A new tight binding parameterization for carbon

To cite this article: L Goodwin 1991 J. Phys.: Condens. Matter 3 3869

View the article online for updates and enhancements.

A new tight binding parametrization for carbon

Leif Goodwin†

Department of Mathematics, Imperial College, Queen's Gate, London SW7 2BZ, UK

Abstract. Working within a minimal orbital sp basis set with fixed site energies and a repulsive pairwise interaction we fit a set of hopping integrals and a repulsive pair potential to experimental graphite and diamond band structures, binding energies, lattice constants and bulk moduli, and to accurate local density functional data for the binding energies and equilibrium volumes of face centred cubic, simple cubic and beta tin phases of carbon. We find that an approximately inverse cube form for the hopping integrals as a function of interatomic separation and an approximately inverse nine-halves power for the pair potential leads to an improved fit to the data including the band structure of graphite. Both the hopping integrals and the pair potential are seen to decay more rapidly than similar parameters for silicon, reflecting the absence of nuclear screening by core electron states.

1. Introduction

Amongst techniques for studying electronic structure and atomic cohesion the tight binding method has found favour for its simplicity and its versatility. As a result of its relatively light demand on computational resources the method has been widely used for atomistic simulations of complex structures as well as for qualitative trends across the periodic table. The range of materials that the method has been applied to includes hydrogen, sp bonded systems, pd bonded systems and transition metals. As recent examples of the use of the method we cite the work of Majewski and Vogl on pd bonded binary compounds [1] and that of Cressoni and Pettifor on sp bonded solids [2]. For an overview we refer the reader to the review article by Finnis *et al* [3].

A much sought after goal of tight binding is to find for each element a so called universal parametrization which would, without modification, be applicable to a whole range of bonding environments. In practice a certain degree of transferability can be ensured by fitting the parameters to as large a data base as possible, which usually means the experimental bulk modulus, the experimental lattice constant and the experimental band structure for the equilibrium bulk phase. An example of this approach is to be found in [4] which includes for carbon a set of parameters fitted to the experimental diamond lattice constant and the experimental diamond band structure. As well as these experimental data there are the results of accurate *ab initio* local density functional (LDF) calculations. The quite remarkable accuracy of these calculations is seen from a comparison of the calculated data with experimentally measurable quantities such as the bulk modulus, the lattice constant and the binding energy of the

† Present address: Département de Chimie, Faculté des Arts et des Sciences, Université de Montréal, CP 6128. Succursale A, Montréal, Québec H3C 3J7, Canada.

equilibrium phase. These have provided the energy as a function of volume for many different elements in experimentally inaccessible lattice structures [5, 6] and raise the possibility of improved fits.

In this paper we use this recent LDA data to improve Harrison's parametrization for the hopping integrals and the pairwise potential of carbon [4]. The method used is similar to that applied to silicon in two recent papers by Goodwin, Skinner and Pettifor [7] and Goodwin and Skinner [8] although the different chemistry of carbon leads to a rather different fit. The parametrization is for use in the tight binding bond model (TBBM) formulation of Sutton *et al* [9] which we describe in section 2 of this paper. In section 3 we introduce Harrison's parametrization for the hopping integrals and the pair potential and present results calculated for some representative bulk phases. The results of LDF calculations [6] are used for comparison. In section 4 we introduce modifications to Harrison's forms in order to improve the modelling of the bulk phases. These improvements to the modelling are summarised at the beginning of the section. The modifications are introduced in section 4 via the rescaling method [7, 8] which we describe in section 4.1. The fitting process and the results of calculations with the fitted parameters are described in section 4.2.

