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Calculation of the electronic and elastic properties of carbon

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Abstract. By accurately fitting tight-binding parameters to *ab initio* band structures from different tetrahedral volumes, tight-binding parameters have been developed for carbon. The model has scaling form similar to the tight-binding Hamiltonian of Xu *et al*. However, the properties of the higher-coordinated metallic structure are well described by the model in addition to those of the lower-coordinated covalent structures. This one reproduces accurately the band structures of carbon polytypes and gives a good description of the elastic constants for carbon in diamond structure. Results for phonon frequencies in crystalline carbon are also presented.

1. Introduction

Carbon is unique among the elements in its ability to form strong chemical bonds with a variety of coordination numbers from two (e.g. linear chains or carbine phase), to three (e.g. graphite) and four (e.g. diamond). Combining strong bonds with light mass and high melting point, condensed carbon phases have many unique properties that make them technologically important as well as scientifically fascinating. Despite extensive studies over the past few decades, many interesting problems remain unresolved. Examples including those of the high-temperature, high-pressure phase diagram of carbon [1] and the geometric and electronic structure of various disordered carbon phases [1, 2]. In particular, the recent exciting discovery of carbon fullerenes [3, 4] opened up an entirely new area of research with many unanswered questions.

Previous theoretical studies on condensed carbon fell into two main categories: Calculations using *ab initio* techniques [5–9] and calculations based on empirical interatomic potentials [10–16]. These potentials are very fast and can be applied to large numbers of atoms. However, they do not treat electronic structure at all and are relatively inaccurate in predicting many properties [17]. In contrast, in the last ten years, accurate and reliable results have been obtained for the various bulk crystalline phases by first-principles calculations using density functional theory within the local-density approximations (LDA) [5, 6], but are limited to about 100 atoms or fewer, except when great computer resources are available or reduced convergence of the results is accepted.

The tight-binding method [18–24] offers a reasonable compromise between these other methods. Compared with *ab initio* methods it is reasonably fast and can handle many atoms. Compared with classical potentials it offers great accuracy, with a reasonably correct treatment of electronic structure.

Early versions of tight-binding (TB) models [14, 15] were quite successful in describing the properties of the solid when it is near the diamond structure. However, these early TB

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models can be quite unreliable when extrapolated to other crystalline or disordered structures. It is clear that the usefulness of a TB model in describing the disordered carbon complex systems is closely related to its transferability. Recently, Goodwin, Skinner and Pettifor (GSP) [18] and Sawada [19] have shown that it is possible to obtain a TB model for silicon that accurately describes the energy-versus-volume behaviour of silicon in crystalline phases with different atomic coordination as well as the structure of small clusters. In this paper, we develop for carbon a similar TB model in which we adopt the scaling form given by Xu *et al* [22] for the dependence of the TB hopping parameters on the interatomic separation. However, we address the problem of the model of Xu *et al* [22] by examining alternative scaling form that can be used with a single unique radial cutoff in the calculalution of the electronic properties of the higher-coordinated metallic structure of carbon. The model is shown to have good transferability when applied to a wide variety of crystal structures. Our goal is to describe accurately the electronic properties with our tight-binding model. We provide a tight-binding sp^3 Hamiltonian for carbon in the diamond lattice; our calculations may range from first-nearest neighbours (NN), orthogonal, to third-nearest neighbours. In this paper we demonstrate that transferable tight-binding model for carbon can be found by a careful fitting to LDA calculations. As will be demonstrated, this tight-binding model is in many cases comparable in accuracy to LDA calculations.

2. Tight-binding model for carbon

The semi-empirical tight binding (STBM) method is particularly suited to describe electronic structures when the crystal arrangement is distorted by pressure; it is also of considerable importance in the search for transferable tight-binding (TB) Hamiltonians for group IV semiconductors and in total-energy calculations [18–21]. In all these situations, the knowledge of the change of Slater–Koster parameters with the distance is essential. For this aim an often-used prescription is the d^{-2} Harrison scaling law [15]. The inadequacy of the Harrison law has been pointed out in literature [15] and more or less complicated expressions have been introduced to selectively correct each parameter involved in (TB) matrix elements. While this approach is very successful in a variety of applications, the difficulty is its transferability to structural configurations that are very different from diamond structure.

