Nonlocal-density-functional bond-energy calculations of cage-shaped carbon fullerenes: C_{32} and C_{60}

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The bond energies of C_{32} and C_{60} fullerenes have been calculated by a self-consistent molecular-orbital method based on nonlocal-density-functional theory with the generalized gradient approximation (GGA). These results were compared with those obtained with use of the local-density approximation (LDA). The bond energies calculated with the GGA (C_{60}, 7.24 eV/atom; C_{32}, 6.88 eV/atom) were about 1.3 eV/atom (15%) smaller than those calculated with the LDA, and the GGA result for C_{60} was found to be in good agreement with the evaluated value from the experimental formation energy. The differences in bond lengths, force constants, and orbital energies for the same molecular structure — except for the core orbitals—between the LDA and GGA were small, compared with the difference in bond energies.

I. INTRODUCTION

Since the identification of a C_{60} fullerene by Kroto *et al.*[1] among products formed from laser-ablated graphite, experimental and theoretical work on C_{60} has progressed in several directions. Experimentally, NMR, Raman, optical spectra, and the formation energy[2] from graphite to C_{60} have been obtained. Theoretically, the structure and electronic properties of C_{60} have been determined by Hartree-Fock,[3] extended-Hückel-theory,[4] and local-density-approximation (LDA) (Refs. 5–7) calculations. The LDA is a practical approximation for calculations of the electronic states and atomic structures of the ground states of molecules and solids,[8] and the calculated bond lengths and the gap between the highest-occupied molecular orbital and lowest-unoccupied molecular orbital (HOMO-LUMO gap) are in good agreement with those experimental values for C_{60}.[5–7] However, the LDA gives an unreliable description of the actual bond energies.[8] The main source of this error comes from the local-functional approximation in the exchange-correlation energy and potential.

To overcome this difficulty, a generalized gradient approximation (GGA), based on the nonlocal-density-functional formalism (NLDF), was developed by Perdew and Wang.[9–11] The exchange-correlation energy density in the GGA is approximated by a function of the electron density and its coordinate differences, which are not considered in the LDA. In the GGA in Refs. 9–11, the nonlocal-exchange-functional form has no adjustable parameters, and its exchange hole is expanded up to the second-order gradient terms. The exchange-hole density is negative everywhere and integrates to -1. As for the nonlocal-correlation-functional form, Perdew[9] made two modifications of the earlier correlation-functional form of Langreth and Mehl:[12] (1) a natural separation between the exchange and correlation and (2) the incorporation of many-body effects beyond the random-phase approximation. To investigate the validity of the GGA, electron structures and bonding properties of atoms,[9–11] molecules,[13–17] and solids[18–21] have been calculated. These calculations confirmed that the bond-energy overestimations by the LDA can be significantly reduced by the GGA for these molecules and solids.

In this work, we calculate the bond energy and energy levels of the C_{60} fullerene by a self-consistent molecular-orbital method based on the NLDF with the GGA, considering all electrons. These results are compared with those obtained with LDA calculations and the experimental bond energy[2] and the excitation energy.[22] As for the local-correlational function in the LDA, the form parametrized by Perdew and Zunger[23] was used. We also calculate the bond length and force constant of C_{32}, which is the smallest spheroidal (carbon) fullerene formed in the beam experiment.[24] Then the effects of nonlocality in the exchange-correlation potential and energy for the bonding properties of these fullerenes are investigated.

II. CALCULATION METHOD

In our calculations, the molecular orbitals for carbon fullerenes were expanded by linear combinations of Slater-type atomic orbitals. As the basis orbitals, the double basis plus one d orbital (DBD: neutral atomic carbon orbitals plus $2s$ and $2p$ orbitals for C^{2+}, and one $3d$ orbital) basis set was used. In order to check for completeness, we calculated the differences in bond energies by DBD and DBDF (DBD plus one $4f$ orbital) basis sets for C_{32}. The difference in the results was 0.07 eV/atom for both the GGA and LDA. So, the error due to incompleteness of the basis orbital in the difference in bond energies between GGA and LDA was sufficiently small. Overlap and Fock matrix elements whose explicit forms were presented in Ref. 17 were numerically calculated by the integral method developed by Becke.[25] In order to estimate the errors of numerical integrals in calculating those matrix elements, the bond energy of C_{32} was calculated with three different sampling meshes (984, 1300, and 2000 points per atom). The results showed that the bond energies with the 1300- and 984-point sampling

meshes differed by about 0.05 and 0.1 eV/atom, respectively, from that with the 2000-point sampling mesh. The differences in the results were the same in both the GGA and LDA calculations. The version with 1300 sampling mesh points was sufficiently accurate and used for the following calculations to investigate the difference in bond energy between GGA and LDA.