2. The tight binding bond model

In this section we briefly describe the tight binding bond model of Sutton *et al* [9]. More detailed treatments of the tight binding method in general, and in particular the repulsive pair potential, are to be found in [9–12]

To evaluate the energy we calculate and then sum together three terms referred to as the bond energy, the promotion energy and the repulsive energy:

$$E_{bind} = E_{bond} + E_{prom} + E_{rep}. \tag{1}$$

The bond energy (equation (2)) takes into account the energy gain from the formation of quantum mechanical bonds ignoring the energy loss due to changes in the occupation of the basis orbitals. To calculate this term we find the band energy for the bonding case and subtract from it the sum of the electronic energies for isolated non-interacting atoms with identical orbital occupations. Denoting each site and each orbital type by i and α, the local densities of states by $n_{i\alpha}(\epsilon)$ and the energy levels of the free atoms by $\epsilon_{i\alpha}$ the bond energy is thus as follows

$$E_{bond} = \sum_{i\alpha} \int_{-\infty}^{\epsilon_F} (\epsilon - \epsilon_{i\alpha}) n_{i\alpha}(\epsilon) \, d\epsilon. \tag{2}$$

The local density of states which occurs in the above energy terms and in the following term is found in the usual fashion by solving the tight binding eigenvalue problem.

The promotion energy (equation (3)) takes into account the energy loss due to changes in the occupation of the basis orbitals. To calculate this term we find the sum of the electronic energies for isolated non-interacting atoms in the ground state and subtract off the sum of the electronic energies for isolated non-interacting atoms whose orbital occupations are equal to those in the bonding state under study. Denoting the changes in the orbital occupations by $\Delta n_{i\alpha}$ the promotion energy is thus as follows

$$E_{prom} = \sum_{i\alpha} \epsilon_{i\alpha} \Delta n_{i\alpha}. \tag{3}$$

For a structure such as the simple cubic lattice in which the p orbitals are degenerate and for which each site is identical the promotion energy is just the difference between the s and p site energies multiplied by the change in the s orbital occupation on any given site.

The TBBM includes the so-called local charge neutrality (LCN) approximation in which each atom is constrained to have the same number of valence electrons as the free atom. The LCN approximation was introduced to provide the model with a simple first approximation to self-consistency by preventing unphysically large interatomic charge redistributions. For the ideal lattices considered in this paper LCN is automatically satisfied by symmetry considerations. For structures in which this is not the case LCN can be achieved by adjusting the on-site energies by small amounts using some iterative technique [7, 8].

The repulsive energy (equation (4)) takes into account the non-orthogonality, electrostatic and exchange–correlation terms in the binding energy. To calculate this term we assume that it can be approximated by a sum of pairwise interactions with the summation over all pairs of atoms. Denoting a pair potential by $V_{\mathrm{rep}}(r_{ij})$ and an interatomic vector by r_{ij} the repulsive energy is thus as follows

$$E_{\mathrm{rep}} = \sum_{i<j} V_{\mathrm{rep}}(r_{ij}). \tag{4}$$

The above equations can be differentiated without too much difficulty to provide expressions for the forces on the constituent atoms. As an example of the use of the atomic forces we refer the reader to a recent study of silicon clusters [7, 8] in which the atomic forces were used as input to an annealing algorithm. In this study the atomic forces were calculated exactly via an exact diagonalization of the tight binding Hamiltonian.

3. Harrison's parametrization

In this section we describe briefly Harrison's parametrization for the tight binding Hamiltonian and the pair potential of group IV elements [4].

Harrison provides a prescription for both the Hamiltonian and the pair potential. The Hamiltonian matrix is constructed in the usual fashion [13] from a set of functional forms for the two-centre hopping integrals and a set of fixed on-site energies within a minimal orbital basis of one atomic-like s orbital and three atomic-like p orbitals. The approximation is made that the three-centre terms, the crystal field terms and the contributions from more distant neighbours are of secondary importance in describing the principal features of the interatomic cohesion. The form of the hopping integrals is as given in the following equation:

$$V_{ll'm}(r) = V_{ll'm}(r_0)(r_0/r)^2 \tag{5}$$

There are thus four hopping integrals for pure $ss\sigma$, $sp\sigma$, $pp\sigma$ and $pp\pi$ hopping. Although this form is essentially semi-empirical Froyen and Harrison [14] have attempted a theoretical justification of the inverse square form about equilibrium. For the values of the hopping integrals at equilibrium $V_{ll'm}(r_0)$) we have taken those values quoted by Papaconstantopoulos [15]. These were obtained by fitting out to third neighbours

