Letter

Toward a transferable parametrization for carbon in a periodic semi-empirical molecular orbital scheme

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Abstract. A new parametrization for carbon is proposed within the framework of the complete neglect of differential overlap molecular orbital theory in a scheme for systems with periodic boundary conditions using large-unit-cells and Γ point sampling, with an accurate treatment of the long-range Coulomb tails of the interaction potentials. The new parametrization is obtained by fitting simultaneously experimental and theoretical data for electronic and structural properties of diamond and graphite. Remarkably, compared with other parametrizations existing in the literature and typically based on molecular data, it provides a better description of the relative stability between the two phases, but it is still unsatisfactory in the description of the elastic properties.

Key words: Semi-empirical methods – Tight binding – Periodic systems

1 Introduction

Carbon has always attracted the attention of both physicists and chemists for its fundamental role in the living world as well as in technology. Recently, the interest has been revived by the discovery of a new form of elemental carbon, i.e., fullerenes, and by the production and characterization of a wide variety of carbon-based nanostructures such as nanotubes, onions, and other low-dimensional structures.

Understanding the physical and chemical properties of many of these structures requires accurate electronic-structure calculations, but the size and the complexity of the systems ask for a compromise between accuracy and computational burden. These considerations point to semi-empirical methods as very promising tools for this kind of problem.

Among the semi-empirical methods, tight binding (TB) [1, 2] is the most widely used by the solid-state physics community. It was originally developed to model atoms in simple and perfect crystals, and, typically, a particular tight-binding parametrization is optimized for a single crystalline structure. The various geometries and different chemical environments characterizing the wide variety of carbon-based systems ask, conversely, for a highly transferable parametrization. Although good TB Hamiltonians are nowadays available for some elements (e.g. for carbon [3, 4]), extensive transferability remains an open problem. This limitation is intrinsic to the method, and it is due to the crude treatment of the electron-electron interaction, which is not included explicitly in the standard TB Hamiltonians. The repulsive energy is taken into account empirically, typically with a pair-wise potential. Additional terms (usually in the form of a Hubbard-like term [2]) are sometimes added to the Hamiltonian in order to improve the description of systems involving large charge rearrangements. This type of ad hoc correction, however, is not satisfactory, and often not sufficient to ensure transferability. Recent attempts have been made to include in a TB framework the many-body character of the bond: satisfactory results for the structural properties of diamond and graphite are obtained [5], but with a high computational price.

Another class of semi-empirical methods is the family of Hartree-Fock-based methods, originated from the pioneering work of Pople and coworkers in the late 1960s, and developed in the computational chemistry community also for large and complex molecules. These methods range from the simplest one, the complete neglect of differential overlap (CNDO) [6], to the more sophisticated methods like the modified neglect of differential overlap (MNDO) method [7], the Austin model 1 (AM1) method [8], and the parametric method number 3 (PM3) [9]. They all make use of a linear combination of atomic orbitals for the one-electron wave functions to

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construct the single (or multiple) Slater determinant(s); this (these) is (are) in turn used as ansatz for the many-body wave function. In all these methods the electron-electron interaction is explicitly considered at the Hartree-Fock level. The inclusion on the same footing of both the nuclear-electron and electron-electron interactions eliminates the need for ad hoc terms in the Hamiltonian, and improves substantially (on average) the accuracy and transferability with respect to the TB methods.

However, semi-empirical methods were originally addressed to finite systems, and most of the available parametrizations are derived from properties of gas-phase elements or optimized for molecules, so that there is no guarantee that they will work properly when transferred to solid-state systems. There are also additional technical problems in the extension of semi-empirical methods from finite to infinite systems with periodic boundary conditions (PBC): not much care was given originally to the treatment of the tails of long-range interactions, which is, conversely, necessary in case of infinite systems; furthermore, the methods are not optimized for efficient use in very large systems.

