

## TOTAL ENERGY CALCULATIONS FOR EXTREMELY LARGE CLUSTERS: THE RECURSIVE APPROACH

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We present a computationally efficient scheme to evaluate the total energy of clusters that treats the nonlocality of bonding in very large systems, yet scales linearly with the number of atoms. The local electronic density of states and the corresponding band-structure energy, based on a Slater–Kloster parametrized Hamiltonian, is evaluated using the recursion technique. Other energy contributions are combined into pairwise repulsive energies. We demonstrate the utility of our approach by presenting total energies and densities of states for the different bulk forms of carbon.

THE RELATIVELY recent discovery of carbon fullerenes with a similar bonding topology as the  $C_{60}$  “buckyball” [1, 2] has ignited the imagination of physicists, chemists and materials scientists alike in search of new man-made materials with unusual properties. For carbon alone, a whole plethora of structures has been proposed [3], ranging from giant hollow fullerenes [4] to elongated “bucky tubes” [5] and three-dimensional graphitic membranes with “plumber’s nightmare” structures [6, 7]. In spite of the strong interest in the equilibrium geometry and total energy of these structures, only in very limited cases *ab initio* calculations — using methods such as the Local Density Approximation (LDA) [8] — have been attempted due to the complexity of these systems. In the case of carbon in particular, the local bonding geometry depends sensitively on the electronic configuration at each given site. This fact limits the predictive power of local two- or three-body potentials for this purpose. Approximate schemes have been used with limited success for small carbon clusters which have a substantially different structure than graphite [9–11]. Other approaches based on a parametrized tight-binding Hamiltonian have been more successful in this respect [12, 13]. While these latter schemes do predict the correct bonding geometry in different  $C_N$  clusters, the computations are limited by the diagonalization of the corresponding Hamiltonian matrix which scales as  $N^3$ . This computational requirement is not acceptable when studying the dynamics of very large structures or performing

molecular dynamics simulations of the growth process.

In this paper we present a new approach to calculating the electronic structure, which scales as  $N$  rather than as  $N^3$ . The idea underlying our approach is that the electronic configuration at a given site is determined primarily by the local environment. When calculating the electronic structure, we consider the neighboring atoms of the particular site and embed the corresponding cluster in a medium which is typical of the local bonding geometry. The method of determining the electronic structure is closely related to the cluster Bethe lattice [14] of the nearly equivalent recursion technique [15]. The latter method in particular has been very successful in the determination of the electronic structure of amorphous systems. The formalism which we develop below, and which is inspired by the recursion technique, provides a very efficient way to estimate accurately the total energy of large covalently bonded clusters.

We have found it useful to separate the cohesive energy of the system (with respect to isolated atoms) into two parts, as

$$-E_{\text{coh}} = E_{\text{band}} + E_{\text{rep}}. \quad (1)$$

The first energy contribution,  $E_{\text{band}}$ , is the electronic band-structure energy, which is nonlocal by nature and reflects the hybridization in the system. The second term,  $E_{\text{rep}}$ , contains the internuclear repulsion and all other corrections to  $E_{\text{band}}$  such as the closed-shell repulsion, exchange-correlation and energy

double-counting corrections. We approximate  $E_{\text{rep}}$  by a sum of pairwise functions  $E_r$ , as

$$E_{\text{rep}} = \sum'_{ij} E_r(r_{ij}, Z_i). \quad (2)$$

In the summation, each pair of nearest neighbor sites  $i$  and  $j$  is counted twice. The functions  $E_r$  are isotropic and can depend on the coordination number  $Z_i$  of the atoms.

As shown previously [12], the one-electron spectra of different carbon structures can be obtained to a sufficient accuracy by mapping *ab initio* LDA band structures for the corresponding systems onto a tight-binding Hamiltonian. In this procedure, the essential information about the electronic structure and many-body effects in the system is kept intact.

The one-electron band-structure energy is given by

$$E_{\text{band}} = \sum_i \left( \int_{-\infty}^{E_F} EN_i(E) dE - \sum_{\alpha} n_{i,\alpha} \epsilon_{\alpha} \right). \quad (3)$$

Here, the summation extends over all atomic sites  $i$ ,  $N_i(E)$  is the local electronic density of states, and  $E_F$  is the Fermi energy which is a global quantity. The reference energy of an isolated atom is expressed in terms of the energy levels  $\epsilon_{\alpha}$  and the corresponding occupation numbers  $n_{i,\alpha}$  which satisfy the condition

$$\sum_{\alpha} n_{i,\alpha} = \int_{-\infty}^{E_F} N_i(E) dE. \quad (4)$$

With this definition,  $E_{\text{band}}$  is zero for both empty and full bands.

