Fundamental excitations in C_{60}

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The geometrical and electronic structure of the neutral C_{60} molecule and of $C_{60}{}^{X-}$ anions ($X = 1$, 2, and 3) is calculated using a Pariser-Parr-Pople-type of Hamiltonian in combination with single and double configuration interaction. The model couples the bond length to the bond order, as well as to charge-charge and bond-order–bond-order interactions between nearest-neighbor sites. The total energy is minimized with respect to variations in the bond lengths. Although the energy differences between the molecular orbitals close to the Fermi energy are small, correlation effects in terms of configuration interaction are observed to be of minor importance for the ground-state geometrical and electronic structure. In accordance with this result, the cyclic polaronic defect (Jahn-Teller distortion of the molecule along the equatorial line) produced by Hückel-type calculations for $C_{60}{}^{X-}$ anions is observed to be stable within the correlated description presented in this study. Exactly the same type of defect also exists in the relaxed structure of the first excited state of the neutral molecule. Thus, the cyclic polaron corresponds to a low-lying fundamental excitation in C_{60}.

I. INTRODUCTION

Since the discovery[1] and isolation[2] of the C_{60} molecule, a number of properties of different materials based on this molecule have been discovered. The anionic state of the molecule is particularly interesting since metallic and superconducting properties are observed in crystals of C_{60} mixed with alkali metals, e.g., K_3C_{60}.[3-5] The charge-transfer state of the molecular anion is $C_{60}{}^{3-}$ in these systems. Furthermore, unusual magnetic properties below $T_c = 16$ K are observed in $C_{60}(TDAE)_{0.86}$,[6-8] where TDAE means tetrakis(dimethylamino)ethylene. In this system, one electron per TDAE molecule is transferred to the C_{60} molecule, which then becomes the radical anion $C_{60}{}^-$.

The electronic structure of the neutral C_{60} molecule is such that the highest occupied molecular orbital (HOMO) has a fivefold degeneracy (h_u symmetry) and the lowest unoccupied molecular orbital (LUMO) has a threefold degeneracy (t_{1u} symmetry). Consequently, in a rigid level picture there is a degeneracy at the Fermi level if less than six electrons are added to the C_{60} molecule. In such cases, there is a possibility of a Jahn-Teller distortion, i.e., a geometrical relaxation which leads to lowering of the symmetry of the molecule and a corresponding lifting of the degeneracy at the Fermi level. Such relaxations have been obtained in Hückel type calculations.[9-12] The bond-length alternation pattern which characterizes the neutral molecule[13] is distorted along an equatorial line in monoanionic and dianionic C_{60}. The additional electronic charge is localized to this geometrical defect, which then constitutes a cyclic polaron.[12] However, the molecular orbitals around the Fermi level are still rather close in energy. In such a situation, it is likely that the single determinantal Hartree-Fock ground-state configuration mixes with excited determinants to form a correlated ground state. In order to investigate this possibility we have calculated the electronic and geometrical structure of neutral and charged C_{60} molecules using a Pariser-Parr-Pople (PPP)-like Hamiltonian in combination with a limited single and double configuration interaction (SDCI). Thus the influence of dynamical correlation of the electrons on the electronic and geometrical structures of neutral and charged C_{60} molecules is accounted for in this work.

The CI calculation also provide the correlated excited state energies. We have calculated the energy of the low-lying excited states of the C_{60} anions. Although the oscillator strength is not calculated, these energies and their corresponding CI wave functions give an indication of the evolution of the band gaps as a function of the charge of the molecule.

The tendency toward self-localization of electrons transferred to the C_{60} molecule is a general feature of systems exhibiting strong electron-phonon coupling. The reason for this property is that the ground state of the neutral system is very stable. Therefore, instead of deforming the structure over the whole molecule, which is energetically very costly, the deformation is local, and a large part of the system remains in the same state, both electronically and geometrically, as the neutral species. The same type of effect can occur in excited states of these type of systems, namely a self-localization of the electron and the hole (an exciton) to a (localized) structural defect. Matus, Kuzmany, and Sohmen[14] have argued that the luminescence from solid C_{60} is explained in terms of the formation of such a polaron exciton in the initial state of the radiative decay process. We have calculated the relaxed geometry of the first excited state of a single C_{60} molecule and compared it with the structure of the polaron formed upon charging of the system. These results are discussed in relation to similar studies on conjugated polymers.

