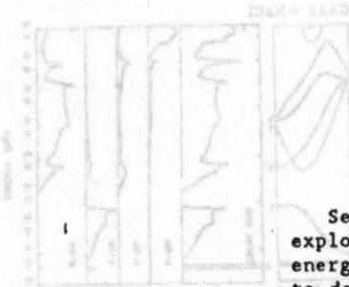


GaAs TIGHT BINDING HAMILTONIANS



JEREMY BROUGHTON, DIMITRI PAPACONSTANTOPOULOS,
MARK PEDERSON and DAVID SINGH
Complex Systems Theory,
Naval Research Laboratory,
Washington, DC 20375.

ABSTRACT

Semi-empirical tight-binding Hamiltonians have been explored to describe the electronic structure and total energies of GaAs in a wide range of structures with a view to determining reliability and transferability. Dispersion relationships and total energies of bulk and molecular structures were calculated via local density functional theory as a data base to fit these Hamiltonians.

1. Introduction

The target of this work is to find a Hamiltonian which is fast, accurate, reliable and capable of describing two component systems in which there is charge transfer for a wide range of coordinations and geometries.

The first phase involved determining whether a non-orthogonal Slater-Koster⁽¹⁾ fit out to fourth nearest neighbors for three different bulk structures of GaAs could reproduce dispersion curves very accurately. This is described in Section 2 below. The second phase involved generating a wide data base of total energies for crystalline and molecular GaAs by local density functional theory (Section 3) with which to fit a new semi-empirical total-energy tight-binding (TB) Hamiltonian (described in Section 4) for use in molecular dynamics simulations. Such a Hamiltonian has to be fast - it is necessary to be able to simulate systems of order hundreds of atoms in seconds per time step on a supercomputer; so that extended defect and two phase systems may be examined. Also, the Hamiltonian must be accurate - relative energies for all thermally accessible atomic configurations must be calculable to milliHartree accuracy so that phase transitions and dynamical quantities may be predicted with confidence. The data base must be well balanced so as to span such accessible configurations and the Hamiltonian sufficiently flexible to interpolate reliably to different parts of phase space.

2. Slater-Koster Dispersion Curves

Using Linear Augmented Plane Wave (LAPW)⁽²⁾ results for GaAs in the NaCl and CsCl structures and also an empirical pseudopotential calculation of the ZnS structure at the minimum energy lattice parameters, we were able to fit dispersion curves (including the d-functions of Ga which are just below the valence band) using the non-orthogonal Slater-Koster procedure in two-center approximation in which matrix elements extend out to fourth nearest neighbor to accuracies of 1 mRy (rms error) for the first five bands. Fig.1. shows the dispersion curves and densities of states for the NaCl structure.

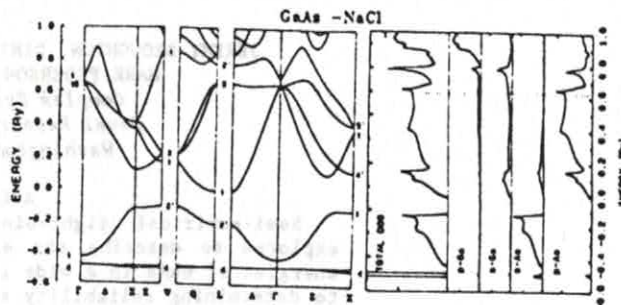


Fig.1. Dispersion curves and densities of states, decomposed by angular momentum component, for GaAs in the NaCl structure.

3. Total Energy Data Base

The semiconducting crystalline structure of GaAs involves four nearest neighbors whereas the metallic liquid involves approximately six. The data base has to cover at least such coordinations. Further, since intended simulations involve surfaces, lower coordination must be included. Crystalline and molecular structures were included in the data base.

The solid state total energy calculations were performed within local density functional approximation (LDA) using the general potential LAPW method. All the electronic states were treated self-consistently; the core electrons fully relativistically in an atomic approximation and the valence electrons in a scalar relativistic approximation. Because of the proximity of the Ga 3d states to the valence band minimum, these states were included in the valence window. The calculations were performed using equal Ga and As sphere radii of 2.2 a.u. with LAPW basis sets determined by a 17.5 Ry plane wave cut-off. The Brillouin zone samplings were performed using special k-point sets. The basis set size and the k-point sets were chosen to yield convergences of total energies to better than 0.5 mRy per atom. Distorted zinc-blende structures involving molecular dipolar units and hexagonal layered structures were also included in the data base. For each structure, many densities were run on either side of the energy minimum. Some of the results for GaAs are shown in Fig.2. They agree well with the plane wave pseudopotential work of Yin and Cohen⁽²⁾ except at high density where d-function overlap occurs. The density of states for experimental rhombohedral structure As is also given, exhibiting a pronounced dip at the Fermi level.

