

Point-ion approximation within the March model for the fullerene molecule

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We present an approach of the March model [N. H. March, Proc. Cambridge Philos. Soc. **48**, 665 (1952)] for the fullerene molecule by employing a point-ion approximation. Accordingly, the model with which we shall be concerned is a high-density gas of π electrons in its ground state with a discrete positively charged background disposed in a t -icosahedral symmetry. The density of π electrons is derived within the first-order approximation of the perturbation theory and then Poisson's equation is solved analytically by imposing natural limits for the fullerene molecule. We have found both inside and outside the fullerene cage distinctive peaks for the electron distribution and a larger fraction of the π electrons contained inside the molecule. We must stress here that the other results recorded in a continuum positive charge approximation of the March model for the fullerene molecule predict that only less than half of all the π electrons are inside the shell. [S0163-1829(98)00612-2]

Progress in the investigations of the Buckminster fullerene has until recently been largely confined to the molecule model within which the positive ions are uniformly smeared over the surface of a sphere and the valence electrons constrained to move on the sphere surface. The model has successfully been used in describing some electronic and optical properties of C_{60} .¹⁻⁴ Recent interest centers on the approach⁶⁻⁹ of the continuum positive charge model, which employs the Thomas-Fermi theory in describing the electron distribution and the stability of the fullerene. The latter molecule model was inspired from March's one-center model⁵ for heavy, almost spherical molecules. The results were decidedly encouraging, and led them to suggest possible improvements. One of them we attempt to present in this paper. We shall use a point-ion approximation within the March model for the fullerene molecule, and we shall self-consistently derive the electron distribution of a fullerene molecule by a systematic application of the well-known results of the many-body perturbation theory.

Previously,⁵ March's one-center model was employed to investigate special molecules XY_n , like CH_4 or SF_6 , and it has been provided with a sound theoretical basis.¹⁰ Shortly, the positive charges of the Y nuclei are smoothed out uniformly over the surface of a sphere with the X atom at the center, and then the essential problem is to apply self-consistent field methods for the delocalized electrons.

As a theory in its own right, the method developed by March has not been without its successes, and it seemed a natural step therefore to investigate whether the method could be extended to the fullerene molecule. The March model strictly corresponds to the endofullerene molecule and it has been explored recently by Clougherty.⁹ For the fullerene case, there is no central atom and the boundary conditions imposed in the March model change at the origin.^{6,7}

The molecule model assumes that the valence electrons cover the inner and the outer surfaces of the uniformly charged fullerene cage moving in a common potential generated both by the positive charges and by their distribution. One point needs stressing here: Smearing the positive ions

into a continuum surface charge distribution, as indicated above, leads to electrons moving in a less rapidly varying spatial potential than for the point ions in the fullerene molecule. (Note that inside a sphere, the electrostatic potential due to a surface charge distribution is constant.) Mostly, the inside electron distribution seems to be affected by employing the continuum positive charge approximation; only less than half of all the valence electrons of the fullerene molecule are inside the shell.^{7,8} Therefore, the fullerene molecule being too "rarefied" within its natural limits, some objections can be risen on its mechanical stability.⁶⁻⁸

This situation can be overcome in a case that we shall present here by employing a point-ion approximation. In this case, the valence electrons are found to be confined, for the most part, inside the shell as a consequence of the adequate changing of the internal electrostatic potential. Moreover, both the inside and the outside electron distributions show distinctive peaks near the fullerene cage, a fact that differs from the other results recorded in the field.⁶⁻⁸

The model with which we shall be concerned is a quantum-mechanical high-density electron gas in its ground state with a discrete positively charged background disposed in a t -icosahedral symmetry. Due to the Coulomb interactions, the electrons redistribute themselves so as to shield the positive charges at large distances. The whole system must be neutral.

