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Effects of basis set quality on the prediction of structures, energies, and properties of amorphous tetrahedral carbon

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We systematically investigate the effects of basis set quality on the prediction of a representative amorphous tetrahedral (a-tC) carbon structure. In fully self-consistent first-principles calculations, variations in the quality of the basis set do result in significant variations in predicted structure. Substantial differences between the calculations, ranging from a minimum basis to a high-quality double-zeta plus polarization (DZP) basis, for amorphous carbon stem from two sources. We discover that to properly relax candidate a-tC structures requires a high-quality basis set in the calculation. A minimum basis set is inadequate to negotiate the transition geometries involved in the making and breaking of bonds while relaxing a structure. Relaxation of an a-tC structure proposed by Drabold, Fedders, and Stumm [Phys. Rev. B **49**, 16 415 (1994)] using a minimum, and a DZP basis demonstrates this point. The minimum basis set calculation leaves the bonding topology essentially unchanged, while relaxation using a DZP basis removes most of the small rings and triples the number of threefold bonded atoms. In addition, we find that to accurately represent the energetics of highly defected local structures, as found in a-tC, also requires a high-quality basis set. We demonstrate this point by using molecular analogs of local structures found in a-tC. Notable is how little rebonding and energy separates a-tC structures that have qualitatively different densities of threefold atoms. [S0163-1829(98)03106-3]

I. INTRODUCTION

Dense, dominantly tetrahedrally coordinated, amorphous carbon (a-tC) has promising potential for a variety of technological applications. It is dense, hard, transparent, and a good dielectric,[1,2] and has a significant gap.[1–3] Radial distribution functions, generated by electron diffraction[4,5] and neutron scattering,[6,7] reveal dominantly tetrahedrally coordinated carbon atoms.[8,2,5] Despite this wealth of experimental data, understanding of a-tC remains limited. It is widely believed that the electronic properties of a-tC, and especially electron emission, are related to the proportion and topology of threefold carbon atoms in the material, but the relationship between growth energetics and microstructure, and materials properties and emission is unknown. Therefore, determining the microscopic structure of a-tC and verifying it by relating to experimental data is a necessary prerequisite to understanding the properties of this material, and has driven many recent theoretical studies.[9–20] However, realistic simulation of amorphous materials places extreme demands on computational approaches. The lack of crystallinity requires using relatively large bulk unit cells, while still accurately computing the energetics of the component atoms despite large variations in local bonding environment. Studies of a-tC pose a particularly difficult challenge from a computational perspective because of the unique richness in bonding that carbon exhibits. This material has a mixture of mostly fourfold and some threefold bonded atoms, connected by single, double, and conjugated bonds in a strained network of rings both smaller and larger than the sixfold rings that characterize crystalline carbon. Figure 1 illustrates a distribution of the bond lengths and bond angles found in a structure we obtained by relaxing the a-tC structure from Drabold, Fedders, and Stumm.[12] Such large bond-length and bond-angle distortions about the carbon atoms severely test the assumption of transferability that semiempirical methods require to be accurate. These same large local distortions may necessitate substantial variational freedom in the basis set for accurate first-principles calculations. This paper investigates the effect of the quality of the basis set on the prediction of representative structures of a-tC.

Fully self-consistent first-principles calculations have pro-

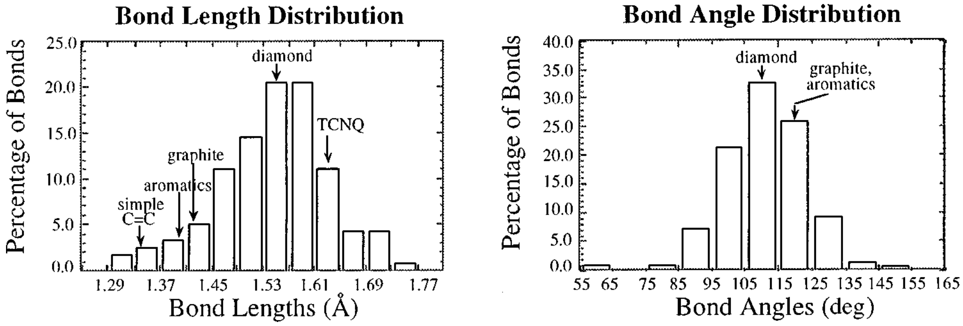

FIG. 1. Distribution of bond length and bond angles in the DFS structure, broken down in a histogram in analogy to types of bonds found in molecular systems.

duced candidate structures for amorphous carbon.[21,18,19] However, because of computational demands these have been few and limited to relatively small unit cells, typically 64 atoms or less. For routine calculations of realistic processes, incorporating time dependence and temperature effects, it would be highly desirable to use less computationally demanding, more approximate methods. In this vein, structural models have been generated by Wang and Ho (WH) (Refs. 11, 14, and 16) using tight-binding molecular dynamics (TBMD) and Drabold, Fedders, and Stumm (DFS) (Ref. 12) using a local-basis density-functional (LBDF) method.[22] Both are effectively minimum basis methods, though the latter has the additional distinction of a first-principles treatment within a Harris functional form of density-functional theory.[23] Previously,[17] we showed that large forces exist on the atoms of the DFS structure when the structure was tested using first-principles calculations with a converged basis set (that also added self-consistency). Reference 17 demonstrated that non-self-consistent methods with limited basis sets do not give an accurate representation of atomic forces. In this follow-on work, we systematically investigate basis set effects in the prediction of a-tC *structure*, and show that limitations in the basis set and a lack of self-consistency can have profound consequences for the predicted geometry of this amorphous material. Nevertheless, we do find that a minimum basis scheme may serve as a reasonable starting point to generate a viable representative a-tC structure if it is subsequently fully relaxed using a converged basis. An analysis of the relaxed structure yields results in good agreement with a structure generated from the quench with a plane-wave basis in a recent Car-Parrinello calculation by Marks *et al.*,[18,20] and in agreement with key experimental observations.

