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Research Workshop on Computational
Condensed Matter Physics:

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**Total Energy Methods
and
Physics of III-V Semiconductors**

January 4th - 6th, 1990

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Auditorium Jacques Monod, Tour 42 , ground floor
Université P. et M. Curie, 4 pl. Jussieu, Paris, France

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Research Workshop on Computational
Condensed Matter Physics:

**Total Energy Methods
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PREFACE

The present workshop continues the series of meetings on Computational Solid State Physics initiated in Oxford (1983) and followed since then by reunions in Braunschweig, Trieste, Glion and, again, Trieste (January 1989). It covers the field of total energy calculations (essentially the density functional method), pseudopotential theory and the Car-Parrinello method.

The purpose of the meeting is to review the recent theoretical developments and to discuss the most interesting applications - those pertinent to the III-V compounds and new materials were retained for this workshop. The Quantum Monte Carlo techniques for treating correlation effects, which also fall within the scope of the series, are absent from this year's program.

Because of the precisely defined subject and small size of the meeting, ample time has been reserved for discussion. I hope that all participants will bring - and get - many new ideas.

Karel Kunc

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University of P. and M. Curie, Paris

PROGRAM

Thursday, January 4th, 1990 (A.M.)

9:00 REGISTRATION

12:00 Lunch

Thursday, January 4th, 1990 (P.M.)

14:00 Welcome and information

K. Kunc

14:05 Computational Solid State Physics: Present State and Future Trends

Chairman: F. Herman

14:05 M. L. Cohen (30 min): Predicting new solids and superconductors

14:35 Discussion (10 min)

14:45 A. R. Williams (20 min): Massively Parallel Computation and Science

15:05 Discussion (10 min)

15:15 **Coffee break** (Tour 43, 5th floor);

Interactions with administration (T.C., 16th floor)

16:00 Fundamental properties of III-V semiconductors deriving from the electronic ground state

Chairman: O. H. Nielsen

16:00 A. Morita (20 min.): Crystal structure and phonon frequencies of black phosphorus under pressure

16:20 Discussion (10 min.)

16:30 K. J. Chang (20 min): Total energy calculations for hydrogen in crystalline Si and GaAs

16:50 Discussion (10 min.)

17:00 R. J. Needs (20 min.): A first-principles calculation of the temperature dependence of the indirect band gap of silicon

17:20 Discussion (10 min.)

17:30 J. Kudrnovský (20 min.): The electronic structure of random $A^{III}B^V$ and $A^{II}B^VI$ semiconductor alloys by tight-binding linear muffin-tin orbital method

17:50 Discussion (10 min.)

18:00 R. Resta (20 min) Absolute deformation potentials in semiconductors

18:20 Discussion (10 min.)

18:30 **Break**

Friday, January 5th, 1990 (A.M.)

9:00 Density-Functional Molecular Dynamics (Car-Parrinello method)

Chairman: R. Car

9:00 W. Andreoni (20 min.): Electronic and structural properties of III-V compound microclusters

9:20 Discussion (10 min.)

9:30 M. C. Payne (20 min.): A conjugate gradients method that works

9:50 Discussion (10 min.)

10:00 R. M. Martin (20 min.): The nature of carbon: electronic calculations on solid and liquid phases

10:20 Discussion (10 min.)

10:30 Coffee break (Tour 43, 5th floor)

10:50 III-V Superlattices and Interfaces

Chairman: S. Baroni

10:50 B. Jusserand (20 min.): Current problems in the superlattice lattice dynamics

11:10 Discussion (10 min.)

11:20 A. Qteish (20 min.): Calculations of the electronic structure of highly strained GaAs-GaSb heterostructures

11:40 Discussion (10 min.)

11:50 E. Molinari (20 min.): Phonon spectra of ultrathin GaAs/AlAs superlattices from density-functional linear-response theory

12:10 Discussion (10 min.)

12:20 Lunch break

Friday, January 5th, 1990 (P.M.)

14:00 New materials: High-Tc Superconductors, Magnetic layers

Chairman: O. K. Andersen

14:00 F. Herman (20 min.): Electronic and magnetic structure of novel multilayers and interfaces

14:20 Discussion (10 min.)

14:30 C. O. Rodriguez (20 min.): Ab initio study of lattice dynamical properties of La_2CuO_4 and $\text{YBa}_2\text{Cu}_3\text{O}_7$

14:50 Discussion (10 min.)

15:00 M. Schlüter (20 min.): The electronic structure of La_2CuO_4 : renormalization from density functional theory to strong coupling models

15:20 Discussion (10 min.)

15:30 **Coffee break** (Tour 43, 5th floor);
Interactions with administration (T.C., 16th floor)

16:15 Ab initio Chemistry

Chairman: M. Scheffler

16:15 M. Karplus (30 min.): Dynamics on quantum / classical potentials

16:45 Discussion (10 min.)

16:55 J. Hafner (20 min.): Structural and electronic properties of the molten elements: pseudopotential perturbation theory vs. first-principles density-functional molecular dynamics

17:15 Discussion (10 min.)