Several authors devoted their attention to these problems, emphasizing one or the other. The problem of transferability, for instance, has been addressed in [10] and [11, 12]. In [10], periodic calculations using MNDO, AM1, and PM3 methods are performed for different systems, using parametrizations extracted from the gas phases: the results are of different quality, depending on the ionicity of the systems, and suggest in some cases the necessity of a re-parametrization. In [12] a parametrization derived from the solid-state phase [11] is applied to surface problems. The convergence of long-range term series in semi-empirical methods has also been discussed by some authors [10–15]; the necessity of a careful handling has been pointed out, with different recipes, from simple truncation schemes [11–15], to manipulation of multipole series expansion [10], to the use of the Ewald sum technique [12], but in the last case only in the context of surface studies. The problem of efficiency has also been investigated in the last few years, especially searching almost linear scaling of computational times with respect to system size, with or without PBC. We only quote here some representative work [16].

We devote our efforts here to the problems of transferability and of correct handling of lattice sums. We concentrate on the simplest of the methods mentioned above, i.e., the CNDO. We address the problem of an efficient implementation to solid-state systems, focusing our attention on carbon. To this aim, we study the electronic and structural properties of diamond and graphite, using first the CNDO parametrizations for carbon already existing in the literature. The results obtained point out some deficiencies, concerning in particular the relative stability of diamond and graphite and their elastic properties. We propose a new CNDO/2 [6] parametrization, which substantially improves the description of the structural and cohesive properties of graphite and diamond, but is still unsatisfactory for the vibrational frequencies. In the new parametrization, however, only the acoustic frequencies are implicitly

accounted for through the equation of state. The difficulty in reproducing the vibrational properties seems to be a general failure of CNDO and this suggests that a more refined semi-empirical scheme (like MNDO) is required for further improvement and better transferability.

Our calculations are performed within a computational scheme designed for large-unit-cell (LUC) and Γ point sampling, with an accurate treatment of the long-range Coulomb tails of the interaction potentials, as described in the following section. Then, Sect. 3 is specifically devoted to the comparison of the results obtained using two standard parametrizations for carbon, and to the development of the new one. A discussion on the correct treatment of the long-range term series and more details of our new computational scheme can be found in another paper [17].

2 CNDO supercell calculations

Originally developed [6] for total energy calculations for isolated finite systems (molecules in vacuum), CNDO was subsequently applied to infinite systems (polymer chains [18] and perfect or defected crystals [15, 19, 20]) with PBC.

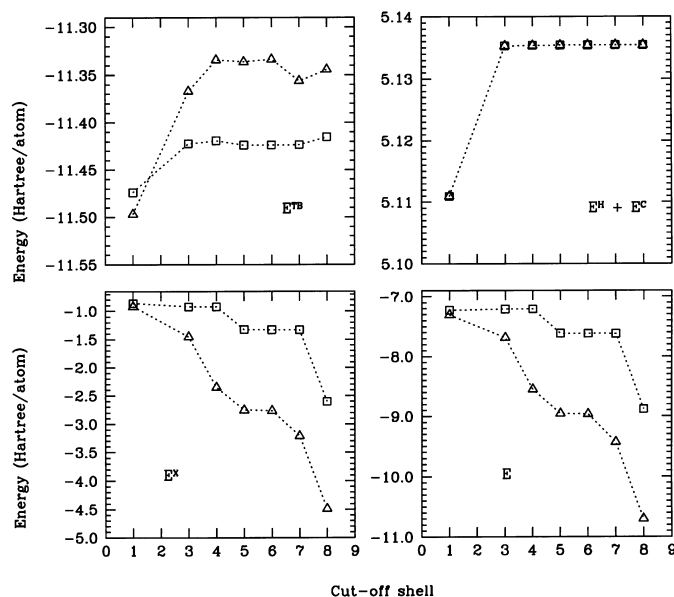In this method, the total energy E of the system is given by:

$$E = E^{TB} + E^{H} + E^{X} + E^{c}$$

where E^{TB} is the tight-binding energy (sum of on-site and hopping contributions), E^{H} is the Hartree energy, E^{X} the exchange energy, and E^{c} represents the core-core repulsion energy.

The ground state electronic structure and energy is determined by standard Roothaan-Hall self-consistent equations, as described in [6]. For extended systems, the solution of the CNDO equations requires an integration over the first Brillouin zone (BZ) which must be performed discretizing the problem in two different ways. In the first one, a finite set of representative (special) $\mathbf{k}$ points is used. In the second one, only the Γ point is used, but, in order to ensure a good BZ sampling, a LUC [15] is considered even for simple bulk systems. This type of calculation, often referred to as LUC-$\mathbf{k}=\mathbf{0}$ calculations, is often preferred for the simplicity of its formulation.