It is not our purpose to generate new model structures for a-tC, but rather to examine the minimum characteristics, and particularly basis set, necessary for any theoretical model that would attempt to generate such models. It is likely that a realistic simulation of a-tC will require much larger unit cells than used here, but 64-atom cells are sufficient to test the basic assumptions that would go into a construction of larger models, and hence, we use, as reference points, models already developed in the literature. The intent is to use the insight garnered in these small simulations to build larger simulations that contain the essential physics.

Deficiencies in the basis set manifest themselves in two ways. First, forces do need to be computed accurately in order to properly relax the geometry of a candidate structure, or that structure might be incorrectly trapped in an artificial minimum due to inflexibility in the basis. To illustrate this point, we adopt the DFS structure as our starting point and quench the structure using basis sets of increasing quality. Relaxing the DFS structure using a minimum basis ''single-ζ'' set calculation leaves the bonding topology mostly unchanged. Given the minimum basis nature of the LBDF calculation, this is a gratifying verification that the two methods represent the same physics. In a relaxation of the DFS structure using a high-quality ''double-ζ plus polarization'' basis set, however, the structure is no longer trapped in this minimum, and a full quench triples the number of threefold bonded atoms while removing half the four-member and all but one of the three-member rings present in the original structure. Second, to accurately compute the *relative* energetics of the various defected local structures present in the a-tC unit cell requires a high-quality basis set. *The different local atomic configurations present in the a-tC models incorporate different amounts of strain, and without adequate variational freedom, biases are created that artificially favor or disfavor one local structure over another*. We demonstrate this point by computing basis set dependencies in the energies of simple molecular analogs of local structures found in a-tC. Threefold rings and double bonds are found to require much greater flexibility in the basis set than other local configurations of atoms, and hence are likely to be under represented in any calculation employing nonconverged bases. A high-quality calculation is critical given how topologically close (in the number of bonds made or broken to bridge between) two different models with qualitatively different numbers of threefold atoms can be. We begin by giving a brief description of computational details, present our results of the geometry relaxations, perform some topological analyses of the final structure and compare to a structure derived without severe basis limitations,[18,20] and close with a discussion and our conclusions.

II. COMPUTATIONAL DETAILS

The first-principles calculations for this study used the local-density approximation (LDA) (Ref. 24) to density-functional theory[25] in a linear combination of atomic orbitals (LCAO) scheme, and were performed using the massively parallel Gaussian-based code QUEST.[26] For the exchange-correlation functional, QUEST uses the Perdew/Zunger parametrization[27] of the Ceperley/Alder electron-gas results,[28] and uses the generalized norm-conserving pseudopotentials of Hamann.[29] Within the LCAO scheme implemented in QUEST, there is no need for softer pseudopotentials—carbon is already well behaved. The method is a full-potential scheme that makes no empirical approximations about the shape of the charge densities or potentials, beyond the use of the pseudopotential to remove explicit treatment of the chemically inert core electrons. The Gaussian basis sets for carbon are systematically varied from single-ζ (SZ) quality, with a single contracted radial function each for the s and p orbitals, to double-ζ plus polarization (DZP), with two radial degrees of freedom each for these orbitals, plus a d orbital to allow for angular polarization. This level reproduces well the results of fully basis-converged calculations.[17] The computation of the forces incorporates the Pulay corrections[30] necessary to account properly for the dependence of the LCAO basis orbitals on atomic positions.

Two structural models are used as starting points for geometry relaxations: first, a 64-atom unit cell generated by the LBDF calculation of Drabold, Fedders, and Stumm,[12] with a density of $2.94\ \mathrm{g/cm^3}$, and, second, a $2.91\ \mathrm{g/cm^3}$ structure generated by Marks *et al.*,[18] using a Car-Parrinello calculation.[31] We also examine a larger 216 atom model generated by Wang and Ho[14,32] having a density of $3.35\ \mathrm{g/cm^3}$. We used only the Γ point in sampling the Brillouin zone for the relaxation calculations. The geometries were relaxed using a combination of a steepest descents quench, and a modified Broyden method[33] to determine the final configuration

TABLE I. Computed forces on atoms in the DFS-LBDF and WH-TBMD a-tC structures using varying basis sets. Listed are the average and maximum force (in eV/Å) and index of atom with largest force.

Basis	F (av.)	F (max)	Atom No.
		DFS-LBDF structure	
SZ	0.85	1.77	21
DZ	0.72	1.63	23
DZP	0.65	1.68	40
		WH-TBMD structure	
SZ	1.20	3.48	180
DZ	1.21	3.33	180
DZP	1.26	3.39	52
		Marks structure	
SZ	0.81	1.75	44
DZ	0.29	0.62	64
DZP	0.38	0.67	2

once the geometry had evolved to near a metastable minimum. This latter method proves unstable unless the structure is near a true local minimum. While the positions of the atoms within the unit cell were fully relaxed, the volume and shape of the cell itself were held fixed.

III. RELAXATION

A. Structure

Table I summarizes the calculations for the forces on the atoms in the DFS,[12] Marks,[18] and WH (Ref. 14) structures using SZ, DZ, and DZP basis sets. The DFS and WH structures both yield large forces in all the calculations, while the forces computed for the Marks structure are much smaller with the better DZ and DZP bases. While it might be inferred that the forces are similar between the different basis set calculations for the DFS structure (from the fact that the average and maximum force magnitudes are similar), a detailed comparison[17] reveals that the SZ and DZP forces are, for the most part, uncorrelated. The forces using the SZ basis are larger than the forces computed with the better bases, somewhat surprising given a minimum basis was used to generate the DFS structure. The principal difference of the current SZ calculation from the LBDF calculation generating the DFS structure is the addition of self-consistency in the current calculation; while differing in details, both are effectively minimum basis LDA calculations. The existence of large forces alone does not guarantee, however, that the structure will necessarily change markedly upon relaxation.[19] A difference in potentials and the addition of self-consistency will lead to some relaxation, but could, in principle, leave the bonding topology unaltered. To test this hypothesis, we start with the DFS structure and relaxed it using a SZ basis for the carbon atoms. The same was not attempted for the 216-atom WH structure because the relaxation was not deemed worth the computational expense and the issue of basis set dependence is adequately explored using the smaller 64-atom DFS structure.