17:25 R. Dovesi (20 min.): Ab initio Hartree-Fock LCAO total energy calculations for periodic compounds. Application to III-V semiconductors and ionic crystals.

17:45 Discussion (10 min.)

17:55 E. Wimmer (20 min.): Density-functional Gaussian-type orbital approach for total energy and force calculations of large, aperiodic systems

18:15 Discussion (10 min.)

18:25 **Break**

Saturday, January 6th, 1990 (A.M.)

9:00 Pseudopotentials: The latest developments

Chairman: V. Heine

- 9:00 S. Froyen (20 min.): How accurate are first-principles pseudopotentials?
9:20 Discussion (10 min.)
- 9:30 X. Gonze (20 min.): Problems with Kleinman and Bylander potentials?
9:50 Discussion (10 min.)
- 10:00 J. D. Joannopoulos (20 min.): Optimized pseudopotentials
10:20 Discussion (10 min.)
- 10:30 D. Vanderbilt (20 min.): Soft self-consistent pseudopotentials in a generalized eigenvalue formalism
10:50 Discussion (10 min.)

11:00 Coffee break (Tour 43, 5th floor)

11:20 Semiconductor Surfaces

Chairman: R. J. Needs

- 11:20 S. Ciraci (20 min.): Calculations of current between two electrodes
11:40 Discussion (10 min.)
- 11:50 F. Ancilotto (20 min.): Surface phonons from ab initio molecular dynamics : Si (111) 2 x 1
12:10 Discussion (10 min.)

12:20 Closing Session

Chairman: A. Baldereschi

- 12:20 R. M. Martin (20 min.): Conference Summary
12:40 Discussion (5 min.)
- 12:45 K. Kunc (2 min.): Closing the Workshop

12:47 End

**ABSTRACTS
OF TALKS**

PREDICTING NEW SOLIDS AND SUPERCONDUCTORS

Marvin L. COHEN

Department of Physics, University of California
Materials and Chemical Sciences Division, Lawrence Berkeley
Laboratory, Berkeley, California 94720, USA.

One of the breakthroughs in condensed matter physics is the newly acquired ability of theorists to explain and predict properties of solids using quantum theory. Starting with minimal information about the constituent atoms, accurate calculations of electronic, structural, vibrational, and even superconducting properties of solids have been performed. The discussion will provide an overview of this area with emphasis on the predictive capacity of the approach.

Applications include the analysis of high pressure structures of solids such as group IV and III-V semiconductors, metallic hydrogen, and compounds having very low compressibilities. A pseudopotential approach is used in most of the above applications. In some cases empirical theories and scaling laws are employed as a guide to facilitate the investigation of trends in material properties. Specific compounds are suggested as candidates for superhard materials and new superconductors.

Handwritten notes:
2. Kohn-Sham method
3. pseudopotential method
4. band structure calculations
5. phonon calculations
6. superconductivity

MASSIVELY PARALLEL COMPUTATION AND SCIENCE

A.R. WILLIAMS

Thinking Machines Corp., Cambridge, MA 02142 - 1214, USA.

Massively parallel computers are the fastest computers available today. More importantly, they represent the only known path to significantly greater performance in the future. It is therefore very likely that such machines will become, to an ever increasing extent, the numerical laboratories of science.

The Connection Machine built by Thinking Machines is particularly well suited to the solution of partial differential equations, such as the Schrodinger equation. The Connection Machine achieves its multiple GIGAFLOP performance using thousands of individual processors performing the same operation on different data elements simultaneously. The fundamental appropriateness of such machines to the solution of partial differential equations reflects the fact that the differential equation represents identical code which must be executed for the different data elements, the solution and the potential, at the many spatial (or transform variable) points in the domain of interest. The fact that the differential aspect of the equation requires very limited communication among the processors is an additional bonus.

The talk will include illustrative examples of the solution of partial differential equations on the massively parallel Connection Machine. These machines and high-level languages for them, like FORTRAN, have been available only recently. The early applications offer lessons for this rapidly emerging field.

CRYSTAL STRUCTURE AND PHONON FREQUENCIES OF BLACK PHOSPHORUS UNDER PRESSURE

A. MORITA¹, K. SHIBATA² and K. SHINDO³

¹ Dept. of Basic Science, Ishinomaki Senshu Univ., Ishinomaki 986, Japan.

² Dept. of Electronic Systems, Aomori Polytechnic College, Goshogawara 037, Japan.

³ Dept. of Humanities and Social Science, Iwate Univ., Morioka 020, Japan.

Black phosphorus is the most stable allotrope of phosphorus at normal pressure and is a narrow-gaped semiconductor with an orthorhombic layered structure. Its properties at normal pressure has been investigated widely experimentally and theoretically.

Black phosphorus also shows various interesting behaviors under high pressure. Its crystal structure changes into the semimetallic rhombohedral (A7) phase at about 5.5GPa and into the metallic sc phase at about 10GPa, which is reported to exist stably even at 60GPa.

