The Self-Consistent and Environment-Dependent Hamiltonian and Its Application to Carbon Nanoparticles

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Computer simulation studies of nanoscale materials, in particular nanoparticles or finite-length nanotubes/nanowires, via ab initio methods are challenging or impossible due to computational costs associated with the calculation of total energy and atomic forces of nanometer-sized systems. While molecular mechanics methods can handle large systems, they cannot describe manifestations of quantum effects in nanoscale materials. Therefore, we have developed a quantum-mechanics based semi-empirical Hamiltonian to bridge the accuracy and system-size gap between the above two methods. The key feature of this self-consistent and environment dependent (SCED) Hamiltonian is that it takes into account of environment-dependency, electron screening, and charge re-distribution effects within the LCAO (linear combination of atomic orbitals) framework. In the present study, we have used a relaxation scheme based on the SCED/LCAO Hamiltonian to determine the structure and electronic density of states of multi-shelled fullerenes ("fullerene onions") up to six shells. Our study reveals that inter-shell interactions are weak with a small charge transfer from the outer to the inner shells. The structure (or geometry) of fullerene shells in the onion structure is very similar to the geometries of corresponding isolated fullerenes, and, therefore, the energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital of a fullerene onion is similar to that of the corresponding outermost shell.

Keywords: Nanotube, Fullerene, Self-Consistent, Charge Transfer, Fullerene Onion, Gap, Atomic Orbitals.

1. INTRODUCTION

Particles in nanometer range have attracted extensive attention from diverse communities including physicists, chemists, biologists, and material scientists because of their unique properties arising from quantum-confinement effects of electrons. However, it is challenging to treat nanoparticles using quantum mechanics based molecular dynamics. First-principles based methods, which treat quantum effects of electrons explicitly, come in two flavors: (i) wavefunction based ab initio methods1,2 and (ii) charge density based density functional theory (DFT) methods.3,5 These methods, while accurate,6,7 are computationally expensive and practically impossible to simulate systems containing more than a few hundred atoms in molecular dynamics even with the availability of present-day supercomputing and parallel computing resources and the computational speed-up offered by linear scaling algorithms.8,9 On the other hand, molecular mechanics based methods,10-12 where the electronic Schrödinger equation is not solved, can handle systems with millions of atoms even on a modest workstation. However, the neglect of quantum effects in molecular mechanics based methods makes these methods inadequate to treat nanoparticles in which quantum effects play an important role.

The compromise between efficiency and accuracy has resulted in yet another route for materials simulations that is based on semi-empirical methods with parameterized Hamiltonians.13-23 Depending on the application, semi-empirical Hamiltonians have two major flavors, one is chemistry and biology related13-15 and mainly isolated molecule oriented, another one is physics (mainly condensed matter) and material science oriented.16-23 These semi-empirical Hamiltonians have been extensively used to treat both extended (bulk) and low-dimensional systems (atomic/molecular clusters, nanowires/nanotubes, surfaces/interfaces, etc.) that are of interest in condensed matter physics, nanoscience, chemistry, and biology. With the emergence of nanoscience as a new research field, the need to develop reliable and transferable
semi-empirical methods has become urgent so that the structure and properties of nanoscale materials containing thousands of atoms can be reliably predicted from theoretical/computational studies.

In most semi-empirical methods, the common problem is the lack of the transferability of the Hamiltonian to different types of environments. This may be attributed to the neglect or insufficient treatment of:
(i) interactions beyond the two-center terms,
(ii) electron screening, and
(iii) the self-consistent treatment of charges.

Recently, we developed a semi-empirical method in the framework of the linear combination of atomic orbitals (LCAO) that included a self consistent (SC) treatment of the charge redistribution and the environment dependent (ED) multi-center interactions in the formulation and construction of the parameterized Hamiltonian.20 This method used in combination with the order-N scheme, as developed in Refs. [24, 25], will enable structural studies of large nanoparticles (i.e., beyond 1000 atoms). The SCED/LCAO Hamiltonian has been developed and tested previously to study the structural and electronic properties of silicon clusters, silicon surfaces, bulk silicon, and intermediate-sized carbon clusters.20 In the present work, we will extend these studies to investigate the structural and electronic density of states of multi-shelled fullerene (fullerene onions) using the SCED/LCAO method.

