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Tight-binding molecular dynamics in liquid III–V compounds: I. Potential generation

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Abstract. We present a novel tight-binding scheme designed for total-energy and molecular-dynamics simulations in III–V compounds. The role played by orbital overlap and charge transfer is critically addressed and suitably modelled. Comparisons to first-principles density-functional and Hartree–Fock data are presented and commented on in view of the interpolative character of the present method.

1. Introduction

In a recent letter [1], we have reported some preliminary results for a molecular-dynamics simulation of liquid GaAs (l-GaAs). The new, relevant feature of that work was the adoption of a tight-binding (TB) potential, which included a phenomenological, still very efficient form of charge transfer potential. Since no other semiempirical scheme is present in literature for molecular dynamics (MD) simulations of liquid III–V compounds, we report here a detailed discussion of our potential, whereas its performances in the MD simulation of liquid GaAs and GaSb are contained in the second part of our work, hereafter indicated as II.

The general philosophy of our work is that a flexible, semiempirical potential should be able to interpolate the cohesion energy curves of a few crystalline phases, as calculated by first-principles methods. Flexibility is achieved if the limited set of parameters do not change very much in passing from the fitting of one set of input data to a different one [2]. This was observed by comparing results obtained with density-functional–LDA [3] and Hartree–Fock [4] input data. They provide nearly the same simulation results for l-GaAs (see part II), even if the relative cohesion energies of the ZnS and NaCl phases are quite different.

On the other hand, changes in the functional form of the scaling law for the TB hopping parameters, as obtained for instance by extending to III–V compounds the scheme of Goodwin, Skinner and Pettifor (GSP) [5], actually generate very bad results in the MD simulations when compared to the available experimental [6] and theoretical [7, 8] data. It is pretty clear that the scaling law is the key feature in MD simulations rather than the actual value of numerical parameters.

In addition to the analysis of the interatomic potential, we present in part II the new and complete results of the structural, vibrational and electronic properties of liquid GaAs and GaSb which agree quite well with the existing experimental information [6, 9].

This part (I) is organized as follows: firstly (section 2) we outline the TB scheme for the total-energy calculations in semiconductors. In section 3 we discuss our form of the repulsive potential, which includes a charge transfer term, and we derive the corresponding parameters for GaAs. Section 4 presents our parametrization for four other III–V materials, for which *ab initio* calculations of the ZnS, NaCl and CsCl phases are available [3, 10].

2. Cohesive energy by tight binding

Our first goal is to reproduce the cohesive-energy phase diagram for GaAs in the stable ZnS (fourfold coordination) and in the metastable NaCl (sixfold coordinated) and CsCl (eightfold coordinated) phases at zero temperature. In a tight-binding approach, the total energy is partitioned into two terms, depending on the atomic configuration, i.e. a band-structure (bs) and a repulsive (rep) energy:

$$E_{\text{tot}} = E_{\text{bs}} + E_{\text{rep}}. \quad (1)$$

The band-structure energy is the sum over the occupied single-particle eigenstates $\epsilon_n(\mathbf{k})$ of a Slater–Koster (SK), TB Hamiltonian [11]. Here, we have used an orthogonalized, extended set sp^3s^* [12], which provides good electronic densities of states with only nearest-neighbour interactions (see figure 1 and table 1). By keeping the on-site elements frozen, the inter-site (hopping) ones depend on bond angles through angular momentum expansion [11], whereas the two-centre integrals (SK parameters) are functions of the interatomic distance through a suitable scaling law.

Table 1. The tight-binding parameters for GaAs used in the present work [12, 23].

	Ga–Ga	Ga–As	As–As
E_s	-2.656	-2.656(Ga) -8.343(As)	-8.343
E_p	3.669	3.669(Ga) 1.041(As)	1.041
E_{s^*}	6.739	6.739(Ga) 8.591(As)	8.591
V_{ss}	-2.0	-1.613	-1.42
V_{sp}	2.1	2.504(Ga) 1.940(As)	2.1
$V_{pp}(\sigma)$	2.2	3.028	3.1
$V_{pp}(\pi)$	-0.67	-0.781	-0.79
V_{s^*p}	2.0	2.082(Ga) 2.097(As)	1.8

