On the Stability of Endohedral Rare Gas Fullerenes

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Abstract

The stability of He@C_{60} and Ne@C_{60} is discussed in the context of a spherical model where the carbon atoms are smeared out into a uniform shell. The electronic properties of the sixty \( \pi \) electrons together with those of the central atom are treated in the Thomas-Fermi approximation. Simple electrostatic reasoning elucidates the nature of the radial stability of the complex. A method to include non-spherical corrections is outlined. Possible bonding topologies of the central atom and the C_{60} cage are discussed, as well as the relevance of these topologies to incipient central atom distortions.
I. INTRODUCTION

An interesting consequence of the closed cage structure of C\textsubscript{60} is that atoms and molecules may be trapped inside, forming endohedral complexes (“dopeyballs”). A variety of such complexes have been produced \cite{1} where the dopant may be a metallic or a rare gas atom/cluster. The electronic structure and mechanical stability of two such endohedral rare gas complexes, He@C\textsubscript{60} and Ne@C\textsubscript{60}, are considered here.

It has previously been noted \cite{2} that the high symmetry of the C\textsubscript{60} cage suggests the following geometrical approximation: the one-electron potential of icosahedral symmetry is replaced with its spherical average. Physically, the nuclear charge together with the charge from the core electrons is smeared out into a thin spherical shell of uniform surface charge density and radius \( R \). Such a fictitious molecule—“spherene”—has complete spherical symmetry.

In the case of metallofullerenes such as Na@C\textsubscript{60}, it has been shown \cite{3} that the equilibrium position of the dopant is not at the center of the cage, consequently reducing the symmetry of the complex. For rare gas dopants, however, it has previously been asserted \cite{1} that there is no such symmetry reduction. Additionally, previous calculations \cite{4} on Ne@C\textsubscript{60} indicate that the dopant is stable at the center. Consequently, given the large coordination number of the gas atom and the lack of a distortion from the high symmetry configuration, endohedral rare gas fullerenes seem to be good candidates for the spherical approximation.

The endohedrally-doped spherene is treated in the Thomas-Fermi approximation. It is anticipated that the highly delocalized \( \pi \)-electrons of the cage and the closed shell configuration of the gas atom are well-suited to such a statistical description. This method of treating high symmetry molecules was originally suggested by March \cite{5}.

The cage is parametrized by the radius \( R \) and valence electron number \( N \), while the gas atom has nuclear charge \( Z \) and an equal number of electrons. The total electron density is calculated using the Thomas-Fermi equations, subject to the shell boundary conditions.

The total energy of the system is calculated for a variety of radii. A stable equilibrium
radius is obtained, when the cage self-energy is computed from the system of ionic point charges, rather than from the continuum model. A method of treating non-spherical corrections is outlined. Lastly, possible central atom distortions are discussed in the context of the Bader molecular graphs arising from the electron density.

II. THOMAS-FERMI THEORY OF DOPEYBALLS

The nuclear potential from the central atom and the cage atoms can be expanded in a multipole series as

\[ V_n(r) = \sum_{\ell,m} \frac{1}{r^{\ell+1}} \sqrt{\frac{4\pi}{2\ell + 1}} Q_{\ell m}^* Y_{\ell m}^*(\Omega) \]  

\( Q_{\ell m} \) is the \( 2^\ell \)-pole moment, given by

\[ Q_{\ell m} = eR_0^{\ell} \sqrt{\frac{4\pi}{2\ell + 1}} \sum_i Y_{\ell m}^*(\Omega_i) + Ze\delta_{\ell 0} \]

where \( Z \) is the atomic number of the rare gas atom of interest. From the icosahedral symmetry of the molecule, it has been shown \cite{2} that the first three non-vanishing multipole moments are for \( \ell = 0, 6, 10 \). As the occupied one-electron states have an effective \( \ell = 5 \), it is not necessary to consider \( \ell > 10 \) multipole terms in first order perturbation theory.

The spherical approximation consists of retaining only the \( \ell = 0 \) term in the multipole expansion. The error introduced can be estimated by consideration of the relevant dimensionless parameters

\[ \alpha_{\ell m} = \left| \sqrt{\frac{4\pi}{2\ell + 1}} \frac{Q_{\ell m}}{R_0^{\ell} Q_{00}} \right| \]  

The following values are found as function of \( Z \): \( \alpha_{6,0} = 0.026/(1+Z) \), \( \alpha_{6,5} = 0.020/(1+Z) \), \( \alpha_{10,0} = 0.021/(1+Z) \), and \( \alpha_{10,5} = 0.034/(1+Z) \). As \( \alpha_{\ell m} \ll 1 \) for \( \ell \leq 10 \), it may be concluded that the spherical approximation is justified for such a high symmetry structure, and one-electron splittings under the true icosahedral symmetry can be treated perturbationally.

With spherical symmetry imposed, the endohedral cluster is quasi-atomic in form. The sixty \( \pi \)-electrons of the cage plus the \( Z \) electrons of the central atom are now treated in the
Thomas-Fermi (TF) approximation where the $Z + N$ electrons see a point charge of $Ze$ at the origin and a uniform shell of charge $Ne$ and radius $R$. The methodology follows that of March [5].

