PHYSICAL REVIEW B VOLUME 45, NUMBER 23 15 JUNE 1992-I

Electronic structure of neutral and charged C_{60} clusters

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(Received 3 December 1991)

We present first-principles calculations for neutral and multiply charged C_{60} clusters within the local-spin-density approximation. We employ a Gaussian basis and pseudopotentials. The calculated equilibrium geometry, ionization potential, and electron affinity are in good agreement with experimental values. We analyze Jahn-Teller distortions for $C_{60}{}^-$ and find that the distortion energy is $\gtrsim 24$ meV. We also present local-spin-density estimations for the strength of electron-electron repulsion, and for the energy scales associated with different spin and orbital configurations.

I. INTRODUCTION

Since the discovery of stable C_{60} clusters as suggested by the prominent $C_{60}{}^+$ peak in the laser-ablation mass spectrum of graphite,[1] a variety of studies on its chemical and physical properties have been undertaken. Very recently, it has been demonstrated that samples of alkali-metal-doped C_{60} become superconductors at a critical temperature, T_c, of 18 K for K_3C_{60} and 28 K for Rb_3C_{60}.[2,3] In these compounds, the alkali-metal valence electron is transferred to the (threefold-degenerate) lowest empty molecular level of C_{60}.[4] Due to the small overlap between wave functions on neighboring C_{60} molecules in the solid, one expects correlation effects associated with different molecular charge states to be important in describing the electronic properties of these materials. Realistic calculations based on density-functional theory have difficulty in describing these charged states in the solid. Thus, we have decided to study isolated neutral and charged C_{60} clusters to determine the value of parameters which are relevant in describing the electronic properties of the solid. In particular, we have studied Jahn-Teller distortions in charged clusters, the strength of electron-electron repulsion, and the energy scales associated with different spin and orbital configurations.

In this paper, we present local-spin-density calculations for neutral and charged C_{60} clusters. We use a Gaussian basis set and the pseudopotential approximation. We optimize the geometry of neutral C_{60} with icosahedral symmetry, and determined vertical ionization potentials and electronic affinities. For the $C_{60}{}^-$ cluster, we have investigated possible distortions within the D_{5d} point group and obtained an estimate of the Jahn-Teller energy for that cluster. This is a key parameter[5] for models that explain superconductivity in alkali-doped fullerenes by an electron-phonon interaction mechanism.[4,6] The calculated equilibrium geometry, ionization potential, and electronic affinity of C_{60} clusters are found to be in good agreement with experimental values.

II. METHOD OF CALCULATION

Our calculations have been carried out within the local-spin-density (LSD) approximation of density-functional formalism. We solve the Kohn-Sham equations in which core effects are incorporated through the use of the tabulated nonlocal pseudopotentials of Bachelet, Hamman, and Schlüter.[7] We use the exchange and correlation potential of Ceperley and Alder[8] as parametrized by Perdew and Zunger.[9] The Kohn-Sham equations for the molecule are (in atomic units)

$$(-\tfrac{1}{2}\nabla^2+V_{\text{ion}}+V_{\text{H}}[\rho]+V_{\text{xc}}^{\sigma}[\rho_\uparrow,\rho_\downarrow])\psi_{\sigma\nu}=\varepsilon_{\sigma\nu}\psi_{\sigma\nu}\ , \quad (1)$$

where $\nu=1,2,\ldots$ is the orbital index, σ represents spin up or down, and the electronic spin density is given by

$$\rho_\sigma(\mathbf{r})=\sum_\nu f_{\sigma\nu}|\psi_{\sigma\nu}(\mathbf{r})|^2 \text{ and } \rho(\mathbf{r})=\sum_\sigma \rho_\sigma(\mathbf{r})\ , \quad (2)$$

where $0\le f_{\sigma\nu}\le 1$ are the occupation numbers, which are allowed to be nonintegers only for the highest occupied level if it is degenerate. The operators in Eq. (1) correspond, respectively, to the kinetic, ionic pseudopotential, Hartree, and exchange-correlation energies.

Our basis set contains three s and four p Gaussian functions whose exponents were fitted to accurate numerical pseudo-wave-functions (calculated for the same tabulated pseudopotential). To maintain a high degree of variational freedom, we have not contracted our Gaussian basis set. The high quality of our basis is illustrated by the fact that we reproduce the eigenvalues of the accurate numerical wave functions within 0.030 eV, and the total energy of the carbon atom within 0.13 eV.