On the other hand, E_{rep} is a quantum-mechanical term, which can be formally written as the difference between the ion–ion interaction and the electron–electron one. This latter was counted twice in the band structure. In practice, E_{rep} reduces to a short-range term, which includes Coulombic, exchange and correlation residual interactions, that it is useful to cast into charge-transfer contributions and orthogonalization corrections not included in the on-site elements of the TB matrix. It is usually expressed as a sum, limited to first neighbours, of a phenomenological pair potential, $U(r)$, which depends on the bond length r , like $\Phi(r_0/r)^m$ or $\Phi \exp[-(r - r_0)/\alpha]$ (Born–Mayer potential). Therefore, in the considered crystalline phases where all the bonds have the same length r , the total energy per atom can be written as

$$E_{\text{tot}} = 2 \sum_{n,\mathbf{k}} \epsilon_n(\mathbf{k}) + \frac{N_{nn}}{2} U(r) \quad (2)$$

where N_{nn} is the coordination number and the spin degeneration is explicitly taken into account in the band-structure term. In a standard approach, the parameters of $U(r)$ are fitted to the equilibrium bond length r_0 and the bulk modulus (i.e. equilibrium and stability conditions) for one single phase. If the Harrison scaling law [13] is used (i.e. the TB

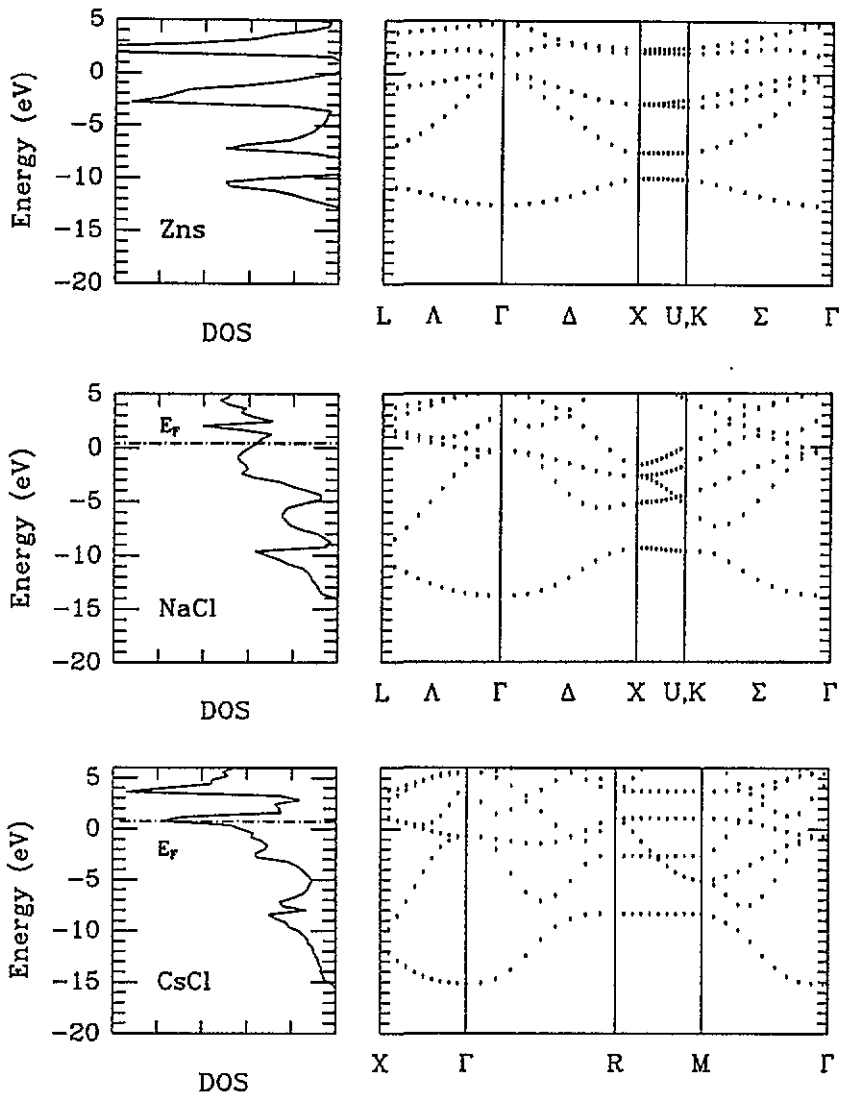


Figure 1. Tight-binding electronic densities of states and band structures for GaAs in the ZnS (top), NaCl (middle) and CsCl (bottom) geometries at the corresponding equilibrium bond lengths.

hopping parameters are scaled as $(r_0/r)^2$, the stable phase is well reproduced, but the same parametrization does not work for the metastable ones.