in a minimal sp basis a set of two-centre orthogonal hopping integrals and a set of on-site energies to a band structure for the equilibrium diamond lattice. Figure 1 shows that we are justified in ignoring the second- and third-neighbour hopping integrals as they contribute a negligible amount to the form of the band structure except in the top of the valence band which is anyway of little interest to us. These on-site energies and nearest neighbour hopping integrals are listed in table 1. The pair potential (equation (6)) varies as the inverse fourth power of the interatomic separation with its equilibrium value ($V_{rep}(r_0)$) fitted to ensure exact reproduction of the experimental lattice constant r_0. The functional form is as follows:

$$V_{rep}(r) = V_{rep}(r_0)(r_0/r)^4. \tag{6}$$

As with the hopping integrals the inverse quadratic form is semi-empirical based on the assumption that the non-orthogonality contribution forms the larger part of the repulsive energy.
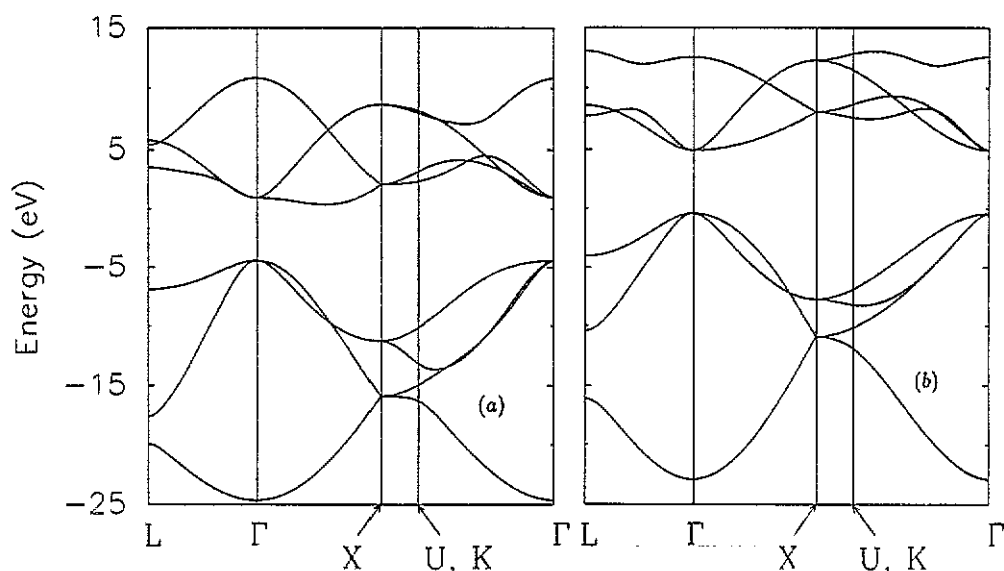

Figure 1. Band structures for diamond carbon calculated using the tight binding parameters of [15]. In (*a*) the interactions extend out to third neighbours, in (*b*) only to first neighbours. Good agreement between the two is seen, demonstrating that the second- and third-neighbour interactions play a negligible role.

Table 1. The equilibrium hopping integrals and on site energies in eV.

ϵ_s	ϵ_p	$V_{ss\sigma}$	$V_{sp\sigma}$	$V_{pp\sigma}$	$V_{pp\pi}$
-5.16331	2.28887	-4.43338	3.78614	5.65984	-1.82861

Results calculated for some bulk lattices using Harrison's parametrization are given in table 2. The table includes for comparison accurate first-principles LDF data of Yin and Cohen [6]. The binding energies were calculated by solving the Hamiltonian

Table 2. The equilibrium energies and volumes calculated with Harrison's tight binding parameters and with an LDF method. Units of energy are eV and all volumes are normalised to the experimental diamond equilibrium volume.