Fullerene onions are multi-layered shell structures of fullerenes with smaller fullerenes encapsulated within bigger fullerenes. The discovery of fullerene onions has been reported previously.23-27 Detailed understanding of the electronic structure of these fullerene onions helps to better utilize these nanoparticles in electronic and optical applications. Various works were dedicated to the structures of the fullerene onions and interactions among the fullerene onion shells.28, 36 The stabilities of the fullerene onions were proposed to come from the van der Waals (VDW) interactions among the fullerene shells28, 36 and weak π→π molecular orbital interactions were suggested as well.37 In the present work, the electronic structures of the fullerene onions and the interactions among the fullerene shells in fullerene onions will be investigated in detail using SCED/LCAO and CNDO (complete neglect of differential overlap).37 CNDO is a semi-empirical method neglecting the overlap distribution ϕ_i(i)ϕ_j(j) of any two different atomic orbital ϕ_i and ϕ_j in all electron-repulsion integrals.38 The eigenvalue (essentially the energy of the atomic orbital) of one-electron Hamiltonian was estimated from ionization potential of atoms. The off-diagonal term (excluding the overlap) of the one-electron Hamiltonian, termed as bonding parameters, was fitted to full LCAO-SCF calculations on diatomic molecules.37, 38 Valence electrons in CNDO are considered for integrals with minimal basis set and core electrons are taken into account with nuclear core. Because of the nature of CNDO, the predictions from CNDO will only be used as a benchmark for comparison to highlight the importance of the inclusion of multi-center interactions in SCED/LCAO and the capability of the SCED/LCAO method to treat large systems.

2. METHODS AND COMPUTATIONAL DETAILS

The SCED/LCAO Hamiltonian has been reported in detail elsewhere.20 For completeness, the SCED/LCAO Hamiltonian is only outlined here.

The general Hamiltonian of a many-atom system can be written as:

\[
H = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{N} \sum_{j=1}^{M} \frac{Z_A}{r_{ij}}
+ \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{N} \sum_{j=1}^{M} \frac{Z_B}{r_{AB}}
\]

accounting for the electronic kinetic energy, nucleus–electron attractions, electron–electron interactions, and nucleus–nucleus repulsions, respectively.

Within the framework of linear combination of atomic orbitals and under the one particle approximation, the diagonal term of the electronic Hamiltonian of SCED/LCAO is written as,

\[
H_{\text{SCED/LCAO}}^{0} = e_{\text{in}} + u_{\text{intra}} + u_{\text{inter}} + v_{\text{intra}}
\]

where \(e_{\text{in}}\) is the sum of the kinetic energy and the energy of interaction with its own ionic core of an electron in the orbital \(\alpha\). The interaction of the electron in orbital \(\alpha\) with other electrons on the same ion is represented by \(u_{\text{intra}}\). \(u_{\text{inter}}\) is the interaction of the electron in orbital \(\alpha\) with other electrons in the orbital \(\beta\) on different ions \(j\). \(v_{\text{intra}}\) is the interaction energy between the electron in orbital \(\alpha\) on the ion \(i\) and the ions at the other sites. These terms can further be represented by

\[
e_{\text{in}} = e_{\text{in}} - Z_iU_i
\]

\[
u_{\text{intra}} = N_iU_i
\]

\[
u_{\text{inter}} = \sum_{k \neq i} [N_iV_{\delta}(R_{ik}) - Z_kV_{\delta}(R_{ik})]
\]

where \(e_{\text{in}}\) is the energy of the orbital \(\alpha\) for the isolated atom at \(i\), \(Z_i\) is the number of positive charge of the ion at \(i\), \(N_i\) the number of valence electrons on the atom at \(i\) in the system, \(U_i\) is a Hubbard-like term for effective electron–electron interaction for electrons on the atom \(i\). \(N_iV_{\delta}(R_{ik})\) is the effective interaction between an electron associated with the ion at site \(i\) and electrons associated with the ion at site \(k\). \(Z_kV_{\delta}(R_{ik})\) is the interaction between an electron associated with the ion at site \(i\) and an ion at site \(k\).
Accordingly, the off-diagonal term \((i \neq j)\) is

\[
H_{ij}^{(\text{SCIDL/CAO})} = \frac{1}{2} \left[ K(R_{ij}) (\varepsilon'_m + \varepsilon'_n) + (N_j - Z_j) U_j + (N_i - Z_i) U_i \right] + \left[ \sum_{k \neq i} (N_i' V_{jk}(R_{ik}) - Z_k V_{jk}(R_{kj})) + \sum_{k \neq j} (N_j' V_{ik}(R_{ki}) - Z_k V_{ik}(R_{ik})) \right] S_{m,n}(R_{ij})
\]

