated within the density functional formalism, making the local density approximation for the exchange-correlation part of the energy functional. The aim is to explore the band structure as well as the geometric structure of such systems and to determine the electron density variation in order to understand hydrogen storage in these materials. Results are presented for superlattices consisting of 1, 3, and 5 monolayers of each constituent.

Estimation of the ideal fracture strength for the jellium model and rigorous theorems for bijellic interfaces

P. Ziesche and R. Kaschner

Technische Universität Dresden, Sektion Physik, Germany

Abstract

Recent considerations of the authors concerning the adhesion between solids, especially a new interpolation formula for the cleavage force as well as the numerical solution of the coupled Euler and Poisson equations of the gradient expansion method applied to the jellium model of cleavage are summarized. Rigorous theorems for the bijellic interface are (i) used to test the calculations, and (ii) generalized to the case of finite slit width. The results include data for the cleavage force as a function of separation and density, the linear and quadratic force constants (which are related to linear and quadratic response functions), and the interfacial energy.

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Structure and Dynamics of Large Clusters: the Icosahedral-Cuboctahedral Transition in Al Clusters and Solid C_{60} *

Jae-Yel Yi, Q. Zhang and J. Bernholc
Department of Physics, North Carolina State University
Raleigh, NC 27695-8202

The 13- and 55-atom clusters are among the smallest clusters for which both cuboctahedral and icosahedral structures exist. We have investigated the relative energetics of the two structures for Al using the Car-Parrinello method. If only breathing mode relaxations are allowed, the icosahedron is the lowest energy structure for Al_{13}, while the cuboctahedron is preferred for Al_{55}.[1] Using especially developed procedures for efficient simulated annealing,[2] we have transformed the ideal cuboctahedra and icosahedra to distorted icosahedra. The icosahedra are thus the ground state structures, although the energetic difference between these structures and "weakly" annealed cuboctahedra is relatively small. The calculated ionization potentials and electron affinities are in much better agreement with experiment after annealing, which demonstrates the importance of including structural relaxations in calculations. For the 55-atom clusters, the structure factors of a "weakly" annealed but definitely cuboctahedral structure and the fully annealed icosahedron are similar and quite different from either of the ideal structures. Therefore, a structural classification of small clusters on the basis of indirect measurements is difficult and not necessarily reliable.

We also report results of Car-Parrinello simulations for the recently discovered C_{60} molecular solid,[3] which is a new and unexpected form of solid carbon. Symmetry unconstrained optimization of the structure results in alternating double and single bonds, similar to the ones predicted for the gas phase molecules. The individual bond angles deviate by at most 1° from their ideal values of 108° and 120.° The computed density of states agrees very well with very recent photoemission results.[4] Although the diameter of each C_{60} fullerene is 7.2 Å, charge density contours show that the intermolecular interactions are small at the experimental lattice spacing (10.04 Å). Dynamical simulations reveal that each molecule rotates at temperatures as low as ~300 K. At T= 1500 K the primary motion is still rotation, with the distortions from the T=0 structure being small. The last result indicates that fullerenes should be stable at very high temperatures and is consistent with their formation under very hot conditions in laser ablation and graphite arc sources. From the T=1500 K simulation we have computed the vibrational frequency spectrum at this temperature. The peaks in the spectrum are in good agreement with infrared absorption data.

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ENERGETICS AND SEGREGATION IN NA/CS HETEROCLUSTERS

M.J. López, A. Mañanes*, M.P. Iñiguez, J.A. Alonso
Departamento de Física Teórica Atómica, Molecular y Nuclear, Universidad de Valladolid, Valladolid, Spain.
* Departamento de Física Moderna. Universidad de Cantabria, Santander, Spain

The equilibrium geometry and the corresponding ground state energy are calculated for Na_mCs_n clusters with composition m=n and m=2n, by minimizing the total cluster energy with respect to both, ionic positions and the electronic density. Density functional theory is used to obtain the energy of the valence electrons is a spherically averaged external ionic potential, and the ionic repulsive energy is calculated by considering point like ions at fixed sites. In the size range studied here (up to 90 atoms per cluster) a layering effect is observed in the cluster geometries. Clusters are composed by well separated homoatomic Na and Cs shells, the external one being always a Cs shell. There is a shong reconstruction of the cluster geometry with increasing size. We have also found that the cohesive energy goes rapidly to the bulk limit and that the mixed cluster is stable with respect to pure unmixed fragments.

