PHYSICAL REVIEW A VOLUME 46, NUMBER 7 1 OCTOBER 1992

Thomas-Fermi model for the C_{60} molecule

F. Siringo, G. Piccitto, and R. Pucci
Dipartimento di Fisica dell'Universitá di Catania, Corso Italia 57, I-95129 Catania, Italy

(Received 13 January 1992)

A solution of the dimensionless Thomas-Fermi equation is presented, which can be considered as a simple model for the C_{60} molecule. In the framework of this model, we derive estimates of the sphere radius R_e at equilibrium, the total energy, and the scattering factor. The limitations of the model are disucssed in relation to some experimental results and to some other approximations.

PACS number(s): 36.40.+d, 31.20.Lr

I. INTRODUCTION

In the framework of the Thomas-Fermi (TF) theory, March [1] has introduced a model for tetrahedral and octahederal molecules in which the outer nuclear charges, say with total nuclear charge $Z_1 e$, are spread uniformly over a sphere of radius R. Within this model, March has given a number of simple results [1] and more recently Pucci and March [2] have derived the prediction of a finite asymptotic limit of the bond length R_e as the nuclear charge $Z_2 e$ at the origin goes to infinity.

In this paper we present a similar model, but without an atom at the origin, i.e., in our case $Z_2=0$. We believe that this model has some interest for the ground-state properties of the C_{60} molecule, which has the structure of the modern European football (a soccer ball). This molecule, also called fullerene, has recently attracted much attention, since it has been possible to prepare it in large quantities [3] and to obtain a solid which presents interesting properties. Furthermore, Hebard *et al.* [4] have found that the material becomes superconducting when doped with alkali-metal atoms.

It is believed [5] that the fullerene cage behaves like an atom with unusual properties. This fact and the presence of a large number of electrons suggest that the TF statistical method is particularly suitable to treat this system.

II. MODEL

The structure proposed by Kroto *et al.* [6] for the C_{60} molecule has *t*-icosahedral symmetry, as does the modern European football (see Fig. 1). In this structure all sp^2 valences are satisfied and we are left with one π electron per carbon atom. The sea of π electrons covers the inner and outer surfaces. We believe that, as in the other aromatic molecules, many properties depend essentially on the π electrons and we will consider explicitly only these electrons. The division between π and σ electrons has been discussed by Haddon [7,8] in connection with the problem of nonplanarity which gives rise to a small residual hybridization between σ and π orbitals. In our model the charge of the nuclei and the core electrons (including σ electrons) are uniformly spread over the surface of a sphere of radius R. With this "smoothing" approximation we recover the spherical symmetry, which allows us to use the TF method in a simple way. In this method the self-consistent potential energy $V(r)$ can be written in the form

$$V(r)=-\frac{Ze^2}{r}\phi(x) , \tag{1}$$

where Z is the total surface charge (equal to 60 in our case) and $x=r/b$ $[b=(a_0/4)(9\pi^2/2Z)^{1/3}]$ is a dimensionless measure of the distance from the center of the sphere.

The dimensionless dependent variable ϕ satisfies the usual nonlinear TF equation

$$\frac{d^2\phi(x)}{dx^2}=\frac{\phi^{3/2}(x)}{x^{1/2}} , \tag{2}$$

with boundary conditions

$$\begin{aligned} &\phi_1(0)=0 , \\ &\phi_2(0)\rightarrow 0 \quad \text{as } x\rightarrow\infty , \\ &\phi_1(X)=\phi_2(X) , \\ &\left[\frac{d\phi_1}{dx}\right]_X-\left[\frac{d\phi_2}{dx}\right]_X=\frac{1}{X} , \end{aligned} \tag{3}$$

where indexes 1 and 2 refer to the two regions $r<R$ and $r>R$ $(R=bX)$. The first boundary condition derives from the fact that we have not an atom at the origin and that the potential $V(r)$ does not diverge for $x\rightarrow 0$. The

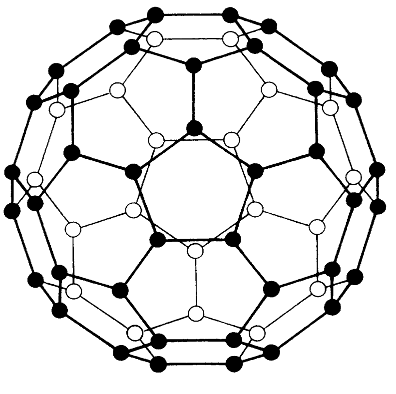

FIG. 1. The structure of the C_{60} fullerene.