This paper is organized as follows. Section II contains a description of the methodology developed for this

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study. The results for the anions and the excited state of neutral C_{60} are presented and discussed in Sec. III A and III B, respectively. A summary and conclusions are given in Sec. IV.

II. METHODOLOGY

The calculations are based on the Pariser-Parr-Pople (PPP) Hamiltonian.[15] Only the π electrons are treated quantum mechanically; the energy of the σ bonds is described by a classical harmonic term. The uncorrelated wave functions and the corresponding total energies are obtained by solving the Schrödinger equation self-consistently within the restricted open shell Hartree-Fock (HF) approximation. Based on this solution, the ground-state bond lengths are calculated iteratively by minimizing the total energy with respect to deviations in the bond lengths. The geometry and electronic structure corresponding to the correlated wave function are obtained from a CI calculation involving singly and doubly excited determinants. In this case each iteration consists of a self-consistent PPP-HF calculation of the charge densities for a given geometry, followed by a CI calculation from which new bond lengths and charge densities are calculated.

The Hamiltonian consists of an electronic part describing π electrons only, and a classical part which describes the σ part of the C-C bonds:

$$H = \sum_{i,j}' \sum_{\sigma} t_{i,j} c_{i,\sigma}^{\dagger} c_{j,\sigma} + \frac{1}{2} \sum_{i,j} \sum_{\sigma_1,\sigma_2} \gamma_{i,j} c_{i,\sigma_1}^{\dagger} c_{j,\sigma_2}^{\dagger} c_{j,\sigma_2} c_{i,\sigma_1}$$
$$+ \frac{K}{2} \sum_{i,j}' (v_{ij} - C_0)^2 . \tag{1}$$

The primed summations over i and j include nearest-neighbor terms only, whereas the unprimed summations over i and j also include on-site terms ($i = j$). The $c_{i,\sigma}^{\dagger}$ ($c_{i,\sigma}$) operator creates (annihilates) an electron with spin σ on site i. Under the assumption that the deviations of the bond lengths are small, the nearest-neighbor hopping integrals can be approximated as follows:

$$t_{i,j} = t_0 - \alpha v_{i,j} , \tag{2}$$

where t_0 is the hopping parameter at uniform bond lengths ($t_0 = -2.5$ eV), α is the electron-phonon-coupling parameter ($\alpha = 6.31$ eV/Å), and $v_{i,j}$ is the deviation from uniform bond lengths. Consistent with the treatment of the hopping integrals, the Coulomb integrals $\gamma_{i,j}$ are also linearized. From the Ohno formula for these integrals[16] we obtain, to first order in $v_{i,j}$,

$$\gamma_{i,j} = U_0 , \quad \gamma_{i,j} = V_0 - \chi v_{i,j} , \tag{3}$$

where $U_0 = 11.3$ eV, $V_0 = 3.75$ eV, and $\chi = 1.44$ eV/Å. Since Coulomb interactions are included up to nearest-neighbor sites only, the cutoff in the electron-electron interaction is rather abrupt. For this type of interaction it is common to reduce the nearest-neighbor interaction as compared to the case where long-range interactions are included.[17] The values of V_0 and χ presented above are therefore scaled down by a factor of 2 as compared to the

values that result from the Ohno expression.

The effect of the counterions is not included in Eq. (1). In order to take this effect into account, we have also performed calculations where a point charge potential is added to the total Hamiltonian. This potential is screened by the static dielectric constant of solid C_{60}, $\varepsilon_{\infty} = 4.0$.[18] However, the actual screening in doped C_{60} crystals, e.g., $K_3 C_{60}$, is expected to be stronger since these materials have very small band gaps.[3] To treat this additional screening of the dopant potential we have also studied the effect of an exponentially screened potential from the counterions.