Lattice	*dia*	SC	β-Sn	FCC	*gra*
E_0^{TB}	−11.51	−8.86	−9.66	−5.99	−10.30
E_0^{LDF}	−7.69	−5.03	−4.87	−3.10	−7.70
V_0^{TB}	1.00	1.07	0.95	1.92	1.71
V_0^{LDF}	0.99	0.98	0.98	1.28	1.57

eigenvalue problem approximately using the recursion method [16] with the continued fraction taken to five exact levels and terminated according to the scheme of Beer and Pettifor [17]. The calculations were for the binding energy as a function of volume per atom for diamond (*dia*), simple cubic (SC), beta-tin (β-Sn), face centred cubic (FCC) and graphite (*gra*) phases. For the calculations on β-Sn the closeness of the first- and second-neighbour distances (see table 3) necessitated the inclusion of both first- and second-neighbour hopping integrals in the Hamiltonian (using the same functional form for each). For the other four lattices only first neighbour interactions were included. A value of the pair potential at equilibrium $V_{rep}(r_0)$ of 8.68 eV ensured the exact reproduction of the experimental lattice constant for the diamond phase.

Table 3. The neighbour distances for five lattices from *ab initio* calculations out to 3.05 Å. Coordination (*C*) and neighbour index (*N*) are indicated.

Lattice	*gra*	*dia*	SC	β-Sn	β-Sn	FCC	β-Sn	SC	*dia*	*gra*
r/Å	1.41	1.55	1.78	1.79	1.89	2.18	2.23	2.51	2.52	2.60
N	1	1	1	1	2	1	3	2	2	2
C	3	4	6	4	2	12	4⊖	12	12	6

We see that qualitatively the parameters have reproduced the trends in the LDF data: FCC which is the most closely packed of the lattices is correctly calculated to have a large atomic volume per atom and the smallest binding energy of the five phases; the SC and β-Sn lattices are correctly calculated to have binding energies which lie midway between the *dia* and FCC binding energies.

Quantitatively though it must be said that the modelling is poor. A serious shortcoming of Harrison's parameters is the incorrect modelling of the *dia gra* binding energy separation which is both of the wrong sign and three orders of magnitude too large as can be seen from table 2. We would expect this to cast serious doubts on the results of any surface calculations or indeed on the results from any calculations in which like *gra* some or all of the atomic coordinations are less than four. Secondly the binding energy of β-Sn is incorrectly calculated to be less than the binding energy of SC. Although both of these structures are experimentally unrealizable we would expect this error to show up in the results of calculations on disordered structures in which the local atomic environments reflect that seen in either β-Sn or SC. Thirdly the equilibrum volume for FCC is about one third larger than the LDF value and again we would expect this to cause problems for the study of disordered structures. Fourthly all binding energies are far too large and it is easy to believe that this would also be the case for other structures not studied here. Lastly the bulk modulus of *dia* at

3.91 Mbar is in reasonable agreement with the experimental value of 4.42 Mbar the error being roughly fifteen per cent.

4. The new parametrization

The previous section has identified a number of shortcomings of Harrison's parametrization some of which we are able to correct for. The first of these is the *dia gra* equilibrium energy separation which we have found by trial and error can be fitted exactly by reducing the pair potential exponent relative to the hopping integral exponent. This also has the effect of reducing the calculated binding energies to more realistic values as we shall see. The second is the *dia* bulk modulus which as we will show we can fit exactly to the experimental value using the rescaling method [7, 8]. Lastly we have throughout the last section considered only first-nearest neighbour interactions with the exception of β-Sn. In fact the second-neighbour interactions are far from zero. We thus need to reduce the range of the parameters and this we shall do, again using the rescaling method.

4.1. The rescaling method

In this section we describe the rescaling method [7, 8].

To understand what we mean by a rescaling imagine the energy plotted against nearest neighbour separation for two lattices whose equilibrium lattice constants we denote as r_0 and r_1. Let us suppose that the equilibrium binding energies of each lattice closely reproduce the corresponding experimental values, that r_0 has been fitted exactly to the experimental value but that r_1 is considerably too large. In this case the plot can be improved by redefining a new horizontal axis according to the definition

$$R(r) = r \, f(r)/f(r_0) \tag{7}$$

and choosing the function $f(r)$ appropriately. The particular form of equation (7) ensures that the equilibrium bond length r_0 is conserved under the *rescaling*. Alternatively rather than calculating a set of energy curves and then rescaling the r-axis we can replace r wherever it occurs in the parameters and then calculate the energy and obtain the same results. Although this may seem trivial it is not. The important feature of rescaling as a means to improving the hopping integrals and pair potential is the preservation of the equilibrium energy separations.