In order to obtain a transferable potential, we need to adopt a more flexible approach, taking into account also information on the high-coordination geometries, mainly coming from first-principles calculations. To this end, we may modify the scaling law of the hopping parameters, the repulsive potential or both. Our goal is to give an interpolative method which is able to reproduce different sets of *ab initio* data, frequently contradictory to each other, especially for metastable phases. This is the case for GaAs where a pseudopotential density-functional calculation (DFT-LDA)³ (figure 2, left) and Hartree-Fock plus Perdew correlation corrections (HF+C)⁴ (figure 2, right) results provide cohesive-energy curves.

The two calculations give quantitatively different estimations for the cohesive energy of the metastable phases. It has been established that such a disagreement originates in the approximation for correlation [14], still we are left with the problem of understanding which is the real picture, and molecular-dynamics simulations with these potentials may provide an answer.

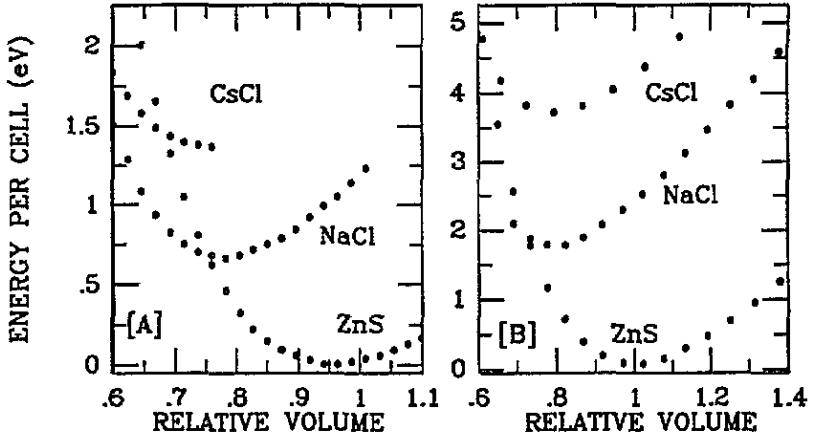


Figure 2. *Ab initio* cohesive-energy phase diagrams for crystalline GaAs: DFT-LDA [3] [A] and HF+C [4] [B] results.

If we use Harrison's scaling function [13], fitting the repulsive potential parameters (Φ, m) of the $\Phi(r_0/r)^m$ form to the equilibrium bond length of the ZnS geometry and the energy difference ($E_{\text{NaCl}}^{\text{eq}} - E_{\text{ZnS}}^{\text{eq}}$) between the NaCl and the ZnS minima, we obtain three cohesion-energy curves which are correctly positioned with respect to the energy scale. However, the highly coordinated structures display too large equilibrium volumes. We have firstly tried to use an unconventional scaling function that preserves the positions of the energy minima and readjusts the high-coordination-phase equilibrium volumes. This approach has been proposed for silicon [5] and in that case it works very well for both total-energy and molecular-dynamics calculations [15]. Here we have generalized the same procedure to GaAs.

In principle, we can re-write expression (2) in such a way that it depends on the scaling function $s(r)$ in the following way:

$$E_{\text{tot}}[s(r)] = E_{\text{bs}}[s^2(r)] + N_{nn}\Phi(s(r))^m \quad (3)$$

where a scaling function dependence is introduced also in the repulsive energy. This $s(r)$ function has to be squared in order to obtain the scaling law of the hopping terms. The substitution of a scaling function $s_1(r)$ by a different one, $s_2(r)$, implies a remapping of the bond length from r to r' , given by

$$r' = s_2^{-1}[s_1(r)]. \quad (4)$$

The energy positions of the minima for different phases and the equilibrium bond length of the ZnS geometry r_0 (if we require $s_1(r_0) = s_2(r_0)$) do not change with the functional form of the scaling function.