In the orthorhombic phase of black phosphorus, the linear compressibility along the [100] direction in the layer plane is almost equal to the one of the [001] direction perpendicular to the layer plane, while the one along the [010] direction is essentially zero, and the pressure slopes of the lattice constants and internal structural parameters show anomaly at about 2GPa. In the phase, with increasing pressure, though most of phonon frequencies increase, the zone edge phonon in the $A7_{\gamma}$ [001] branch seems to show saturation of its hardening for pressure higher than 1.5GPa and the $A1_{\gamma}$ [100] branch shows unexpected softening.

There are several theoretical investigations of the structural stability of black phosphorus. But any comprehensive theoretical study of the properties of black phosphorus under pressure mentioned above has not yet been reported.

In this report we present the results of our *ab initio* pseudopotential calculations about orthorhombic phosphorus under pressure. The cohesive energy, bulk modulus, pressure derivative of bulk modulus, lattice constants and internal structural parameters as a function of atomic volume, and also energies of various phonon modes as a function of atomic volume are calculated and compared with experiments. We also investigate the relative stability of the orthorhombic phase with the A7 and sc phases.

TOTAL ENERGY CALCULATIONS FOR HYDROGEN IN CRYSTALLINE Si AND GaAs

K.J. CHANG

Department of Physics, Korea Advanced Institute of Science and
Technology, P.O. Box 150, Chongryang, Seoul, Korea.

Using an *ab initio* total-energy-pseudopotential method, the nature of hydrogen bonding and diffusion in bulk crystalline Si and GaAs is investigated. For various interstitial positions, the relative energies of atomic hydrogen, diatomic hydrogen complexes, and shallow dopant-hydrogen complexes are examined. For passivated dopant-H complexes, similar atomic structures are found between Si and GaAs; a bond-center model and an anti-bonding site geometry for H provide the most stable configurations in *p*-type and *n*-type samples, respectively. However, there exists some difference in hydrogen bonding that for acceptor-H complexes the H atom in GaAs is more strongly bonded to one of the acceptor neighboring atoms than to the acceptor while a strong interaction between the acceptor and H atoms exists in Si. For donor-H complexes, both the bulk Si and GaAs show bond-breaking displacements for the atom adjacent to H, which is substantially displaced towards its interstitial position from the substitutional site. Despite the passivated complexes are the same Si-H bonds for hydrogenated Si and GaAs doped with P (or As) and Si, respectively, the donor atom itself is displaced in GaAs while the [111] neighboring Si atom of the donor takes place the same displacement in Si. For the stable dopant-H complexes, the calculated hydrogen vibrational frequencies are in good agreement with available experimental data. The calculations are also extended to the passivation of deep DX centers by hydrogen in AlGaAs alloys. Recently, Chadi and Chang proposed a negatively-charged state model for DX centers. The present results suggest that the H passivation occurs via the reaction of $DX^- + d^+ + 2H \rightarrow 2(dH)^0$, where *d* and DX denote a shallow donor and a deep DX center, respectively. For hydrogen diffusion, two modes involving monatomic hydrogen and hydrogen diatomic-complexes are examined. Hydrogen atom is found to behave as a weak negative-*U* center in Si. For the diffusion mode dominated by atomic species, hydrogen diffuses as an ionized H^+ and charged H^- in *p*-type and *n*-type samples, respectively. However, in *n*-type materials, the diffusion via the formation of diatomic complexes is found to be energetically more stable, thus its diffusion is highly expected.

A FIRST-PRINCIPLES CALCULATION OF THE TEMPERATURE DEPENDENCE OF THE INDIRECT BAND GAP OF SILICON

**R.D. KING-SMITH, R.J. NEEDS, Volker HEINE and M.J.
HODGSON**

Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, U.K.

We have evaluated the contribution to the temperature dependence of the indirect band gap of silicon arising from electron-phonon interactions. All quantities are computed from first principles using the total energy pseudopotential method; the calculation is performed without recourse to either phonon models or the rigid ion approximation. Our calculation is formulated within Brooks-Yu theory, which gives the electron-phonon interaction energy and the temperature dependence of the band gap in terms of the changes in the phonon frequencies induced by the excitation of a single electron across the band gap. Numerical results are in reasonable agreement with experiment. Our calculations show that, at high temperatures, each phonon branch gives approximately the same contribution to the temperature dependence of the band gap. We find that the *degree of phonon softening* caused by the excitation of an electron across the gap is a strong function of phonon wavevector.

THE ELECTRONIC STRUCTURE OF RANDOM A^{III}B^V AND A^{II}B^{VI} SEMICONDUCTOR ALLOYS BY TIGHT-BINDING LINEAR MUFFIN-TIN ORBITAL METHOD

J. KUDRNOVSKÝ^{1,3}, V. DRCHAL¹, M. ŠOB²,
N.E. CHRISTENSEN³ and O.K. ANDERSEN³

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² Institute of Physical Metallurgy ČSAV, Zizkova 22, 616 62 Brno,
CSSR.