The influence of the core of σ bonds on the total energy is accounted for by the last term in Eq. (1), which is a classical harmonic potential where $K = 49.7$ eV/Å^2 is the spring constant and C_0 is proportional to the mean bond order $\langle P_{i,j} \rangle$ of the molecule as

$$C_0 = 2 \frac{\alpha}{K} \langle P_{i,j} \rangle . \tag{4}$$

The values of the electron-phonon-coupling constant α and the spring constant K (see above) are those chosen in Hückel-type calculations to produce the experimentally observed difference between single and double bonds of 0.05 Å for neutral C_{60}.[9]

In a first study, the bond-length deviations $v_{i,j}$ are calculated by minimization of the total HF ground-state energy ($E_{\text{tot}}^{\text{HF}}$) of the system [the expectation value of the Hamiltonian in Eq. (1) using the Hartree-Fock ground-state determinant]. From the condition

$$\frac{\partial E_{\text{tot}}^{\text{HF}}}{\partial v_{i,j}} = \frac{\partial \langle \Psi_0 | H | \Psi_0 \rangle}{\partial v_{i,j}} = 0 , \tag{5}$$

the ground-state bond-length deviations are expressed in terms of the elements of the density matrix ($P_{i,j}$) and the parameters K, α, and χ [see Eqs. (1)–(3) above]:

$$v_{i,j} = \frac{1}{K} \{ 2\alpha P_{i,j} + \tfrac{1}{2}\chi[P_{i,j}^2 - P_{i,i}(P_{j,j}-2)$$
$$- P_{j,j}(P_{i,i}-2)] \} + C_0 + Z . \tag{6}$$

The term Z contains contributions which are nonlinear in $v_{i,j}$. This term is neglected during the iterative procedure since $Z=0$ at equilibrium. Note that the closed expression for $v_{i,j}$ is a result of the linearization of the hopping and Coulomb integrals [see Eqs. (2) and (3)].

In the calculations where correlation effects are included, the PPP-HF calculation is followed by a CI calculation. The CI wave function

$$|\Psi^{\text{CI}}\rangle = b_0 |\Psi_0\rangle + \sum_{S} b_S |\Psi_S\rangle + \sum_{D} b_D |\Psi_D\rangle \tag{7}$$

includes the $N_C = 1000$ singly ($|\Psi_S\rangle$) and doubly ($|\Psi_D\rangle$) excited determinants (SDCI) with lowest energy selected from 6000 generated configurations. In order to increase the number of relevant configurations and to simplify the interpretation of the CI wave function, all configurations are spin adapted and restricted to doublets in the case of C_{60}^{-} and C_{60}^{3-} and to singlets in the case of C_{60} and C_{60}^{2-}. The bond-length deviations are calculated by

minimizing the total energy of the system ground state (E_{tot}^{CI}) by putting the derivative with respect to the bond deviations $v_{i,j}$ of the CI energy to zero:

$$\frac{\partial E_{tot}^{CI}}{\partial v_{i,j}} = \frac{\partial \langle \Psi_{CI} | H | \Psi_{CI} \rangle}{\partial v_{i,j}} = 0 , \tag{8}$$

where H is the Hamiltonian in Eq. (1). Equation (8) is solved for $v_{i,j}$:

$$v_{i,j} = -\frac{1}{K} \frac{\partial \langle \Psi_{CI} | H_e | \Psi_{CI} \rangle}{\partial v_{i,j}} + b_0^2 C_0 + \sum_S b_S^2 C_S + \sum_D b_D^2 C_D , \tag{9}$$

where H_e is the electronic (nonclassical) part of the Hamiltonian in Eq. (1). The constants C_S and C_D are proportional to the mean bond orders of the molecule as described by the singly and doubly excited determinants, respectively, in the same way as C_0 in Eq. (4) is proportional to the mean bond order of the HF ground state.

III. RESULTS

A. C_{60} anions

In Fig. 1 are shown the variations in the bond lengths (v_{ij}) for C_{60}^-, C_{60}^{2-}, and C_{60}^{3-}. Both the results of the noncorrelated (dashed line) and the correlated (solid line)
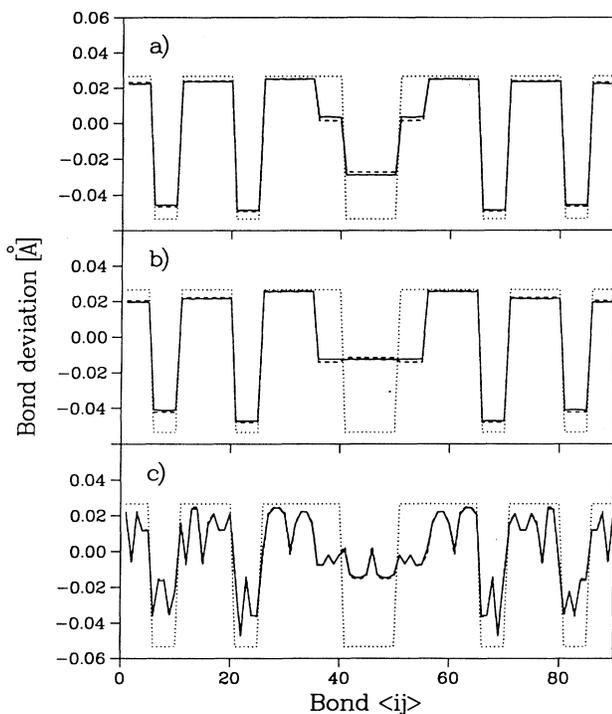
FIG. 1. Displacements of the bond lengths relative to the average bond length of the neutral C_{60} molecule for (a) C_{60}^-, (b) C_{60}^{2-} and (c) C_{60}^{3-}. Solid and dashed lines represent the results with and without CI, respectively. The dotted line is the result, including CI, for the neutral C_{60} molecule.