The SZ quench of the DFS structure was straightforward, lowering the total energy by 1.12 eV ($\sim$0.02 eV/atom), and, indeed, does not involve a significant change of bonding topology. Only one bond ruptures, and no new ones form. Adopting a bond distance criterion of 1.9 Å (to capture two anomalously long bonds of length 1.85 and 1.82 Å—without including these the structure is left with dangling bonds), the DFS bond network contains four three-member rings, and one of these vanishes when the bond ruptures in the SZ relaxation. The number of threefold bonded atoms increases slightly from six to eight, and one of the anomalously elongated ‘‘stretched bond defects’’ [12] heals in the relaxation, but, overall, the bonding topology of the self-consistent DFS+SZ-relaxed structure strongly resembles the unrelaxed DFS structure. Given that the SZ calculation gives the largest forces of the various bases, this would appear to support the premise that a non-self-consistent minimum basis calculation can faithfully reproduce the results of a converged self-consistent calculation (the principal difference of the current SZ calculation and the LBDF method).

Despite the smaller starting forces, however, the effects of relaxing the geometry using the DZ or DZP bases are much more dramatic. Both lead to the same bonding topology, so the following discussion focuses on the DZP results, which also compares favorably with the results of a recently reported relaxation of the DFS structure using a plane-wave calculation.[19] In addition to the bond pair ruptured in the SZ calculation, six more pairs split and one new bond pair forms. The longest bond distance is now 1.75 Å, while the smallest second-neighbor distance is 2.01 Å. The stretched bond defects,[12] those bonds between 1.8 and 1.9 Å, disappear. As a result of the recoordination, the bonding network has undergone significant changes. Most notably, the number of threefold atoms triples in the relaxed structure, from 6 to 18, or 9% to 28%. In the DFS structure these appeared only in isolated pairs (true double bonds); in the relaxed structure many have coalesced into extended chains, composed of even numbers of threefold atoms (conjugated bonds). Of the four three-member rings at the start, only one remains, and of the six original four-member rings, only half survive the bond rearrangement produced by the relaxation.

Following the path of the relaxation illustrates the need to have a very flexible basis set to obtain a relaxed geometry. Excluding the first few steps after the initial geometry (with its forces of order eV/Å) the average magnitude of the forces on the atoms for any single atomic configuration typically ranged from 0.01 to 0.10 eV/Å during the course of the relaxation, and at one point the average force dipped to 0.007 eV/Å, with the largest force on any single atom being only 0.027 eV/Å. In most ordinary molecular and crystalline systems, these small forces would imply a well-converged geometry, yet for this amorphous system, three more bonds would be broken and a new one formed before arriving at the final relaxed result. That forces this small are important in the determination of structure places extreme demands on the quality of the basis set to be able to compute forces to significant accuracy. Note that the average forces on the unrelaxed DFS atomic configuration using the SZ and using the DZP basis sets differ by an amount greater than the typical average forces observed during the course of the relaxation, i.e., the *errors* in the SZ minimum basis computed forces are much larger than the *total* forces needed to be resolved in order to correctly relax the structure.

TABLE II. Average/largest forces (in eV/Å) on the atoms in calculations using different basis sets for relaxed *a*-*t*C structures.

	Basis		
Structure	SZ	DZ	DZP
DFS	0.85/1.77	0.72/1.63	0.65/1.68
DFS+SZ	0/0	0.51/1.08	0.64/1.75
DFZ+DZ	0.65/1.26	0/0	0.18/0.70
DFS+DZP	0.79/2.15	0.20/0.75	0/0

To handle the transition states that the structure must navigate through as it evolves require greater variational flexibility to treat accurately than equilibrium or near-equilibrium geometries. The DFS+SZ structure is trapped after breaking one bond, the limitation in the basis set causing the error in the computed force to be too large to negotiate the barrier to breaking the next bond. Table II presents the results of force calculations using the different basis sets for structures relaxed using the SZ, the DZ, and the full DZP basis. The relaxed DFS+DZ and DFS+DZP structures share the same bonding topology, and the cross forces between them average only 0.2 eV/Å. On the other hand, the forces on the final DFS+SZ structure, using the DZP basis, are as large as the DZP forces on the original DFS structure. Conversely, a SZ basis calculation on the DFS+DZ and DFS+DZP structures produces forces as large as the SZ forces for the unrelaxed DFS structure. For the DFS+DZP structure, the SZ basis calculation yields a force on a single atom as large as 2.2 eV/Å. The large error in computing forces using a minimum basis set does not diminish in the fully relaxed local equilibrium geometry.

One last geometry relaxation was undertaken. Starting with the relaxed DFS+DZP structure, we tested whether this final structure would change markedly if given the opportunity to relax using the SZ minimum basis. The net lowering in energy in the SZ quench from the DFS+DZP structure was about 0.53 eV, suggesting possibly significant local structural changes (by comparison, a DZ basis calculation for the DFS+DZP structure gives an energy only 0.04 eV higher than the DFS+DZ structure, and vice versa). However, despite the sizeable energy change, the bonding network does not change—the (DFS+DZP)+SZ calculation was confined in the same bonding topology as the DFS+DZP converged basis calculation. While it is not able to relax to the correct structure on its own, the SZ calculation does get trapped within the optimal bonding topology provided it is started there. This would seem to support the assertion that an anneal/quench scheme might be sufficient to generate representative structures despite a deficient basis and Hamiltonian.[19] While the shape of the potential surface and forces (and hence the dynamics) would be poorly approximated in such a calculation, an anneal might overcome the artificial barriers separating local minima and find the correct low-energy structures (correct in the sense that a converged basis calculation would arrive at the same topology) representative of *a*-*t*C. However, the validity of this assertion is dependent on the calculation being able to accurately determine relative energetics of different structures. In this section we have discussed how one needs an accurate computation of the forces to navigate the potential surface and accurately relax *a*-*t*C structures. In the next section, we address the question how flexible a basis-set representation is needed to treat the energetics, and provide an example where the minimum basis calculation does not stay confined in the same bonding topology as a converged basis calculation.