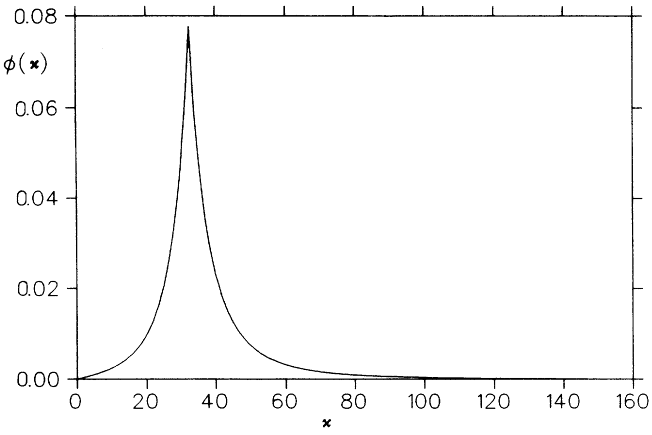

FIG. 2. The solution of the dimensionless TF equation (2) with boundary conditions given by Eq. (3) as a function of x. The radius of the sphere was fixed to $X=32.5$ (corresponding to $R_e=3.89$ Å).

last condition follows from a well-known result in electrostatics. The solution of Eq. (2) with the boundary conditions (3) is presented in Fig. 2 for $X=32.5$, corresponding to $R=3.89$ Å.

For the evaluation of the total energy E, we have to consider the potential $V_N(r)$ due to the surface density $\sigma=Z_e/4\pi R^2$,

$$\begin{aligned} V_{N_1}(r) &= \frac{Z_e}{R}, \quad r<R \\ V_{N_2}(r) &= \frac{Z_e}{r}, \quad r>R . \end{aligned} \tag{4}$$

Furthermore, in the evaluation of the ion-ion potential energy U, we use the exact expression

$$U=\frac{1}{2}\sum_{i,j}^{60}\frac{e^2}{r_{ij}}=\frac{Z^2e^2}{R}c , \tag{5}$$

where $c=0.431$, if we assume that all the C–C bond lengths are equal (even considering the real structure of the C_{60} molecule the difference in the value of c would be less then 0.02%).

III. RESULTS

By adopting the above described model, the expressions for the total energy E and its derivative dE/dR can be written

$$E=\frac{3}{7}\frac{(Ze)^2}{b}\left[\frac{4}{3}\frac{\phi_1(X)}{X}-\frac{1}{3}\phi_1'(X)-\frac{1}{X}+\frac{7}{3}\frac{1}{X}c\right] , \tag{6}$$

$$\frac{dE}{dR}=\frac{(Ze)^2}{R^2}[X\phi_1'(X)-\phi_1(X)-c] . \tag{7}$$

Equation (7) can be derived from the virial theorem which is satisfied in the form

$$2T+V=-R\frac{dE}{dR} , \tag{8}$$

where T is the total kinetic energy and V is the total potential energy. In Fig. 3 we report E as a function of R. The value of R at equilibrium R_e can be extracted from the minimum of this curve and is $R_e=3.89$ Å, which compares well with the value $R_e=3.55$ Å given by Zhang, Yi, and Bernholc [9]. An alternative way to derive this value is by following the work of March and Pucci [10], who noted that at equilibrium, corresponding to $dE/dR|_{R_e}=0$, the following condition must be satisfied

$$Q_2(R_e)=(1-c)Z , \tag{9}$$

where $Q_2(R_e)$ is the total charge outside a sphere of radius R_e. Evidently

$$Q_2(R)=\int_R^\infty 4\pi r^2\rho(r)dr , \tag{10}$$

$\rho(r)$ being the electron density. Equation (9) allows us to note that the equilibrium sphere radius R_e is determined not by detailed electron distribution but by the total number of electrons $Q(R_e)$ outside distance R_e.

From the electron density $\rho(r)$ calculated in our model it is possible to estimate the scattering factor $f(\mathbf{K})$, which is defined by

$$f(\mathbf{K})=\int\rho(\mathbf{r})e^{i\mathbf{K}\cdot\mathbf{r}}d\mathbf{r} . \tag{11}$$

In Fig. 4 we report the results of this calculation (solid line). If we consider the molecular density as a superposition of atomic densities

$$\rho(\mathbf{r})=\sum_{i=1}^{60}\rho_c(\mathbf{r}-\mathbf{r}_i) , \tag{12}$$

we can write the spherical average

$$f(\mathbf{K})=60\frac{\sin KR_e}{KR_e}f_c(K) , \tag{13}$$

where $f_c(K)$ is the scattering factor of the single C atom, tabulated by Hoerni and Ibers [11]. The results of this