III. RESULTS AND DISCUSSIONS

To check our calculation procedure and to investigate the improvement in the bond energy with use of the GGA over the LDA in the case of small molecules, we calculated the bond energies of five well-known hydrocarbon molecules, CH_4, C_2H_2, C_2H_4, C_2H_6, and C_6H_6. As the basis orbital of hydrogen, a neutral atomic hydrogen orbital plus three $2s$ and $2p$ basis set was used. Our results by LDA were confirmed to be in excellent agreement with those values calculated in Ref. 26 within 0.3% differences except for C_2H_4. Our self-consistent GGA results were also in good agreement with those GGA values in Ref. 26 within 1% differences except for C_2H_4. Compared with the experimental bond energies, the LDA overestimated them by 0.5 eV/atom on average; the GGA did so only by 0.1 eV/atom.

In Table I bond lengths and bond energies calculated by the GGA and LDA methods are listed. For comparison with the C_{32} and C_{60} fullerenes, the results of C_2 are also included in Table I.

For C_{32}, the molecular structure is assumed to be a cage-shaped one with D_3 point-group symmetry, composed of 12 five-membered and six six-membered rings. The bond lengths are assumed to be equal, and one-bond optimization is performed. The difference between bond energy obtained by a complete structure optimization and that by one-bond optimization is expected to be small

according to the results in Ref. 27.[28] The bond length calculated with the GGA is slightly longer, by 0.02 Å (1%), than that with the LDA. The bond energy calculated with the GGA is 1.3 eV/atom (16%) smaller than that by LDA, because of the nonlocal effect of the exchange-correlation energy and potential. The dependence of bond energy on bond length is shown in Fig. 1. The LDA and GGA curves are similar except for a 1.3-eV/atom difference in bond-energy size, and the force constants in the bond direction are 9.04×10^5 (LDA) and 9.05×10^5 (GGA) dyn/(cm atom). Also for C_2, the force constant obtained with the GGA is in agreement with that obtained with the LDA within a 2% difference.

For C_{60}, the molecular structure is a truncated icosahedron with 12 five-membered and 20 six-membered rings, and the experimentally observed bond lengths (1.40 and 1.45 Å) (Ref. 29) are assumed in both the LDA and GGA calculations. The difference in bond energies calculated with the experimental structure and the optimized structures calculated with either the LDA or GGA may be small, for the following reasons: (1) The bond lengths calculated with the LDA (1.39 and 1.45 Å) in Ref. 6 are in good agreement with the experimental values, and the bond lengths obtained with the LDA are in agreement with those obtained with the GGA within a difference of 0.02 Å for C_2 and C_{32}. (2) Regarding the energy curve for C_{32} in Fig. 1, the bond-energy difference between a stable structure and an unstable one whose bond length even differs 0.05 Å from the former is smaller than 0.1 eV/atom.

As shown in Table I, the bond energy of C_{60} calculated with the GGA is 7.24 eV/atom and is 1.3 eV/atom (15%) smaller than that calculated with the LDA. It is in good agreement with an evaluated value (6.94–6.98 eV/atom) (Ref. 30) from the experimental formation energy from graphite to C_{60}.[2] The reductions of the bond energy with use of the GGA over the LDA are 14% (C_2), 16% (C_{32}),

TABLE I. Bond lengths and bond energies for a carbon dimer and cage-shaped carbon fullerenes; C_{32} (12 five-membered and six six-membered rings) and C_{60} (12 five-membered and 20 six-membered rings). For the C_{32} fullerene, bond lengths were optimized under the assumption that all bond lengths were equal. The experimentally obtained bond lengths (Ref. 29) were used for C_{60}.

| | | Carbon clusters | | |
	Method	$C_2(^1\Sigma_g)$	C_{32}	C_{60}
Bond length (Å)	Expt.	1.25[a]		1.40, 1.45±0.015[b]
	GGA	1.26	1.46	c
	LDA	1.25	1.44	c
Bond energy	Expt.	3.16[a]		6.94–6.98[d]
(eV/atom)	GGA	3.11	6.88	7.24
	LDA	3.61	8.17	8.50

[a]Reference 33.

[b]Reference 29.

[c]Experimental bond lengths (Ref. 29) were used for calculating bond energies.