A very important development toward both of these problems was made by GPS [18]. However, we adopt the functional form suggested by Xu *et al* [22] for the scaling function $h(r)$:

$$h(r) = \left[\frac{r_0}{r}\right]^n \exp\left\{n\left[-\left[\frac{r}{r_c}\right]^{nc} + \left[\frac{r_0}{r_c}\right]^{nc}\right]\right\}.$$

Here $h(r)$ represents the distance-dependent tight-binding parameters, where r_0 denotes the nearest-neighbour atomic separations in diamond, and n, n_c , r_c are parameters that need to be determined. r_c controls the range of the interactions, and n_c the decay of the scaling form. The electronic eigenvalues are obtained by solving an empirical tight-binding Hamiltonian H_{TB}. The off-diagonal elements of H_{TB} are described by a set of orthogonal sp^3 two-centre hopping parameters, $h_{ss\sigma}$, $h_{sp\sigma}$, $h_{pp\sigma}$, $h_{pp\pi}$, scaled with interatomic separation r as a function $h(r)$; and the on-site elements E_s and E_p are the atomic orbital energies of the corresponding atom. The model of Xu *et al* reproduced the bulk phase energy of carbon when the TB parameters were restricted to the first-neighbour shells of all the structures. However, it is impossible to chose a cutoff distance that satisfies the condition that all crystalline structures of carbon have only nearest-neighbour interactions. When we do use this cutoff distance of 2.6 Å, notable effects are found on the metallic structures which are shifted to higher energy values. In our TB model, the values of the matrix elements are non-negligible near the second-neighbour distances in carbon, which yield a good description of the electronic properties for carbon in various bulk crystal structures. This implies a cutoff between the second- and third-neighbour distances, 2.87 Å.

The parameters in the model are chosen primarily by fitting first-principles (LDA) results of the band structures for different carbon polytypes [5, 6], i.e. diamond, graphite, linear chain, (hexagonal compact) h.c.p structures. For these parameters (h_α, $n_{c\alpha}$, $r_{c\alpha}$ and n) the energy bands of the bulk phases of carbon were fitted with a nonlinear least-squares-fitting routine. The final set of parameters is $n = 2$, $r_c = 2.87$ Å, $n_c = 6.85$. The parameters obtained from such fitting are listed in table 1. Additional checks have also been made to ensure that the model gives reasonable results for elastic and vibrational properties.

Table 1. The parameters of the energy integrals obtained with the adjustment of our parameters to LDA calculations, with $E_s = -5.163\,31$ eV and $E_p = 2.288\,87$ eV. The hopping parameters (h) are in eV.

R (Å)	$h_{ss\sigma}$	$h_{sp\sigma}$	$h_{pp\sigma}$	$h_{pp\pi}$
1.54	−4.433 38	3.786 14	5.659 84	−1.828 61
2.51	0.135 79	−0.015 36	0.626 02	−0.243 84
2.95	−0.011 24	0.163 36	−0.066 70	0.065 17

3. Results

We have first calculated the band structure of diamond cubic carbon with all of the input parameters obtained by fitting to the electronic band structure obtained from first-principles LDA calculations [25]. In figure 1, the TB band structure of carbon in the diamond lattice is plotted at the experimental lattice constant of 3.56 Å. The dispersion of all the TB valence bands as well as the lowest conduction bands agree very well with the LDA results [25]. Interactions up to third neighbours are considered; inclusion of third neighbours is