Electronic Structure of Adsorbates Near Surface Irregularities: Cluster Models for CO on Cu Surfaces.

K. Hermann, Abt. Theorie, Fritz-Haber-Institut Berlin, Germany

Workfunction and PAX experiments have shown that surface irregularities such as kinks, steps, or imperfections can give rise to large local inhomogeneous electric fields. Consequences for the chemisorptive interaction are studied in cluster models for CO adsorbed on Cu surfaces. The CO-Cu interaction is modelled by $Cu_5(1,4)CO$ clusters with the external electric field simulated by that of a point charge of size q. Positive q values simulate the situation near a surface step where an effective positive charge exists (Smoluchowski effect) while negative q simulate the field of a negatively charged coadsorbate ion. The electronic cluster wavefunctions are obtained from ab initio Hartree-Fock-LCAO calculations. For positive q the 1-electron energies of all cluster orbitals shift downwards which can be explained by a (dominantly linear) surface Stark effect. Further, the two e-type cluster orbitals responsible for π backdonation in Cu_5CO increase their CO 2π admixture in the presence of the field. The increased effective CO 2π occupation leads to a field-induced C-O bond weakening. This explains the increased C-O equilibrium distance and the reduced frequency of the C-O stretching vibration found in the present model calculations which is consistent with experimental findings for CO adsorbed near surface steps. The results for negative q are complementary to those for positive q which is consistent with the experimental result that negative coadsorbate ions can reduce the CO dissociation probability at metal surfaces.

Hydrogen-Magnesium Interaction Energies

U. Yxklinten, Z. J. Tian, A. Mällo, C. Engdahl, and B. I. Lundqvist

Institute of Theoretical Physics,
Chalmers University of Technology, S - 412 96 Göteborg, Sweden

Abstract

Total-energy calculations with the effective-medium theory, EMT, have been performed on the hydrogen-magnesium system in order to obtain hydrogen chemisorption and dissolution properties. The EMT has been applied to a single H adatom on the Mg(0001) and $(11\bar{2}0)$ surfaces, to a layer of H atoms adsorbed on the Mg(0001) surface, to H coadsorbed with Mg, to an additional H atom coadsorbed with a full H overlayer on the Mg(0001) surface, and to H_2 on the Mg(0001) surface. Heat of solution for H in bulk Mg, and Mg lattice expansion as a function of the H concentration, have also been calculated. At several instances comparisons with first-principles calculations and experimental data can be made, and the fair agreement gives confidence in the method used. Out of the calculations emerge a picture with activated dissociative chemisorption of H_2 on the Mg(0001) surface, initial adsorption in subsurface sites, low activation barriers for H-atom diffusion on the surface and in the bulk, and with H-H-interactions having several important consequences. The calculations also provide numbers for direct comparison with experiment, such as, adsorbate vibrational frequencies and diffusion barriers for adsorbed and dissolved hydrogen, and illustrate the great importance of allowing for relaxation of the atomic configurations.

Ab-initio calculations of relaxations and workfunctions of transition metalsurfaces: The *anomalous* relaxation of Pd(100) and Rh(100)

D. Hennig[1], M. Methfessel, S. Weber, and M. Scheffler
Fritz-Haber Institut der MPG
Faradayweg 4-6, D-1000 Berlin 33, Germany

Experimentally, most clean surfaces show an inward relaxation, i.e. the inter-layer spacing between the first and second layer is smaller than the bulk inter-layer spacing. However, some transition-metal are found to relax outward. Current theories focus on the effect of charge-density smoothing at the surface and can only explain inward relaxation. We therefore performed density-functional theory calculations for several fcc transition-metal surfaces, in order to analyse this hitherto non explained effect. In particular we investigated the trend for different low index fcc crystal surfaces: (111), (100), and (110). We used the full-potential linear-muffin-tin orbital method and a slab geometry. Calcutated relaxations and workfunctions agree well with experimental results. For Pd(100) and Rh(100) we find indeed the so-called *anomalous* behavior. The results are explained in terms of a competition between charge-density smoothing and the bonding and antibonding nature of *d*-derived states.

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[1] **Permanent address**: Department of Theoretical Physics, Humboldt-University of Berlin Invalidenstr. 110, Berlin O-1140 Germany

Interaction of the Pt(111) surface with adsorbed Xe atoms

J.E. Müller
Institut für Schicht- und Ionentechnik, Forschungszentrum Jülich,
D-5170 Jülich, Federal Republic of Germany

The interaction potential between the Pt(111) surface and Xe atoms adsorbed upon it, was calculated using the cluster method with the Kohn-Sham scheme. For a single Xe atom, an energetically most favorable *on-top* adsorption site, 3.0 Å above a Pt atom was found, with an activation energy for surface diffusion of 22 meV, and a perpendicular vibration energy of 8.5 meV. This vibration energy is reduced drastically by clustering of the adsorbed Xe atoms.