The total energy calculations for the molecules were performed using LDA with recently developed all-electron Gaussian-orbital cluster codes⁽⁴⁾. The core and valence states were expanded in terms of a linear combination of contracted Gaussian orbitals. For each atom, we used a total of ten s-, five p- and four d-type contracted orbitals which are constructed from a set of eighteen optimized even-tempered Gaussians. The potential is calculated analytically on a mesh of points and all requisite integrals are obtained using an essentially exact variational integration mesh^(4,5). The molecular results for As are given in Fig.3.

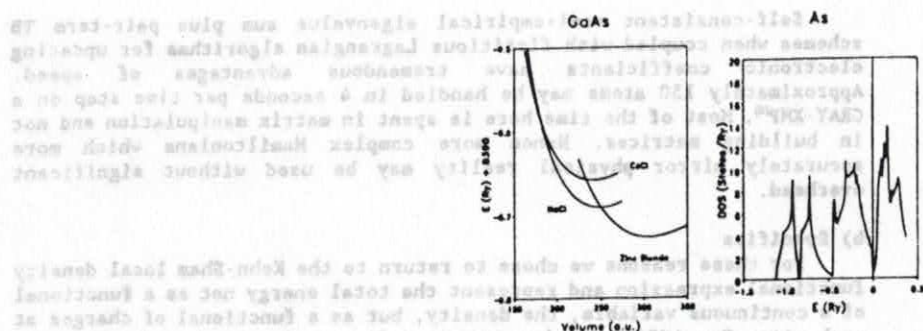
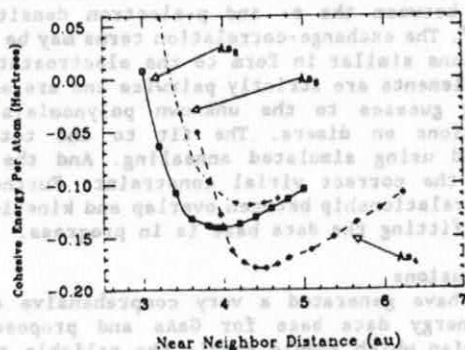


Fig. 2. Total energies of GaAs in different crystal structures. Densities of states for As.



Note that the As_4 cluster is the most stable; it is the cluster observed experimentally in the gas phase.

Fig. 3. Cohesive energies for As_n clusters.

4. Tight-Binding Hamiltonian.

a) Preamble

The data base generated above requires additional experimental information to put the molecular and bulk systems on the same energy scale - experimental cohesive energies and dimer bond strengths are included in the data base. (In general, LDA obtains very accurate relative energies between similar structures - but cohesive energies are poorly reproduced.)

The usual semi-empirical total-energy TB Hamiltonian involves an eigenvalue sum plus pair terms in which matrix elements between local basis functions are functions only of distance and angles between s- and p-functions. But in systems involving large amounts of charge transfer, matrix elements have to be parameterized in terms of charges. Thus bare matrix elements obtained from the fit to dispersion curves are non-trivially related to one another from structure to structure. Also the pair-terms in the standard Hamiltonian must now be charge dependent.

Self-consistent semi-empirical eigenvalue sum plus pair-term TB schemes when coupled with fictitious Lagrangian algorithms for updating electronic coefficients have tremendous advantages of speed. Approximately 150 atoms may be handled in 4 seconds per time step on a CRAY-XMP[®]. Most of the time here is spent in matrix manipulation and not in building matrices. Hence more complex Hamiltonians which more accurately mirror physical reality may be used without significant overhead.

b) Specifics

For these reasons we chose to return to the Kohn-Sham local density functional expression and represent the total energy not as a functional of a continuous variable, the density, but as a functional of charges at each site. Our ANSATZ is that we can define a charge on each atom, and we can do this by either Mulliken analysis⁽⁷⁾ or Lowdin localization⁽⁸⁾. At long range, the electrostatic part may be written to lowest order as a Madelung sum. At shorter range the charge around each atom is decomposed into s- and p-contributions. Matrix elements then become functions of charges, polynomials of distances between atoms and simple powers of cosines between the s- and p-electron densities and the interatomic vectors⁽⁹⁾. The exchange-correlation terms may be cluster expanded to yield expressions similar in form to the electrostatic terms. Kinetic energy matrix elements are strictly pairwise and are of Slater-Koster form. The starting guesses to the unknown polynomials are obtained from LDA calculations on dimers. The fit to the total energy data base is performed using simulated annealing. And the Hamiltonian is made to fulfill the correct virial constraint. Further, the fit invokes the correct relationship between overlap and kinetic energy matrix elements. Work on fitting the data base is in progress.

5. Conclusions

We have generated a very comprehensive electronic structure and total energy data base for GaAs and proposed a physically correct Hamiltonian which should enable the reliable simulation of statistical mechanically interesting systems of order hundreds of atoms over physically useful periods of time of order tens to hundreds of thousands of time steps within reasonable supercomputer budgets.

6. Acknowledgements

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7. References

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