(6)

where the first term in the off-diagonal Hamiltonian corresponds to the two-center hopping term, similar to the Wollfberg-Helmholtz relation in the extended Hückel theory.\(^9\) Since \(V_{jk}(R_{ik}) [V_{ik}(R_{ki})]\) is defined as the energy of effective interaction per ionic [electron] charge between an ion [electron] at site \(k\) and an electron on the ion at site \(i\), \(V_{jk}(R_{ik})\) may be represented by the following function form

\[
V_{jk}(R_{ik}) = \frac{E_{0}}{R_{ik}} \left[ 1 - (1 + B_{jk} R_{ik}) e^{-x_{jk}/R_{ik}} \right]
\]

(7)

Furthermore, since \(V_{jk}(R_{ik})\) and \(V_{ik}(R_{ki})\) have similar form as they approach \(E_{0}/R_{ik}\) for \(R_{ik}\) beyond a certain distance, they are expected to differ by a short range function \(\Delta V_{jk}\) given by

\[
\Delta V_{jk} = (A_{N} + B_{N} R_{ik}) \left[ \frac{1 + e^{-\alpha_{jk}/R_{ik}}}{1 + e^{-\beta_{jk}/(d_{jk} - R_{ik})}} \right]
\]

(8)

In Eq. (6) \(K(R_{ij})\), a scaling function, is chosen to be \(K(R_{ij}) = e^{\frac{\phi_{ij}}{R_{ij}}}\). Finally, the overlap matrix elements \(S_{m,n}(R_{ij})\) are parameterized as

\[
S_{ij} = (A_{\sigma} + B_{\sigma} R_{ij}) \left[ \frac{1 + e^{-\alpha_{\sigma}/R_{ij}}}{1 + e^{-\beta_{\sigma}/(d_{\sigma} - R_{ij})}} \right]
\]

(9)

Within the framework of SCIDL/CAO, the total number of electrons associated with an ion is given by \(N_i = \sum_{\alpha} \sum_{\beta} \sum_{\gamma} c_{\alpha \beta}^{i} c_{\gamma \beta}^{i} f_{\alpha} S_{m,n}^{\gamma}\), where \(c_{\alpha \beta}^{i}\) is the coefficient vector of the eigenvalue corresponding to the eigenvalue \(\varepsilon_{\alpha}\) of the general eigenvalue equation \(Hc_{\alpha} = \varepsilon_{\alpha} c_{\alpha}\). Charge redistributions reflected by two-center and multi-center interactions are realized through the self-consistency in solving the general eigenvalue equation.

The parameters defining the SCIDL/CAO Hamiltonian will be optimized through an appropriately chosen database for a particular element. In particular, the parameter set defining the SCIDL/CAO Hamiltonian for carbon had been constructed using the database that includes properties of carbon clusters of different bonding up to six atoms and the bulk carbon (diamond and graphite phases).\(^{26}\) The database was prepared from the DFT-based mPW1PW91 method\(^{40}\) with Dunning's basis set (cc-pVTZ).\(^{41}\) The constructed SCIDL/CAO parameter set for carbon had been shown to be reliable and transferable in its applications to study properties of carbon-based systems that include families of carbon clusters such as icosahedral \((I_h)\) clusters, buckydiamonds, and different caged structures.\(^{26}\) The parameter set used in the present work is listed in Table 1 and is the same as the one used previously.\(^{26}\)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\varepsilon_{\text{C}}) (eV)</td>
<td>-17.360</td>
</tr>
<tr>
<td>(\alpha_{\text{m}}) (Å(^{-1}))</td>
<td>2.153</td>
</tr>
<tr>
<td>(\alpha_{\text{s}}) (Å(^{-1}))</td>
<td>-0.0329</td>
</tr>
<tr>
<td>(d_{\text{m}}) (Å)</td>
<td>0.547</td>
</tr>
<tr>
<td>(d_{\text{s}}) (Å)</td>
<td>0.547</td>
</tr>
<tr>
<td>(\sigma_{\text{m}}) (Å(^{-1}))</td>
<td>1.881</td>
</tr>
<tr>
<td>(\sigma_{\text{s}}) (Å(^{-1}))</td>
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</tr>
<tr>
<td>(\phi_{\text{m}}) (Å(^{-1}))</td>
<td>1.85</td>
</tr>
<tr>
<td>(\phi_{\text{s}}) (Å(^{-1}))</td>
<td>1.85</td>
</tr>
</tbody>
</table>