We choose a simple reference $s_1(r) = r_0/r$, by which the scaling-invariant repulsive potential parameters Φ and m are fitted to the equilibrium ZnS bond length and the difference in energy between the NaCl and the ZnS minima ($E_{\text{NaCl}}^{\text{eq}} - E_{\text{ZnS}}^{\text{eq}}$). Then, in order to adjust the large values of the high-coordination-phase equilibrium volumes, a new scaling function $s_2(r)$ is introduced:

$$s_2(r) = \frac{r_0}{r} \exp \left[- \left(\frac{r}{r_c} \right)^{n_c} + \left(\frac{r_0}{r_c} \right)^{n_c} \right]. \quad (5)$$

The above functional form is conceived in order to obtain a rapid attenuation between first and second neighbours in the ZnS structure, by multiplying the usual scaling law by a smoothed step function: r_c and n_c are parameters and represent the position and the sharpness of the step, respectively. This particular choice of the scaling function implies redefinitions of the bond length (from r to r') and of the bulk modulus (from B to B'), satisfying the following equations:

$$r = r' \exp \left[\left(\frac{r'}{r_c} \right)^{n_c} - \left(\frac{r_0}{r_c} \right)^{n_c} \right] \quad (6)$$

$$B'(r'_{\text{eq}})^3 = \left[1 + n_c \left(\frac{r'_{\text{eq}}}{r_c} \right)^{n_c} \right] B(r_{\text{eq}})^3 \quad (7)$$

where B , B' , r_{eq} and r'_{eq} are the bulk moduli and the equilibrium bond lengths calculated with the two different scalings. n_c and r_c are estimated by means of the previous equations, to reproduce the *ab initio* values for B_{ZnS} and r_{NaCl} .

Obviously, two independent fits have been made for the two sets of first-principles data and the values of the calculated parameters are reported in table 2. Here we see that n_c nearly doubles from the DFT-LDA to the HF+C fitting, so that the actual physical meaning of such a parameter is questionable. In figure 3 our results for DFT-LDA and HF+C interpolations (light dots are for $s_1(r) = r_0/r$) are displayed: we see that the agreement with the corresponding *ab initio* results is reasonably satisfactory in the former case, but the method fails to reproduce the latter. As a matter of fact, the fitting procedure for GaAs results is more complex than for silicon (for which the reference geometries are the diamond and the 12-coordinated FCC ones): this is mainly due to the difficulties in correctly determining the minima of the NaCl curves calculated with $s_1(r)$, especially in the HF+C case, due to their low curvature. Apart from these calculation details, the physical conclusion is that the real problem in GaAs is not to tailor the decay of the hopping parameters and repulsive potential, as is the case for elemental semiconductors, but to take into account the charge-transfer effects originated by the coexistence of anions and cations.

Table 2. Parameters of the GSP method for GaAs, fitted to DFT-LDA [3] and HF+C [4] data.

	m	Φ (eV)	n_c	r_c (Å)
DFT-LDA	4.67	3.7924	13	3.511
HF+C	3.84	4.6121	25	2.830

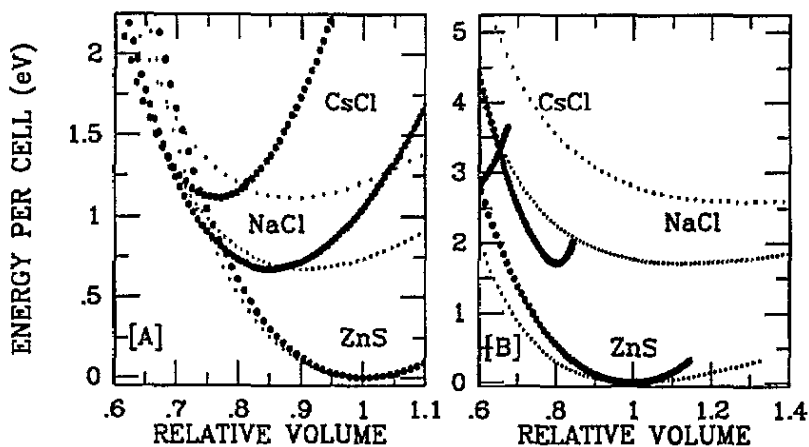


Figure 3. Cohesive-energy phase diagrams for GaAs calculated with the unconventional scaling function method: DFT-LDA [A] and HF+C [B] fittings. The light points correspond to the Harrison scaling function.

