Stability and Teller's theorem: Fullerenes in the March model

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We study C_{60} with the use of the March model [N. H. March, Proc. Camb. Philos. Soc. **48**, 665 (1952)]. A spherical shell model is invoked to treat the nuclear potential, where the nuclear and core charges are smeared out into a shell of constant surface charge density. The valence electron distribution and the electrostatic potential are efficiently computed by integration of the Thomas-Fermi equation, subject to the shell boundary conditions. Total energy is numerically calculated over a range of shell radii, and the mechanical stability of the model is explored with attention to the constraints of Teller's theorem [E. Teller, Rev. Mod. Phys. **34**, 627 (1962)]. The calculated equilibrium radius of the shell is in fair agreement with experiment. [S1050-2947(97)03707-4]

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I. INTRODUCTION

The highly symmetrical structure of C_{60} has motivated geometrical approximations which have previously been invoked to study electronic and optical properties of the molecule. While consideration of the icosahedral structure of the molecule is necessary for detailed comparison with experiment, previous studies have had success in describing some of the properties of C_{60} within the continuum approximation, where a system of free electrons is constrained to move on the surface of a sphere [1–4].

While the peak electron density should be found on the shell, electrostatic consideration of the mechanical stability of the entire system requires that a sizable fraction of the total number of valence electrons be *inside* the shell. Motivated by this observation, we study here a generalization of the previously considered continuum model: we allow the valence electrons to move in three dimensions in the external potential generated by a spherical shell of constant surface charge density. We call such an artificial molecule whose nuclear potential has spherical shell symmetry "spherene."

We treat spherene by the Thomas-Fermi (TF) method. While TF results are typically rather rough, it is often used to efficiently generate starting potentials for more exact self-consistent-field methods. We have had success [5] using the resulting TF potential in this fashion. Of course, TF theory has historically had value in its own right. Here, we use the TF results to discuss the stability of C_{60}. This is rather a subtle business, as it is well known that systems treated with TF are subject to Teller's theorem [6], which states that molecules in TF theory will unbind. We prove Teller's theorem in the context of a spherical shell, and we circumvent it by considering the true point-charge distribution in the calculation of the "nuclear" energy.

The approach used here was previously employed by March [7] to investigate molecules in the form of a central atom with tetrahedrally or octahedrally coordinated ligands, such as in the case of CH_4 or SF_6. We closely follow March's work, applying it to the case of C_{60}, where there is no central atom and an icosahedral arrangement of ligands. The absence of a central atom changes the boundary condition of March at the origin. The case of C_{60} would seem to be ideally suited to this approach, given its high "coordination" number. Such a model has also been investigated by Siringo *et al.* [8]. Our results are in agreement with those of Siringo *et al.* and we offer an analysis of the molecular stability of the March model of C_{60}. The case of an endohedrally doped fullerene, such as He@C_{60}, is of the exact form considered by March, and it has been explored recently [9].

II. MODEL

We start with a positively charged spherical shell of radius R and charge Ze. The shell charge arises from the sum of the positive nuclear charges with the core electrons of the constituent atoms. We take $Z=60$ for the case of C_{60}; thus, the valence electrons are the remaining 60 π electrons. These valence electrons interact with the shell via a spherically symmetric cut-off Coulomb potential. This nuclear electrostatic potential V_n is everywhere positive and is given by

$$V_n(\vec{r})=\begin{cases} Ze/R, & 0<r<R \\ Ze/r, & r\geqslant R. \end{cases} \tag{1}$$

We can view this model as arising from an approximation of the true nuclear electrostatic potential, where all but the monopole term is neglected. The validity of the spherical shell model can be examined by expanding the nuclear potential in multipole moments. We denote the location of the ith atom by a radius R and a set of spherical angles $\Omega_i=(\theta_i,\phi_i)$. We center our coordinate system on the geometric center and we align our axes with the fivefold and twofold axes of the molecule. Thus, for the region external to the cage,

$$V_n(\vec{r})=\sum_{\ell,m}\frac{1}{r^{\ell+1}}\sqrt{\frac{4\pi}{2\ell+1}}Q_{\ell m}Y^*_{\ell m}(\Omega). \tag{2}$$

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

$$Q_{\ell m}=eR^{\ell}\sqrt{\frac{4\pi}{2\ell+1}}\sum_i Y_{\ell m}(\Omega_i). \tag{3}$$

The summation in Eq. (2) is only over even ℓ as a result of the inversion symmetry of C_{60}. Furthermore, in general we note that $Q_{\ell m}$ is nonvanishing only if the spherical irreducible representation, denoted by ℓ, when decomposed in terms of the irreducible representations of I_h, contains the trivial (a_{1g}) representation.