TABLE III. Relative total energies of *a*-*t*C structures relaxed with different basis sets, in eV.

	Basis		
Structure	SZ	DZ	DZP
DFS	0.0	0.0	0.0
DFS+SZ	−1.12	−1.04	−0.64
DFS+DZ	−4.41	−5.36	−4.63
DFS+DZP	−4.24	−5.32	−4.67
Marks	−0.63	−4.76	−4.43
Marks+SZ	−1.79	−4.29	−3.75
Marks+DZP	−0.14	−4.77	−4.59
Diamond (Γ)	−54.12	−45.11	−44.15

B. Basis sets and energetics

Table III summarizes the relative total energetics computed for the *a*-*t*C unit cells. The DFS+SZ relaxation may be trapped in the wrong minimum, but it nonetheless finds the energy in the DFS+DZP structure to be lower—and to be lower by roughly the same amount as the calculations with a DZP basis. The computed energy difference between the DFS+SZ structure and DFS+DZP structure is 0.049 eV/atom in calculations using a SZ basis, and 0.063 eV/atom using a DZP basis. In contrast, the DFS+DZP structure is 0.62 eV/atom higher in energy than diamond (using a DZP basis). That the SZ and the DZP basis sets give energy lowerings from the DFS to the DFS+DZP structure that differ by 0.014 eV/atom seems insignificant in comparison. Nonetheless, these small energies can signal large changes in structure. The DZP change of 0.073 eV/atom from the DFS to the DFS+DZP structure heralds a major change in composition, from 6 threefold (9%) bonded carbon atoms to 18 (28%).

Expressing differences on a per-atom basis masks the reality that these energy changes are concentrated at a few sites—near those locations undergoing bond rearrangements. In *a*-*t*C, the local bonding can sample a tremendous variety of configurations due to the bonding flexibility characteristic of carbon. Figure 2 illustrates this point, showing a few sample local structures encountered in this study. Figure 2(a) shows an extended string of threefold bonded carbons. Figure 2(b) shows a highly defected local structure centered about a fourfold ring that shares one edge with a three-member ring and the other edges with several five-member rings. To realistically model *a*-*t*C requires that the relative energetics of all possible configurations be treated accurately.

In an amorphous system it is difficult to isolate the various effects that contribute to the energetics. Atomic coordination, bonding topology, and strain are intertwined. Hence, to investigate the basis set dependence of the energetics of

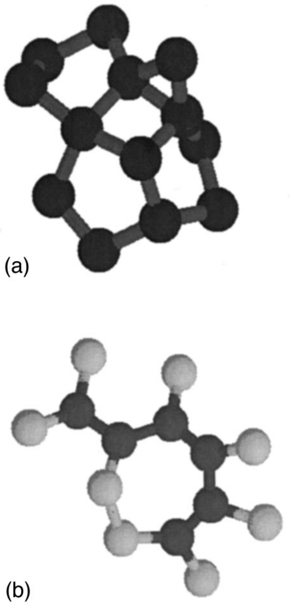

FIG. 2. Examples of highly strained local structures found in a-tC models. (a) Extended string of threefold bonded carbon atoms. (b) A tangle of linked small rings.

different structures, we appeal to simple molecular analogs of the kinds of structures typically found in the amorphous system. We concentrate on typical ring structures, since these constitute a convenient means to characterize amorphous systems. The molecules considered start with cyclo-hexane, to provide a reference that ideally contains no strain. To examine the energetics of simple three- and four-member rings, we examine cyclo-propane and cyclo-butane. To study the relative energetics of threefold vs fourfold bonding, we add ethylene, which can be thought of as a two-member ring. Finally, we add benzene to investigate the consequences of conjugated bonding. This collection does not exhaustively sample the range of bonding possible in a-tC (bond strains, and mixed bonding in smaller rings are not included), but does treat several very different bonding configurations that should give a flavor of how the quality of the basis set affects the relative energetics.

The carbon basis sets considered were SZ, SZP, DZ, DZP, and TZP. The final ''triple-ζ'' (TZP) basis set provides a third radial degree of freedom for the s and p orbitals, while the SZP adds a d orbital for angular polarization to the SZ basis. This probes the relative importance of flexibility in different parts of the basis set, e.g., angular vs radial polarization. For each molecule we varied the basis set on the carbon atoms (keeping the basis sets of the terminating hydrogen atoms fixed at DZP quality). The energy using each of the different carbon basis sets was computed relative to the energy using a minimum SZ basis. Figure 3 shows the results, with the relative energies of using different basis sets plotted per carbon atom. As might be expected due to its relatively unstrained isotropic bonding, the effect of adding radial flexibility to the carbon atom basis (SZ vs DZ, SZP vs DZP vs TZP) is small in cyclohexane. Furthermore, the total deficiency in the SZ basis is modest, of order 0.2 eV/atom, and mostly taken up by the addition of a d orbital for angular polarization.