³ Max-Planck-Institut FKF, Heisenbergstrasse 1, D-7000
Stuttgart, FRG.

We present a new approach for calculating the electronic structure of substitutionally disordered semiconductor alloys $A_xB_{1-x}C$. Our approach combines the tight-binding (TB) linear muffin-tin orbital (LMT0) method with empty interstitial spheres to describe the electronic structure of open structure materials, the coherent potential approximation (CPA) to treat the alloy disorder and Löwdin downfolding to establish the minimal basis character of the method inherent to empirical theories.

The TB-LMT0 Hamiltonian in the orthogonal LMT0-representation is defined on the bcc lattice with halved lattice constant, divided into four interpenetrating fcc sublattices. The zinc-blende, rock-salt or fluorite semiconductor alloys then differ only by arrangements of cations, anions and empty spheres on fcc sublattices. The differences in AC and BC bond lengths are modelled via variations of AC and BC hopping matrix elements.

The CPA averaging is done in a suitably chosen LMT0-representation, where it can be done without limitations inherent to empirical TB-CPA theories, and the results are consequently transformed back to the original, physical LMT0-representation.

The set of 36 orbitals (the s-, p-, d-states on each sublattice) is for a chosen energy range and for a given material partitioned into lower and higher subsets. The former one, constituting the minimal basis, is treated exactly while the latter one is approximated, but without the loss of accuracy in a chosen energy range. This is done in a suitably chosen LMT0-representation for higher states.

The theory allows the generalization to alloy surfaces or superlattices using the surface Green's function method. Its feasibility is illustrated for (Cd, Hg)Te and (Pb, Cd)F₂ random alloys.

ABSOLUTE DEFORMATION POTENTIALS IN SEMICONDUCTORS

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² SISSA, Strada Costiera 11, I-34014 Trieste, Italy.

The absolute position of a given energy level in an infinite solid is ill defined since it depends on the arbitrary choice of the zero of the electrostatic potential; in any finite system this zero is well defined, but it depends on shape and surface effects. This implies that the *absolute* deformation potentials (ADP's) for uniform strain are possibly ill defined. There is indeed much interest in the ADP's, since the band-offsets in strained superlattices crucially depend on them; furthermore some intriguing measures of the ADP's under homogeneous strain have been published. On the theoretical side, an important step forward has been recently made¹ by mapping this problem onto an equivalent band-offset problem at an ideal strained/unstrained homojunction. Here we outline the complete solution of the problem.

Only the potential *difference* between two regions of the solid is well defined. These regions can be joined without misfits if the system is *periodic* in the planes parallel to a given direction: we therefore specialize to the case where, for a given *arbitrary* axis \hat{n} , the uniaxial strain $\epsilon_{\alpha\beta} = \epsilon n_\alpha n_\beta$ is present, but this strain is inhomogeneous. The potential drop between two regions in different strain states is well defined, and the issue we address here is whether or not this drop is a function of the local strain only. Our answer is negative for a polar crystal, while it is affirmative for some nonpolar ones. The basic ingredients of the theory are the long-range fields linearly induced by unit displacements of individual atoms: to leading order these are—in a dielectric—either dipolar (in polar lattices), quadrupolar (in the diamond lattice), or octupolar (in Bravais lattices). We prove that the ADP for a given direction of the uniaxial strain is a well defined bulk property of the crystal if (and only if): (i) the dipoles vanish individually; (ii) the sum of the quadrupoles over the unit cell vanishes. Both conditions are fulfilled in the diamond lattice and in Bravais lattices.

Our result for a cubic material is that the (uniaxial) ADP depends on two independent parameters and has the form $C_1 + C_2 f(\hat{n})$, where the explicit \hat{n} dependence is embedded in the geometrical factor $f(\hat{n}) = 3(1 - \sum_\alpha n_\alpha^4)/2$, varying between 0 (001 direction) and 1 (111 direction). We calculate the C constants for bulk Si and Ge using state-of-the-art density functional theory and norm-conserving pseudopotentials. Our results are compared with existing experiments, with previous ADP calculations¹, as well as with some preliminary calculations of the band offsets at strained Si/Ge heterojunctions.

[1] C.G. Van de Walle and R.M. Martin, Phys. Rev. Lett. **62**, 2028 (1989).

ELECTRONIC AND STRUCTURAL PROPERTIES OF III-V COMPOUND MICROCLUSTERS

Wanda ANDREONI

**IBM Research Division, Zurich Research Laboratory, 8803
Rüschlikon, Switzerland.**

Selected microclusters of GaAs, AlAs and GaP are studied using the Car-Parrinello method. Equilibrium structures determined via simulated annealing are compared with those found for silicon and germanium with the same techniques. The temperature dependence of structural and electronic properties is also investigated.