In both solution strategies, however, lattice sums of Coulomb-tailed functions are involved for the evaluation of Coulomb and exchange contributions. It is well known that the lattice sum of Coulomb-tailed potentials gives rise to conditionally convergent series [21]. Therefore, if these sums are not computed properly, the total energy may show an unphysical divergent behavior with respect to the range of the interactions, even for the simplest case of a neutral bulk system. In order to obtain physically realistic results, an artificial cut-off to the neighboring shells of interacting atoms has been imposed in many computations for extended systems [11, 13, 15]. We will briefly discuss here the reliability of this simple approximation.

By performing CNDO/2 calculations on diamond following the standard parametrization by Pople and Beveridge [6] and using different LUC's from an 8-atom simple cubic (SC) cell up to a 54-atom face-centered cubic (FCC) cell, we have studied in detail the behavior of the different contributions to the total energy with respect to the neighbor cut-off distance. The results are shown in Fig. 1. For perfect crystals, the long-range contributions in E^H cancel exactly those from the electron-nuclei term, leading to a rapidly converging behavior of $E^H + E^c$. The tight-binding energy E^{TB} is also rapidly converging, since, by definition, it contains only short-range contributions. Instead, the exchange energy E^X is responsible for an incorrect divergent behavior of the total energy E. Any choice of truncating conditions can be therefore only empirically justified a posteriori and also depends on the choice of LUC. The results obtained including the third and the fourth neighbor shells, as proposed in [14] and [15] for the 16-atom FCC, seem to be accidentally close to the correct values, being valid only for that particular LUC.

The standard method of Ewald sums can be applied to CNDO LUC-$\mathbf{k} = \mathbf{0}$ calculations and provide a more adequate treatment of the lattice sums of Coulomb-tailed functions [17]. The results are shown in Fig. 2. It can be clearly seen how now the exchange energy E^X, and consequently the total energy E, do not depend on the cut-off neighbor shell which, in the proposed scheme, controls only the lattice sums of short-range terms. Differences in the results between the various LUCs are due to the different sampling of the BZ, which comes from the use of the Γ point only, but for BZs of different size.
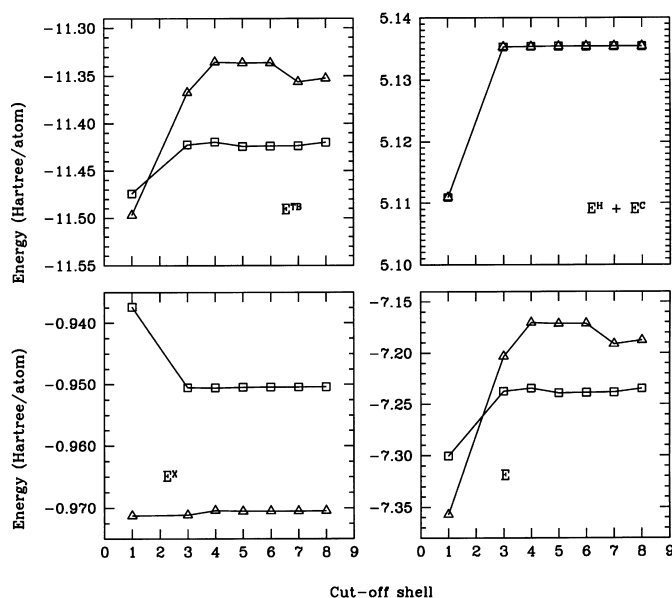
3 CNDO parametrizations for carbon

Our computational scheme provides a robust framework to evaluate unambiguously the performance of approximate molecular orbital (MO) theories on solid-state systems. We first discuss in this section the results obtained using the parametrizations available in literature; then we propose a new parametrization with the aim of improving the description of the relative stability of diamond and graphite phases, and in general of achieving better accuracy and transferability.