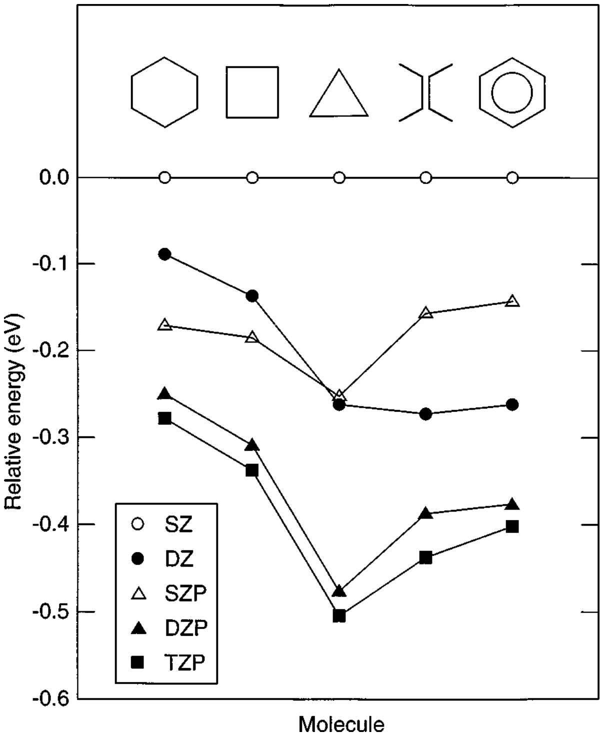

FIG. 3. Relative energies (in eV/carbon-carbon bond) of cyclo-hexane, cyclo-butane, cyclo-propane, ethylene, and benzene as the basis set on all carbon atoms is varied, to illustrate the basis set dependent treatment of strain. The lines are solely to guide the eye.

The effects of enhancing basis-set flexibility for the remaining molecules are substantially larger. Basis set flexibility becomes progressively more important as strain increases in the sequence from cyclo-hexane through cyclo-propane. The DZP basis lowers the energy by 0.48 eV/atom (with respect to SZ) for cyclo-propane, approximately evenly divided between radial and angular polarization, or 0.23 eV/atom more than it does for the unstrained cyclo-hexane ring. The SZ to DZP lowering for ethylene is 0.39 eV/atom, attesting to a 0.14 eV/atom bias against threefold atoms in the SZ basis set with respect to the fourfold bonded carbons of cyclo-hexane. Promoting the basis has the largest effect for benzene and its conjugated bonding, with a gain of 0.56 eV/atom. This is perhaps misleading as it may be more appropriate to compare the relative energetics per bond rather than per atom. Counting nine bonds in the benzene ring, the basis-set effects in benzene match those in ethylene.

Two factors obscure the direct observation of this bias in the different relaxations of the DFS structure. The SZ calculation incorporates a strong bias against small rings, and yet the SZ relaxation keeps most of the small rings while the DZP calculation relaxes most of them away. First, the destruction of small rings is counterbalanced by the creation of a number of threefold atoms, also biased against in the SZ calculation. The second factor is illustrated in the schematic of Figure 4. The elimination of small rings is net downhill for both SZ and DZP calculations, and even if this effect is artificially overestimated in the SZ basis (six-member rings are the global minimum), the bias in computing the transition path to reach more stable structures is even higher. The key observation is that the rings may be *artificially* trapped in an

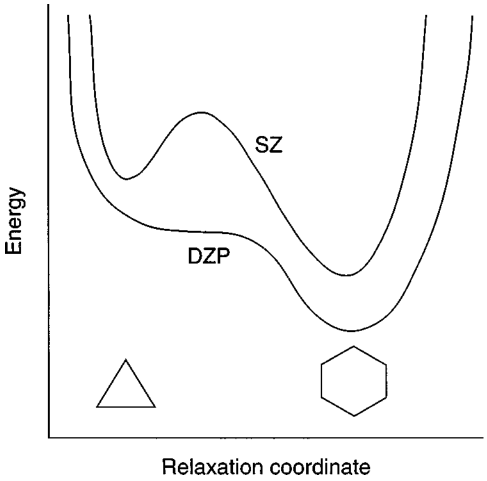

FIG. 4. Illustration of trapping of SZ calculation in artificial minimum. SZ calculation is trapped while DZP calculation is not, along an idealized relaxation coordinate.

SZ calculation yielding a false minimum, while the DZP calculation is downhill through what in the SZ calculation are ‘‘barriers.’’

In relaxations starting with the Marks structure,[18] the effect of bias in the basis set (with respect to threefold atoms) is more clearly seen. The SZ basis and DZP basis relax to structures with distinct bonding topologies. A Marks+SZ relaxation makes an additional bond and changes a pair of threefold atoms into fourfold atoms, while a Marks+DZP relaxation[34] does the opposite: it breaks a bond, changing two fourfold atoms into threefold atoms. Starting from the Marks+DZP structure, a SZ calculation returns to the Marks+SZ structure, lowering the total energy by 1.65 eV. Conversely, starting from the Marks+SZ structure, a DZP calculation returns to the Marks+DZP structure, lowering the energy by 0.84 eV. The total error in the relative energy of the Marks+SZ and Marks+DZP structures in the minimum basis SZ calculation is 2.49 eV. Unlike the case for the DFS-derived structures discussed in Sec. III A, the SZ calculation does not stay in the correct minimum energy bonding topology. The key difference between the two relaxed structures is that the Marks+DZP structure has four more threefold bonded atoms than the Marks+SZ structure; the number of small rings remains the same.

The structures resulting from DZP relaxations of the DFS structure and of the Marks structure, the result of a Car-Parrinello calculation without severe basis and self-consistency limitations, bear a number of similarities despite their very different origins. The presence of modest numbers of three- and four-member rings and comparable proportions of threefold bonded atoms are just a few superficial similarities. Even more striking is that the computed total energies of the two (DZP-relaxed) models differ by only a total of 0.08 eV (1.2 meV/atom in a DZP) basis calculation (see Table III). At least energetically, the DZP-relaxed Marks and DFS models are startlingly similar. An approach that starts with a TBMD- or LBDF-derived structure, and adds a first-principles relaxation with a good basis would represent a less expensive means to obtain representative models of a-tC, but would this approach yield models equivalent to a fully converged calculation such as that of Marks *et al.*? Structural analyses of amorphous systems are problematic, and, hence, comparison of different models is difficult. Statistical averages of atomic properties are required for comparison, and a sample size of 64 atoms limits the quality of the statistics. In the following section we try to quantify a number of structural properties and make comparisons among the various models discussed above.