Thus, after the nonvanishing monopole moment, the next nonvanishing elements are in $\ell=6$, followed by $\ell=10$. For C_{60}, we need not consider $\ell>10$, as the highest-lying electron orbital is derived from an $\ell=5$ manifold. $Q_{\ell m}$ is also only nonvanishing for $m=0$ and ± 5.

We estimate the error of neglecting $\ell\neq 0$ terms by evaluating the relevant dimensionless parameters

$$\alpha_{\ell m}=\left|\sqrt{\frac{1}{2\ell+1}}\frac{Q_{\ell m}}{R^{\ell}Q_{00}}\right|. \tag{4}$$

We find that $\alpha_{6,0}=0.007, \alpha_{6,5}=0.006, \alpha_{10,0}=0.006$, and $\alpha_{10,5}=0.01$. As $\alpha_{\ell m}\ll 1$ for $\ell\leqslant 10$, we conclude that the spherical approximation is reasonable for our purposes.

We consider the dimensionless TF equation without exchange effects at temperature $T=0$:

$$\frac{d^2\phi}{dx^2}=\frac{\phi^{3/2}}{x^{1/2}}. \tag{5}$$

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

$$b=\frac{1}{4}\left[\frac{9\pi^2}{2Z}\right]^{1/3}a_0, \tag{6}$$

where a_0 is the Bohr radius of hydrogen. ϕ is related to the total electrostatic potential V in the usual way:

$$V(r)=\frac{Ze}{r}\phi(x). \tag{7}$$

Without a nuclear charge at the origin, the standard atomic boundary condition at $x=0$ is altered to $\phi(0)=0$, as the potential is now finite at the origin. The presence of the shell gives rise to a discontinuity in the derivative of ϕ at the shell. Thus,

$$\phi'(X^-)-\phi'(X^+)=\frac{1}{X}, \tag{8}$$

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

III. NUMERICAL RESULTS

We obtain numerical solutions to Eq. (5) subject to the above boundary conditions for different values of X. A variation of the shooting method [10] is used, where we choose a trial slope for ϕ at the origin, and we integrate outward to the asymptotic region ($x\gg X$). The boundary condition at infinity is replaced by requiring ϕ to vanish at an outer shell of large radius. The slope is subsequently varied in a systematic way until the boundary condition on the outer shell is satisfied.

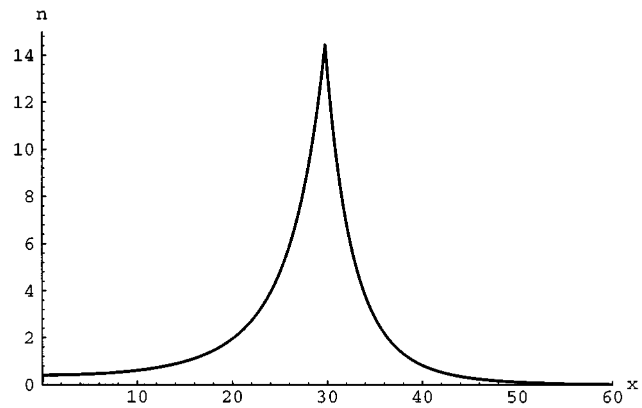

FIG. 1. Electron charge density n (in units of $15/\pi\times 10^5 b^{-3}$) vs x for $Z=60$ and $R=6.73a_0$.

The following identities are used as a final check of the numerical procedures: (1) conservation of electron number requires that ϕ satisfy

$$\int_0^\infty \phi^{3/2}x^{1/2}dx=1; \tag{9}$$

and (2) the virial theorem for shell systems requires that

$$\frac{9}{35}\int_0^\infty \phi^{5/2}x^{-1/2}dx+\int_0^\infty\frac{\phi^{3/2}x^{1/2}}{x_>}dx=-2\left[\phi'(X)-\frac{\phi(X)}{X}\right], \tag{10}$$

where $x_>$ is the larger of x and X. The resulting solutions obey the above relations to an accuracy of better than three parts in 10^4.

In Fig. 1, we show the electron (volume) charge density n as a function of x obtained from our solution for ϕ for parameters corresponding to those modeling C_{60}, where $X=29.7592$ ($R=6.73a_0$) and $Z=60$. While the potential is found from Eq. (7), n is computed from the relation

$$n(x)=\frac{Z}{4\pi b^3}\left[\frac{\phi(x)}{x}\right]^{3/2}. \tag{11}$$

We note that ϕ (and consequently n and V) is strongly peaked at the shell, in a consistent fashion with the continuum models which constrain the valence electrons to the surface of the shell; however, it is significant that nearly 43% of the valence electrons are contained inside the shell. We return to this point in our discussion of stability.