calculations are presented together with the results for the neutral molecule (dotted line; the noncorrelated and the correlated result are essentially the same in this case). The bonds in the molecule are numbered "layer by layer" starting with the five bonds in a pentagon. Bond numbers 6 to 10 constitute the next "layer" and connect each of the five first atoms to their nearest neighbors. The next two "layers" consist of bonds number 11 to 20 and 21 to 25, respectively. The numbering of bonds proceeds in a similar way until the complete molecule is covered.

The localized cyclic polaronic defect mentioned in Sec. I is easily identified in Figs. 1(a) and 1(b) for the monoanion and dianion of C_{60}. The bond-length alternation is seen to be significantly reduced compared to the neutral system for bonds 36 to 55, i.e., the bonds along the equatorial line of the C_{60} molecule, whereas the rest of the bonds are left essentially unchanged. Evidently, the same type of defect is created in both the monoanion and the dianion, the difference being that the deformation is larger in the latter system where the bond lengths along the cyclic defect are essentially uniform. For the trianion, however, a new type of structure appears [see Fig. 1(c)]. A careful analysis of the bond-length data shows that the defect of the dianion is still present and additional deformations, due to the "third" electron, occur mostly in the region outside this defect. We note, however, that about 30% of the bond remains unchanged as compared to the neutral molecule. Thus the geometrical defect is somewhat localized also in the case of C_{60}^{3-}.

A very clear picture of the self-localization of charges in C_{60} is given in Fig. 2, where the net atomic charges of the different anions are displayed. The molecule has been mapped on a plane in such a way that the top and bottom pentagons appear in Fig. 2 as the central and outer pentagons, respectively. In Figs. 2(a) and 2(b), the "equatorial line" of the C_{60} molecule corresponds to the connected sequence of sites with a major net atomic charge, i.e., the net charge of the monoanions and dianions is localized to the same region where the bond-length alternation is reduced [see Figs. 1(a) and (b)]. The geometrical defect together with the net charges constitute the cyclic polaron in the case of C_{60}^- and a cyclic bipolaron in the case of C_{60}^{2-}. As already indicated in the geometrical data, the cyclic bipolaron still exists in C_{60}^{3-}. The additional electron, as compared to the dianion, is localized to regions outside of the bipolaron, symmetrically on the upper and lower hemispheres of the spherical molecule [see Fig. 2(c)]. Therefore, the net atomic charges due to all three additional electrons in the trianion are rather spread over the molecule. The individual molecular orbitals, however, are still localized to different regions of the molecule; the HOMO is localized to a circumference which intersects the north and south poles of the molecule, and the HOMO-1 is localized to the equatorial region.

The basic structure of the defect persists when the potential due to the counterions is included (see Figs. 3 and 4). The strongest polarization of the defects occurs for the monoanion since the potential in this case is more asymmetric than in the case of the dianion, where the counterions are placed symmetrically on opposite sites of the equatorial line, or in the case of the trianion, where

the counterions are placed in the form of a triangle concentric with the C_{60} molecule. The results presented in Figs. 3 and 4 are for the unscreened potential. The additional screening of the counterions which occur in the metallic state (see Sec. II) reduces the effect of the counterions further. Therefore, we believe that the effect of the counterions on geometrical and electronic structures of the anions can be neglected in systems like K_3C_{60}.