IV. STRUCTURAL ANALYSES

A. Local bonding

Table IV summarizes the local bonding properties of the atoms in five different models: DFS,[12] DFS+DZP relaxed, Marks,[18] Marks+DZP relaxed, and the 216-atom WH (Ref. 14) structure. All are within range of experimental estimates from electron-energy-loss spectroscopy[8,2] and neutron scattering[5,6] for the first coordination number N_1, though the DFS model, with significantly fewer threefold bonded atoms than the other models, agrees slightly better. However, the Marks model (and our DFS+DZP relaxed model) produces a radial distribution function (RDF) in much better agreement with experiment,[18] while possessing a larger proportion of threefold coordinated carbon atoms than experimental estimates. This observation suggests that the simplifying assumptions that go into constructing the experimental estimates of atomic coordination numbers need to be reconsidered.

TABLE IV. Statistical averages of nearest-neighbor properties in at-C models. Distances in Å.

	Structure				
	DFS	DFS+DZP	Marks	Marks+DZP	WH
N_1	3.91	3.72	3.66	3.62	3.73
R_1	1.566±.077	1.552±.089	1.534±.091	1.528±.087	1.542±.077
R_1^-	1.295	1.326	1.327	1.333	1.331
R_1^+	1.854	1.752	1.785	1.779	1.783
$N_1^{3\text{-}3}$	0.094	0.375	0.562	0.625	0.407
$R_1^{3\text{-}3}$	1.347±.046	1.384±.053	1.405±.059	1.416±.060	1.403±.050
$N_1^{3\text{-}4}$	0.375	0.938	0.938	1.000	0.796
$R_1^{3\text{-}4}$	1.512±.054	1.525±.060	1.495±.035	1.502±.060	1.522±.052
$N_1^{4\text{-}4}$	3.438	2.406	2.156	2.000	2.528
$R_1^{4\text{-}4}$	1.578±.068	1.589±.065	1.585±.071	1.575±.067	1.571±.058

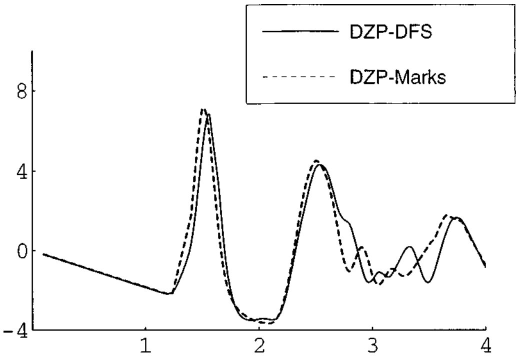

FIG. 5. Computed radial distribution functions for a DFS+DZP relaxed structure (solid) and Marks+DZP relaxed structure (dashed).

In comparison to the 1.52 Å inferred from experimental radial distribution functions,[35,7] the directly computed average nearest-neighbor bond distance R_1 varies from 1.53–1.56 Å among the different models. In Figure 5 we show superimposed the RDF of the DFS+DZP structure and the Marks+DZP structure. However, we note that a peak position in a RDF is not equivalent to an average bond distance. For example, Marks *et al.*[18] report an average bond distance of 1.520 Å, reflecting the position of the first peak in a RDF analysis of their structure, yet the directly computed average bond distance is significantly longer, at 1.534 Å.

The average bond distance is less than that in diamond because of the incorporation of a significant number of bonds involving threefold bonded atoms. The average bond distances between fourfold atoms $R_1^{4\text{-}4}$, are all larger than in diamond, while the distances between two threefold atoms $R_1^{3\text{-}3}$, and between a threefold and a fourfold atom $R_1^{3\text{-}4}$, are smaller. This differentiation also contributes to the standard deviation. The structures having more threefold atoms have smaller average bond lengths and larger standard deviations in that length. The relatively large average bond distance in the unrelaxed DFS structure merely reflects the much lower number of threefold bonded atoms in that structure. The bond lengths in the different models range from 1.33 −1.78 Å ($R_1^- - R_1^+$), except for the wider spread of bond lengths in the DFS model, reflecting a range of bonding from pure double bonds to highly stretched single bonds. The basis-converged calculations have standard deviations in the bond distance that agree well with each other, about 0.09 Å, and with experiment,[7] 0.10 Å. The minimum basis methods yield slightly smaller values, at less than 0.08 Å.

The second-nearest-neighbor analysis presented in Table V again illustrates the danger of taking the RDF results too literally. In their analysis of the contribution to the RDF from second-nearest neighbors, Marks *et al.*[18] quote a second-nearest-neighbor distance of 2.507±0.16 Å (see Figure 5). Yet an explicit average obtains 2.554±0.180 Å. The width is approximately reproduced, but the center is shifted by 0.047 Å. All the models obtain roughly the same value, in reasonable agreement with experiment, though again the DFS value tends to be larger, and has a wider spread as well.