In order to take advantage of the high symmetry of the system under study (here the icosahedral point group I_h), we built up a symmetry-adapted basis set starting from the unsymmetrized basis by means of the projection technique of group theory,[10] which decomposes the functional space in orthogonal subspaces. Each of these is characterized by a type of irreducible representation of the symmetry group. The advantages of using a symmetrized basis are multiple. First, when the irreducible representation carried by a partially filled shell is known, the possible modes of the Jahn-Teller distortions can be predicted, as we will discuss later. Second, because of the symmetry, the matrices of the operators in Kohn-Sham equations (1) are in a block diagonal form. Thus, the number of matrix elements to be calculated is drastically reduced, compared to the unsymmetrized basis, making the problem computationally manageable.

III. ICOSAHEDRAL C_{60} CLUSTERS

The geometry of C_{60} is fully determined by two bond lengths: the pentagon edge and the hexagon-hexagon bond. Minimizing the total energy of neutral C_{60} gives bond lengths of 1.453 Å for the (long) pentagon edge and 1.386 Å for the (short) hexagon-hexagon edge. These lengths are typical of aromatic carbon-carbon bonds. The calculated bond lengths are in excellent agreement with experimental NMR (Ref. 11) values of 1.45±0.015 and 1.40±0.015 Å and x-ray-diffraction values of 1.432(9) and 1.388(5) Å.[12] Our theoretical values for the molecule are also in excellent agreement with the calculated local-density bond lengths of 1.444 and 1.382 Å for solid C_{60}.[13] The bond lengths obtained from molecular Hartree-Fock calculations[14] are 1.453 and 1.369 Å, while second-order Møller-Plesset (MP2) perturbation theory yields values of 1.446 and 1.406 Å.[15]

The basic electronic structure of C_{60} has been discussed by one of us and co-workers based on local-density calculations for the solid and experimental photoemission and inverse-photoemission spectra.[13] Our calculations for the isolated cluster are consistent with the solid-state calculations, and we will therefore concentrate in this paper on the aspects of the electronic structure that are specific to clusters. The most important electronic states for C_{60} are the highest occupied molecular orbital (HOMO), which is fivefold degenerate and has h_u symmetry, and the lowest unoccupied molecular orbital (LUMO), which is threefold degenerate with t_{1u} symmetry. The calculated energy difference between HOMO and LUMO is 1.87 eV, in reasonable agreement with the separation between the two first peaks of the photoelectron detachment spectra.[16,17] Both HOMO and LUMO are π molecular orbitals and their wave functions are dominated by an $l=5$ component when they are decomposed into cluster-centered spherical harmonics.[13,19]

We have calculated the electronic structure and total energy for $C_{60}{}^{+}$, $C_{60}{}^{-}$, $C_{60}{}^{2-}$, and $C_{60}{}^{3-}$ at the equilibrium geometry of the neutral species. In a highly symmetrical species like the icosahedral C_{60}, the presence of orbital degeneracies creates problems in local-density theory when the degenerate orbitals are only partially occupied, as discussed by von Barth.[20] Here, fractional occupation numbers are used to force icosahedral symmetry for the charge density. Both C_{60} and $C_{60}{}^{3-}$ are closed-shell systems where the problem of fractional occupation does not exist. For $C_{60}{}^{+}$ we remove $\frac{1}{5}$ of an electron from each of the h_u HOMO with spin down, for $C_{60}{}^{-}$ we add $\frac{1}{3}$ of an electron to each of the t_{1u} LUMO with spin-up orbitals, and in the case of $C_{60}{}^{2-}$ we add $\frac{2}{3}$ of an electron for the t_{1u} LUMO orbitals with spin up.