A CONJUGATE GRADIENTS METHOD THAT WORKS

M.C. PAYNE¹, M.P. TETER^{2,3} and D.C. ALLAN²

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In this talk three different approaches to performing total energy pseudopotential calculations will be described. The difficulties associated with the instability in the electronic screening will be discussed with particular emphasis on the problems encountered in achieving self-consistency in each of the approaches. The first approach, typified by conventional matrix diagonalisation methods, consists of searching for a self-consistent charge density by mixing 'old' and 'new' charge densities. In this approach the self-consistent Kohn-Sham eigenstates are never obtained and there can be considerable errors in the computed Hellmann-Feynman forces. In the second approach, typified by Car and Parrinello's molecular dynamics method¹, the self-consistent Kohn-Sham eigenstates are obtained directly. Methods based on this approach are a considerable improvement over methods based on conventional matrix diagonalisation techniques. However, these methods do not overcome the self-consistency problem but merely introduce a parameter that can be adjusted to control the instability in the electronic screening. In the case of the molecular dynamics method this parameter is the timestep. The self-consistency problem is the biggest obstacle to performing total energy calculations on extremely large systems and any technique that does not directly address this problem, such as the conjugate gradients method of Stich et al.², will be limited in its power. The third approach to total energy calculations is based on the direct minimisation of the Kohn-Sham energy functional. It will be shown that there is no instability in the electronic screening when this approach is adopted. A conjugate gradients method³ based on this approach will be described. This method should allow total energy pseudopotential calculations to be performed for systems containing hundreds of atoms.

1. R. Car and M. Parrinello, Phys.Rev.Lett. **55** 2471 (1985).

2. I. Stich, R. Car, M. Parrinello and S. Baroni, Phys.Rev. **B39** 4997 (1989).

3. M.P. Teter, M.C. Payne and D.C. Allan, submitted to Phys.Rev. B (1989).

THE NATURE OF CARBON : ELECTRONIC CALCULATIONS ON SOLID AND LIQUID PHASES

Richard M. MARTIN¹, Giulia GALLI¹, Roberto CAR² and
Michele PARRINELLO^{2,3}

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² International School for Advanced Studies, 34014 Trieste, Italy.

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The propensity of carbon to bond with two- three- and four-fold coordination leads its great diversity of forms, including graphite, diamond, and disordered films whose properties span the range between these two crystalline forms. Electronic structure calculations using the local density functional approximation have previously been shown to describe accurately the different bonding in the crystalline forms. Here we describe results on complex forms including simulations of the liquid at high temperatures using the combined molecular dynamics - density functional techniques pioneered by Car and Parrinello[1]. These can accurately simulate thermal atomic motion in solid and liquid phases, with the electrons treated quantum mechanically to properly describe the complex bonding. We have used these methods to determine the radial density distributions, typical local structures, and electronic properties of both liquid and quenched amorphous states [2] and have preliminary results on melting under pressure. The results discussed in this talk will concentrate upon the least understood state of carbon, the liquid state which exists only above 4500K. We will discuss the nature of the liquid at low pressure, for which there are many speculations but little knowledge; e.g., and two recent experimental works have come to opposite conclusions on whether the liquid is metallic or insulating. We will also describe preliminary results on diamond melting at high pressures that indicate an increase in the melting temperature with pressure, which is opposite to the behavior of Si and Ge and has possible important implications for geophysics.

1. R. Car and M. Parrinello, Phys. Rev. Lett. 55, 2471 (1985).

2. G. Galli, R. M. Martin, R. Car and M. Parrinello, Phys. Rev. Lett. 62, 555 (1989) and 63, 988 (1989).

CURRENT PROBLEMS IN THE SUPERLATTICE LATTICE DYNAMICS

Bernard JUSSEMAND

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Bagneux, France.

The lattice dynamics of GaAs/AlAs superlattices with perfect interfaces is now well understood. However the effect of interface roughness onto the frequency of the confined optical vibrations remains an open problem. I will present Raman scattering results giving evidence of the strong perturbation experienced by the phonons confined in thin GaAs layers due to interface roughness. I will analyse semiquantitatively the respective roles of the extension of the roughness along the superlattice axis and of its lateral scale.

In other systems, like Si/Ge and GaAs/InAs superlattices, the lattice mismatch is very large and interface roughness is more likely to appear than in the model GaAs/AlAs system. Moreover a detailed understanding of superlattice vibrations in these systems requires the knowledge of the bulk phonon dispersion curves under strain which is not presently available. This prevented us to get a quantitative description of our results on InAs/GaAs superlattices which nevertheless unambiguously support the existence of a large but rough modulation in this system.

CALCULATIONS OF THE ELECTRONIC STRUCTURE OF HIGHLY STRAINED GaAs-GaSb HETEROSTRUCTURES

A. QTEISH and R. J. NEEDS

Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK.

The band offsets at the highly strained GaAs-GaSb (7 % lattice-mismatch) and the lattice matched GaAs-AlAs interfaces have been determined using self-consistent pseudopotential techniques. The linear and non-linear deformation potentials of GaSb under uniaxial strain along the $[001]$ direction and under hydrostatic pressure have also been calculated. The valence band offset at the ideal GaAs-GaSb interface is predicted to be 1.1 eV with the strained GaSb valence band being higher in energy. The confinement energy of the first heavy-hole state, in a well of width 15 Å, is estimated to be 0.3 eV. Given that the band gap of GaAs is 1.5 eV, it follows that the lowest direct optical transition at Γ is 0.7 eV, which is considerably smaller than the value of 1.3 eV obtained in recent experiments. We conclude that this discrepancy is due to the incorporation of As atoms in the GaSb region in the experimental samples.