Table 1. The fitted or optimized parameters of the SCIDL/CAO Hamiltonian for element carbon.

To validate the appropriateness of using the SCIDL/CAO Hamiltonian to study fullerene onions, we first investigated the structure of \(C_{60}\) using our SCIDL/CAO Hamiltonian and compared our results with experiment. The bond length of \(C_{60}\) from SCIDL/CAO is 1.477 Å for the 6–5 bond (cf. 1.455 Å observed\(^{32}\)) and 1.430 Å for the 6–6 bond (cf. 1.391 Å observed\(^{33}\)), respectively. The predictions of bond lengths of \(C_{60}\) by the SCIDL/CAO Hamiltonian with less than 3% error verify the robustness of the parameters of SCIDL/CAO for carbon.

3. RESULTS AND DISCUSSION

The fullerene onions studied in the present work using SCIDL/CAO molecular dynamics are \(C_{60@C_{200}}, C_{60@C_{240}}, C_{60@C_{280}}, C_{60@C_{320}}, C_{60@C_{360}}, C_{60@C_{400}}, C_{60@C_{450}}, C_{60@C_{500}}, C_{60@C_{550}}, C_{60@C_{600}}, C_{60@C_{650}}, C_{60@C_{700}}, C_{60@C_{750}}, C_{60@C_{800}}, C_{60@C_{850}}, C_{60@C_{900}}\). Experimentally, \(C_{60@C_{600}}\) has been observed.\(^{43}\) All the geometries of fullerene onions were relaxed by the SCIDL/CAO molecular dynamics (MD) with the last two optimized via O(N)/SCIDL/CAO. On the other hand, because of the size limitation of CNDO, only \(C_{60@C_{200}}, C_{60@C_{240}}, C_{60@C_{280}}, C_{60@C_{320}}, C_{60@C_{360}}, C_{60@C_{400}}, C_{60@C_{450}}, C_{60@C_{500}}, C_{60@C_{550}}, C_{60@C_{600}}, C_{60@C_{650}}, C_{60@C_{700}}, C_{60@C_{750}}, C_{60@C_{800}}, C_{60@C_{850}}, C_{60@C_{900}}\) were fully optimized by CNDO, with the largest fullerene onion relaxed having only 1800 atoms. This comparison demonstrates the capability of the O(N)-SCIDL/CAO to carry out MD simulations for large systems. The relaxed geometries for fullerene onions \(C_{60@C_{240}}, C_{60@C_{280}}, C_{60@C_{320}}, C_{60@C_{360}}, C_{60@C_{400}}, C_{60@C_{450}}, C_{60@C_{500}}, C_{60@C_{550}}, C_{60@C_{600}}, C_{60@C_{650}}, C_{60@C_{700}}, C_{60@C_{750}}, C_{60@C_{800}}, C_{60@C_{850}}, C_{60@C_{900}}\) obtained by both methods are very similar. The relaxed configurations of all the fullerene onions studied in the present work possess \(I_h\) symmetry and the separations between neighboring shells of these fullerene onions all fall in the neighborhood of 0.34 nm.

As shown in Figure 1, as the size of the fullerene onion gets bigger, the faceted shape of its shell
becomes more evident. It should be noted that the initial configurations for the relaxation of the fullerene onions used in the SCED/LCAO simulation, for example C_{60} \circledast C_{240} \circledast C_{360} \circledast C_{900} \circledast C_{1380} \circledast C_{2160} \circledast, are composed of co-centered spherical fullerene shells. It is indeed remarkable that the full-geometric relaxation of such fullerene onions with spherical shapes leads to faceted ones in the optimization based on the SCED/LCAO Hamiltonian, and thus demonstrating the predictive power of this Hamiltonian.