In Table I we give total-energy differences between neutral and charged C_{60}, calculated at the equilibrium geometry of the neutral species. These are presented in the table as electronic affinities (EA). The ionization potentials (IP) of $C_{60}{}^{n-}$ are identical to the electronic affinities of $C_{60}{}^{(n-1)-}$. For C_{60}, we obtain the vertical electronic affinity of 2.78 eV, which is in excellent agreement with photodetachment values between 2.6 and 2.8 eV (Ref. 16) and 2.65±0.05 eV,[17] and with the predicted values of 2.70 and 2.88 eV calculated by Ref. 18. The calculated vertical ionization potential of C_{60}, 7.74 eV, is also in agreement with the recent experimental value of 7.6±0.2 eV,[21] and is close to a previous local-density value of 7.8 eV,[23] and to the Hartree-Fock value of 7.92 eV.[14]

The $C_{60}{}^{2-}$ species has recently been observed[22] in the gas phase with a measured lifetime greater than 1 ms. Our calculations predict $C_{60}{}^{2-}$ to be higher in energy than $C_{60}{}^{-}$ by 0.26 eV, indicating that the double anion is unstable in disagreement with experiment. Because of the incomplete cancellation of the self-interaction term of the Hartree potential by the local-density exchange and correlation, local-density calculations fail to predict correctly the stability of atomic anions.[9,24] The fact that we obtain a small negative value for the ionization potential of $C_{60}{}^{2-}$ in local-density calculations would be consistent with either a metastable double anion or with a stable doubly charged anion with a very small (a few tenths of an eV) ionization potential.

The problem of using local density with anionic species is reflected by the appearance of occupied orbitals with positive energies in our calculations for $C_{60}{}^{2-}$ and $C_{60}{}^{3-}$. Formally these orbitals are unbound, and we must check our results with the utmost care to make sure that our results have a physical meaning. For $C_{60}{}^{n-}$, the effective

TABLE I. The calculated vertical electronic affinities (in eV) of C_{60} ions are compared with the values of the appearance potentials observed by photoionizaion and photodetachment experiments. The calculated negative electron affinities for the anions are the result of the effective electron confinement due to the localized basis set and their physical interpretation is discussed in the text.

	Theory	Experiment
$C_{60}{}^{+}$	7.74	7.6±0.2[a]
C_{60}	2.78	2.65±0.05[b]
$C_{60}{}^{-}$	−0.26	(>0)[c]
$C_{60}{}^{2-}$	−3.26	

[a] Reference 17.
[b] Reference 21.
[c] Reference 22.

potential in Eq. (1) has an asymptotic repulsive behavior for large distances, r, from the molecule given by $V_{\rm ion}+V_{\rm H}+V_{\rm xc}\simeq n/r$. Our calculations are an excellent numerical approximation for the problem of the cluster confined in a box, if our basis set has large variational freedom in the region inside the second outermost classical turning point of the effective potential and negligible variational freedom outside the outermost classical turning point. The first condition is satisfied by the choice of a good atomic basis set. The outermost classical turning point is given in a first approximation by the condition $n/r=\epsilon_{\rm HOMO}$, where $\epsilon_{\rm HOMO}$ is the (positive) energy of the highest occupied orbital. In our case, these turning points are at 32 and 17 a.u. for $C_{60}{}^{2-}$ and $C_{60}{}^{3-}$, respectively; at these distances our most extended Gaussians have negligible weight. Our calculations are therefore representative of systems with the electrons confined in a sphere of radius of 17 a.u., which is much larger than the 7-a.u. C_{60} molecule radius. We can therefore use the results shown in Table I to estimate the strength of the electron-electron interaction for the t_{1u} orbitals. The value of the Hubbard U parameter that we obtain from the difference in electronic affinities of (confined) $C_{60}{}^{-}$ and $C_{60}{}^{2-}$ is 3 eV.

From our calculations, we can further estimate other parameters that are relevant for a physical discussion of the electronic structure of C_{60}. For $C_{60}{}^{2-}$, we calculated both "singlet" and "triplet" states constraining the total charge and spin densities to have icosahedral symmetry, resulting in a "triplet" state lower in energy by 0.04 eV (in agreement with Hund's rules for atoms). On the other hand, the energy of icosahedral $C_{60}{}^{-}$ with equal fractional occupation of the three t_{1u} orbitals is lower by 0.02 eV than with full occupation of a single orbital. The energy scale for spin and orbital configurations in the molecule is therefore small.

IV. JAHN-TELLER DISTORTION IN $C_{60}{}^{-}$

A priori, we do not expect large Jahn-Teller distortions in $C_{60}{}^{-}$, because we are adding a single electron to a delocalized orbital of a large molecule.