The most difficult part of the total energy evaluation is an efficient scheme to determine the local density of states. While  $N_i(E)$  should contain the essential physics associated with the nonlocality of bonding, the exact function is not very important since the band structure energy, given by equation (3), is an integral quantity of  $N_i(E)$ . Even though the local density of states can in principle be determined using *ab initio* techniques [16], we prefer a tight-binding parametrization for its computational efficiency. Calculations based on the tight-binding formalism are much easier to perform than analogous *ab initio* calculations especially when describing large unit cells and low symmetry situations. Even in absence of symmetry, the tight-binding Hamiltonian can be used to determine the local density of states from a moment expansion, using the recursion technique [15].

For carbon systems, we based our electronic structure calculations on a Slater-Koster parametrized [17] four-state tight-binding

Hamiltonian [12]. The energy levels of carbon atoms are  $E_s = 7.3 \text{ eV}$  and  $E_p = 0.0 \text{ eV}$ . The off-diagonal matrix elements are the hopping integrals with an exponential distance dependence. Their values for  $d = 1.546 \text{ \AA}$ , which is the equilibrium nearest-neighbor distance in diamond, are  $V_{ss\sigma} = -3.63 \text{ eV}$ ,  $V_{sp\sigma} = 4.20 \text{ eV}$ ,  $V_{pp\sigma} = 5.38 \text{ eV}$ , and  $V_{pp\pi} = -2.24 \text{ eV}$  [12]. Instead of using a fixed cutoff distance for determining nearest neighbors, we reduce the interatomic interactions by multiplying the hopping integrals with the cutoff function [18]  $\exp(-(r/r_c)^{n_c} + (r_o/r_c)^{n_c})$ , where  $r_o = 1.546 \text{ \AA}$ ,  $r_c = 1.5r_o$ , and  $n_c = 10$ .

As mentioned above, the idea underlying this approach is that the interactions between two sites do not depend significantly on the bonding topology far away. This approach has been used successfully in the calculation of the electronic structure of amorphous semiconductors [14]. The local density of states at the site  $i = 0$  is given by

$$N_0(E) = \lim_{\epsilon \rightarrow 0} \left( -\frac{1}{\pi} \right) \text{Im} G_{00}(E + i\epsilon). \quad (5)$$

The  $G_{00}$  element of the Green function matrix is given by the Dyson equation as

$$G_{00}(E) = \left( \frac{1}{E - H} \right)_{00} = \left( \begin{array}{cccc} E - a_0 & -b_1 & 0 & \dots \\ -b_1 & E - a_1 & -b_2 & \dots \\ 0 & -b_2 & E - a_2 & \dots \\ \dots & \dots & \dots & \dots \end{array} \right)^{-1}_{00} = \frac{1}{E - a_0 - \frac{b_1^2}{E - a_1 - \frac{b_2^2}{\dots}}}. \quad (6)$$

The continued fraction coefficients  $a_n$  and  $b_n^2$  are related to energy moments  $\mu_{\alpha} = \int_{-\infty}^{+\infty} dE E^{\alpha} N_0(E)$  of the local density of states at the site  $i = 0$ . These coefficients are obtained by tridiagonalizing the Hamiltonian matrix of the system,

$$H_{TD} = \left( \begin{array}{cccc} a_0 & b_1 & 0 & \dots \\ b_1 & a_1 & b_2 & \dots \\ 0 & b_2 & a_2 & \dots \\ \dots & \dots & \dots & \dots \end{array} \right). \quad (7)$$

Charge transfer between inequivalent sites in the structure is reduced by an on-site Coulomb interaction which, in the mean-field approximation, can be mapped onto a crystal potential. Variations of

the crystal potential impose a rigid shift on the local densities of states. This shift of the core and valence levels does not affect the crystal cohesion, yet is reflected in different core level binding energies. In our calculation, we determine this shift by imposing a local charge neutrality condition

$$\int_{-\infty}^{E_F} N_i(E) dE = \text{const.} \quad (8)$$

In the following, we describe useful simplifications which lead to an efficient computation of the local density of states for different structures. The specific case of carbon is likely to be computationally the most demanding due to the complexity of carbon bonding. Directional bonding, i.e. the preference for definite bond angles for  $sp$ ,  $sp^2$ , or  $sp^3$  type bonding, requires that at least the four lowest moments  $\mu_\alpha$  be included in the continued fraction. Furthermore, it is essential to treat the  $s$ ,  $p_x$ ,  $p_y$  and  $p_z$  subbands in the density of states separately in order to represent correctly the bond stretching and bond bending forces.