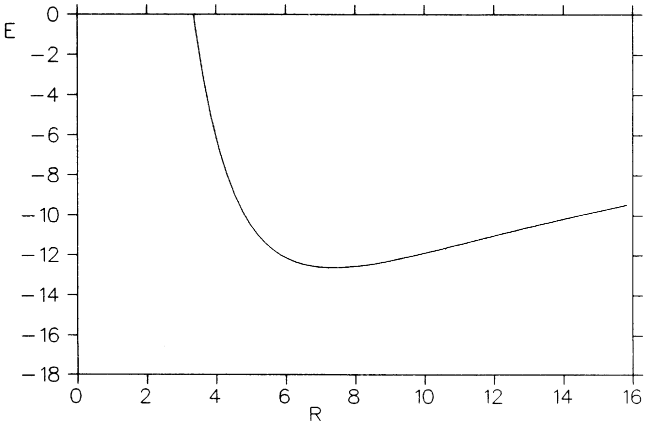

FIG. 3. Total energy E (in hartrees) of the C_{60} molecule calculated in our model as a function of the radius R of the sphere (in a.u.).

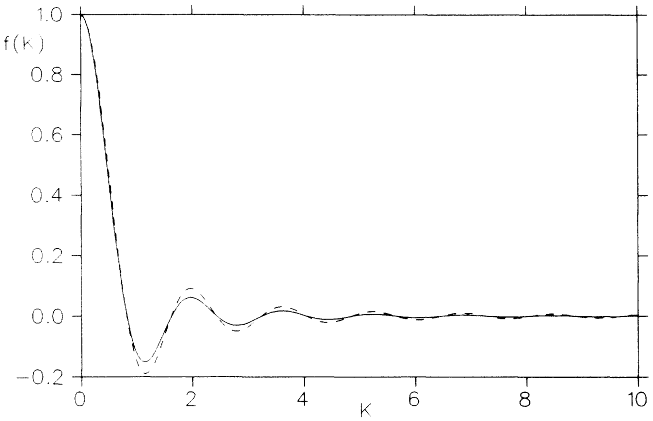

FIG. 4. Scattering factor $f(K)$ (normalized to 1) of the C_{60} molecule as a function of K (in Å^{-1}) calculated by using our TF density (solid line) and the density obtained by superimposing the atomic densities (dashed line). The radius of the sphere R was fixed to the calculated equilibrium value $R_e = 3.89$ Å.

calculation are reported as a dashed line in Fig. 4. This second scattering factor shows oscillations of greater amplitude with respect to the Thomas-Fermi result. The message of this behavior is that in the TF method the electron density decays too slowly. Indeed, it is known [12,13] that the exact asymptotic form of the electron density at large r is $\rho(r) \sim A r^{\gamma} \exp[-2(2I)^{1/2} r]$, where I is the exact ionization potential. The slow long-range decay of the TF theory is well known [14] and in turn reflects the choice of a vanishing ionization potential in the derivation of Eq. (2). This prevents us from comparing the TF density of states with any realistic or experimentally determined spectrum.

IV. DISCUSSION

In this paper we have presented a simple model to treat the ground-state properties of the nearly spherical molecule fullerene. The model is clearly oversimplified in comparison with the number of calculations existing in literature [15–19], however, being based on the statistical TF method it provides a direct estimate of the density and of the self-consistent potential which could be of some interest for further calculations of pseudopotentials in the solid. The main approximation adopted in our model consists in the smearing of the charge of the nuclei and of the σ electrons on the surface of a sphere. This approximation has as a consequence the weakening of the C–C bonds. In fact the cohesive energy per atom results to be in our model 5.7 eV, while Saito and Oshiyama [19] find 7.4 eV in the framework of the local-density approximation. Consistently with this effect we obtain an equilibrium radius of the sphere somewhat larger of the observed one. However, the results show that the model is able to take into account at least semiquantitatively the main properties of the C_{60} molecule. This is due, in our opinion, to the goodness of the Thomas-Fermi approximation when a large number of electrons are involved and to the central role played by the π electrons. A possible way to improve the model could be to consider the so called "floating" approximation [10,20], in which the C atoms are allowed to "float" in along the sphere radius so that they were at a distance less than R_e from the origin. With this method one has a free fitting parameter, while in the model here proposed no external parameters are introduced: all is derived very simply in terms of the fundamental constants. Of course, in order to get full quantitative description of the ground-state properties of the C_{60} molecule one has to consider in detail the σ electron effects.

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