A useful identity which follows from rescaling is that the calculated equilibrium energies are dependent only on the ratio of the hopping integral exponent to the pair potential exponent. We can prove this with the following rescaling where s is a free variable:

$$R(r) = r_0(r_0/r)^s \tag{8}$$

Substituting $R(r)$ in place of r in a hopping integral which varies as the inverse interatomic separation to the power of n and a pair potential which varies as the inverse separation to the power m we obtain the following forms:

$$V_{ll'm}(r) = V_{ll'm}(r_0)(r_0/r)^{ns} \tag{9}$$

$$V_{\text{rep}}(r) = V_{\text{rep}}(r_0)(r_0/r)^{ms}. \tag{10}$$

As the equilibrium energies are unchanged by a rescaling they must also be independent of s. By inspection of equations (9) and (10) we see that the equilibrium energies are also independent of the hopping integral and pair potential exponents so long as their ratio is held constant.

The rescaling in equation (8) can be used to fit the bulk modulus to the experimental value by a suitable choice of the parameter s. Denoting the original calculated value of the *dia* bulk modulus by B_0^{old} and the rescaled calculated value by B_0^{new} we find via some simple algebra the following relationship:

$$B_0^{new} = s^2 B_0^{old}. \tag{11}$$

The following rescaling (equation (12)) can be used to reduce the range of the interactions so as to include only the first-nearest neighbour values as originally assumed.

$$R(r) = re^{(r/r_c)^{n_c} - (r_0/r_c)^{n_c}}. \tag{12}$$

Equation (12) provides a smooth drop to zero which starts around an interatomic separation equal to r_c and whose sharpness is set by the value of n_c. As long as the cut-off is relatively sharp and the value of r_c sufficiently large relative to r_0 we need not worry about the effect on the bulk modulus which will be negligible as seen from the following equation which describes how the truncation affects the bulk modulus:

$$B_0^{new} = B_0^{old}(1 + n_c(r_0/r_c)^{n_c}/2)^2. \tag{13}$$

4.2. The improved parametrization

The procedure we have followed for the fitting is as follows. First we adjusted the ratio of the hopping integral exponent to the pair potential exponent such that the *dia gra* equilibrium energy separation was given correctly. Then keeping this ratio fixed we simultaneously adjusted both exponents according to the rescaling in equation (8) so as to correctly reproduce the experimental bulk modulus for the *dia* lattice. Thirdly and lastly we smoothly truncated the parameters using the rescaling in equation (12) so as to keep the interactions down to a minimum and also ensure a reasonable value for the FCC equilibrium volume. This leads to the following forms for the hopping integrals and the pair potential:

$$V_{ll'm}(r) = V_{ll'm}(r_0)(r_0/r)^{2.796}e^{2.796(-(r/2.32)^{22}+(r_0/2.32)^{22})} \tag{14}$$

$$V_{rep}(r) = V_{rep}(r_0)(r_0/r)^{4.455}e^{4.455(-(r/2.32)^{22}+(r_0/2.32)^{22})}. \tag{15}$$

The values from the fitting are thus 2.796 and 4.455 for the hopping integral and the pair potential exponents and 2.32 Å and 22 for r_c and n_c.

Results calculated with the rescaled parameters are summarized in table 4. The calculational details are as given in section 3 with the equilibrium value of the pair potential $(V_{rep}(r_0))$ equal to 10.92 eV. The bulk modulus is of course exactly equal to the experimental value of 4.42 Mbar.

The results table shows that the improvement in the modelling is not limited just to the bulk modulus, the *dia gra* energy separation and the range of the parameters. It

Table 4. The equilibrium energies and volumes calculated with the rescaled tight binding parameters. The corresponding LDF data are to be found in table 1. Units of energy are eV and the volumes are normalized to the *dia* equilibrium volume.