3. A new potential for GaAs

We guess that the repulsive energy can still be expressed as a sum of pair potentials and propose a new form for such a potential, keeping the Harrison scaling rule in the TB hopping elements. We add to the Born–Mayer potential (mainly originated by the overlap of occupied orbitals) a term that slowly varies as the inverse of the interatomic distance:

$$U(r) = \Phi_1 \exp[-(r - r_0)/\alpha] + \Phi_2 \left(\frac{r_0}{r}\right). \quad (8)$$

This additional term takes charge-transfer effects into account in a phenomenological and simplified way. Its microscopic foundation stands in the self-consistent TB calculations performed by Majewski and Vogl for the cohesion energy in binary compounds [17, 18] in the crystalline phases. In principle, charge transfer generates both intra-site Hartree repulsion and inter-site Madelung attraction of charges, which, in turn, raises and lowers, respectively, the corresponding TB on-site elements. This implies a self-consistent procedure on the occupation numbers on the one hand and long-range Coulombic summations on the other. Both procedures are undesirable in molecular-dynamics simulations, since they heavily affect the computational workload.

Majewski and Vogl have shown [18] that charge-transfer effects originate a complex, additional term in the repulsive energy. Numerical estimations of this term for a definite crystalline phase have demonstrated it to be positive (the Hartree term is dominant) and to decay approximately as the inverse of the interatomic distance. We took advantage of this information and extrapolated it into a two-body potential, which is summed up to first neighbours. In figure 4 we display the different contributions to the total-energy curves for GaAs in the ZnS phase as a function of the interatomic distance, for both the DFT–LDA fitting and the HF+C one.

The apparent contradiction between the slowly decaying form of such a repulsive potential and the evaluation of its contributions only to first-neighbour distance is removed by considering that $\Phi_2(r_0/r)$ mainly describes the coordination-dependent intra-site charge transfer mechanism, while the inter-site Coulomb interactions are screened by the gapless

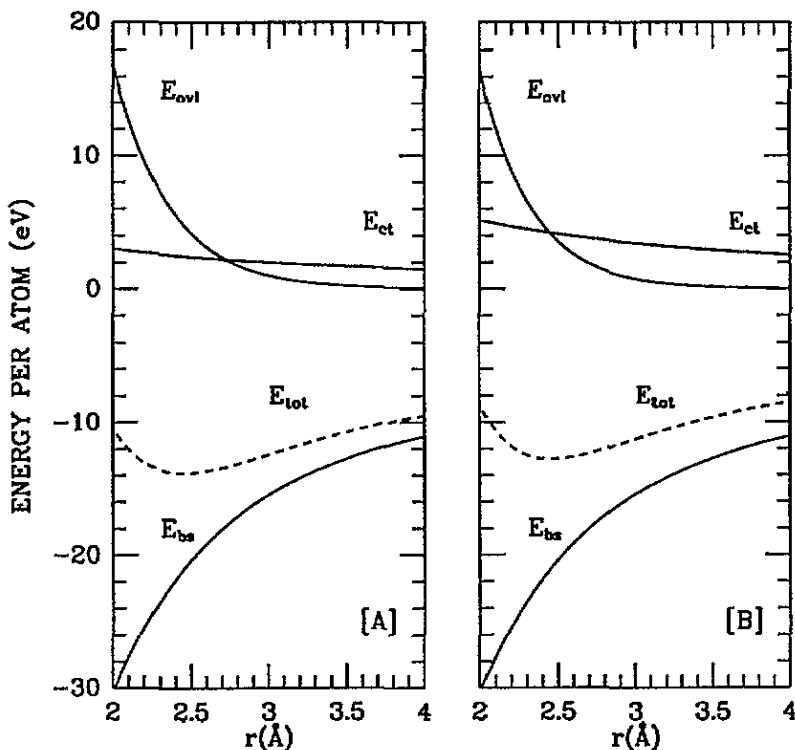


Figure 4. The overlap (E_{ovl}), charge-transfer (E_{ct}) and band-structure (E_{bs}) contributions to the total energy (E_{tot}) of GaAs in the ZnS phase. The $U(r) = \Phi_1 \exp[-(r - r_0)/\alpha] + \Phi_2(r_0/r)$ repulsive potential was fitted to DFT-LDA [A] and HF+C [B] data. The dashed curves represent the total energy (E_{tot}).

electronic structure of all the GaAs phases other than the ZnS one (liquid state included). The $\Phi_2(r_0/r)$ term is actually barely dependent on the interatomic distance whereas it is linearly dependent on the number of first-neighbouring atoms, so that it plays an important role when the coordination is changed because it raises the energy of the higher-coordination phases. Therefore it allows energy to reset almost independently of interatomic distances and corresponds to the fact that charge-transfer effects are globally more sensitive to coordination rather than to interatomic distances.