ADSORPTION AND MAGNETISM.LCGTO-MP-LSD STUDY OF ADATOMS ON FERROMAGNETIC Ni(100) SURFACE.

Franca Mele, N.Russo and Marirosa Toscano

Dipartimento di Chimica,Università della Calabria, I-87030 Arcavacata di Rende(CS), Italy.

The relationships between adsorption of adatoms (H, C, N, O and CO) and changes in the saturation magnetization Ms of ferromagnetic Ni(100)surface have been investigated with the first-principle LCGTO-MP-LSD method.
Our results show that:

i. the most stable adsorption sites for H, C, N and O atoms is the four-fold hollow one, while CO adsorbs preferentially in on top position.

ii. the computed geometric and spectroscopic equilibrium parameters are in good agreement with available experimental data.

iii. the spin polarized calculations show that H, C and N adsorption causes a decrease of 1, 2 and 3 μ_B in the total magnetic moment. In the case of O and CO adsorption no change in the total magnetic moment is observed but significant variations are found for the local atomic moments of surface Ni atoms directly involved in the interaction with the adatoms.

A Study of Alkali Adlayers on Al(111) as a Function of Coverage

P. A. Serena
IBM Research Division, Zurich Research Laboratory
8803 Rüschlikon, Switzerland
and N. García
Departamento de Física de la Materia Condensada
Universidad Autónoma, 28049 Madrid, Spain

We have studied the adsorption of Na, K and Cs on Al(111) as a function of coverage Θ by performing self-consistent calculations on thick slabs where the local ionic pseudopotentials are first averaged parallel to the surface. As Θ is increased, the difference charge density induced by the adlayer dramatically shows electron transfer towards the substrate up to a critical $\Theta_c \sim 0.3$ ML, followed by a slower accumulation in the outer adlayer region. The work function change $\Delta\Phi$ exhibits a concomitant asymmetric minimum (in agreement with experiments). So does also the equilibrium adlayer-substrate distance, whereas the frequency ω of relative perpendicular vibrations shows a maximum and is quite low, especially for Cs This implies significant shifts and smearing of d and $\Delta\Phi$ at room temperature. Agreement with three-dimensional calculations for Na adlayers on jellium can be obtained for a reasonable choice of the alkali core radius r_c. The binding energy monotonically decreases as Θ is increased. It is rather insensitive to r_c and in reasonable agreement with the above-mentioned calculations.

Ab-initio calculations of chemisorption and diffusion of Al and Si on Al(111)

R. STUMPF, J. NEUGEBAUER and M. SCHEFFLER,
Fritz-Haber-Institut der MPG, Berlin, Germany

We studied the clean Al(111) surface and the chemisorption of Al and Si atoms at low and at high coverages (Θ = 0.1–1 ML) on this surface. We therefore used density-functional theory, a plane wave basis set for the electronic wave functions, the local density approximation for the exchange-correlation functional and ab-initio, norm-conserving, fully separable pseudopotentials. Calculating self-consistently the electronic structure, we simultaneously relaxed the adsorbate and the two top surface layers. We discuss the nature of the bonding, which is mainly covalent, and the rather large atomic relaxation around the adsorbate. The relaxations in our calculations are clearly more important than a recent article[a] about adsorption on the Al(100) surface indicates. These unexpected results have important consequences for the binding energy at different sites and for surface diffusion.

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CALCULATION OF MIGRATION ENERGIES FOR DIFFUSION ON THE Si(100) SURFACE.

G. Brocks, P.J. Kelly,
Philips Research Laboratories, 5600 JA Eindhoven, The Netherlands.

R. Car
SISSA, Trieste, Italy.

The Car-Parrinello approach to electronic structure calculations enables us to use supercells containing a sufficiently large number of atoms that we can study the interaction between adatoms and a surface in the limit where the adatom-adatom interaction is negligible. Results are presented for the binding position and the migration barriers of single Si, P or Al adatoms on the reconstructed Si(100) surface. These results are extracted from an energy surface which is constructed by calculating the total energy for a number of positions of the adatom on the surface. At each position, the total energy is minimized simultaneously with respect to the electronic charge density and all remaining (adatom and substrate) ionic degrees of freedom. The calculations are carried out within the local density approximation, using plane waves and pseudopotentials in a supercell containing 96 substrate atoms plus the adatom. We predict that, at room temperature, the diffusion of P and Si adatoms is quasi-one-dimensional in the direction parallel to the dimer rows making up the Si(100) surface. Dimers of adatoms are found to form stable structures on the Si(100) surface. The binding energy and geometry of a number of Si ad-dimer structures are calculated and their structural stability is investigated by means of ab initio molecular dynamics simulations.