As it is known,¹¹ the many-body perturbation procedures do not attempt to solve the quantum-mechanical many-body problem, but instead introduce physically reasonable approximations in a self-consistent manner. We are interested in a regime where Bohr's Correspondence Principle applies, namely, in the limit of large quantum numbers. This limit is certainly achieved when the number of electrons becomes sufficiently large, so that one can apply the methods of statistical mechanics. Thus, let us suppose that we are dealing with N_e noninteracting electrons moving in a common potential $V(\vec{r})$. In our case $V(\vec{r})$ is generated both by the electron distribution and by positive charge of the fullerene cage. The density of Fermions within the first-order approximation of the many-body perturbation theory is given in terms of the unperturbed density ρ_0 , as¹¹

$$\rho(\vec{r}) = \rho_0 - \frac{k_f^2}{2\pi^3} \int d\vec{r}' V(\vec{r}') \frac{j_1(2k_f|\vec{r}-\vec{r}'|)}{|\vec{r}-\vec{r}'|^2}, \quad (1)$$

where k_F is the Fermi wave vector and $j_1(x)$ is the first-order spherical Bessel function. Within primary form 1, the electron density $\rho(\vec{r})$ makes very difficult further mathematical computations and, therefore, we need a linearization formula. Usually, the linearization proceeds by assuming $V(\vec{r})$ as having a slow variation in space (Thomas-Fermi approximation). Accordingly, $V(\vec{r}')$ is replaced in 1 by $V(\vec{r})$.

At this point it is useful to recall that by involving a point-ion approximation, the electrostatic potential achieves a more rapid spatial variation than for the continuum distributed surface charge, as we stressed above. Here, one can raise a very important question as to whether linearization 1 is possible. In the present context, let us emphasize first that in a high-density electron gas a point charge is screened out very rapidly,¹¹ namely, at distances beyond a characteristic screening length, say, q_0^{-1} (which is in inverse proportion to $\sqrt{k_f}$). Also, we notice that, as usual in an electron gas, the slow variation of $V(\vec{r})$ is supposed to be over a de Broglie wavelength for an electron at the Fermi surface, which is $2\pi/k_f$. In this view, as an answer to the above question, we may say that a conflict with the use of the Thomas-Fermi approximation occurs only close to the point charges of the fullerene cage, beyond a distance ranging between $R - q_0^{-1}$ and $R + q_0^{-1}$, where R is the radius of the fullerene molecule, $R \approx 6.73a_H$.¹² Crudely, we shall disregard this limitation and doing so, we replace $V(\vec{r}')$ in 1 with $V(\vec{r})$ to obtain after a straightforward integration

$$\rho(\vec{r}) = \rho_0 - \frac{q_0^2}{4\pi} V(\vec{r}), \quad (2)$$

where

$$q_0^2 = \frac{4k_f}{\pi a_H} \sim \frac{N_e^{1/3}}{R a_H}, \quad (3)$$

with a_H standing for the Bohr radius and N_e being the number of the electrons. Errors due to the approximation made in the above would be expected when we check the conservation of the electron number, but, as we shall see, there is good confidence within the natural limits of the fullerene molecule.

At the same time we may see that the density follows the potential closely, which means that the validity of the theory is ensured, as we already stipulated above, by the number of electrons being much greater than unity. Of course, at large distances from the outer surface of the fullerene cage, the theory is not valid because the electron density vanishes, nor at very short distances, towards the molecule center, where the electron density vanishes also.

With these in mind, and combining 2 with Poisson's equation to yield

$$\Delta V = -4\pi\rho_0 + q_0^2 V(r, \theta, \varphi), \quad (4)$$

we have a self-consistent field problem that accounts for the electron distribution profile in both the density and potential.

Note that, taking into account higher terms in the perturbation series for the density matrix, which leads to more terms in the density formula 2, one can straightforwardly rederive the well-known Thomas-Fermi theory.¹¹

Note that, further on, we will refer only to the π electrons; the charge of an electron is taken to be $-e$ and atomic units will be used. Here it is convenient to exploit the fact that 4 separates in spherical polar coordinates r, θ, φ . Then, the solution of Poisson's equation may be written in the form

$$V(r, \vartheta, \varphi) = \sum_{l,m} F_{lm}(r) Y_{lm}(\theta, \varphi), \quad (5)$$

where $Y_{lm}(\theta, \varphi)$ are the spherical harmonics. F_{lm} satisfies the radial equation

$$\frac{1}{r} \frac{d^2}{dr^2}(rF) - \frac{l(l+1)}{r^2} F = q_0^2 F - 4\pi\rho_0. \quad (6)$$