PHONON SPECTRA OF ULTRATHIN GaAs/AlAs SUPERLATTICES FROM DENSITY-FUNCTIONAL LINEAR-RESPONSE THEORY

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Trieste, Italy.

² IRRMA-Institut Romand de Recherche Numérique en Physique
des Matériaux, Lausanne, Switzerland.

³ CNR, Istituto "O.M. Corbino", Roma, Italy.

The phonon spectra of ultrathin $(GaAs)_n(AlAs)_n$ (001) superlattices (SL's) are studied from first principles using linear-response density-functional techniques. Results are presented for ideally ordered SL's with $n = 1, 2, 3$, along with prototype supercell calculations aimed at simulating some completely and partially disordered structures. The full dispersions of bulk *GaAs* and *AlAs* along all high-symmetry directions are also calculated, in order to relate SL modes with the spectra of their constituents.

Our results for bulk *GaAs* are in excellent agreement with neutron scattering data. In the case of bulk *AlAs*, experimental information is very poor; for this compound, our results — which are the first *ab-initio* predictions— indicate that the LO branch is much flatter in the $\Gamma - X$ direction than in other directions, contrary to expectations from phenomenological models. The reliability of such predictions is supported by the fact that we obtain very similar results for the closely related *AlSb* compound, in excellent agreement with recent neutron scattering measurements.

The calculated spectra for superlattices are compared with experimental data by several groups. We conclude that the Raman spectra of ultrathin samples in the LO range cannot be explained without assuming a substantial substitutional disorder affecting even inner cationic planes. In particular, we show that —due to the anisotropy of the bulk *AlAs* dispersion and to its large LO-TO splitting— superlattice *AlAs*-like LO modes are very sensitive to wavevector-mixing induced by disorder in the cationic sublattice, and their study is of relevance for characterization purposes.

Finally, we demonstrate that a very accurate description of the vibrational properties of both ordered and disordered structures of *GaAlAs* can be obtained by using *ab-initio* interatomic force constants calculated for the virtual crystal, and treating the difference between *Ga* and *Al* ions just through their difference in masses. This result is of special importance in order to perform systematic studies on the role of substitutional disorder in the vibrational properties of very large unit cell systems.

ELECTRONIC AND MAGNETIC STRUCTURE OF NOVEL MULTILAYERS AND INTERFACES

Frank HERMAN¹ and Mark van SCHILFGAARDE²

¹ IBM Almaden Research Center, San Jose, CA 95120, USA.

² SRI International, Menlo Park, CA 94025, USA.

We will review some recent developments in the study of the electronic and magnetic properties of heterostructures involving semiconductors, transition metals, and rare earths. The major part of our talk will be concerned with metallic multilayers^{1,2} such as Co/Cr and Fe/Cr, which exhibit striking magnetic properties. These include giant magnetoresistance effects in magnetic layered structures having antiferromagnetic coupling.³ We will discuss recent theoretical studies of magnetic multilayers^{4,5} and point out the role that spin-polarized electronic structure and total energy calculations can play in clarifying the nature of spin arrangements and electronic transport mechanisms at such interfaces.

1. P. Lambin and F. Herman, *Phys. Rev. B* **30**, 6903 (1984).
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3. M. Baibich et al, *Phys. Rev. Lett.* **61**, 2472 (1988).
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AB-INITIO STUDY OF LATTICE DYNAMICAL PROPERTIES La_2CuO_4 AND $\text{YBa}_2\text{Cu}_3\text{O}_7$

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The phonon frequencies, and mode-Grüneisen parameters at selected high symmetry points together with structural related properties of La_2CuO_4 and $\text{YBa}_2\text{Cu}_3\text{O}_7$ are calculated from first principles within the local density functional formalism. The full potential linear muffin tin orbital (FP-LMTO) method was used and special attention was paid at the Brillouin zone integration. The results are in good agreement with experiment. The electronic energy bands and wavefunctions at the fermi surface, as well as their deformation due to the frozen phonon displacements, are presented and discussed.

THE ELECTRONIC STRUCTURE OF La_2CuO_4 : RENORMALIZATION FROM DENSITY FUNCTIONAL THEORY TO STRONG COUPLING MODELS

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Starting from a realistic quantum-chemical description of the Cu-O based superconductors, strong coupling models, appropriate for small energy scales are derived in subsequent renormalization steps. We take as starting point the Density Functional approach, which accurately describes the cohesive properties of materials like La_2CuO_4 . The results are analyzed and mapped onto a multiband Hubbard Hamiltonian using the method of constrained charge fluctuations. One extracts a complete set of numerical parameters representing specific features of the Cu-O planes. A variety of experiments probing high (1-10 eV) energies are well described. In a second renormalization step finite clusters are exactly diagonalized and the low (≤ 2 eV) energy results are mapped onto effective one-band models. The insulating phase is well described by a Heisenberg model with excitation energies in excellent agreement with experiment. Finally, effective one-band models are found to describe the spectral features in the presence of added carriers (electrons or holes). The specific values for the parameters of these models have implications for possible descriptions of the superconducting state.