For diamond we perform total energy calculations on a 128-atom FCC supercell for different values of the bulk unit cell lattice parameter a. Up to third nearest-neighbor interactions are included in the lattice sums of the short-range terms. The calculated total energies E for the original Pople [6] and Harker-Larkins [14] parametrizations are shown in Fig. 3. The equilibrium lattice parameter a_0, obtained from a fit to the Murnagham equation of state, is 6.624 a.u. or 6.802 a.u. for the Pople or Harker-Larkins parametrizations, respectively, in good agreement with both experimental (6.7410 a.u. [22]) and accurate theoretical results, ranging from about 6.66 a.u. to 6.79 a.u., including Hartree-Fock [23], ab initio pseudopotentials [24–26], and recent improved TB data [4, 5]. Conversely, the estimated bulk modulus is largely overestimated with both parametrizations. Moreover, the absolute value of the cohesive energy E is significantly larger or smaller than the experimental one for the Pople or Harker-Larkins parametrizations, respectively. The quality of these findings is analogous to that of results for the molecules, i.e. very good equilib-

Fig. 1. Total energy E (*right lower panel*) and its constituting terms (*other panels*) obtained for diamond from CNDO calculation with the 8-atom SC (*triangles*) and 16-atom FCC (*squares*) LUCs and using the standard truncation scheme for the treatment of the Coulomb lattice sums. The energies are plotted as a function of the nearest-neighbors cut-off shell. The lattice parameter a_0 was fixed at the experimental value of 6.741 a.u. Dotted lines are a guide to the eye
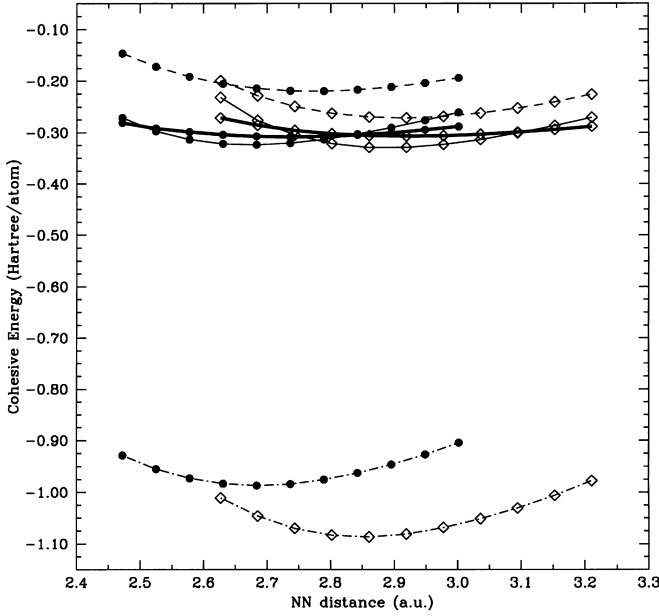

Fig. 2. Total energy E (*right lower panel*) and its constituting terms (*other panels*) obtained for diamond from CNDO calculation with the 8-atom SC (*triangles*) and 16-atom FCC (*squares*) LUCs and using the Ewald method for the treatment of the Coulomb lattice sums. The energies are plotted as a function of the nearest-neighbors cut-off shell. Solid lines are a guide to the eye

Fig. 3. Equation of state for carbon in the diamond (*diamonds*) and in the graphite (*circles*) structures. Lines are a guide to the eye, joining data obtained using CNDO with the original Pople (*dashed-dotted lines*) [6] or Harker-Larkins (*dashed lines*) [14] parametrizations, and with the new one proposed in this work (*thin solid lines*). Calculations have been performed with the correct treatment of the lattice sums of long-range terms, as proposed in this work. For comparison also, DFT *ab initio* results (*thick solid lines*) from [4] are shown

rium geometries and poor predictions for binding energies and elastic constants.

Graphite is a layered solid with a large interlayer distance (6.34 a.u. [22], i.e. almost 2.4 times the interatomic distance within planes). Lattice planes have the honeycomb arrangement. To optimize the in-plane geometry, interlayer interactions can be neglected in a first approximation since their contribution to the total energy of the system is small (0.0013 Hartree/atom [27]), so that we study in practice a graphite monolayer. We have performed total energy calculations on a 2D 128-atom supercell with basic vectors eight times those of the two-atom Wigner-Seitz primitive unit cell. Lattice sums of short-range interactions include up to third neighbors. In Fig. 3 we show the cohesive energy per atom calculated by the two CNDO parametrizations listed above, compared to the results obtained from density functional theory (DFT) (reported in [4]). The calculated in-plane lattice parameter a_0 is 4.648 a.u. or 4.810 a.u. for the Pople or Harker-Larkins parametrizations, respectively, in good agreement with the experimental value (4.669 a.u.[22]) and more accurate calculations [4, 5, 24–26], whereas the cohesive energy and the bulk modulus deviate significantly from the correct values.