IV. STABILITY AND TELLER'S THEOREM

We follow March [7] and conclude that the electronic energy E_e can be simplified to a form requiring only values of ϕ and its derivative evaluated just inside the shell:

$$E_e = \frac{Z^2e^2}{7bX}[4\phi(X^-) - X\phi'(X^-) - 3]. \tag{12}$$

For the C_{60} parameters, we find $E_e = -486$ Ry.

Using the Hellman-Feynman theorem, we calculate the radial force that the electrons exert on the shell, F_r:

$$F_r = -\frac{dE_e}{dR} \tag{13}$$

$$= -Ze\frac{dV(R)}{dr} \tag{14}$$

$$= -\frac{Z^2e^2}{b^2X^2}[X\phi'(X^-) - \phi(X^-)]. \tag{15}$$

Only electrons in the interior of the shell can exert a force on the shell, a consequence of Gauss's law. Hence, the presence of charge in the interior provides a centripetal, stabilizing force that opposes the centrifugal self-force of the shell.

From dimensional considerations, we write the self-interaction energy of the shell as

$$U_n = c\frac{Z^2e^2}{R}. \tag{16}$$

For the uniform shell, $c=\frac{1}{2}$. Within TF theory, Teller's theorem [6] implies that the stabilizing force of the electrons on the shell is of insufficient magnitude to compensate for the repulsive self-force of the shell. Thus, there is no finite equilibrium radius for the shell for $c=\frac{1}{2}$. We sketch a proof specific to the shell. The proof proceeds by *reductio ad absurdum*.

We assume that there exists a finite equilibrium shell radius R_0. Using $c=\frac{1}{2}$, Eqs. (15), (12), and (16) imply that

$$E(R_0) = \frac{3}{7}ZeV(R_0^-). \tag{17}$$

Since $V(r)$ is positive for finite r, we conclude that $E(R_0)$ is positive as well. However, the virial theorem states that, at equilibrium,

$$E(R_0) = -T, \tag{18}$$

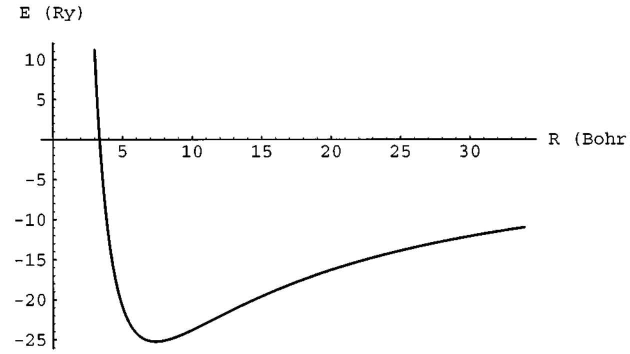

FIG. 2. Total energy E vs shell radius R.

where T is the total kinetic energy of the electrons. Since T must be positive, we conclude from Eq. (18) that $E(R_0)$ is negative. But this is in contradiction to the result of Eq. (17). Hence, there is no finite R_0.

The continuum approximation overestimates the shell self-force. If one computes the self-force by considering the point structure of the ions, a stable equilibrium is obtained. For the system of Z ions of charge e located on the vertices of a truncated icosahedron of radius R, we find $c \approx 0.4311$. We use this value of c to compute the total energy of the system, $E = E_e + U_n$, at different shell radii. The resulting energy curve is plotted in Fig. 2. From the minimum of the curve, we extract an equilibrium radius, $R_0 = 7.36a_0$, that is in fair agreement with the experimental value [11] of $6.73a_0$.

It is amusing to observe that at equilibrium, c is precisely the fraction of valence electrons contained inside the shell. This condition follows from simple electrostatic considerations.

V. DISCUSSION

In addition to giving an equilibrium radius in good agreement with experiment, TF gives a potential that is an excellent starting potential for more rigorous self-consistent-field techniques. Furthermore, there are many enhancements of this method that can be easily incorporated, such as the inclusion of exchange and correlation and density gradient corrections to the kinetic energy.

The method can be extended to other fullerene systems of interest. It is a simple matter to treat endohedrally doped fullerenes [9] or positively charged fullerenes. Last, by generalizing to finite temperature, equations of state can be calculated, as was done previously in the case of atoms [12].

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