Because of the hybridization of the \( \sigma \) and \( \pi \) orbitals associated with the curvature of the fullerene shells in a fullerene onion, the interactions between carbon atoms in neighboring shells of a fullerene onion will be stronger than those between carbon atoms in neighboring graphene sheets in graphite. Therefore, a change of geometry of the fullerene shells in the fullerene onions as compared to the corresponding isolated fullerene is expected. To give quantitative measures of this change, we calculated \( \Delta r \) defined as the average of \( r_{\text{(atom) of a fullerene onion}} - r_{\text{atom of a fullerene onion}} \) that measures the radial change of the fullerene shells, and \( \Delta \bar{d} \) defined as the average change in bond length in the shells in a fullerene onion with respect to the isolated fullerenes. The results are summarized in Table II. It can be seen from Table II that although the predictions (\( \Delta r \) and \( \Delta \bar{d} \)) by both SCED/LCAO and CNDO are small, indicating the effects of the shell–shell interactions on the geometries of the fullerene onions are weak, those predicted by SCED/LCAO are about one order of magnitude greater. This is not surprising because multi-center interactions beyond the two-center interactions are neglected in CNDO. A key feature in the predictions by the two methods requires further clarification. From the values of \( \Delta r \) and \( \Delta \bar{d} \) listed in Table II, it can be seen that the innermost C_{60} shell always shrinks while the outermost shell always expands for all the fullerene onions optimized by SCED/LCAO. On the other hand, the trend demonstrated by the predictions of the CNDO is just the opposite, namely, the innermost C_{60} shell always expands while the outermost shell always shrinks for the three smaller fullerene onions relaxed by CNDO. The resolution of the discrepancy in the predictions of structures of fullerene onions by these two Hamiltonians requires either predictions from higher levels of theory or experimental benchmarks. Because of the size of fullerene onions, it renders the relaxation of fullerene onions considered in the present work unfeasible by \textit{ab initio} methods except probably the smallest fullerene onion, i.e., C_{60} \circledast C_{240}. However, even for C_{60} \circledast C_{240}, we had to use the DFT based method B3LYP\textsuperscript{4} with Slater minimum basis set (STO-3G) to carry out its geometry optimization. Although quantitative measures of the predictions based on the minimum basis set (STO-3G) may not be very accurate, the qualitative trend predicted by it is expected to be correct. In the B3LYP/STO-3G predictions, C_{60} shrinks (\( \Delta r \) is \(-0.0036 \text{ \AA} \) for all 60 atoms) and C_{240} expands (\( \Delta r \) is 0.0069 \text{ \AA} for 180 atoms, the pentagons region shrinks about 0.0006 \text{ \AA}). The bond distances of the 6–6 and 6–5 bonds in C_{60} are 1.413 and 1.477 \text{ \AA}, respectively.
Table II. Change of geometry (+Δr, overall expanding of cage; −Δr, overall shrinking of cage; +Δd, overall elongation of bond distances; −Δd, overall shortening of bond distances) of fullerene shells in fullerene onions with respect to the isolated fullerenes. Δr is the change of distance of carbon atom from the center of mass in fullerene onion with respect to that in the isolated fullerene. The number in the parenthesis identifies the number of atoms that either move out or move-in, corresponding to either +Δr or −Δr, respectively. Δd is defined as the average of Δr. All lengths are in angstrom. The number in the parenthesis in this case is the number of bonds.