The dependence of such a term on a site property, such as coordination inside the cut-off radius, suggests an analogy to an important class of potentials for metallic materials, such as the embedded-atom model [19] and the effective-medium theory [20], even if the covalent contribution to E_{bs} is here still very important.

The three parameters Φ_1 , Φ_2 and α are fitted on the equilibrium bond lengths of ZnS and NaCl phases and to the difference of their cohesion energies: the values corresponding to DFT-LDA and HF+C are reported in table 3. The calculated cohesion-energy curves, displayed in figure 5, show quite a good agreement with both sets of cohesion-energy curves of figure 2. In figure 4 the separate components of the total energy are shown. Similar results are obtained if the exponential is replaced by a power law $\Phi_1(r_0/r)^m$ (table 4, figure 6). We prefer a Born-Mayer potential whose validity and physical foundation have been proved in several situations [16]. Moreover the numerical values for α are comparable in the two

fittings and agree quite well with the estimations made for alkali halides [21] and silicon [22].

Table 3. Parameters of the repulsive potential $U(r) = \Phi_1 \exp[-(r - r_0)/\alpha] + \Phi_2(r_0/r)$ for GaAs, fitted to DFT-LDA [3] and HF+C [4] data.

	α (Å)	Φ_1 (eV)	Φ_2 (eV)
DFT-LDA	0.3555	2.3906	1.2347
HF+C	0.321	2.047	2.085

Table 4. Parameters of the repulsive potential $U(r) = \Phi_1(r_0/r)^m + \Phi_2(r_0/r)$ for GaAs, fitted to DFT-LDA [3] and HF+C [4] data.

	m	Φ_1 (eV)	Φ_2 (eV)
DFT-LDA	6.0	2.816	0.8145
HF+C	6.75	2.362	1.766

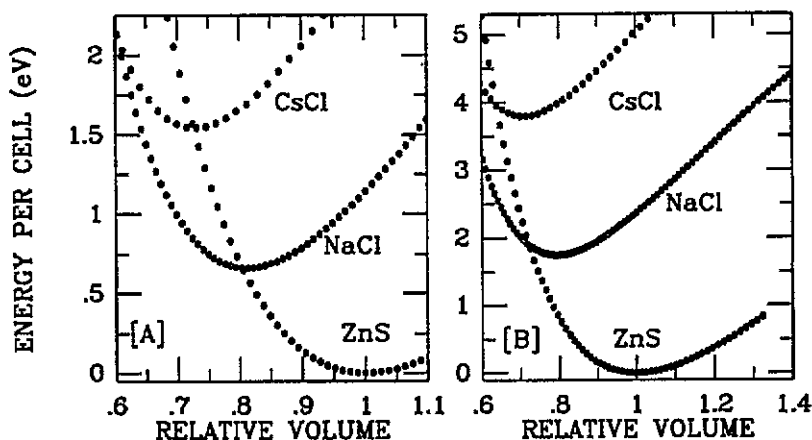


Figure 5. Cohesive-energy phase diagrams for GaAs calculated with $U(r) = \Phi_1 \exp[-(r - r_0)/\alpha] + \Phi_2(r_0/r)$: DFT-LDA [A] and HF+C [B] fittings.

So far, our first-neighbour approach has taken into account only anion-cation interactions, in different coordinations. In a liquid or in an amorphous material, however, like-atom bonds (the so-called ‘wrong bonds’) occur and represent an essential feature of the disordered phases. The TB set that we use has been completed with like-atom hopping parameters by O’Reilly and Robertson [23] (see table 1), in the framework of an electronic-structure investigation of amorphous binary compounds: As-As interactions are actually taken from crystalline arsenic and Ga-Ga interactions from c-GaSe. As concerns the repulsive term, we use the same potential per bond as determined for Ga-As even in the case of like-atom interactions. This could look like a rough approximation that can only be justified *a posteriori* on the basis of our results. One possible explanation is that the charge-transfer term describes an average effect, that mainly depends on the local coordination.