Atomic Arrangement of Alkali Adatoms on Si(001)-2×1 Surface

K. KOBAYASHI, S. BLÜGEL+, K. TERAKURA
ISSP, University of Tokyo, Tokyo 106, Japan
+IFF, Forschungszentrum Jülich, D-5170 Jülich, Germany

Adsorption sites of Na and Li on the Si(001)-2×1 surface at the saturation coverage are determined theoretically by using the simulated annealing method proposed by Williams and Soler. For Na, the most stable configuration is the combination of the hollow site along the dimer chain and the trough site on top of the third layer Si atom in contradiction with an earlier calculation. The substrate relaxation is a crucial factor for stabilizing this configuration. On the other hand, Li atoms are adsorbed at low symmetry positions. For both of Na and Li, we observe a significant movement of the substrate atoms towards the ideal surface configuration.

AB INITIO MOLECULAR DYNAMICS WITH THE CONJUGATE GRADIENT METHOD : APPLICATION TO GERMANIUM

V.Yu.Milman, Xudong Weng, M.C.Payne, V.Heine, R.J.Needs
Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, UK

The use of *ab initio* Car-Parrinello type molecular dynamics (MD) simulations is playing an increasingly important role in the understanding of dynamical properties of solids and liquids. In this contribution we describe an implementation of the MD technique based on the conjugate-gradient method for electronic minimization [1]. This method differs from the original Car-Parrinello idea in that it is not necessary to introduce an artificial dynamics for the electronic degrees of freedom. Due to the high numerical stability and rapid convergence of the conjugate-gradient algorithm it was possible to introduce two different time scales for the MD simulation, performing the electronic minimization with a time step which was longer than the step used for the updating of Ewald forces on the ions.

Test MD runs were performed for germanium at temperatures close to the melting point. We used the Starkloff-Joannopoulos local pseudopotential and a Γ-point sampling for several different supercells and cutoff energies. A Nosé thermostat in Hoover's formulation was used to hold the temperature constant, and the equations of motion of the ions were integrated using the Gear predictor-corrector method. Preliminary results for structural and thermodynamic properties are in reasonable agreement with the experimental data for either liquid or amorphous germanium depending on the temperature and the prehistory of the run.

We envisage subsequent implementation of this technique with the transition state theory to obtain free energies and diffusion coefficients at low temperatures where the characteristic time for diffusion is much longer than the possible length of an *ab initio* run.

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Application of Car-Parrinello Method to Solid and Liquid Metal and Metallic Alloy Guo-Xin QIAN, M. WEINERT, G. W. FERNANDO and J. W. DAVENPORT Brookhaven National Laboratory* — We have performed first-principles molecular dynamics simulations for solid and liquid metals such as Na and Al, and for solid metallic alloy such as Al-Sn. We suggest a variable occupation scheme to solve the problem of degenerate states near fermi level. Simulations were carried out at several different temperatures for each metal. The calculated static and dynamic properties such as pair-distribution function $g(r)$ coefficient of self-diffusion D and activation energy E_a of liquid Na and Al are either in good agreement with X-ray and neutron scattering measurements or suggest further experimental verification. Furthermore, we studied a metallic alloy Al-Sn using the same technique. We have calculated its energy versus temperature in the solid phase which yields a specific heat of 3.5k_B slightly above the Dulong-Petit value of 3k_B.

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Guo-Xin Qian

Guo-Xin Qian
Department of Physics
Brookhaven National Laboratory
Upton, NY 11973
U. S. A.