In studying the structural phase stability of carbon, a difficult point is the relative stability of diamond and graphite structures, which are nearly degenerate. This is afforded in the theoretical works previously cited, both using TB schemes [3–5] and ab initio pseudopotentials [24–26]. Both experiments and recent calculations [5, 25, 26] indicate that graphite is more stable

than diamond, but the difference in the cohesive energy is very small (from 0.00003 Hartree/atom in [26] up to 0.0015 Hartree/atom in [5]), comparable or even smaller than the difference between the zero-point vibrational energies (estimated to about 0.0005 Hartree/ atom [26]) and in some cases smaller than the numerical accuracy. Both the Pople [6] and the Harker-Larkins [14] parametrizations give diamond more stable than graphite by a non negligible amount, i.e. by 0.087 Hartree/atom and 0.052 Hartree/atom respectively (see Fig. 3).

We tried to obtain a new CNDO parametrization aimed at improving the description of diamond and graphite. The new parametrization should give proper account of both sp^3 and sp^2 hybridizations. If successfully accomplished, we expect this to improve accuracy and transferability.

The on-site energy integrals ϵ_s and ϵ_p as well as the proportionality constants β_I of the hopping energy integrals $\beta_{\mu\nu}$ (see [6] for the definition of the CNDO parameters and functions) were assumed to be free adjustable parameters. The electron-electron repulsion energy and the electron-core attraction energy potentials γ_{IJ} and V_{IJ} were recast into the following expressions:

$$\gamma_{IJ}(r) = \frac{1 - (1 - \gamma_1 P_\gamma(r))\mathrm{e}^{-2\xi_\gamma r}}{r} \tag{1}$$

$$V_{IJ}(r) = Z_J \frac{1 - (1 - V_1 P_\mathrm{v}(r))\mathrm{e}^{-2\xi_\mathrm{v} r}}{r} \tag{2}$$

where $P_\gamma(r)$ and $P_\mathrm{v}(r)$ are polynomials in $\xi_\gamma r$ and $\xi_\mathrm{v} r$, obtained from the integrals over Slater-type orbitals [6]. For $\gamma_1 = 1$ and $V_1 = 1$ we recover exactly the original CNDO/2 functions. We recall that in CNDO/2 the electron-core attraction energy potential V_{IJ} is taken as a multiple of the electron-electron repulsion energy potential γ_{IJ}, more precisely $V_{IJ} = Z_J\gamma_{IJ}$. All along the re-parametrization described here, the coefficients of the polynomial $P_\mathrm{v}(r)$ are taken to be the same as those of the polynomial $P_\gamma(r)$; however, the exponent ξ_v as well as the constant V_1 will be varied independently from ξ_γ and γ_1, and therefore the functions V_{IJ} and γ_{IJ} can be different. The possibility of a different choice of the functional form for V_{IJ} has to be investigated in future attempts of re-parametrization.

We also assume the exponents $\xi_{ss\sigma}$, $\xi_{sp\sigma}$, $\xi_{pp\sigma}$, and $\xi_{pp\pi}$ of the hopping functions $\beta_{\mu\nu}$ as free parameters. We have thus in total 11 free adjustable parameters.

We first optimize the seven parameters controlling the band-structure energy (ϵ_s, ϵ_p, β_I, $\xi_{ss\sigma}$, $\xi_{sp\sigma}$, $\xi_{pp\sigma}$, and $\xi_{pp\pi}$) to reproduce correctly the accurate theoretical band-structure of diamond in the high-symmetry points Δ, X, Q, L, Σ, and Γ [28]. Then the parameters characterizing the electron-electron repulsion function γ and the electron-core attraction function V (γ_1, V_1, ξ_γ, and ξ_v) were modified to reproduce the DFT ab initio diamond and graphite cohesive energy curves of [4]. The resulting parameters (in atomic units; energies in Hartree) are the following: $\epsilon_s = -1.066$, $\epsilon_p = -0.762$, $\beta_I = -2.665$, $\xi_{ss\sigma} = 2.877$, $\xi_{sp\sigma} = 2.983$, $\xi_{pp\sigma} = 2.883$, and $\xi_{pp\pi} = 2.642$, $\gamma_1 = 1.141$, $V_1 = 1.844$,