Table V further breaks down the second-nearest-neighbor analysis in terms of the smallest ring that contains the second-nearest-neighbors atoms along with an atom that connects them. Gaskell *et al.*[6] later reproduced by Gilkes *et al.*[7] noted that it was necessary to include a peak at approximately 2.1 Å to fully describe the experimental RDF, and the analysis here reveals that this peak corresponds to second-nearest neighbors along diagonals in four-member rings R_2^{4m}. The strain given by a four-member ring is the only means to obtain such a short second-neighbor coordination, as Marks *et al.* noted.[20] The first-principles derived models all have roughly the correct number of four-member rings. The WH structure, however, is clearly distinct in its lack of four-member rings. Note that as a result of this the second coordination number N_2 in the WH structure satisfies the corrected relation $N_2 = 6(N_1 - 2)$ put forward by Marks *et al.*[20] Despite its rather good agreement in other structural properties presented above, the WH model fails to reproduce an experimentally verified feature in a-tC. Five-member rings also incorporate enough strain to produce a second-nearest-neighbor distance R_2^{5m}, less than diamond, but otherwise the second-nearest-neighbor distances are larger than in diamond, even for six-member rings (R_2^{6m}). Unfortu-

TABLE V. Statistical averages of second-nearest-neighbor properties. Distances in Å.

	Structure				
	DFS	DFS+DZP	Marks	Marks+DZP	WH
N_2	10.69	10.03	9.47	9.28	10.39
R_2	2.583±.209	2.569±.184	2.554±.180	2.544±.174	2.537±.168
R_2^-	1.997	2.007	2.076	2.065	2.133
R_2^+	3.335	3.159	3.361	3.126	3.138
N_2^{4m}	0.375	0.188	0.188	0.188	0
R_2^{4m}	2.182±.107	2.111±.081	2.213±.066	2.202±.066	–
N_2^{5m}	3.312	2.969	3.281	3.125	2.454
R_2^{5m}	2.454±.130	2.453±.123	2.460±.108	2.451±.108	2.440±.114
N_2^{6m}	4.188	4.094	3.156	2.969	5.232
R_2^{6m}	2.602±.152	2.607±.154	2.593±.150	2.592±.152	2.544±.152
N_2^{6+m}	7.000	6.875	6.000	5.969	7.935
R_2^{6+m}	2.666±.185	2.631±.165	2.616±.179	2.603±.170	2.567±.170
R_3^-	2.478	2.436	2.499	2.439	2.266

TABLE VI. Ring statistics, normalized to a 64-atom unit cell.

		Ring size						
Structure	F_4	3	4	5	6	7	8	9
DFS	91%	4	6	22	31	16	13	7
DFS+DZP	72%	1	3	20	28	15	9	9
Marks	65%	3	3	21	19	7	11	8
Marks+DZP	62%	3	3	20	18	7	10	7
WH	73%	0	0	16.0	40.6	27.9	9.5	6.8

nately, we know of no direct experimental evidence that would verify or deny the existence of three-member rings in a-tC (perhaps vibrational data can provide a distinctive signature), but given how well the simulations reproduce other a-tC properties, their existence in the simulations provides good evidence that they are present in a-tC.

In the 64-atom models, there are several six-atom chains that connect an atom to its image in a neighboring unit cell. Hence, a discussion of many third-neighbor properties is ill-defined, as atoms can be third neighbors from two different directions, and have two distinct and equally valid separations. Worth noting, however, is that these distances can range to less than 2.5 Å, or less than the peak in the RDF usually associated with second-nearest neighbors. The first observation relates to the difficulty that these models have in reproducing the parts of experimental RDFs beyond second-nearest neighbors.[7] The second observation demonstrates the difficulties in extracting coordination numbers N_2 and N_3 from a RDF.

B. Topology

Characterizing and comparing bonding topologies in a-tC is conveniently done via ring statistics. We implement the shortest path criterion of Franzblau[36] in the analysis presented in Table VI for the various models, along with the proportion of fourfold bonded atoms (F_4). For rings of size six and larger, it proves necessary to check for ring closure as chains of length six are sufficient to connect many atoms to their images in neighboring unit cells. There are no five-member chains which connect an atom to its image, and no shorter chains can with the bond-length criterion used in this study (four or fewer bonds cannot span the lattice parameter).

All models are dominated by relatively unstrained rings of size five, six, or seven, with five-member rings being (nearly) as common as six-member rings. Beyond seven, the ring distributions fall off only very slowly with size. The various models share similar distributions with the exception of the WH model, which lacks three- and four-member rings, and emphasizes seven-member rings over five-member rings. There appears to be, in the TBMD calculation of WH, a strong bias against small rings that embody strain in the form of small bond angles. The first-principles derived models all show reduced numbers of seven-member rings, and the Marks-derived models even show the number of five-member rings to equal the number of six-member rings.

Threefold bonded atoms in these models clearly tend to coalesce, and they coalesce into even-numbered clusters, mostly in chains. The six three-fold atoms of the DFS model are distributed only in pairs. The larger threefold atom population in the relaxed DFS structure produces a chains of six and four threefold atoms to go along with four pairs. In each of the Marks-derived models and the WH model, there is a branched chain, but in none of the models does a threefold atom chain close on itself to form an aromatic ring. The longer conjugated chains would be instrumental in providing a means for improved electrical conductivity in a-tC, and it is interesting that the structural relaxations produced increased numbers of threefold atoms.

While the threefold bonded atoms appear dominantly in even-number clusters in the various models, this is not exclusively the case. First, two pairs of atoms have to be counted as bonded in the DFS model, despite extraordinarily large separations. However, these elongated bond distances disappear upon relaxation, giving even-numbered clusters of threefold atoms. The threefold atoms of the Marks model are all in even-numbered clusters, but a DZP relaxation of this structure, with only a 0.16 eV lowering in the total energy, actually results in an isolated threefold atom and an odd-sized larger cluster. The WH model also has an isolated threefold atom, along with a chain of three threefold atoms.

The manner in which the threefold atoms congregate has consequences for the computed band gap. First we note that the 64-atom unit cells used in this study are not large enough to provide a clean evaluation of a band gap and density of states. The statistics of so few states will not be very good, as noted previously. Also, within the atomic basis we use, it can be explicitly seen that the orbitals of an atom interact non-negligibly with their images in neighboring unit cells, i.e., isolated defects cannot possibly exist. Bearing in mind this caveat, the computed band gap in the different models follows roughly the degree to which three-fold atoms pair off and cluster into even sets. The DFS+DZP structure has a gap (between the highest occupied and lowest unoccupied eigenvalue) of 1.3 eV, larger than the 0.5 eV gap computed for the Marks and the Marks+DZP structure, while the WH model produces essentially no gap. The DZP calculation for the unrelaxed DFS structure is the exception. Despite the presence of two overly stretched bonds that nearly produce dangling bonds, the calculation produces a much larger gap of 2.0 eV.