Lattice	*dia*	SC	β-Sn	FCC	*gra*
E_0^{TB}	−7.03	−3.48	−4.06	−1.76	−7.06
V_0^{TB}	1.00	1.24	1.14	1.31	1.65

also includes a considerable improvement in the absolute values of the binding energies for all of the lattices. These were previously much too large. In addition the FCC equilibrium volume has been markedly improved although this has been at the expense of the β-Sn and SC equilibrium volumes. In figure 2 the improved hopping integrals have been plotted as a function of the interatomic separation. The figure shows that the improved hopping integrals tend rapidly to zero before second neighbours for all lattices except the β-Sn lattice (see table 3 for neighbour separations). In figure 3 the band structure for the *gra* lattice calculated with the improved parameters is shown alongside a band structure calculated using a set of tight binding parameters fitted to the equilibrium *gra* structure. The figure illustrates that the improved parameters lead to a reasonable reproduction of the qualitative features of the bands although the ppπ band is rather narrower than it should be [18].
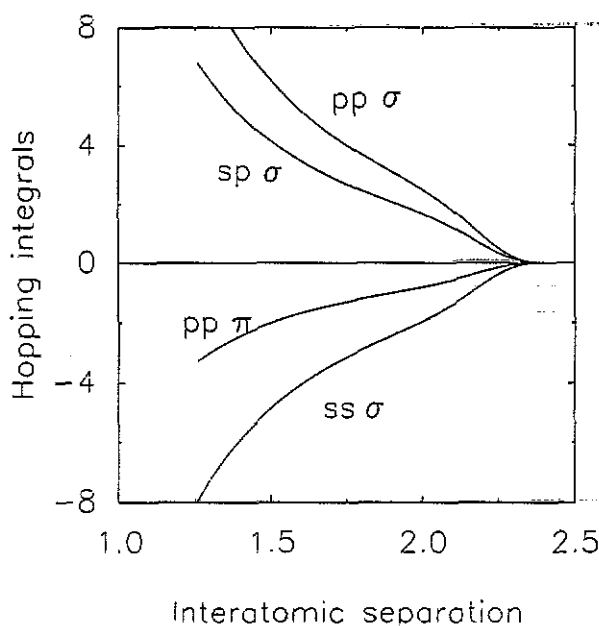

Figure 2. The fitted hopping integrals plotted as a function of interatomic separation. The neighbour distances are given in table 3.

5. Discussion

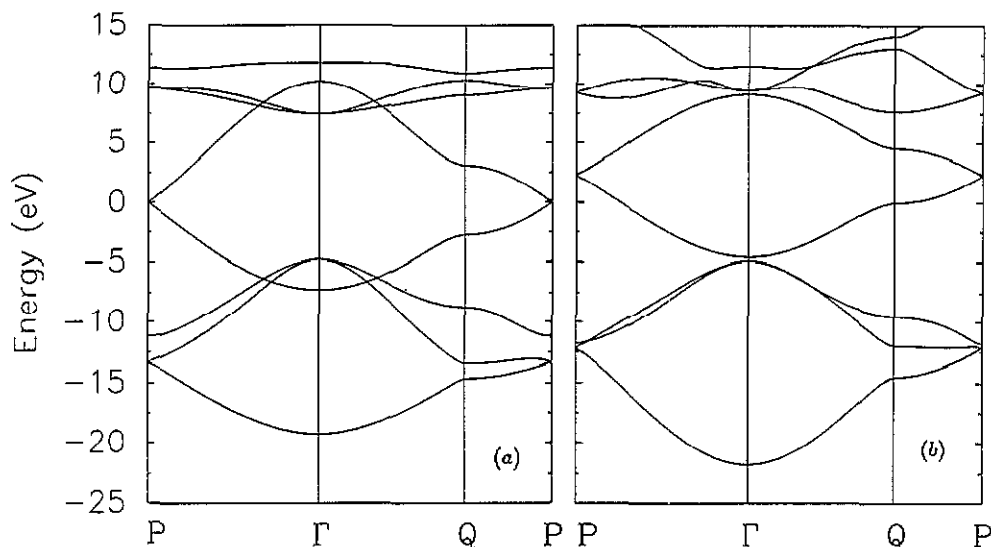It is interesting to compare the form of the parameters for carbon with a set recently