The fifth moment of density of states depends only on the first and second neighbors of any given site. The corresponding information, contained in the recursion coefficients  $a_n$ , and  $b_n^2$ ,  $n = 0, 1, 2$ , is determined by tridiagonalizing the corresponding small submatrix of the Hamiltonian matrix. Truncation of the continued fraction after  $b_2^2$  would lead to a set of  $\delta$ -functions for the density of states, corresponding to a small isolated cluster with many dangling bonds [19]. A physically more reasonable approach to describe very large structures is to embed the small cluster in an average environment with similar bonding. This can be achieved by attaching a Bethe lattice to the cluster [14] which, to a large degree, is equivalent to using

$$t(E) = \frac{b_\nu^2}{E - a_\nu - t(E)}, \quad (9)$$

giving the square root terminator  $t(E)$  [20] in the continued fraction in equation (6). The terminating coefficients  $a_\nu$  and  $b_\nu^2$  are easily determined in the bulk limit from the lower and upper band edges. In our calculation, these values are taken from the linear chain, the graphite monolayer or bulk diamond, depending on the local coordination of the site  $i = 0$ . The density of states for these structures, obtained within the tight-binding formalism is shown in Figs. 1(a), (b) and (c).

As mentioned earlier, the essential information for the calculation of deformation energies is contained in the recursion coefficients  $a_n$ ,  $b_n^2$  with  $n \leq \eta$ ,  $\eta \approx 2$ . Attaching a square root terminator to

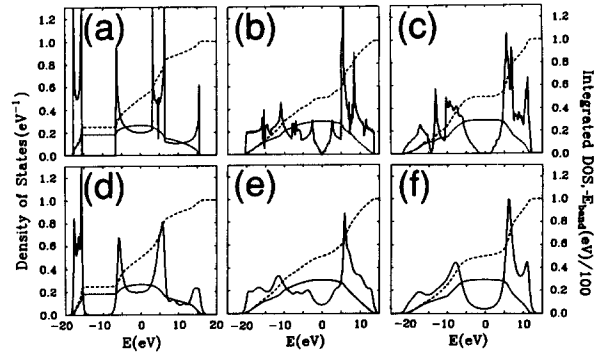


Fig. 1. Electronic local density of states  $N(E)$  (solid lines), integrated density of states  $\int_{-\infty}^{E_F} dEN(E)$  (dashed lines), and the band structure energy  $-E_{\text{band}}(E_F)$  as a function of band filling (dotted lines) for different carbon structures. Results of a tight-binding band-structure calculation for an infinite carbon chain (bondlength  $d_{\text{CC}} = 1.286 \text{ \AA}$ ) (a), a graphite monolayer ( $d_{\text{CC}} = 1.418 \text{ \AA}$ ) (b) and bulk diamond ( $d_{\text{CC}} = 1.546 \text{ \AA}$ ) (c) are compared with the simplified recursive results in (d), (e) and (f). The energy zero coincides with the Fermi level for a half-filled band, corresponding to neutral carbon.

the continued fraction of equation (6) at this point would mean to ignore the specific bonding topology and the corresponding connected loops which modify the *higher* moments and continued fraction coefficients beyond  $\eta$ . We have found it useful to consider continued fraction coefficients beyond  $\eta = 2$  in the expression for the density of states. Rather than calculating these coefficients explicitly by tridiagonalizing an accordingly much larger Hamiltonian submatrix, we use previously calculated coefficients  $a_n$ ,  $b_n^2$  ( $3 \leq n \leq 8$ ) for the bulk structures as a “patch” which we splice onto the continued fraction. The set of coefficients for a linear chain, graphite and diamond is selected according to the coordination number of the site of interest. In order to avoid strong oscillations in the density of states due to this “patch” and the square root terminator, we mix in the “patch” coefficients with  $a_\eta$ ,  $b_\eta^2$  and the terminating coefficients  $a_\nu$ ,  $b_\nu^2$  so that no strong discontinuities occur in  $a_n$  and  $b_n^2$  at  $n = \eta$  and  $n = \nu$  [21]. The continued fraction coefficients in the “patch”  $\eta < n < \nu$  are given by