The function F is, of course, independent of m . Terms corresponding to $l=0$ have been considered separately in solving the above equation. After some convenient substitutions, we have obtained the general solution for the radial equation as

$$F_l(r) = \frac{(4\pi)^{3/2} \rho_0}{q_0^2} + \frac{A_{00}}{r} \sinh(q_0 r) + \frac{B_{00}}{r} \cosh(q_0 r) + \sum_{j=0}^l C_{lj} \frac{(-1)^j A_{lm} \exp(q_0 r) + B_{lm} \exp(-q_0 r)}{q_0^j r^{j+1}}, \quad (7)$$

where

$$C_{lj} = \frac{l(l+1)(l+j)!}{2^j j! (l-j)!}, \quad (8)$$

and A and B are constants that will be determined. Introducing $F_l(r)$ in Eq. (5) it then follows that

$$V(r, \vartheta, \varphi) = \frac{4\pi\rho_0}{q_0^2} + \frac{B_{00}}{r} \cosh(q_0 r) + \frac{A_{00}}{r} \sinh(q_0 r) + \sum_{l,m} ' \sum_{j=0}^l C_{lj} \times \frac{(-1)^j A_{lm} \exp(q_0 r) + B_{lm} \exp(-q_0 r)}{q_0^j r^{j+1}} \times Y_{lm}(\theta, \varphi), \quad (9)$$

where the prime in the right-hand side of the equation means that the summation over l begins from $l=1$.

As for our case the electrostatic potential must be finite in origin, we have imposed in Eq. (9) the conditions $B_{00}=0$ and $B_{lm}=(-1)^{l+1}A_{lm}$. Thus, inside the fullerene cage, the electrostatic potential has the explicit form

$$V_{\text{int}}(r, \vartheta, \varphi) = \frac{4\pi\rho_0}{q_0^2} + \frac{A_{00}}{r} \sinh(q_0 r) + \sum_{l,m}' \sum_{j=0}^l C_{lj} \frac{(-1)^j A_{lm} [\exp(q_0 r) + (-1)^{l-j} \exp(-q_0 r)]}{q_0^j r^{j+1}} Y_{lm}(\theta, \varphi). \quad (10)$$

At infinitely long distances the potential vanishes and, accordingly, $A_{00}=0$ and $A_{lm}=0$ in 9. We get outside the fullerene cage

$$V_{\text{out}}(r, \vartheta, \varphi) = \frac{4\pi\rho_0}{q_0^2} + \frac{B_{00}}{r} \exp(-q_0 r) + \sum_{l,m}' \sum_{j=0}^l C_{lj} \frac{B_{lm} \exp(-q_0 r)}{q_0^j r^{j+1}} Y_{lm}(\theta, \varphi). \quad (11)$$

According with 2, the inner electron density is

$$\rho_{\text{int}}(r, \vartheta, \varphi) = \frac{q_0^2 A_{00}}{4\pi r} \sinh(q_0 r) + \sum_{l,m}' \sum_{j=0}^l C_{lj} \frac{(-1)^j A_{lm} [\exp(q_0 r) + (-1)^{l-j} \exp(-q_0 r)]}{4\pi q_0^{j-2} r^{j+1}} Y_{lm}(\theta, \varphi), \quad (12)$$

and, similarly, for the outer electrons, one gets

$$\begin{aligned} \rho_{\text{out}}(r, \vartheta, \varphi) &= \frac{q_0^2 \cdot B_{00}}{4\pi r} \exp(-q_0 r) \\ &+ \sum_{l,m}' \sum_{j=0}^l C_{lj} \frac{B_{lm} \exp(-q_0 r)}{4\pi q_0^{j-2} r^{j+1}} Y_{lm}(\theta, \varphi). \end{aligned} \quad (13)$$

As it is known, the carbon ions have a *t*-icosahedral disposal within the fullerene molecule that closely assimilates with the spherical one. Consequently, by considering a system of N carbon ions located on the vertices of a truncated icosahedron of radius R the positive charge density may readily be written as

$$\sigma(\theta, \varphi) = \frac{z}{R^2} \sum_{i=1}^N \delta(\varphi - \varphi_i) \delta(\cos\theta - \cos\theta_i), \quad (14)$$

where the charge $z=1$, and the i is an index running over the carbon ions ($N=60$ for the fullerene molecule). The expansion of $\sigma(\theta, \varphi)$ in spherical harmonics $Y_{lm}(\theta, \varphi)$ reads

$$\sigma(\theta, \varphi) = \frac{z}{R^2} \sum_i \sum_{lm} Y_{lm}^*(\theta_i, \varphi_i) Y_{lm}(\theta, \varphi). \quad (15)$$