Figure 3. Tight binding band structures calculated for graphite carbon. (*a*) was calculated using the parameters from [18], which were obtained by fitting directly to an experimental band structure, which is consequently faithfully reproduced. (*b*) was calculated using the improved parameters from this paper. Comparison between the two shows that the improved parameters reproduce the essential features of the graphite band structure.

obtained for silicon [7, 8] which is also a Group IV element. For silicon it was found that the hopping parameters could each vary approximately as the inverse square of the interatomic separations and the pair potential as the inverse fourth power. In contrast the carbon parameters vary inversely with interatomic separation with powers of 2.796 and 4.455. This is commensurate with a high value of the bulk modulus for the *dia* lattice as is seen from equations (9), (10) and (11). This in turn is a reflection of the absence of core p states which would otherwise screen more effectively the nuclear Coulomb potential.

6. Conclusion

In conclusion we have shown that Harrison's hopping integrals and pairwise potential can be improved by two modifications. These are: firstly a considerably more rapidly varying form for the hopping integrals and a slightly more rapidly varying form for the pair potential and secondly a shortening of the range of the interatomic interactions. This last is important as it allows the use of the parameters in molecular dynamics simulations. The original forms were unsuitable due to the use of an arbitrary interaction cut-off. The modifications lead to an acceptable band structure for *gra*, an improved bulk modulus and improved equilibrium energies and volumes for the bulk lattices studied and in particular for the *dia gra* binding energy separation which is now essentially exact. The improved parameters should give improved results for the study of a wide range of structures.

Acknowledgments

References

[1] Majewski J A and Vogl P 1986 *Phys. Rev. Lett.* **57** 1366
[2] Cressoni J C and Pettifor D G 1991 *J. Phys.: Condens. Matter* **3** 495
[3] Finnis M W, Paxton A T, Pettifor D G, Sutton A P and Ohta Y 1988 *Phil. Mag.* A **58** 143
[4] Harrison W A 1983 *Phys. Rev.* B **27** 3592
[5] Jones R O and Gunnarson O 1989 *Rev. Mod. Phys.* **61** 689
[6] Yin M T and Cohen M L 1984 *Phys. Rev.* B **29** 6996; 1983 *Phys. Rev. Lett.* **50** 2006
[7] Goodwin L, Skinner A J and Pettifor D G 1989 *Europhys. Lett.* **9** 701
[8] Goodwin L and Skinner A J 1990 *Many Atom Interactions in Solids* ed R M Nieminen, M J Puska and M J Manninen (Berlin: Springer)
[9] Sutton A P, Finnis M W, Pettifor D G and Ohta Y 1988 *J. Phys. C: Solid State Phys.* **21** 35
[10] Harris J 1985 *Phys. Rev.* B **31** 1770
[11] Foulkes W M C and Haydock R 1989 *Phys. Rev.* B **39** 12520
[12] Skinner A J and Pettifor D G *J. Phys.: Condens. Matter* submitted
[13] Slater J C and Koster G F 1954 *Phys. Rev.* B **94** 1498
[14] Froyen S and Harrison W A 1979 *Phys. Rev.* B **20** 2420
[15] Papaconstantopoulos D A 1986 *Handbook of the Band Structures of Elemental Solids* (New York: Plenum)
[16] Heine V, Haydock R, Bullett D W and Kelly M J 1980 *Solid State Physics* vol 30 (New York: Academic)
[17] Beer N and Pettifor D G 1984 *Electronic Structure of Complex Systems (Proc. NATO Advanced Study Inst.)* ed P Phariseau and W Temmerman (New York: Plenum)
[18] Robertson J 1983 *Phil. Mag.* B **47** L33