$\xi_\gamma = 1.186$, and $\xi_v = 1.433$. Although the present attempt is only a preliminary one, being based on few input data, our basic general idea is that the use of a large set of accurate theoretical structural and electronic data which must be representatives of several different chemical environments would ensure accuracy and transferability to the parametrization, at variance with the most common schemes based on few experimental data and referred to a particular environment. For the sake of truth, a MO parametrization optimized only for diamond [11] seems to give satisfactory results also when applied to surfaces [12]; however, this parametrization is not directly comparable with the present one, being within the MNDO [7] scheme, and using the standard truncation approach for the long-range interaction series. Moreover, it is not applied to other phases, so that extensive transferability cannot be judged.

The on-site energies are smaller than those of Pople and Harker-Larkins sets; however, this is in accordance with many tight-binding parametrizations in the literature. The hopping functions $\beta_{\mu v}$ are more rapidly decaying, making the resulting scheme practically a nearest-neighbor one. The electron-electron repulsion and electron-core attraction functions obtained with the optimized parameter set are not very different from those reported previously [6, 14].

The cohesive energy curves for diamond and graphite obtained with the optimized parameter set are shown in Fig. 3. Equilibrium lattice parameters are well reproduced for both structures. Although diamond turns out again to be more stable than graphite, the difference in cohesive energy between both structures is reduced to 0.005 Hartree/atom, i.e. by at least one order of magnitude with respect to the previous CNDO parametrizations. The bulk modulus is again overestimated, as typically occurs also with the other CNDO parametrizations. This is an indication that differential overlap cannot be completely neglected. In this sense we expect that it will be more meaningful and successfully to work for a new parametrization for carbon in the MNDO [7] framework or other more sophisticated semi-empirical MO schemes.

4 Conclusions

In this paper we have used a correct scheme for treating Coulomb-tailed lattice sums for approximate MO supercell calculations, in particular we have analyzed the CNDO scheme. By an adequate use of the Ewald [21] sum technique we are able to obtain a robust computational scheme [17]. When applied to calculations on perfect crystals it eliminates the problems related with the exchange contributions to the total energy. The method is also well suited to perform supercell calculations on systems like defected or amorphous solids and systems with a limited translational symmetry (planar sheets of carbon of increased complexity, nanotubes, etc.), where the long-range contributions present in the core-core interaction energy E^c will not cancel exactly those coming from the valence electron Hartree energy E^H. Its applicability is not limited to CNDO. More sophisticated semi-empirical MO schemes such as MNDO [7], AM1 [8], and PM3 [9] are also characterized by slowly decaying potential energy functions; lattice sums of these functions will then be present in supercell calculations, both in Hartree and exchange terms. The implementation of the Ewald sum technique is therefore useful in order to avoid convergence problems.

The proposed computational scheme was preliminary applied to the study of the relative stability of diamond and graphite within CNDO. Because of its robustness, it was possible to evaluate unambiguously the performance of the CNDO/2 implementation of CNDO for carbon-based solid-state systems. Analogously to the results predicted for molecules in vacuum [6], CNDO/2 gives very good results for equilibrium bond lengths, i.e. errors with respect to experiment within about 2%, and poor results for elastic properties and cohesive energies. These trends seem to be a common feature of the CNDO method and may be ascribed to its neglect of the overlap between atomic orbitals.

However, we find some important improvement with a new parametrization obtained by fitting reference electronic structure and structural ab initio data. The new parameter set gives a better description (with respect to the old parametrizations) of diamond and graphite structural geometries and energies, but not substantial improvement for the elastic properties.

The preliminary study presented here for a new parametrization within a correct treatment of long-range terms can be extended to other MO methods, in order to definitely establish whether it is necessary to include overlap terms in both electron-electron and electron-core interaction energy functions to achieve better results. This is left to future work.

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