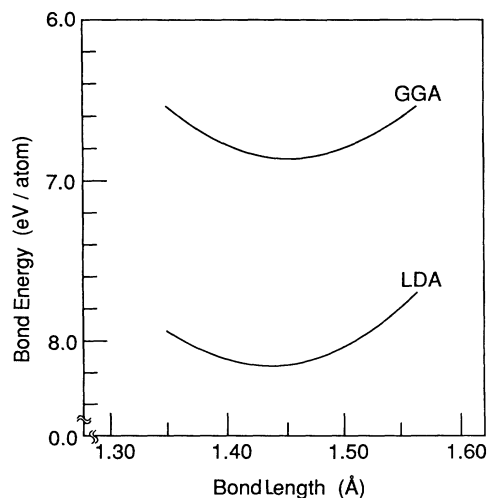[d]Evaluated (Ref. 30) from the experimental formation energy from graphite to C_{60} in Ref. 2.

FIG. 1. Bond energy versus bond length of a C_{32} (12 five-membered and six-membered rings) fullerene calculated by the LDA and GGA methods. All bond lengths are assumed to be equal.

and 15% (C_{60}) and are relatively constant. As the bonding properties of these molecules are different from each other, the reason for the nearly equal reduction rate for the bond energy is that the improvement of the exchange-correlation potential and energy in the atomic region by using the GGA may be important for the reduction of the overestimated error of the LDA.

In addition, for an infinitely long fullerene C_∞ capped at both ends with half of C_{60}, the bond energy is estimated to be 7.44 eV/atom based on the following discussion, and is comparable to that of graphite (7.37 eV/atom). According to the results[31] of bond energies of fullerenes in Ref. 27, the following rule[32] between the total bond energy E and the number n of carbon atoms of C_n is found to hold: $E = Fn - A$, where F is the bond energy (per atom) of C_∞. The value of A may denote the excess strain energy of the five-membered rings, and is almost constant (12 eV) for a series of C_n ($n = 60-120$).[31] The difference in the bond energies between C_∞ and C_{60} is $A/60 = 0.2$ eV/atom. If this estimated value is the same as in the present self-consistent GGA calculation, the size of F would amount to 7.44 eV/atom. On the other hand, $A/60$ is estimated to be about 0.4 eV/atom, from the present result of the bond-energy difference between C_{60} and C_{32}. This value is larger than that of C_n ($n = 60-120$).[31] It means that the excess strain energy of the five-membered rings in C_{32} may be larger than those in C_n ($n = 60-120$).[31] This result is consistent with the fact that there are some adjoining triples of five-membered rings in C_{32}.

The energy levels of C_{32} and C_{60} are also calculated. The energy levels calculated with the GGA are about 3-eV deeper for the localized carbon $1s$ orbitals, and are a little higher (within 0.3 eV; 3%) for the valence orbitals than those calculated with the LDA for the same molecular structure. The HOMO-LUMO gaps of C_{60} for the experimental molecular structure are 1.63 and 1.65 eV for the GGA and LDA, respectively, and are in good agreement with the experimentally observed excitation energy (1.7 eV).[22]

IV. CONCLUSION

We have calculated the bonding properties and energy levels of the cage-shaped C_{32} and C_{60} fullerenes by using the self-consistent molecular-orbital calculation method with the GGA. The bond lengths in C_{32} were optimized under the assumption of equal bond lengths, and the experimentally observed bond lengths were used for C_{60}. The results were as follows.

(1) The differences in bond energies calculated with the GGA and LDA were 1.3 eV/atom (15–16%), and the GGA could remove a major portion of the overestimated error in LDA, because of the nonlocal effect of the exchange-correlation energy and potential. However, the differences in bond lengths, force constants, and energy levels for the same molecular structure—except for the core orbitals—were small compared with the difference in bond energy.

(2) The bond energy calculated with the GGA for C_{60} (7.24 eV/atom) was in good agreement with the evaluated value from the experimental formation energy.[2]

(3) Calculated HOMO-LUMO gaps of C_{60} (GGA, 1.63 eV; LDA, 1.65 eV) were in agreement with the experimentally observed excitation energy (1.7 eV).[22]

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[31]The bond energies calculated by a non-self-consistent Harris-functional approximation with the GGA using the minimum atomic basis set in Ref. 27 were 5.58 (C_{60}), 5.61 (C_{70}), 5.63 (C_{80}), 5.65 (C_{90}), 5.66 (C_{100}), 5.67 (C_{110}), and 5.68 (C_{120}) eV/atom. Each C_n consists of 12 five-membered rings and $0.5(n-20)$ six-membered rings. The shapes of the C_{70} and C_n with $n=80$–120 fullerenes may be considered as being formed by separating two halves of C_{60} and by introducing some six-membered rings of ten extra carbon atoms. The bond lengths in each C_n were assumed to be equal and the one-bond optimization was performed.

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