$$\begin{aligned} \tilde{a}_n &= \frac{1}{2} \left[ \left(1 - \sin \frac{\pi\alpha}{2}\right) a_\eta + \left(1 + \sin \frac{\pi\alpha}{2}\right) a_\nu \right], \\ \tilde{b}_n^2 &= \frac{1}{2} \left[ \left(1 - \sin \frac{\pi\alpha}{2}\right) b_\eta^2 + \left(1 + \sin \frac{\pi\alpha}{2}\right) b_\nu^2 \right], \end{aligned} \quad (10)$$

with  $\alpha = (2n - \eta - \nu) / (\nu - \eta)$ . While the above procedure gives an improved description of the density of states, the higher “patched” coefficients

Table 1. Band-structure energy  $E_{\text{band}}$  (per atom) for different carbon structures, based on tight-binding calculations (TB) or a simplified calculation using the recursion technique (RT)

	C (chain)	C (graphite)	C (diamond)	C <sub>60</sub>
$E_{\text{band}}^{\text{TB}}$ (eV)	-28.194	-30.460	-29.220	-30.143
$E_{\text{band}}^{\text{RT}}$ (eV)	-28.104	-30.392	-29.117	-30.004

do not affect the lower moments of the density of states and hence have a small effect on the band structure energy. We would like to point out that our method of termination is tolerant of a possible inaccuracy in the terminating coefficients and does not include unphysical oscillations in the local density of states. Moreover, the straightforward parametrization of the Hamiltonian and our simplified treatment of the density of states make an analytic evaluation of the forces possible, at least within the Hellman–Feynman scheme.

The densities of states of the infinite chain, a graphite monolayer, and bulk diamond, obtained using the above procedure, are shown in Figs. 1(d), (e) and (f). Also shown in this figure are the integrated density of states and the band structure energy as a function of band filling (or the position of the Fermi level). The bands in perfect neutral carbon structures are half filled. The numerical results for the band structure energies in this case are given in Table 1. These results indicate that our approximate recursive treatment of the local density of states can describe bonding in the different carbon structures with adequate precision.

Once the band structure energy is known, the total energy of the system can be evaluated using equation (1). The required pairwise repulsive energies  $R_{\text{rep}}$  are obtained from LDA total energies for symmetric bulk structures such as infinite chains, graphite and diamond, and band structure energies based on the tight-binding Hamiltonian with no

further approximations. In Table 2 we list formation energies of different systems [24] with respect to graphite, defined by  $\Delta E_f = E_{\text{coh}} - E_{\text{coh}}(\text{graphite})$ . We find very good agreement between our results and the experiment. We note that our approach represents a significant improvement over the well-established Tersoff potential [9], especially for linear structures.

As a test of our approach, we calculate the electronic structure and formation energy of the C<sub>60</sub> molecule. All atoms in this cluster are equivalent, so the calculation of the local density of states requires only the tridiagonalization of a single Hamiltonian submatrix associated with a 10-atom cluster and the knowledge of the recursion coefficients of a graphite monolayer. In this calculation, we have assumed the lengths of the single and the double bonds to be the same,  $d_{\text{CC}} = 1.418 \text{ \AA}$ . The distribution of the energy eigenvalues of C<sub>60</sub>, based on the diagonalization of a  $240 \times 240$  Hamiltonian matrix, is shown in Fig. 2(a). The local density of states, obtained from our recursive method, is given in Fig. 2(b). The occurrence of a large HOMO–LUMO gap in the C<sub>60</sub> molecule is related to the nonvanishing curvature of the C<sub>60</sub> surface. In comparison to the flat graphite monolayer, the surface curvature increases the interaction in the weakly bound  $\pi$  electron system. The main reason for this effect is the interaction between neighboring  $p_{\perp}$  orbitals (which are locally perpendicular to the surface), which is a pure  $pp\pi$  interaction in graphite, but gains a nonzero  $pp\sigma$  component at the curved C<sub>60</sub> surface. This physics is contained in the fourth moment of the local density