Electronic and Structural Properties of Liquid Gallium

X. G. Gong[a,b], Guido L. Chiarotti[a,c], M. Parrinello[a,d], E. Tosatti[a,b]

a) International School for Advanced Studies (SISSA), Strada Costiera 11, I-34014 Trieste, Italy

b) International Centre for Theoretical Physics (ICTP), P.O. Box 586, I-34014 Trieste, Italy

c) Laboratorio Tecnologie Avanzate Superfici e Catalisi(TASC), del Consorzio Interuniversitario Nazionale per la Fisica della Materia (INFN), Padriciano 99, I-34012 Trieste, Italy

d) IBM Research Division, Zurich Forschunglaboratorium, CH-8803 Rüschlikon, Switzerland

Abstract

We have studied the high temperature (T=1000k) properties of liquid Gallium (l-Ga), by using the first principle molecular dynamics simulation [1] at three different densities (change of density is chosen instead of temperature, because of the shorter equllibration time). The structure factor S(k) and pair correlation function computed at the experimental density agree well with available experiment at T=959K [2] . Study of direct space configuration reveals that about half of Ga atoms are instantaneously engaged in a covalent bond. Of these again only half form binary bonds, while the rest form 3-atoms chains and occasionally 4-atom chains or 4-atom sp^2 "star". This offer a very instructive picture of how l-Ga mediate between the physics of solid α-Ga (binary bond) and that of β-Ga (infinite chains) [3]. As the density increase, a shoulder devoleps in S(k), similar to that observed experimentally at low temperatures. We find a direct connection between the presence of this shoulder and the proportion of chains over binary bonds which we observed at higher densities. We also provided a first *ab-initio* description of other electronic properties of liquid Ga.

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LMTO based methods for local electronic structure in substitutional and structural disorder

T Jarlborg (1), E Moroni (2), J Häglund (3) and J Sjöström (3).

(1) DPMC, University of Geneva, Switzerland
(2) IRRMA and University of Lausanne, Swizerland
(3) Royal Inst of Technology, Stockholm, Sweden

Abstract

Methods for calculations of the local electronic structure at a given site surrounded by disorder of various kinds are developed. The methods are based on the self-consistent LMTO method. In one application substitutional disorder as in alloys is considered and the local electronic structure at each constituent is obtained. The results are compared with results from LMTO super-cell calculations and with published CPA-calculations. In a second application, we consider structural disorder as in amorphous systems, in liquids or in solids at elevated temperatures. Results for Pd with disorder around the basic fcc structure are presented and compared to other calculations and to experiment. The results include exemples of density-of-states functions and total energies, and the possibe use from further development of the two methods, or from a combination of them, is discussed.

MICROSCOPIC APPROACH TO THE ATOMIC AND ELECTRONIC STRUCTURE OF TRANSITION-METAL GLASSES

CH. HAUSLEITNER AND W. JANK

Institut für Theoretische Physik, TU Wien, Wiedner Hauptstraße 8-1o, A-1o4o Wien

We present a novel hybridized NFE-TBB approach for the interatomic forces in disordered transition-metal alloys to construct realistic models for the atomic structure of amorphous alloys. These pair potentials show clearly the interrelation between short-range-order (SRO) and the shape and filling of the d-band. Here we present calculations of the atomic and electronic structures of amorphous transition-metal alloys at the example of Ni_xZr_{1-x} (x=o.35, o.5o, o.65) based on molecular dynamics simulations, supercell-electronic structure calculations, and on a single-scatterer final-state approximation for the photoemission spectra.

Effect of disordered *Ba* addmixture upon pre-Fermi electron spectra and constant energy surfaces in high-T_c oxide $La_{2-x}Ba_xCuO_4$

A.V.Zhalko-Titarenko, V.V.Nemoshkalenko, S.N.Chernukhin
L.M.Sheludchenko

As it was previously experimentally established by Simonov at al., high-Tc oxide of interest demonstrate superconductivity at $x=0,12$ only when admixture is disordered . Thus one can not expect to adequately describe its electronic structure via traditional band-structure approach. We have carried cut cluster calculation for perovskite sub cells of its structure, containing both *La* and *Ba* atoms. Cluster level half - width was adjusted to band-structure data for $x=0$, and was treated as proportional to x for $x\neq 0$. For $x\neq 0$ electronic structure was treated as weighted admixture of correspondent broaden *La*- and *Ba*- containing cluster energy levels. Calculation results allowed us to state, that for optimal $x=0,12$ $La_{2-x}Ba_xCuO_4$ electron spectra demonstrate a sharp oxygen peak in a close vicinity of Fermi level with energy less, than phonon limiting frequency. This peak is dominantly formed by *La* layer oxygen. Pre-Fermi constant energy surfaces where evaluated via Fourier transformation of real-space charge density. There where not found any pronounced changes in its structure due to disordered *Ba* addition exactly at E_F.

AUTHOR INDEX