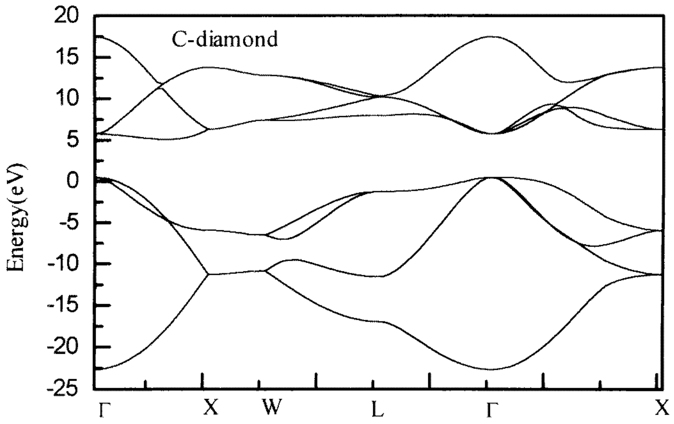


Figure 1. The band structure of diamond carbon calculated within the two-centre orthogonal approximation.

essential for accurate description of the region around the fundamental gap and of the lowest conduction bands. The (root mean square) rms deviations of these bands is 0.01 eV, which is almost the same as the best that has previously been achieved [25]. We summarize in table 2 the known experimental [26] and LDA eigenvalues at high-symmetry points Γ, X and compare them with those of our calculation. Interestingly, our band gap data are in good agreement with the LDA, and experimental results (see table 2). The occupied states are almost exactly reproduced. In addition, our calculation yields accurate results for the two lowest unoccupied states. However, the agreement for the two highest conduction bands is not so good, possibly because these two highest-energy bands involve contribution from d states.

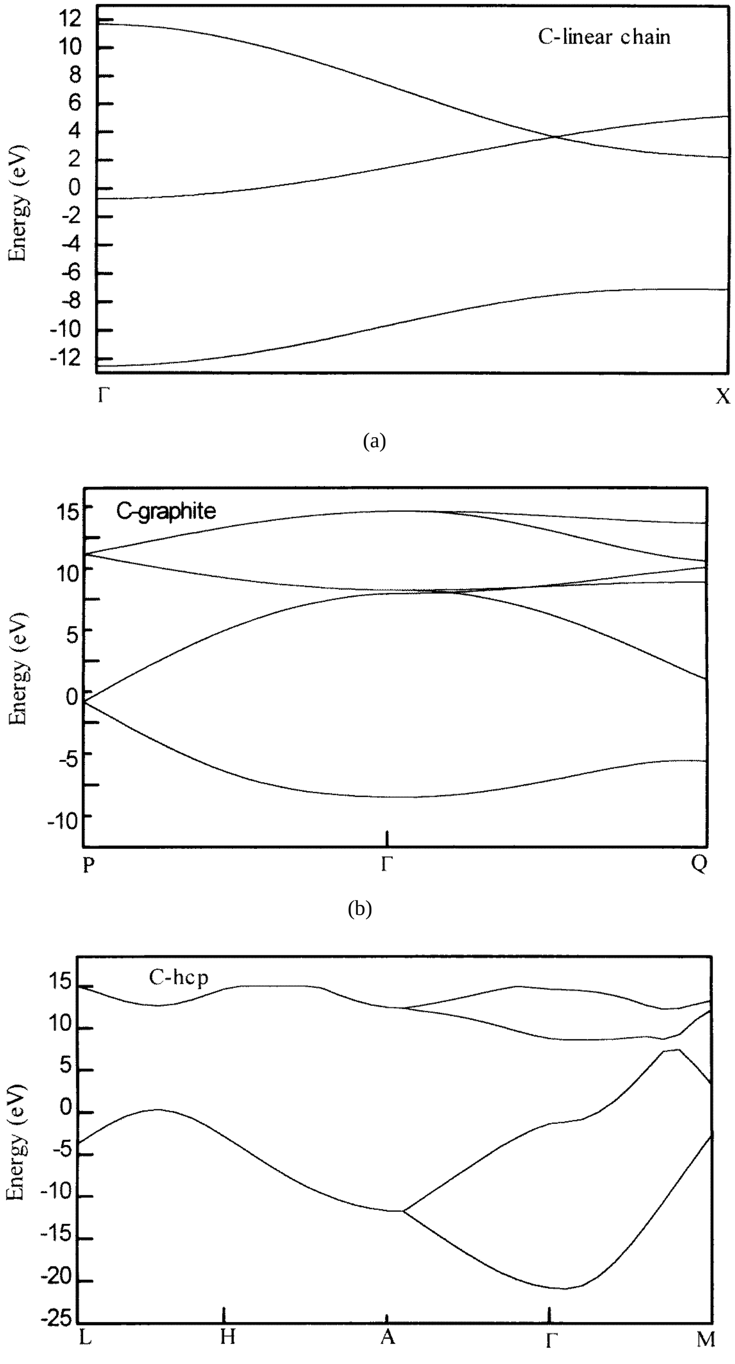
Table 2. Eigenvalues in units of eV at high-symmetry points Γ and X of diamond carbon obtained within our calculation compared to LDA [25] and experimental data. The experimental data are quoted from [26].