Table 2. Formation  $\Delta E_f = E_{\text{coh}} - E_{\text{coh}}(\text{graphite})$  (in eV, per atom) for different carbon structures. Our present results, based on the recursion technique (RT), are compared to tight-binding (TB), Local Density Approximation (LDA), Tersoff potential [9] results, and experimental data

	C (chain)	C (graphite)	C (diamond)	C <sub>60</sub>
Present approach (RT)	1.14	0.0	0.05	0.39
Tight-binding	1.12	0.0	0.02	0.33
LDA	1.10	0.0	0.02	
Tersoff <sup>a</sup>	5.41	0.0	0.03	0.82
Experiment		0.0	0.0 <sup>b</sup>	0.36 <sup>c</sup>

<sup>a</sup> See Ref. [9].

<sup>b</sup> See Ref. [22].

<sup>c</sup> See Ref. [23].

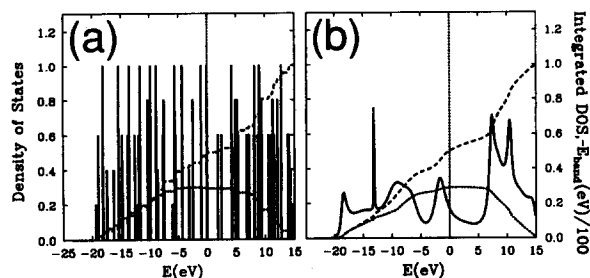


Fig. 2. Local electronic density of states  $N(E)$  (solid lines), integrated density of states (dashed lines), and the band structure energy  $-E_{\text{band}}(E_F)$  (dotted lines) for the  $C_{60}$  cluster. Tight-binding results, obtained by diagonalizing a  $240 \times 240$  Hamiltonian matrix and shown in (a), are compared to simplified recursive results in (b). The position of the “Fermi level” in the HOMO–LUMO gap is emphasized by the dotted line.

of states and hence addressed in our model. Even though our scheme underestimates the complexity of the local density of states, it shows a signature of the large HOMO–LUMO gap in the local density of states of  $C_{60}$  shown in Fig. 2(b).

The differences between the densities of states, obtained using different methods, are nearly washed out when comparing integrated densities of states and band structure energies. This fact is demonstrated in Table 1. A comparison of band structure energies for different carbon structures, based on different levels of sophistication, indicates that the recursive approach is sufficiently precise. Even more interesting is the comparison of the results for graphite and the  $C_{60}$  molecule with the same bond lengths. Since all carbon atoms are three-fold coordinated, the repulsive contribution  $E_{\text{rep}}$  to  $E_{\text{coh}}$  in equation (1) is the same for both the structures. The lower binding energy of the (unrelaxed)  $C_{60}$  structure with respect to graphite is then reflected in the accordingly smaller absolute value of  $E_{\text{band}}$  (and higher formation energy  $\Delta E_f$ ) of the  $C_{60}$  molecule due to the less favorable hybridization of orbitals. Of course, this energy difference is lowered when considering the relaxed structures. We do not expect this number to change much upon relaxation [25].

In summary, we have developed and implemented a computationally efficient scheme to evaluate the total energy of very large systems which lack symmetry. Our approach, based on the recursion technique for the local electronic density of states, accounts for the nonlocality of bonding, yet scales linearly with the number of atoms. This is a significant advantage over standard total energy calculations, based on the diagonalization of a Hamiltonian matrix, which scale as  $N^3$ . We

believe that this fact, combined with a total energy expression which effectively decouples individual sites, will prove to be a strong advantage when performing molecular dynamics calculations on massively parallel computers.

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24. The cohesive energies are evaluated for the observed equilibrium geometry of graphite and diamond. For the infinite chain, the equilibrium bond length is obtained by LDA.
25. Based on our results, we expect the binding energy (per atom) of the  $C_{60}$  structure to be 0.33 eV lower than the graphite value  $E_{\text{coh}}(\text{graphite}) = 7.37 \text{ eV}$ , yielding  $E_{\text{coh}}(C_{60}) = 7.04 \text{ eV}$ . This value is in reasonable agreement with the experimental value  $E_{\text{coh}}(C_{60}) = 7.01 \pm 0.002 \text{ eV}$  [23].