<table>
<thead>
<tr>
<th></th>
<th>SCED</th>
<th></th>
<th>CNDO</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>+Δr</td>
<td>−Δr</td>
<td>+Δd</td>
<td>−Δd</td>
</tr>
<tr>
<td>O2</td>
<td>C100</td>
<td>0.0126(220)</td>
<td>−0.00084(60)</td>
<td>+0.0021(340)</td>
</tr>
<tr>
<td></td>
<td>C110</td>
<td>0.0010(20)</td>
<td>−0.00010(20)</td>
<td>+0.0021(340)</td>
</tr>
<tr>
<td>O3</td>
<td>C10</td>
<td>−0.0005(60)</td>
<td>−0.0003(90)</td>
<td>+0.0025(240)</td>
</tr>
<tr>
<td></td>
<td>C11</td>
<td>0.00027(254)</td>
<td>−0.0017(58)</td>
<td>+0.0048(741)</td>
</tr>
<tr>
<td>O4</td>
<td>C10</td>
<td>−0.0130(60)</td>
<td>−0.0055(390)</td>
<td>+0.0025(240)</td>
</tr>
<tr>
<td></td>
<td>C11</td>
<td>0.0055(160)</td>
<td>−0.0405(180)</td>
<td>+0.0032(139)</td>
</tr>
<tr>
<td>O5</td>
<td>C10</td>
<td>0.0244(254)</td>
<td>−0.0257(286)</td>
<td>+0.0030(478)</td>
</tr>
<tr>
<td></td>
<td>C11</td>
<td>0.0494(640)</td>
<td>−0.0271(320)</td>
<td>+0.0042(1022)</td>
</tr>
<tr>
<td>O6</td>
<td>C10</td>
<td>0.0762(29)</td>
<td>−0.0704(31)</td>
<td>+0.0053(37)</td>
</tr>
<tr>
<td></td>
<td>C11</td>
<td>0.1245(130)</td>
<td>−0.0405(110)</td>
<td>+0.0032(139)</td>
</tr>
<tr>
<td></td>
<td>C12</td>
<td>0.0766(480)</td>
<td>−0.0174(52)</td>
<td>+0.0149(751)</td>
</tr>
<tr>
<td></td>
<td>C13</td>
<td>0.1375(942)</td>
<td>−0.1162(18)</td>
<td>+0.0185(1212)</td>
</tr>
<tr>
<td></td>
<td>C100</td>
<td>0.1023(1184)</td>
<td>−0.0749(316)</td>
<td>+0.0068(1871)</td>
</tr>
<tr>
<td></td>
<td>C110</td>
<td>0.1880(2014)</td>
<td>−0.1612(146)</td>
<td>+0.0118(2949)</td>
</tr>
</tbody>
</table>

This trend is exactly the same as those predicted by SCED/LCAO, validating the robustness of SCED/LCAO in predicting the structures of large systems, specifically structures of fullerene onions.

To acquire further evidences to shed light on the reliability of these two semi-empirical Hamiltonians, we calculated the density of states (DOS) of C60 using both SCED/LCAO and CNDO. These results, together with their comparison to the corresponding DOS obtained by

Table III. Charges on fullerene shells in fullerene onions.

<table>
<thead>
<tr>
<th>Fullerenes</th>
<th>Shells</th>
<th>CNDO</th>
<th>SCED</th>
</tr>
</thead>
<tbody>
<tr>
<td>C60@C20</td>
<td>C20</td>
<td>−0.032</td>
<td>−0.048</td>
</tr>
<tr>
<td>C60@C20</td>
<td>C20</td>
<td>0.032</td>
<td>0.048</td>
</tr>
<tr>
<td>C60@C20</td>
<td>C20</td>
<td>−0.031</td>
<td>−0.050</td>
</tr>
<tr>
<td>C60@C20</td>
<td>C20</td>
<td>−0.105</td>
<td>−0.118</td>
</tr>
<tr>
<td>C60@C20</td>
<td>C20</td>
<td>0.136</td>
<td>0.168</td>
</tr>
<tr>
<td>C60@C20</td>
<td>C20</td>
<td>−0.031</td>
<td>−0.242</td>
</tr>
<tr>
<td>C60@C20</td>
<td>C20</td>
<td>−0.102</td>
<td>0.081</td>
</tr>
<tr>
<td>C60@C20</td>
<td>C20</td>
<td>−0.129</td>
<td>−1.142</td>
</tr>
<tr>
<td>C60@C20</td>
<td>C20</td>
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<td>1.303</td>
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<td>C60@C20</td>
<td>C20</td>
<td>−0.242</td>
<td>0.100</td>
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<tr>
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<td>C20</td>
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<td>−3.155</td>
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<td>C60@C20</td>
<td>C20</td>
<td>3.260</td>
<td>6.814</td>
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<td>C60@C20</td>
<td>C20</td>
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<tr>
<td>C60@C20</td>
<td>C20</td>
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<tr>
<td>C60@C20</td>
<td>C20</td>
<td>0.465</td>
<td>6.670</td>
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Fig. 2. The density of states (DOS) for fullerene C60 predicted from DFT, CNDO, and SCED. The DOS of C60(DFT) was predicted with B3LYP/6-31G(d) with the SCED/LCAO relaxed geometry. The DOSs in each figure are plotted on the same scale for each fullerene onion. The arrow indicates the highest occupied molecular orbital (HOMO). The energy of the HOMO in the DOS of C60 was shifted to −7.61 eV according to the experimental ionization potential of C60 [Ref. 45].