Turning our attention now to the corresponding electrostatic potentials for the inner and outer regions of the fullerene molecule, we impose the appropriate boundary conditions and get, after some manipulations, the constants entering in Eqs. (10) and (11) as follows:

$$A_{00} = \frac{zN}{q_0 R} \exp(-q_0 R), \quad (16)$$

$$B_{00} = \frac{zN}{2q_0 R} \exp(q_0 R), \quad (17)$$

$$\begin{aligned} A_{lm} &= \sum_{i=0}^l \frac{C_{li}}{(q_0 R)^i} \exp(q_0 R) 4\pi z \sum_i Y_{lm}^*(\theta_i, \varphi_i) \\ &\times \left\{ \sum_{j,k=0}^l \frac{C_{lj} C_{lk} (-1)^{j+1} (j+1)}{(q_0 R)^{j+k}} [\exp(2q_0 R) \right. \end{aligned}$$

$$\begin{aligned} &\left. - (-1)^{l-j} \right] \left[1 - \frac{q_0 R}{j+1} \coth^{(-1)^{l-j}}(q_0 R) \right] \\ &+ \sum_{p,s=0}^l \frac{C_{lp} C_{ls} (-1)^p (s+1)}{(q_0 R)^{p+s}} [\exp(2q_0 R) - (-1)^{l-p}] \\ &\times \left(1 - \frac{q_0 R}{s+1} \right) \Bigg\}^{-1}, \end{aligned} \quad (18)$$

$$\begin{aligned} B_{lm} &= \sum_{i=0}^l \frac{C_{li} (-1)^i}{(q_0 R)^i} \exp(q_0 R) [\exp(2q_0 R) - (-1)^{l-i}] \\ &\times 4\pi z \sum_i Y_{lm}^*(\theta_i, \varphi_i) \\ &\times \left\{ \sum_{j,k=0}^l \frac{C_{lj} C_{lk} (-1)^{j+1} (j+1)}{(q_0 R)^{j+k}} [\exp(2q_0 R) \right. \\ &\left. - (-1)^{l-j} \right] \left[1 - \frac{q_0 R}{j+1} \coth^{(-1)^{l-j}}(q_0 R) \right] \\ &+ \sum_{p,s=0}^l \frac{C_{lp} C_{ls} (-1)^p (s+1)}{(q_0 R)^{p+s}} [\exp(2q_0 R) - (-1)^{l-p}] \\ &\times \left(1 - \frac{q_0 R}{s+1} \right) \Bigg\}^{-1}. \end{aligned} \quad (19)$$

Conservation of electron number requires that the following identity be satisfied:

$$\begin{aligned} &\int_0^R r^2 dr \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\varphi \rho_{\text{int}}(r, \vartheta, \varphi) \\ &+ \int_R^\infty r^2 dr \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\varphi \rho_{\text{out}}(r, \vartheta, \varphi) = N_e. \end{aligned} \quad (20)$$

After a straightforward integration we obtain an equation in terms of the electron number N_e given by

$$1 - \frac{1}{\exp(q_0 R)} = \frac{N_e}{zN}, \quad (21)$$

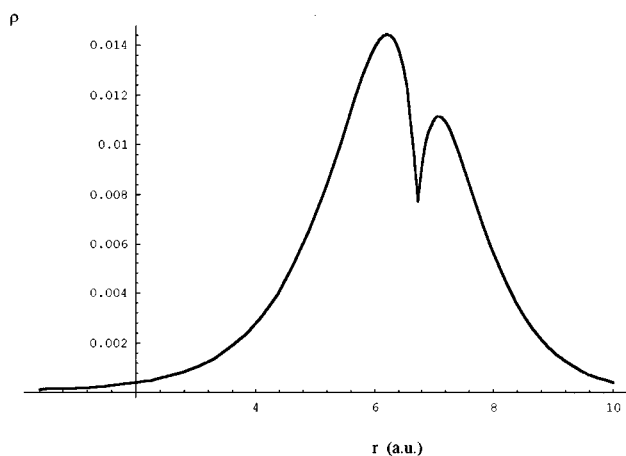


FIG. 1. Electron charge density ρ vs r for $R=6.73a_H$, $z=1$, $N=60$, $\theta=0$, and $\varphi=\pi$.