(In collaboration with M. S. Hybertsen, E. B. Stechel and D. W. Jennison.)

DYNAMICS ON QUANTUM/CLASSICAL POTENTIALS

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Molecular dynamics simulations of large systems making use of
combined quantum mechanical and classical mechanical potentials will
be discussed and illustrated by examples.

STRUCTURAL AND ELECTRONIC PROPERTIES OF THE MOLTEN ELEMENTS : PSEUDOPOTENTIAL PERTURBATION THEORY VS. FIRST-PRINCIPLES DENSITY-FUNCTIONAL MOLECULAR DYNAMICS

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The structural and electronic properties of the liquid s,p-bonded elements are discussed in terms of (a) classical molecular dynamics based on effective pair- and volume forces derived from pseudopotential perturbation theory and dynamical simulated annealing and (b) first-principles density-functional molecular dynamics calculations. We concentrate on (a) the trend from close-packed metallic structures in groups I to III to open, more covalent structures in groups IV to VI of the Periodic Table, and (b) the return to more metallic structures in the heavy elements of groups IV to VI, most pronounced in the series Si - Ge - Sn - Pb.

Somewhat surprisingly these trends are rather well described by pseudopotential perturbation theory: coordination numbers, bond distances, and bond-angles are predicted with good accuracy - only in the molten chalcogenides significant differences of the calculated correlation functions with experiment are observed. A detailed comparison of these results with published DF-MD calculations for l-Si and l-As and with new DF-MD results on l-Te shows that the differences in the structural properties are mainly in the higher-order correlation functions: for l-As perturbation and ab-initio calculations predict a slightly different orientational correlation between the flattened trigonal As-pyramids which also constitute the puckered layers of the crystalline As-structure, in l-Te perturbation theory predicts an essentially random distribution of the dihedral angles, whereas the ab-initio calculations suggest that adjacent bonds are correlated in a way similar to that in the helical chains of the trigonal Te-structure. In the electronic density of states the perturbation calculations lead to a shallower pseudo-gap at the Fermi-edge than the ab-initio calculations.

The comparison of both series of calculations results in a rather simple picture for the driving electronic mechanism behind the structural trends.

AB-INITIO HARTREE-FOCK LCAO TOTAL ENERGY CALCULATIONS FOR PERIODIC COMPOUNDS : APPLICATION TO III-V SEMICONDUCTORS AND IONIC CRYSTALS

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The state of the art of the periodic Hartree-Fock LCAO technique is illustrated with reference to CRYSTAL, the ab initio program implemented by the author and collaborators [1,2].

All electron results (binding energy, lattice parameter, bulk modulus and optical phonon frequency) are reported for diamond, silicon, BN, BP, AlP, SiC. Standard molecular basis sets are adopted; only the exponent of the outer valence gaussian has been reoptimized in the solid. Both the lattice parameter and the bulk modulus are systematically overestimated, on average by 1% and 10%, respectively. A posteriori corrections through correlation-only functionals [3] are applied to the Hartree-Fock total energy; the resulting mean error on the binding energies is 2%. A larger set (17) of III-V semiconductors is under study by using standard pseudopotentials[4]; pseudopotential and all electron results are compared.

Some examples of total energy calculations for other classes of compounds are reported and concern: elastic constants of simple ionic crystals (Li_2O , MgO), geometry optimization in α -quartz, intermolecular energy in crystalline urea.

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DENSITY-FUNCTIONAL GAUSSIAN-TYPE ORBITAL APPROACH FOR TOTAL ENERGY AND FORCE CALCULATIONS OF LARGE, APERIODIC SYSTEMS

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Plane-wave based methods have proven to be extremely useful and accurate in the description of solid-state systems such as transition metals and their surfaces. However, systems like large metal clusters or structures that contain both short bond distances and large open spaces such as molecules reacting with metal surfaces require different approaches. In this contribution, we discuss an implementation of density functional theory using Gaussian-type orbitals and computationally highly efficient algorithms. In the present approach, integrals are evaluated using a modified Obara-Saika scheme, electron densities are calculated via a fitting procedure involving only analytical integrals, and the exchange-correlation contribution is obtained via numerical integration on an adaptive grid. It is shown how the forces can be obtained from derivatives of three-center integrals which in turn can be readily calculated by the same scheme as used in the SCF part. Although the number of integrals scales only with a third power in the number of basis functions, a direct SCF scheme which avoids external storage of the integrals becomes attractive even for a moderate size of the basis set. The code is implemented in a highly parallel fashion thus achieving sustained 1 GFLOPS on an 8-processor CRAY Y-MP machine. The applicability of this method is demonstrated for Zn clusters as well as for the structure of water molecules in a large fragment of a Zn-insulin crystal.