Symmetry points	Our calculation	Experimental	LDA
Γ_{15}	6.01	6.00	6.02
$\Delta_1^{\min}$	5.96	5.5	5.91

Using the same set of input parameters, we then applied the TB method to calculate the band structures of graphite, linear chain and h.c.p. structures at different lattice constants of 1.34, 1.41 and 1.89 Å, respectively, which are theoretically predicted from LDA calculations. We found that a good tight-binding fit could be obtained only if the s and p basis functions on different atoms were assumed to be orthogonal. The use of a minimal basis set is inadequate for describing the higher-energy bands; we focus our fitting on the occupied energy bands. The results are shown in figure 2. However, the TB model reproduces very well the occupied bands for carbon crystalline structures with coordination numbers varying from 2 (linear chain) to 12 (h.c.p.). The lower part of the conduction bands in the h.c.p. structure is also fairly well described. This is due to the absence of higher-energy orbitals in the basis set. Thus, a good description of the occupied energy bands should be adequate for studying the elastic properties of condensed phases. In the present work, we have shown that the TB parameters adjusted for the diamond structure can produce fairly good results for the h.c.p., graphite and linear chain structures. The fact that these systems under consideration have different coordination numbers (2 to 12) demonstrates the good transferability of the TB method. However, it is clear that the present TB model improves significantly the transferability of the model of Xu *et al* [22] to describe the electronic properties of the metallic structure. In table 3, the vibrational and elastic properties of diamond carbon

Table 3. Values of the bulk modulus B, elastic constants and the phonon frequencies of diamond C calculated with the present tight-binding model, and compared to the experimental results (Expt.). The experimental data are quoted from [26].

	Our calculation	Expt.
B (10^{11} erg cm^{-3})	76.01	56.7
$(C_{11} - C_{12})/2$ (10^{11} erg cm^{-3})	32.10	47.60
C_{44} (10^{11} erg cm^{-3})	48.01	43.00
$\omega_{LTO}(\Gamma)$ (THz)	35.21	39.9
$\omega_{TA}(X)$ (THz)	25.29	24.20
$\omega_{LA}(X)$ (THz)	34.06	35.5



(a)

(b)

(c)

Figure 2. (a) The band structure of linear chain carbon. (b) The band structure of graphite carbon. (c) The band structure of h.c.p. carbon.

predicted by the present TB model are presented and compared with experimental data. Very good agreement is achieved between our calculated phonon frequencies and the experimental data [27] (errors all within 5%). However, the elastic constants $(C_{11} - C_{12})/2$ and C_{44} are too soft in comparison with experimental data (errors all within 15%).

4. Conclusion

In conclusion, our TB model gives an accurate description of the electronic, elastic and vibrational properties of carbon. It is able to reproduce the band structures of accurate LDA calculations with excellent transferability among the linear chain, graphite, diamond and h.c.p. structures. The model gives a good description of higher-coordinated metallic structures. This approach is very successful in describing the band structures of carbon structures with coordination numbers ranging from 2 to 12. We expect that our TB model will have widespread applications in the study of complex carbon systems.

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