In a one-electron rigid-band picture, the added electron in $C_{60}{}^{-}$ will occupy one of the three degenerate t_{1u} LUMO states of neutral C_{60} with icosahedral symmetry. These three t_{1u} states transform under the group I_h like a vector (x,y,z). The Jahn-Teller theorem tells us that the three t_{1u} orbitals will couple with molecular distortions of A_g and H_g symmetry. Using group-theory analysis, one finds that there are two A_g and eight H_g vibrational modes in C_{60}. The formal theory of the coupling of the t_{1u} states with these vibrational bonds has been recently discussed.[5] The eigenmodes have been calculated with semiempirical[25] and first-principles methods,[26,27] but numerical values of the ionic displacement vectors associated with the vibrations have not yet been reported by the first-principles calculations.

Here we take a pragmatic approach to obtain a good first-principles estimate of the Jahn-Teller distortion energy of $C_{60}{}^{-}$ without having to perform an expensive study of the full vibrational modes of the molecule. We suppose that the distortion breaks the symmetry in a minimal way, and we look for the largest subgroup of I_h which can stabilize the orbital occupied by this extra electron with respect to the two other orbitals. In our case, the subgroup which leaves invariant an axis of maximal symmetry (the fivefold axis) is the D_{5d} group (D_{5d} can be seen as $C_{5v}\times I$). Furthermore, the A_g vibrations leave invariant all fivefold axes, and for each H_g vibrational manifold we can choose one vibration that leaves invariant one fivefold axis. So when we vary the ten structural degrees of freedom of the D_{5d} symmetry, we are in fact exploring one mode from each of the two A_g and the eight H_g vibrational modes. The distortion of $C_{60}{}^{-}$ in the reduced D_{5d} symmetry splits the three orbitals of the t_{1u} representation of the icosahedral point group to the $a_{2u}\oplus e_{1u}$ representation of D_{5d} of dimension 1 and 2, respectively.

We present in Fig. 1 a contour plot of the orbital $\psi(r,\theta,\phi)$ with a_{2u} symmetry of the D_{5d} point group. This corresponds to one of the t_{1u} LUMO orbitals of neutral C_{60}. The orbital is plotted on the surface of a sphere as a function of the polar coordinates θ and ϕ. The radius of the sphere, 3.17 Å, was chosen to be smaller than the geometrical size of the spherically shaped molecule (3.6 Å), to avoid the radial node associated with the π character of the orbital. In this picture, the poles lie on a pentagon center, and the black points indicate the projections of the atomic positions on that sphere. The figure shows the ringlike character of the LUMO orbitals of C_{60}, with the maxima of the wave function close to the "equator" ($\theta=\pi/2$) of the polar coordinate plot. The thick curves are the nodes of the wave function, and allow us to identi-

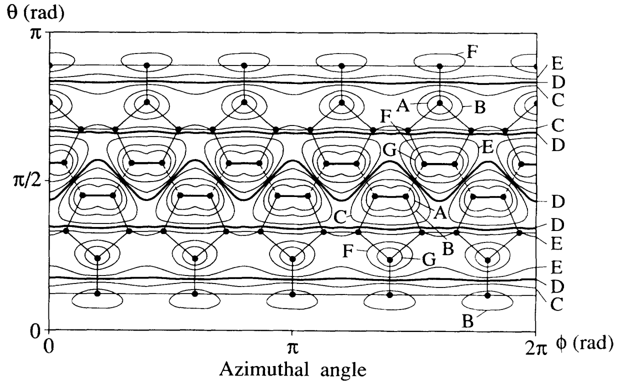

FIG. 1. Contour plot of the $a_{2u}(D_{5d})$ orbital corresponding to the $t_{1u}(I_h)$ LUMO orbital of C_{60} on the surface of a sphere of radius 3.17 Å as a function of the polar angles θ and ϕ. The contours correspond to amplitudes of the normalized wave function ranging (in atomic units) from -0.039 (A) to 0.039 (G). The thick wavy (D) lines are the node of the wave function, which can be used to identify the bonding and antibonding regions of this wave function. The black dots connected by straight lines show the projection of the carbon atoms and carbon-carbon bonds on the surface of the sphere. The thick straight lines connect the atoms strongly bonded by this orbital, the dashed lines strongly antibonded atoms.