HOW ACCURATE ARE FIRST-PRINCIPLES PSEUDOPOTENTIALS ?

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Using α -Sn as an example we compare several different pseudopotential calculations to all-electron (full potential) calculations. We find that lattice constants and electronic energy levels differ by as much as 2.7 % and 0.33 eV, respectively. These differences are larger than what might be expected based on standard atomic pseudopotential tests. However, we find that a new test, comparing compressed pseudo-atoms and all-electron atoms, is able to discriminate between the various potentials.

PROBLEMS WITH KLEINMAN AND BYLANDER POTENTIALS ?

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A few years ago, an interesting type of non-local pseudopotential has been proposed by Kleinman and Bylander (Phys.Rev.Lett.**48**, 1425 (1982)). However, up to now, its use has been very scarce. While calculations are much faster than with the usual form, the Kleinman and Bylander (KB) pseudopotentials sometimes generate "ghosts bands" and instabilities, which then can cause unphysical results in self-consistent calculations of polyatomic systems. Similar difficulties are to be expected also for other fully-non-local potentials, as for example those recently proposed by D.Vanderbilt.

Our short communication describes the identification of the difficulties associated with fully-non-local potentials, which has been performed by two different techniques : a spectral approach, and an analysis of logarithmic derivatives. It is suggested how the problems can be cured.

In particular we present an analysis of KB pseudopotentials for Se, Ga and As and discuss eigenenergies as well as total energies for the GaAs crystal.

OPTIMIZED PSEUDOPOTENTIALS

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An atomic criterion is identified that characterises the convergence of the total energy of a solid with respect to a plane-wave basis set. Using this criterion, tractable norm-conserving pseudopotentials can be generated, for the first time, for transition metals and first-row non-metals.

SOFT SELF-CONSISTENT PSEUDOPOTENTIALS IN A GENERALIZED EIGENVALUE FORMALISM

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A new approach to the construction of first-principles pseudopotentials is described. The pseudopotential is constructed at the outset to be fully non-local (i.e., non-local in both radial and angular variables). It has the following desirable properties. (i) It takes the form of a sum of a few separable terms. (ii) It becomes local and vanishes outside the core. (iii) The scattering properties and their energy derivatives are by construction correct at several energies spanning the range of occupied states, and the transferability can be systematically improved by increasing the number of such energies. (iv) The norm-conserving constraint is removed, so that the pseudo wavefunction can be constructed in such a way as to optimize smoothness. (v) The pseudopotential itself becomes involved in the self-consistent screening process, thereby improving transferability with respect to changes in charge configuration. Together, these features allow the cutoff radius to be increased without sacrificing transferability, even for "problem" cases such as $2p$ and d orbitals. The price to be paid for these desirable features is that a generalized eigenvalue problem is introduced. However, for iterative or Car-Parrinello type solutions of the solid state Schroedinger equation, the operation count is hardly increased. Tests of the pseudopotentials for oxygen, copper, and other systems will be presented.

CALCULATIONS OF CURRENT BETWEEN TWO ELECTRODES

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Tip-sample interaction effects, which are crucial in scanning-tunneling and atomic force microscopy can be analyzed in the atomic scale by using total energy and atomic force calculations. However, the calculation of the current is hindered because of limited number of atoms treated in a periodic supercell. Earlier studies¹ showed that at separations smaller than that corresponding to maximum attraction the corrugation at constant current is slightly reduced by the tip induced elastic deformation, but not enhanced as claimed. The tip induced local modifications of the electronic structure and site-dependent effective barrier were found to have strong effects on the observed STM images. Recently, we have developed a method to calculate the current between two electrodes, in which crucial parameters are obtained from first-principle calculations. In this method, we use the formalism derived earlier² for the conductance through a constriction between two reservoirs of electron gas in GaAs-AlGaAs heterostructure, and represent the electrodes by two jellium metals which are connected by an orifice. The corrugation of the sample surface and the lateral and transverse variation of the potential in the orifice are implemented into the model from the self-consistent calculations. Orifice states solved in a number of segments are matched to the incident 3D wave by using a transfer matrix method. We are able to provide explanation for several experimental results: i) The transition from tunneling regime to ballistic transport and quantized conductance in a point contact. ii) Anomalous and inverted corrugation of the nominally flat (111) surface of Al. iii) Focusing effects in the electron emission from a point source.³

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SURFACE PHONONS FROM AB-INITIO MOLECULAR DYNAMICS : Si (111) 2 x 1

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Surface phonons have been observed on the (111)2x1 surface of silicon at ~ 10 meV and ~ 55 meV, and studied with semi-empirical models. A contradictory interpretation of the nature of the vibrational modes emerges, particularly with respect to their localization, polarization and dipole activity. We present the results of ab-initio molecular dynamics calculations of the lattice dynamics of the π -bonded chain reconstructed surface. The calculated phonon spectrum shows well-defined surface modes at frequency close to the measured values. A detailed description of the atomic motions for these modes is given.

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