At temperature $T = 0$, the dimensionless TF equation without exchange is given by

$$\frac{d^2\phi}{dx^2} = \frac{\phi^{3/2}}{x^{1/2}}$$

(4)

$x$ is the distance from the center of the shell in units of

$$b = \frac{1}{4} \left[ \frac{9\pi^2}{2Z} \right]^{1/3} a_0$$

(5)

where $a_0$ is the Bohr radius of hydrogen. $\phi$ is related to the potential in the usual way

$$V(r) = \frac{Ze}{r} \phi(x)$$

(6)

Eq. 4 is supplemented with the boundary conditions: $\phi(0) = 1$, and

$$\phi'(X^-) - \phi'(X^+) = \frac{N}{ZX}$$

(7)

where $X$ is the shell radius in dimensionless units and differentiation is with respect to $x$. Additionally, $\phi$ itself is continuous over its domain, and $\phi \to 0$ as $x \to \infty$.

**III. NUMERICAL RESULTS**

$\phi(r)$ is found by numerical integration of Eq. 4 subject to the above boundary conditions. The charge density $n(r)$ and total electronic energy $E_e$ are subsequently obtained from $\phi(r)$, as

$$n(x) = \frac{Z}{4\pi b^3} \left[ \frac{\phi(x)}{x} \right]^{3/2}$$

(8)

and

$$E_e = \frac{3Z^2e^2}{7b} [\phi'(0) + \frac{4N}{3Z} \phi(X^-) - \frac{N}{3Z} \phi'(X^-) - \left( \frac{N}{Z} \right)^2 \frac{1}{X} - \frac{7N}{3Z} \frac{1}{X}]$$

(9)
The radial electron density of Ne@C\textsubscript{60} is given as an example in Fig. 1.

The electronic energy $E_e$ is found for various values of the dimensionless cage radius $X$ in the cases of $Z = 2$ and 10, corresponding to He@C\textsubscript{60} and Ne@C\textsubscript{60} respectively. As the boundary condition for $\phi$ at the shell explicitly depends on $Z$, $E_e$ will not have simple “atomic” scaling with $Z$ ($E_e \sim Z^{7/3}$).

If we add to $E_e$ the electrostatic self-energy of the continuum shell, $U$, it is found that this total energy $E = E_e + U$ does not have a minimum for finite $X$, in accord with Teller’s no-binding theorem \[6\] for molecules in TF theory. The continuum shell self-energy is too large and dominates $E_e$. However, if the self-energy is evaluated as a sum over point ions distributed on the shell surface, an energy minimum at finite shell radius is found. The spherical approximation is abandoned for the purposes of calculating the potential energy for the nuclear configuration.

The self-energy of the nuclear configuration may be written in the form

$$U = ZNe^2/bX + cN^2e^2/bX$$

where $c$ is a dimensionless number, computed from the actual equilibrium coordinates of C\textsubscript{60}. It was previously \[2\] computed as $c = 0.43101$.

The total energies for He@C\textsubscript{60} and Ne@C\textsubscript{60} as a function of the shell radius are displayed in Figs. 2 and 3. The resulting equilibrium radii, $R_0$, are listed in Table 1, together with the total energies for the equilibrium configuration. Previous results for C\textsubscript{60} are provided for comparison.

The expansion of the equilibrium cage radius with increasing $Z$ is observed, in agreement with a previous restricted Hartree-Fock calculation \[4\]. It should, however, be noted that $c$ is a result of the detailed atomic positions in C\textsubscript{60}. Certainly, distortions which do not preserve the relative positions of cage ions will give rise to changes in $c$, and consequently, to changes in $R_0$. It is also interesting to note that the monotonic increase of $R_0$ with $Z$ does not follow the “atomic size” scaling relation ($D \sim Z^{-1/3}$).
The shell equilibrium can be understood from electrostatic considerations. At equilibrium, the centrifugal force on the shell resulting from self-interaction is balanced by the centripetal force exerted on the shell by the charge contained inside the shell. The total charge contained inside the shell at equilibrium is \( -cNe \approx -25.86e \), and the total number of electrons inside the shell is \((Z + cN)\). Thus we see that endohedral fullerenes whose central atoms have higher \( Z \) require more electrons inside the shell to maintain equilibrium.

### IV. BEYOND SPHERENE

While approximating the discrete cage ions by a uniform spherical shell is valid approximation with regard to the total energy, it is the corrections to the spherical average which contain all the information regarding the bonding. The spherical approximation reduces the complex to a one-dimensional system. The consequent critical points in the electron density consist of only minima and maxima, and an analysis of the bonding topology requires consideration of the effects of the nuclear multipole moments \( \ell > 0 \). A method for finding the electron density corrugations of endohedral fullerenes is given below.

To treat these non-spherical contributions, one must return to the general TF equation,

\[
\nabla^2 V = \beta V^{3/2} - 4\pi \rho_+ \tag{11}
\]

where \( \beta = \frac{32\pi^2 e^2}{3h^3}(2m)^{3/2} \) and \( \rho_+ \) is the (positive) nuclear charge density.