fy bondinglike and antibondinglike regions. As discussed previously,[13] the C_{60} wave functions can be associated with spherical harmonics of angular momentum l. For the function shown in Fig. 1, the appropriate combination of spherical harmonics is $[6Y_5^0(\theta,\phi)+\sqrt{7}Y_5^5(\theta,\phi)-\sqrt{7}Y_5^{-5}(\theta,\phi)]/5\sqrt{2}$. From the examination of the orbital in Fig. 1, we conclude that it would be stabilized if we shorten the bonds between the pairs of atoms lying near the equator and parallel to it (thick bonds in Figs. 1 and 2) and we lengthen the bonds between those atoms that cross the equator (dashed bonds in Figs. 1 and 2). Based on these tendencies, we calculated a slice of the Born-Oppenheimer (BO) surface for C_{60}^- parametrized by two coordinates. The first corresponds to the variation in the bond lengths for the ten pairs of atoms situated just above and below the equator (Fig. 2). The second is a global vertical displacement of the two hemispheres of the spherically shaped molecule. In this slice of the BO surface, decreasing the bond lengths of the quasiequatorial pairs of atoms or elongating vertically the C_{60} molecule will stabilize the a_{2u} orbital. On the other hand, the system prefers to stabilize the e_{1u} two-dimensional eigenspace for the opposite distortions. In order to explore the branch corresponding to a given orbital occupation, say a_{2u}, we force the occupation of the a_{2u} orbital even if that leaves orbitals with lower energy empty. In order to investigate the effect of the non-totally-symmetric distortion proposed, we first calculated the equilibrium geometry of the C_{60}^- in the spherical shape with this a_{2u} occupied orbital. The two bond lengths obtained are 1.450 and 1.397 Å, and correspond to the starting geometry for the distortions. The energy gained by the distortion is given by the difference in energy between the geometry with icosahedral symmetry and the minimum energy in the explored slice of the BO surface. As expected, the energy gain due to the distortion is very small, $\Delta E=24$ meV, and corresponds to a decrease in bond length on the order of 0.01 Å for the quasiequatorial pairs of atoms. This distortion energy is too small for the system to behave like an effective "negative-U" system, but has the right magnitude to explain superconductivity in alkali-metal-doped fullerides with an electron-phonon mechanism.[6,5]

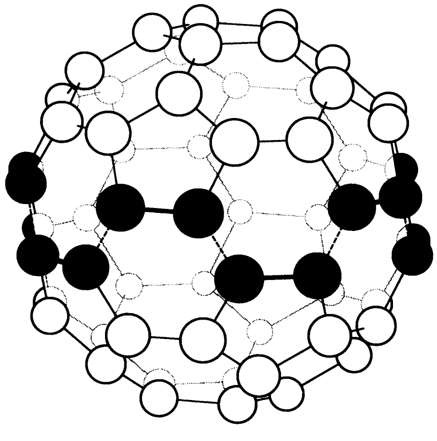

FIG. 2. Model of the C_{60} molecule showing in black the key atoms whose displacement stabilizes the a_{2u} orbital of C_{60}^-. Black balls correspond to atoms which are subject to the distortion in our approach. Thick lines are strengthened bonds, while dashed lines correspond to weakened bonds.

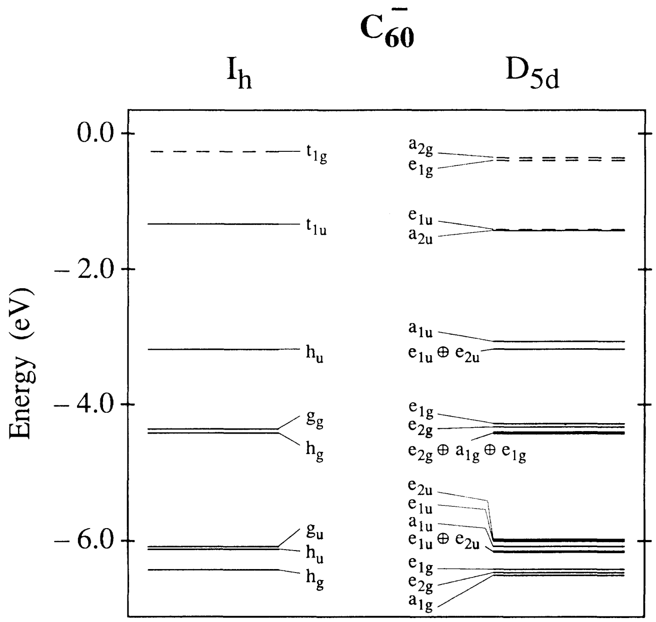

FIG. 3. Eigenvalue spectrum of C_{60}^- in the I_h and the distorted D_{5d} symmetry together with the irreducible-representation labels. Only spin-up orbital levels are shown. Some of the degeneracies are very close and are shown as degenerate. Dashed lines correspond to unoccupied levels.