As discussed in Sec. I, it is expected that in systems where the excited states are nearly degenerated with the ground state, the representation of the ground state in terms of a single determinant is inadequate. Instead a correlated ground state, where a number of determinants mix, is likely to be formed. Indeed, in the C_{60} anions the excited states lie very close in energy to the ground state. Despite this fact, we observe very small effects on the geometrical and electronic structure when CI is included in the calculation (see Figs. 1–4). This feature is confirmed by inspection of the CI wave functions, which to more than 90% are described by the Hartree-Fock ground-state determinant, and by the small gain in total energy (the correlation energy E_{corr}) which is obtained in the CI calculations as compared to the Hartree-Fock result (see Table I). The minimal mixing between determinants in the case of the C_{60} anions is a result of the tendency toward localization of the molecular orbitals (MO's). Since different MO's, for instance those in the

FIG. 3. Same as Fig. 1, but with the potential due to counterions included. (a) $X^+C_{60}^-$, (b) $X_2^{2+}C_{60}^{2-}$ and (c) $X_3^{3+}C_{60}^{3-}$.

FIG. 2. Net atomic charges for C_{60} anions displayed on a C_{60} topological network in the plane: (a) C_{60}^-, (b) C_{60}^{2-}, and (c) C_{60}^{3-}.
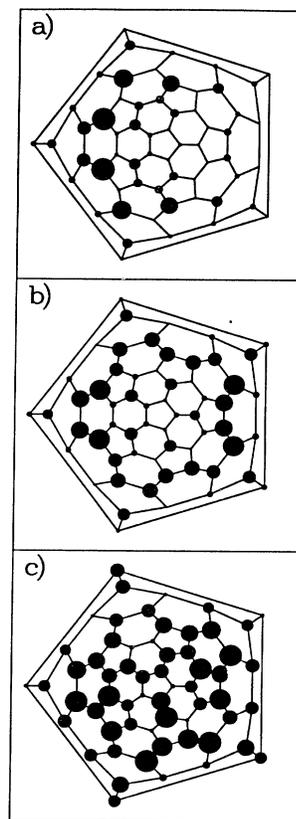
FIG. 4. Same as Fig. 2, but with the potential due to counterions included. (a) $X^+C_{60}^-$, (b) $X_2^{2+}C_{60}^{2-}$ and (c) $X_3^{3+}C_{60}^{3-}$.

TABLE I. CI wave functions and correlation energies (E_{corr}) for the ground state of the C_{60} anions. The notation $|G.S.\rangle$ refers to the Hartree-Fock ground-state determinant, and $|a,b \rightarrow r,s\rangle$ indicates an excited determinant where electrons have been promoted from MO's a and b to MO's r and s.

System	E_{corr} (eV)	CI wave function
C_{60}	-0.094	$+0.992\|G.S.\rangle$
C_{60}^{-}	-0.175	$+0.984\|G.S.\rangle$
C_{60}^{2-}	-0.365	$+0.958\|G.S.\rangle -0.120\|31,31\rightarrow34,34\rangle -0.120\|31,31\rightarrow35,35\rangle$
C_{60}^{3-}	-0.332	$+0.949\|G.S.\rangle -0.171\|31,31\rightarrow34,34\rangle -0.117\|31,31\rightarrow35,35\rangle$
$X^{+}C_{60}^{-}$	-0.200	$-0.971\|G.S.\rangle -0.135\|31\rightarrow34\rangle$
$X_{2}^{2+}C_{60}^{2-}$	-0.393	$-0.955\|G.S.\rangle +0.122\|31,31\rightarrow35,35\rangle +0.118\|31,31\rightarrow34,34\rangle$
$X_{3}^{3+}C_{60}^{3-}$	-0.309	$+0.941\|G.S.\rangle -0.173\|31,31\rightarrow34,34\rangle -0.121\|31,31\rightarrow35,35\rangle$

triad of orbitals originating from the triply degenerate t_{1u} MO of the neutral molecule, are localized to different regions of the molecule, mixing of determinants involving these MO's would lead to delocalization of the electrons. Evidently, the energy gain by localizing the electrons is larger than the correlation energy that would be gained in a state where many determinants mix. Therefore, the cyclic polaronic defect is basically unaffected by the inclusion of the correlation in terms of CI.