where q_0 must be replaced by 3. Taking $N=60$, $R=6.73a_H$, $z=1$ and solving numerically, we get $N_e=60$ with very good accuracy. As we have expected, the number of electrons covering the inner and outer surfaces of the fullerene cage is equal to that of the carbon ions. Thus, the whole system remains neutral. In fact, this is the main physical requirement that must be satisfied in applying here the many-body perturbation theory.

Turning our attention now to the electron densities given by 12 and 13 we must note that, by embodying the overall point-group symmetry of C_{60} ,¹³ the summation over electron orbital number l must be made for even values only. Also, the elements corresponding to $l=2,4,8$ vanish identically, so that the first nonvanishing terms remain for $l=0,6,10$ and for $m=0,\pm 5$. In Fig. 1 we have shown the radial profile of the electron density both inside and outside the fullerene cage. The numerical integration was carried out inside a large sphere of radius $10a_H$, greater than the radius of the molecule. As we may see, the outer electron distribution decreases very rapidly from the fullerene cage vanishing around $10a_H$. In fact, except for the region of short distances, towards the molecule center where the electron density vanishes also, the super sphere of radius $10a_H$ coincides with the domain of validity of the present theory, as we have established in the introductory text. We must also notice two main aspects concerning the point-ion approximation within the March model for the fullerene molecule. The first is that the electron distribution shows two peaks slightly displaced from the interface, the separation length being around $1.25a_H$. The second is that, in this case, a larger fraction of the π electrons is contained inside the molecule. This fraction is equal to 78 percent but, actually, it could be less, because the model does not include properly the p_z character of the π electrons. However, as we have said above, the

other results recorded in the field⁶⁻⁸ predict that only less than half of all the π electrons are inside the shell. In this view, we may conclude that the errors arising from the continuum approximation of the positive charge are twofold. On one hand, the continuum approximation overestimates the shell self-force⁷ and, on the other, it underestimates the number of the inner electrons.

As we know, the effective forces operating in an electron gas are of much shorter range than the bare Coulomb interaction. The Coulomb interaction is seen, in practice, to be screened out very rapidly, beyond a characteristic screening length, $\sim q_0^{-1}$.

With this in mind, we are thus in a position to understand the features of the fullerene electron density shown in Fig. 1. The electrons move in the field of the positively charged carbon ions tending, naturally enough, to contract the charge cloud into the fullerene cage. At the same time, the electrons near the surface electrostatically repel other electrons from their immediate vicinity. This leads to a diminution of negative charge around the fullerene cage. The net effect of positive point charges, together with the inside and outside electron distributions, diminished somewhat into their interface, is a much reduced force of screened Coulomb type. This removes the electron distribution peaks from the positively charged shell. On the other hand, due to their fermionic nature, the electrons prefer to go towards regions where the kinetic energy is lower. Consequently, both the inside and the outside electron distributions have a diffusive trend.

To this end, we must note that there was another related method for including the effects of the discreteness of the positive charges presented by Clougherty⁹ but numerical results were not given. Although Eq. (4) in this paper and Clougherty's Eq. (15) in Ref. 9 are very similar, their method of deduction is different. In Clougherty's paper,⁹ the non-spherical corrections to the potential, originated from the discreteness of the positive charges, are included by consideration of the higher-order multipole moments in the general Thomas-Fermi equation. In further research, it has been assumed that these corrections are much smaller than the spherically averaged solution and, by an adequate approximation, this has led to a linearized equation like Eq. (4). By comparison, in the present study, we have used a direct method to obtain a linearized equation of type (4). Thus, we have derived the density of electrons within the first-order approximation of the many-body perturbation theory and, then, we have solved the appropriate Poisson's equation analytically, by imposing natural limits for the fullerene molecule. As in the above-cited work,⁹ the discreteness of the positive charges intervenes in the boundary conditions.

Another problem that can be handled directly by this method is the endohedrally doped fullerenes, but the results are more complicated and will not, therefore, be recorded here.

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