B3LYP with Gaussian basis set 6-31G(d), are shown in Figure 2. It can be seen that the DOS predicted by the SCED/LCAO method agrees far better with that predicted by B3LYP/6-31G(d) than that by the CNDO method. The key features of the DOS predicted by SCED/LCAO, including the overall shape of the DOS and the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), are much closer to those by B3LYP/6-31G(d). In particular, the HOMO-LUMO energy gap predicted by SCED/LCAO is closer to the experimental values \(^{46,47}\) than the one predicted by CNDO. This comparison has provided the additional evidence for the robustness of the SCED/LCAO Hamiltonian.

Having established the appropriateness of applying SCED/LCAO to study properties of fullerene onions, we calculated and listed in Table III the charge transfers between the shells in fullerene onions obtained by SCED/LCAO. The small geometrical changes of the fullerene shells observed in the fullerene onions have indicated the existence of weak shell–shell interactions (note that if there is no interaction between the shells, there could not be any charge transfer between shells). Therefore, small charge transfers between shells are expected. This is confirmed by the results given in Table III where the total amount of the net charge on a fullerene shell in a given fullerene onion is shown (there should be zero net charge on an isolated fullerene). There is one key and interesting message conveyed by the results shown in Table III. It appears that the charge transfer almost entirely occurs from the outermost shell to the inner shells. To correlate this observation with the electronic structure of fullerene onions, we show in Figure 3 two illustrative examples. In this figure, the DOSs of fullerene onions, \(C_{60}@C_{240}\) and \(C_{60}@C_{240}@C_{540}\), together with the DOSs of isolated fullerenes \(C_{60}\), \(C_{240}\), and \(C_{540}\), are shown. It can be seen that the DOS of \(C_{60}@C_{240}\) is almost the superposition of the DOS of \(C_{240}\) and \(C_{60}\) with only minor modifications in the vicinity corresponding to the HOMO of \(C_{240}\) and that of \(C_{60}\). Specifically, the DOS in the immediate neighborhood corresponding to the HOMO of \(C_{60}\) shows a small increase while the DOS in the immediate neighborhood corresponding to the HOMO of \(C_{240}\) shows a small decrease. This picture is consistent with the small amount of electrons transferred from the \(C_{240}\) shell to the \(C_{60}\) shell. A similar picture holds for the DOS of the fullerene onion \(C_{60}@C_{240}@C_{540}\), namely, it can be considered as the superposition of the DOSs of \(C_{60}\), \(C_{240}\), and \(C_{540}\) with only minor modifications. In this case, a slight increase occurs in the immediate neighborhood corresponding to the HOMO of \(C_{60}\) and that of \(C_{240}\) while a slight decrease occurs in the immediate neighborhood corresponding to the HOMO of \(C_{240}\), consistent with the transfer of a small amount of electrons from the \(C_{540}\) shell to \(C_{60}\) and \(C_{240}\) shells. Because of the weak interaction between shells, the HOMO-LUMO gap of fullerene onions is very similar to that of the outermost fullerene shell.
4. CONCLUDING REMARKS

In this work, we have established the robustness of energy optimization scheme with linear scaling for large systems based on the SCED/LCAO Hamiltonian and, in particular, the appropriateness of the application of the scheme to study properties of fullerene onions. We have predicted the structural and electronic properties of fullerene onions with up to six fullerene shells. We found that because of the weak shell–shell interactions, the fullerene shells in fullerene onions exhibited small geometrical changes. Specifically, the innermost shell shrinks while the outermost shell expands. The slight structural changes were also found to be closely related to the transfer of a small amount of electrons from the outermost to the inner shells. Finally, the extension of the SCED/LCAO method to heterogeneous elements is currently under progress.

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References


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