Häser, Almlöf, and Scurseria[13] have calculated the geometrical structure of neutral C_{60} at the *ab initio* Hartree-Fock level and included correlation in terms of MP/2 perturbation theory. It was pointed out by these authors that correlation plays an important role in the geometrical structure. The origin of this difference compared to our results is likely to be due to the differences in methods. It should be noted that even though the inclusion of MP/2 corrections is of importance, it does not change the geometrical structure qualitatively. Furthermore, by the way our method is parametrized, the ground-state bond-length dimerization of neutral C_{60} obtained in this work is identical to that calculated by Häser, Almlöf, and Scurseria.

The excited states of the C_{60} anions are also calculated. In Table II are shown the excitation energies and the corresponding wave functions of the lowest excited states with and without counterions included. The smallest gap is obtained for C_{60}^{3-}, 0.344 and 0.350 eV, respectively, for systems with and without counterions. This is consistent with the experimental observation that solids formed of these anions are metallic.[3] Again, the effect of the counterions is very small on the electronic properties of the anions.

The electronic transitions corresponding to the first excited states of the anions are shown in Table II to be strongly dominated by the single-particle HOMO-LUMO transition. Inspection of these MO's, which originate from the t_{1u} MO of the neutral system, show that they are odd with respect to the symmetry plane (the equatorial plane) of the molecule. The HOMO-LUMO transition is therefore dipole forbidden. The lowest optically allowed transitions occur instead at 0.796, 1.054, and 0.641 eV for C_{60}^{-}, C_{60}^{2-}, and C_{60}^{3-}, respectively.

As discussed above, the single-particle-like excitation in the anions is a result of the localization of the MO's to different regions of the molecule. In contrast to this result, Braga, Rosén, and Larsson[19] calculated the transi-

tions in C_{60}^{-} using a complete neglect of differential overlap (CNDO)/S-CI method and concluded that these transitions involve a high number of configurations. The reason for this discrepancy is that Braga, Rosén, and Larsson used the geometry of the neutral system when they studied the monoanion. This geometry, which is shown here to be unstable toward the formation of the cyclic polaron, prevents localization of MO's, which in turn leads to extensive configuration interaction.

B. Excited state of neutral C_{60}

The fivefold degeneracy of the HOMO's and the threefold degeneracy of the LUMO's of C_{60} allow for 15 degenerate excited states of the neutral molecule in the single-particle description. These 15 states all have the same symmetry and therefore couple very strongly in the CI picture (in contrast to the case discussed above). The same is true for the optically allowed transitions from the h_{u} level (HOMO-1, HOMO-1, ..., HOMO-4) to the threefold-degenerate t_{1g} level (LUMO+3, LUMO+4, and LUMO+5). Thus it is of fundamental importance to use CI in order to describe the excited state of the neutral molecule correctly. This is very clearly illustrated in Table III (a), where the excitation energies and CI wave functions of the four lowest excited states of neutral C_{60} are shown. The triad of excited states around 2.5 eV correspond to the band gap of C_{60}. Considering a bandwidth of about 0.4 eV of both the valence and the conduction bands,[20] this value is in very good agreement with the corresponding band gap of solid C_{60}, which from a combination of the photoelectron and inverse photoelectron

TABLE II. CI wave functions and excitation energies (E_{exc}) for the first excited states of the C_{60} anions.

System	E_{exc} (eV)	CI wave function
C_{60}^{-}	0.388	$+0.986\|31\rightarrow33\rangle$
	0.389	$-0.986\|31\rightarrow32\rangle$
C_{60}^{2-}	0.566	$-0.964\|31\rightarrow32\rangle$
	0.567	$-0.964\|31\rightarrow33\rangle$
C_{60}^{3-}	0.350	$-0.968\|31\rightarrow32\rangle -0.102\|31,31\rightarrow35,36\rangle$
$X^{+}C_{60}^{-}$	0.396	$-0.983\|31\rightarrow33\rangle$
	0.412	$-0.980\|31\rightarrow32\rangle$
$X_{2}^{2+}C_{60}^{2-}$	0.556	$+0.965\|31\rightarrow33\rangle +0.116\|31,31\rightarrow35,36\rangle$
	0.580	$+0.963\|31\rightarrow32\rangle -0.115\|31,31\rightarrow34,36\rangle$
$X_{3}^{3+}C_{60}^{3-}$	0.344	$-0.951\|31\rightarrow32\rangle +0.147\|31\rightarrow34\rangle$

TABLE III. CI wave functions and excitation energies (E_{exc}) for the first excited states of neutral C_{60}. (a) Unrelaxed geometry. (b) Relaxed geometry.