Figure 3 shows part of the two eigenvalue spectra for the C_{60}^- in both I_h and in the distorted D_{5d} symmetry. Only the spin-up orbital levels are presented. The spin-down orbitals are similar and do not yield any new information. The dashed lines correspond to unoccupied levels. In the icosahedral symmetry (left part of the figure) the t_{1u} levels are occupied by one electron with occupation number $\frac{1}{3}$ for each of them. We see explicitly the levels splitting due to the distortion, and remark that some levels are still very close together, within a few meV, and appear degenerate in the figure.

V. DISCUSSION

The calculated bond lengths, vertical ionization potential, and electronic affinity are in good agreement with experimental data. We found that the energies associated with orbital and spin configurations of C_{60} anions are small. This is a consequence of the delocalized character of the t_{1u} wave function on the surface of C_{60} and the strong screening of the other 240 valence electrons which have a similar spatial distribution. Since the energy scale for the spin and orbital configuration energies is smaller than the 0.5-eV width of the corresponding band in the solid,[13] we do not expect these effects to be important. On the other hand, the $U=3$ eV value of the Hubbard parameter for the cluster is large, and even after screening effects are taken into account for the solid, the value of the effective Hubbard parameter $U_{\rm eff}=U/\epsilon$ will be of the order of magnitude of the bandwidth for any reasonable value of the screening constant ϵ. As many authors have pointed out, alkali-metal-doped C_{60} should have strong electron correlations associated with the charge states of each molecule, and the crystals should be close to the metal-insulator transition. Experimental evidence from the low-conductivity values[28] and photoemission spectra[29] are consistent with such a transition.

The most interesting parameter obtained from our calculations is the estimation of the Jahn-Teller distortion energy, $E_{\rm JT}\gtrsim 24$ meV of C_{60}^{-}. This is again smaller than the width of the t_{1u} band in the solid, and therefore we should not expect static distortions or effective "negative-U" behavior for the negatively charged C_{60} clusters. Since we only explored a two-dimensional cross section of the BO surface, we have a lower bound for that energy, but our analysis of the bonding and antibonding character of the wave functions makes us confident that we are including the most important distortions. Recently Lannoo and co-workers[5] derived a relation, $\lambda=2N(E_F)(5/6)E_{\rm JT}$, between the Jahn-Teller distortion energy, the density of states at the Fermi level, $N(E_F)$, and the electron-phonon interaction parameter λ of McMillan's equation for the superconducting transition temperature. Using an estimation of $N(E_F)=6$ states per eV (3 states in a band 0.5 eV wide), we find $\lambda\gtrsim 0.24$ from our lower bound on the Jahn-Teller energy. Since superconductivity in alkali-doped C_{60} can be explained by an electron-phonon coupling mechanism, if $\lambda\simeq 0.5$ our first-principles calculation of a lower bound of the Jahn-Teller energy has the correct order of magnitude for explaining the observed values of T_c.

ACKNOWLEDGMENTS

We thank Professor J. Buttet for helpful discussions, and K. Glassford for a critical reading of the manuscript. This work was supported in part by the Swiss National Science Foundation under Grant No. 20-30272.90.

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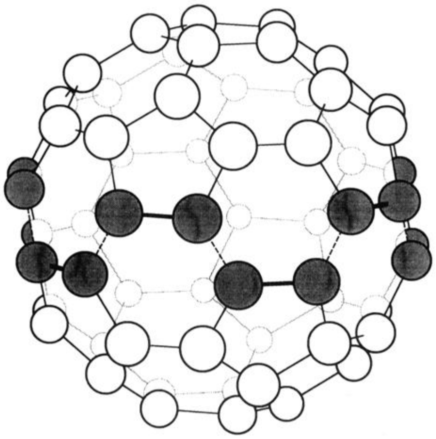

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