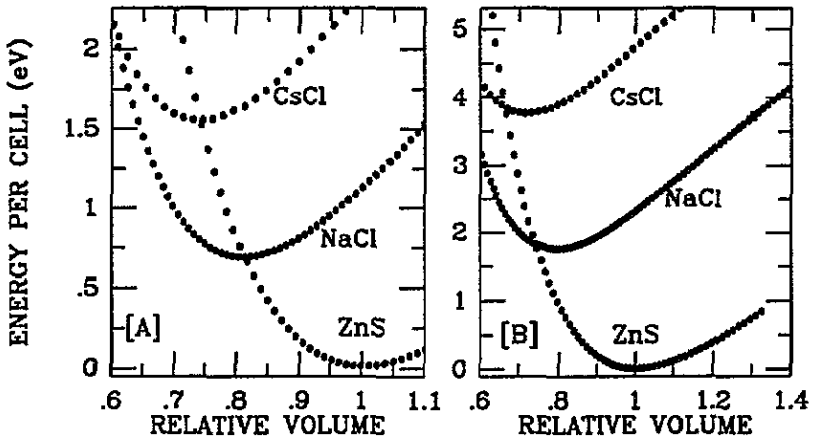


Figure 6. Cohesive-energy phase diagrams for GaAs calculated with $U(r) = \Phi_1(r_0/r)^m + \Phi_2(r_0/r)$: DFT-LDA [A] and HF+C [B] fittings.

As concerns the Born-Mayer potential, the use of cation-anion interactions in the case of like-atom bonds can be justified by the similar covalent radii of gallium and arsenic, even if very satisfactory results are obtained also for GaSb, as reported in the following.

4. Potential parameters for other III-V compounds

The parameters for the repulsive potentials $U(r) = \Phi_1 \exp[-(r - r_0)/\alpha] + \Phi_2(r_0/r)$ and $U(r) = \Phi_1(r_0/r)^m + \Phi_2(r_0/r)$ have been calculated, using the same technique proposed for GaAs, for other III-V compounds, for which DFT-LDA total energy calculations concerning the ZnS and NaCl geometries are available: AlAs, AlP, GaP [3] and GaSb [10]. The TB parameters are still relative to the sp^3s^* basis set [12] and Harrison's scaling law is adopted [13]. The hopping elements for like atoms are obtained by scaling the Ga-Ga and As-As hopping parameters with the inverse of the square of the cation-cation and anion-anion bond lengths of the examined material [23].

In tables 5 and 6, we display the corresponding repulsive potential parameters. The general expected trend for the repulsive potential is that the smaller the size of the anion (cation) when the cation (anion) is kept fixed, the harder should be the overlap repulsion. As for the charge transfer, increasingly extended atomic orbitals should provide a larger and larger overlap and consequently a more sizeable charge transfer. These trends are rather well reproduced by the parameters Φ_1 and Φ_2 , respectively, for common-cation compounds. Only the trend shown by Φ_2 for AlX systems ($X = P, As$) is not in agreement with the above qualitative rule. However, we remark that the absolute variation of Φ_2 between AlP and AlAs is quite small. When considering common-anion compounds, the above trends are not closely reproduced. As a matter of fact, only the evolution of the Φ_2 parameter qualitatively agrees with the expected behaviour. Finally, we observe that it is hard to extrapolate from tables 5 and 6 any trend for α and m , their values being almost constant. In figures 7 and 8 we display the electronic DOS and the cohesion-energy diagrams for the case of GaSb, whose results for the liquid-phase simulation are reported in part II.