System	E_{exc} (eV)	CI wave function
	2.513	$+0.237\|30\rightarrow31\rangle -0.200\|28\rightarrow32\rangle -0.314\|27\rightarrow33\rangle -0.406\|29\rightarrow31\rangle$ $-0.220\|26\rightarrow33\rangle +0.300\|27\rightarrow31\rangle +0.396\|29\rightarrow32\rangle -0.299\|29\rightarrow33\rangle$ $-0.107\|27\rightarrow32\rangle +0.116\|30\rightarrow32\rangle -0.118\|21\rightarrow35\rangle -0.113\|24\rightarrow36\rangle$ $+0.107\|22\rightarrow35\rangle -0.141\|20\rightarrow34\rangle +0.103\|23\rightarrow37\rangle$
	2.514	$-0.506\|26\rightarrow32\rangle -0.388\|28\rightarrow32\rangle +0.121\|27\rightarrow33\rangle -0.185\|29\rightarrow31\rangle$ $+0.315\|26\rightarrow33\rangle -0.414\|28\rightarrow33\rangle -0.144\|27\rightarrow31\rangle -0.142\|28\rightarrow31\rangle$ $+0.139\|23\rightarrow34\rangle -0.138\|25\rightarrow35\rangle +0.171\|17\rightarrow36\rangle -0.111\|22\rightarrow41\rangle$
(a)	2.529	$-0.612\|30\rightarrow31\rangle -0.376\|27\rightarrow33\rangle -0.106\|29\rightarrow31\rangle +0.186\|26\rightarrow33\rangle$ $-0.252\|28\rightarrow33\rangle -0.300\|27\rightarrow32\rangle -0.152\|30\rightarrow32\rangle +0.121\|30\rightarrow33\rangle$ $+0.116\|25\rightarrow34\rangle -0.114\|22\rightarrow36\rangle -0.123\|21\rightarrow36\rangle -0.166\|19\rightarrow35\rangle$
	3.206	$-0.356\|28\rightarrow36\rangle +0.338\|30\rightarrow35\rangle -0.307\|29\rightarrow34\rangle -0.167\|27\rightarrow35\rangle$ $+0.155\|28\rightarrow35\rangle -0.111\|27\rightarrow36\rangle -0.241\|26\rightarrow34\rangle +0.205\|23\rightarrow31\rangle$ $+0.259\|22\rightarrow32\rangle -0.159\|24\rightarrow31\rangle -0.279\|21\rightarrow33\rangle +0.215\|19\rightarrow31\rangle$ $+0.145\|17\rightarrow33\rangle -0.225\|18\rightarrow32\rangle -0.183\|20\rightarrow33\rangle +0.127\|17\rightarrow31\rangle$
(b)	2.010	$-0.908\|30\rightarrow31\rangle +0.161\|29\rightarrow32\rangle +0.161\|28\rightarrow33\rangle -0.122\|25\rightarrow34\rangle$ $+0.122\|24\rightarrow35\rangle -0.113\|21\rightarrow36\rangle$

spectra is determined to 2.3 eV.[21] Leach et al.[22] have measured the absorption of C_{60} in the energy region 1.5–6 eV and found a weak absorption band between 2.0 and 2.5 eV. This band is assigned to vibronic components of the symmetry-forbidden HOMO-LUMO transition. Therefore, two different experimental methods, as well as our theoretical results, all point to a HOMO-LUMO gap in C_{60} which is of the order of 2.5 eV.

As stated above, transitions from the HOMO's (h_u) to the LUMO's (t_{1u}) are dipole forbidden. The first three excited states in Table III (a) are clearly dominated by transitions between these MO's, and are therefore not involved in optical absorption. The fourth state, however, is dominated by transitions from the HOMO levels (MO's 26–30) to the LUMO+3, LUMO+4, and LUMO+5 (MO's 34–36) and corresponds to the first optically allowed excited state. The calculated excitation energy of this state is 3.2 eV, in perfect agreement with the experimental value of 3.2 eV measured by laser depletion spectroscopy,[23] and the value of 3.1 eV found from electronic absorption spectroscopy of dilute C_{60} in hexane solution.[24] Together with the results of the band gap discussed in the previous paragraph, this shows that our method not only gives the correct ground-state bond-length dimerization, as it is parametrized for, but also correctly describes the excited states of C_{60} very accurately. Earlier calculations using the CNDO/S method which include also the σ electrons, but with a smaller number of configurations than in our calculation, give the first optically allowed transition at 3.48 (using 800 configurations) (Ref. 19) and 3.6 eV (250 configurations).[25] The relatively close agreement between the results obtained in this study and the CNDO/S results justifies the π-electron approximation used here.