\( \rho_+ \) can be expressed as a sum of spherical harmonics,

\[
\rho_+(\vec{r}) = Ze\delta(\vec{r}) + \frac{\delta(r - R)}{r^2} \frac{Ne}{4\pi} + \Delta\rho \tag{12}
\]

where

\[
\Delta\rho = \frac{\delta(r - R)}{r^2} \sum_{\ell,m} R^{-\ell} \sqrt{\frac{2\ell + 1}{4\pi}} Q_{\ell m} Y_{\ell m}(\Omega) \tag{13}
\]

The potential \( V \) is now written as

\[
V(\vec{r}) = V_0(r) + \zeta(\vec{r}) \tag{14}
\]

6
where \( V_0 \) is the spherically–averaged solution and \( \zeta \) results from consideration of the higher order multipole moments. It is assumed that \( \zeta \) is much smaller than \( V_0 \). Thus, Eq. 11 leads to a linearized equation for \( \zeta \)

\[
\nabla^2 \zeta = \frac{3}{2} \beta V_0^{1/2} \zeta - 4 \pi \Delta \rho
\]

Eq. 15 is of the form of the single particle Schrödinger Eq. at zero energy with a central “potential,” \( \frac{3}{2} \beta V_0^{1/2} \), which is everywhere positive, and an non-homogeneous boundary term. \( \zeta \) may be expanded in spherical harmonics inside and outside \( r = R \), and the boundary term gives rise to a discontinuity in the radial derivative of \( \zeta \). Thus,

\[
\zeta(\vec{r}) = \sum_{\ell m} \zeta_{\ell m}(r) Y_{\ell m}(\Omega)
\]

where \( \zeta_{\ell m} \) satisfies the following

\[
\left( \frac{d^2}{dr^2} - \frac{3}{2} \beta V_0^{1/2} - \frac{\ell(\ell + 1)}{r^2} \right) r \zeta_{\ell m}(r) = 0
\]

and is subject to the following boundary conditions

\[
r \zeta_{\ell m} \rightarrow 0, \quad \text{as} \quad r \rightarrow 0
\]

\[
r \zeta_{\ell m} \rightarrow 0, \quad \text{as} \quad r \rightarrow \infty
\]

\[
\frac{d}{dr}(r \zeta_{\ell m}) \bigg|_{r=R^+} = -R^{-\ell - 1} \sqrt{4 \pi (2 \ell + 1)} Q_{\ell m}
\]

As the effective “potential” in Eq. 17 is positive for all \( r \), only exponential solutions are possible for \( \zeta \). Without a discontinuity in the radial derivative, only the trivial solution would satisfy the boundary conditions at the origin and at infinity. Thus, \( \zeta_{\ell m} \) is non-zero only when \( Q_{\ell m} \) is non-zero. The first non-spherical corrections to the potential and the electron density then are at \( \ell = 6, 10 \). Not surprisingly, these \( \ell \) values correspond to irreducible representations of the rotation group which contain the trivial representation (A\(_g\)) of I\(_h\). It is interesting to note that the centrifugal term in the effective “potential” will reduce the contributions from large \( \ell \) to the density.
V. STRUCTURE AND BONDING

The simplest bonding configuration consistent with the symmetry constraints is that of sixty bonds between the central atom and the carbon atoms in the cage. However, a second possibility was proposed on the basis of an ab-initio calculation [4] on Ne@C_{60}. There, it was found that with the Ne atom in the center of the cage, thirty bond paths exist, starting on the Ne atom and terminating on the carbon-carbon double bond points. Is this a stable configuration with respect to central atom displacement?

While the total energy calculations in Ref. [4] indicate that Ne is in a stable equilibrium at the center of the cage, unless the bond point at the carbon-carbon double bond is a non-nuclear attractor [8] (“pseudoatom”), it would seem that the bonding topology found in Ref. [4] may correspond to that of the metastable state described by Bader [7] as a “conflict structure.”

Given that the Na\(^+\) is isoelectronic with Ne, and that Na\(^+\) in Na\(^+\)@C\(_{60}\) does distort along a five-fold axis, a similar instability in Ne@C\(_{60}\) would seem possible. The possible incompatibility of the molecular graph with the total energy calculations indicates that additional study is warranted, and central atom distortions in rare gas endohedral fullerenes remain as an intriguing possibility.

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FIG. 1. Radial electron density for Ne@C\textsubscript{60} (in units of \(10/b\)) vs \(x\) for \(R = 7.36a_0\).
FIG. 2. Total energy $E$ (Ry) for He@C$_{60}$ vs shell radius $R$ (Bohr).
FIG. 3. Total energy $E$ (Ry) for Ne@C$_{60}$ vs shell radius $R$ (Bohr).
TABLES

TABLE I. Minimum total energies $E$ (Ry), equilibrium radii $R$ (Bohr), for $Z = 0, 2, 10$.

| $Z$ | $R$  | $E$     |
|-----|------|---------|
| 0$^a$ | 7.35 | -25.313 |
| 2    | 7.41 | -32.98  |
| 10   | 7.64 | -356.30 |

$^a$ Ref. [2]