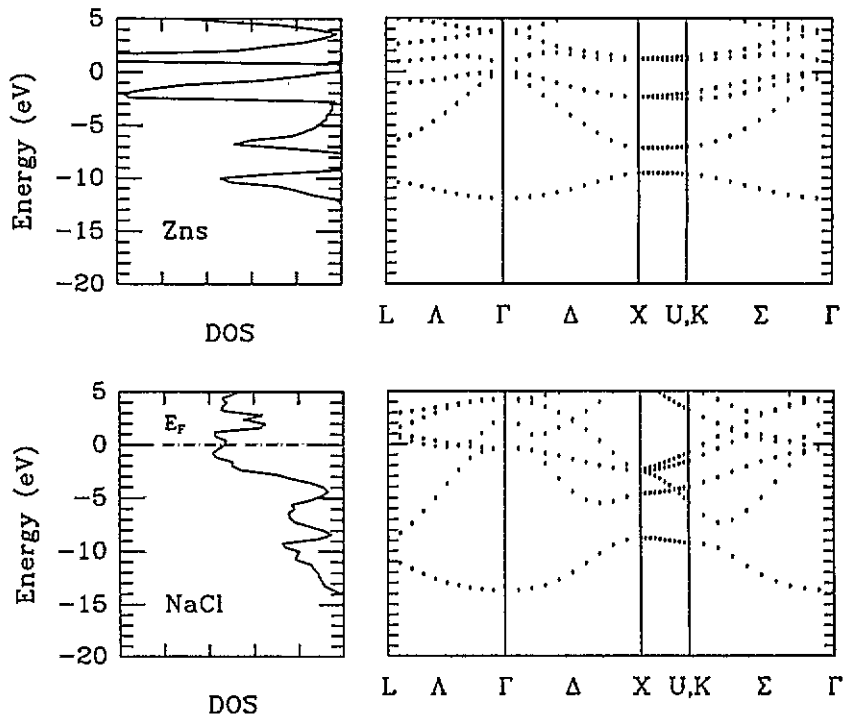
As a final comment on the generation of our potential it is worth saying that the fitting procedure has exploited only crystalline systems which display a high three-dimensional

Table 5. Parameters for the repulsive potential $U(r) = \Phi_1 \exp[-(r - r_0)/\alpha] + \Phi_2(r_0/r)$ for GaAs fitted to DFT-LDA data [3, 10].

	α (Å)	Φ_1 (eV)	Φ_2 (eV)
GaP	0.3580	2.6183	1.2027
GaAs	0.3555	2.3906	1.2347
GaSb	0.3802	2.0136	1.5587
AlP	0.3088	2.2283	1.2270
AlAs	0.3220	2.0866	1.1395

Table 6. Parameters for the repulsive potential $U(r) = \Phi_1(r_0/r)^m + \Phi_2(r_0/r)$ for GaAs fitted to DFT-LDA data [3, 10].

	m	Φ_1 (eV)	Φ_2 (eV)
GaP	5.696	3.1206	0.6880
GaAs	6.000	2.8160	0.8143
GaSb	6.050	2.3700	1.1929
AlP	6.738	2.5803	0.8702
AlAs	6.700	2.4200	0.8079

**Figure 7.** Tight-binding electronic densities of states and band structures for GaSb in the ZnS (top) and NaCl (bottom) geometries at the corresponding equilibrium bond lengths.

symmetry. It is open to question how much our potential could be transferable to surfaces, extended defects and similar symmetry-broken situations. However, our present goal is the simulation of liquid and amorphous structures, where many point defects coexist with

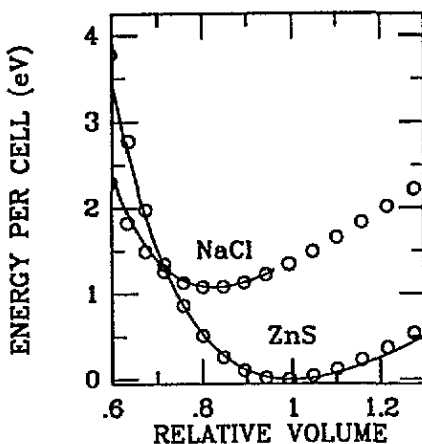


Figure 8. Cohesive-energy phase diagrams for GaSb calculated with $U(r) = \Phi_1 \exp[-(r - r_0)/\alpha] + \Phi_2(r_0/r)$: *ab initio* [10] (open circles) and tight-binding (solid line) results.

a 'global' spherical symmetry and the results that we obtained are very satisfactory (part II and [24]). This is not a trivial test, since different attempts to provide a reliable TB Hamiltonian suitable for molecular-dynamics calculations of III-V compounds [25] have not been followed, to our knowledge, by simulation tests. Moreover, our tight-binding potential has the advantage of being very simple and physically transparent and its computational workload is reduced.

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