The absorption peak at 1.55 eV observed in high-resolution electron-energy-loss spectroscopy (HREELS) was interpreted as being due to exciton formation.[26] Also, Matus, Kuzmany, and Sohmen have interpreted their luminescence spectra of solid C_{60} in terms of a self-trapped molecular exciton.[14] This state is believed to originate from the first excited state of the molecule, which, due to Coulomb interactions, relaxes to form a bound state of the excited electron and the hole. Since the electron-phonon interaction is strong in this system, we can also expect a relaxation of the geometry for the exciton state. The exciton is therefore termed a polaron exciton. The existence of a polaron exciton has been verified in calculations using a Hückel type of Hamiltonian.[27] Our calculations, which include electron-electron interactions and electron-electron correlation effects, produce a result which is very similar to that obtained at the single-particle level, i.e., bond-length deviations (v_{ij}) that are nearly identical to those in the polaron formed by adding a charge to the molecule (see Fig. 5). Thus the cyclic polaron acts as a fundamental low-lying excitation of C_{60}, in very much the same way as for instance the soliton is the fundamental low-lying excitation of trans-polyacetylene.[28]

In comparison with the strongly mixed first excited state of C_{60}, it is striking that the wave function of the first excited state after geometry relaxation is strongly dominated by a single excited determinant, namely the determinant correspond to a HOMO to LUMO excitation. Again this is a result of the localization of the different MO's to different regions of the molecule and the fact that in this type of system, localization (in the form of a cyclic polaron) is energetically more favorable than mixing of determinants. The approximately single determinantal nature of the relaxed first excited state also explains why the single-particle result is in such good
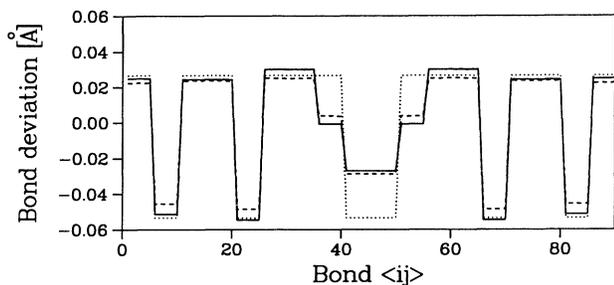
FIG. 5. Displacements of the bond lengths relative to the average bond length of the neutral C_{60} molecule for the first excited state of C_{60} (solid line) and for C_{60}^- (dashed line).

agreement with the result of our calculations.

The net atomic charges of the polaron exciton is essentially zero at each site which confirms the excitonic nature of this excitation, namely that the hole and the electrons are confined to the same region. The relaxation energy of the polaron exciton, as compared to the first excited state of the molecule in the ground-state geometrical conformation, is calculated to be 0.114 eV. This value is in rather close agreement with the experimental estimate of 0.170 eV.[14]

IV. SUMMARY AND CONCLUSIONS

The ground-state bond lengths of C_{60}^- has been calculated using a PPP-CI type of Hamiltonian. The same type of calculation is performed for the bond lengths in the first excited state of neutral C_{60}. Both these systems exhibit a distortion of the bond lengths along the equatorial line of the spherically shaped molecule. This type of defect, a cyclic polaron, thus constitutes a fundamental low-lying excitation of C_{60}. The cyclic polaron is observed also to be stable in C_{60}^{2-}. Additional charging of the molecule results in bond-length distortions and charge accumulation symmetrically below and above the equatorial plane.

The chosen parametrization of the electron-phonon and electron-electron interaction terms in the Hamiltonian, in combination with spin-adapted CI involving 1000 configurations, were shown to produce excitation energies in very close agreement with experimental observations for the neutral molecule. We believe, therefore, that the methodology used here is appropriate for studies of the electronic structure of C_{60}. The method can easily be extended to include calculations of oscillator strengths, to produce spectra in direct comparison with experimental optical-absorption data. The calculations are also very fast and could easily be performed on larger systems, for instance on clusters of C_{60}, which is interesting since this type of calculation would provide information about intermolecular interactions. In the future, we also intend to study larger fullerenes using the method presented here.

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