V. DISCUSSION

The proportion and topology of threefold carbon atoms plays a large role in determining the properties of amorphous carbon. Low density amorphous carbon is composed mostly of threefold carbon atoms, and is opaque and soft. Dense amorphous, dominantly tetrahedrally bonded, carbon is hard, optically transparent, and a good dielectric. However, even small variations of density in a-tC, with presumably modest changes in the proportions of threefold to fourfold bonded atoms, can lead to changes of several orders of magnitude in electrical properties such as resistivity of a material.[37,38] Hence determining the ratio of threefold to fourfold atoms has been a major goal of experimental analyses of a-tC,[2,5–8,37–39] and most theoretical studies, and has been cited as an important figure of merit of the topology of different theoretical models.[40] In the DFS model, threefold bonded atoms are infrequent, at 9% of the atoms, but this increases to a significant 28% when the structure is relaxed using fully self-consistent basis-convergent calculations. This contrast is much more profound than the difference between the WH structure,[11] with 19% of the atoms being threefold bonded, and the 13% that is obtained when the WH structure was relaxed using the LBDF method.[40] The DFS+DZP relaxed structure has a composition very similar to the 34% proportion obtained from a geometry generated from a Car-Parrinello calculation.[18] And, unlike the minimum basis methods, the DFS+DZP structure also exhibits the elongated chains of threefold atoms that Marks *et al.* find.[18,20] The connectivity of threefold atoms is likely to profoundly affect the electrical properties of the material.

Both TBMD and LBDF under represent the population of threefold atoms with respect to basis-converged results, despite LBDF adding a first-principles density-functional treatment of the energetics. What the two methods share is a minimum basis description, and it is this that limits the transferability of both. The molecular calculations presented in Sec. IV show that a minimum basis treatment impacts threefold atoms (in ethylene) 0.14 eV more than unstrained fourfold atoms (in cyclo-hexane), and, hence, that a minimum basis description will bias a bulk calculation against threefold atoms. Naturally, the orbitals needed to describe a single bond are going to be different from those needed to describe a double or conjugated bond, and using the identical orbitals for both will unavoidably impose an artificial bias. Furthermore, the local bonding in a-tC is strongly anisotropic, and it is this aspect that a minimum basis method would have difficulty describing despite being able to reproduce perfectly the relative energetics of various crystalline carbon phases, all with local isotropic bonding environments in equilibrium. The molecular calculations clearly demonstrate the importance of having adequate variational flexibility to describe the energetics of atoms in highly strained environments. Reducing the variational flexibility to a SZ minimum basis costs 0.23 eV more for a carbon atom in a three-member ring (cyclo-propane) than it does for a carbon atom in an ideally unstrained six-fold ring (cyclo-hexane). Moreover, the 0.23 eV/atom bias translates into a total bias against the formation of three-member rings of 0.68 eV. Similarly, the minimum basis treatment incorporates a 0.24 eV bias against the formation of four-member rings. This analysis would account for why, in contrast to a Car-Parrinello calculation,[18] the TBMD calculation[14] produces no small rings, and while the LBDF calculation[12] generates such rings, they are only artificially stable, and perhaps too few survive when the structure is properly relaxed using a more complete basis.

A number of important qualitative features of a-tC are correctly reproduced by minimum basis methods, despite their quantitative deficiencies. The threefold bonded atoms appear mostly in pairs or in even-numbered clusters. In other words, there are few dangling bonds. This is consistent with the experimental observation that unpaired spins exist at very low density.[41] Though threefold bonded atoms do coalesce, there is no sign of aromatic structures, in agreement with earlier observations.[13,15] As a result, a-tC has a sizeable gap, free of defects,[12] in agreement with experimental observations.[1,3] The LBDF computed gap for the DFS structure was 2.5 eV,[12] slightly larger than experiment,[3] but the DFS+DZP gap is 1.3 eV, now consistent with the usual LDA underestimate of band gaps,[42] as are the gaps in the Marks-derived models.

Another aspect that models reproduce reasonably well are general features of radial distribution functions.[7] However, most amorphous models composed dominantly, but not exclusively, of fourfold bonded atoms estimate the positions of the first couple peaks of the RDF well, but miss the finer details of the distribution such as the bond length distribution among near neighbors, i.e., the shape and width of the first peak(s).[7] One cautionary finding of the current analysis is how few bonds need be broken or made to connect very different models. The DFS and DFS+DZP relaxed structures, with threefold atoms rare and common, differ by only eight bond pairs. This highlights the need to be able to treat the relative energetics of different structures with great accuracy in order to find a system that is realistically representative of a-tC.

VI. CONCLUSIONS

We systematically investigated basis-set dependence in first principles predictions of structural properties of a-tC. A minimum basis description is apparently sufficient to capture some of the qualitative properties of the material, but is inadequate to describe the quantitative details of a system having highly strained local bonding topologies with large bond-length and bond-angle distortions. The proportion of threefold atoms and the number of small rings are particularly dependent on the quality of the calculation. To accurately represent the energetics of the locally highly defected structures found in the amorphous material, especially small ring structures, and the high degree of local anisotropy in this very defected material requires self-consistency and high-quality basis sets. A post-relaxation with a fully-convergent method, however, appears to recover the salient aspects of a geometry derived from a first-principles Car-Parrinello calculation[18,20] starting from the melt. We have outlined the minimum characteristics necessary for larger, more realistic simulations of a-tC.

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