Two-dimensional electrostatic analog of the March model of C_{60} with a semiquantitative application to planar ring clusters

Claudio Amovilli*
Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, I-56126 Pisa, Italy

Norman H. March†
Department of Physics, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerpen, Belgium
(Received 20 March 2006; published 22 June 2006)

The so-called March model of fullerene uses the one-center approximation of quantum chemistry to calculate the spherical π-electron density ρ by the Thomas-Fermi (TF) statistical method. Then the variational principle of the TF theory is employed by combining the electronic energy determined entirely by ρ with the discrete C_{60} nuclear potential energy to predict, semiquantitatively, the equilibrium radius. Here the same approach is worked out, but now largely analytically, in two dimensions, as a possible model of planar ring clusters. Again the equilibrium radii are calculated and consistency with realistic clusters of hydrogen and carbon rings is discussed in detail. Finally, an estimate of the "breathing" frequency of C_{14}, C_{18}, and C_{22} is given.

DOI: 10.1103/PhysRevA.73.063205 PACS number(s): 36.40.−c, 31.15.Bs

I. INTRODUCTION

The so-called March model [1,2] of fullerene approximates the 60 π electrons peaked around the surface of the buckyball by a spherical distribution of electron density ρ. This then leads, by a variational calculation based on the Thomas-Fermi (TF) energy functional $E_{TF}[\rho]$, but retaining the nuclear-nuclear potential energy for the correct discrete C nuclei positions [1], to an equilibrium radius of the buckminster fullerene somewhat larger than experiment, but already useful. Similar considerations, but with Hartree-Fock method instead of TF, have been successfully used in quantitative calculations on spherical boron cages [3].

The present study has been motivated by the cluster studies on C reported by Jones and Seifert [4]. In particular, they report by the density functional study (DFT), that the likely lowest isomers of C_N with N between 14 and 22 are planar rings with "cumulenic" spacing between the nuclei on the rings. This has prompted us to consider the analog of the three-dimensional March model of C_{60} to apply to such quasi two-dimensional planar ring clusters.

The outline of the paper is then as follows. In Sec. II below, for completeness, we briefly summarize the TF statistical model for such a two-dimensional (2D) planar electronic assembly. Then we focus on the use of electrostatics and charge interactions satisfying the corresponding 2D Poisson equation. Analogous to the March model of C_{60}, ρ, now the number of electrons per unit area, is taken to have circular symmetry. This is, in the spirit of the one-center expansion, equivalent to smearing N point charges f into a uniform line charge with total charge Nf. Whereas in C_{60}, Nf was, naturally enough, taken to be 60, i.e., one π electron per C atom [5,6], in cluster rings we shall study, now largely analytically, the equilibrium radius R_e of the rings as a function of N. The details of this are set out in Sec. III. In Sec. IV we analyze the consistency of the present model with real *ab initio* and DFT calculations on ring clusters. The paper concludes with a summary plus some proposals directions for further study in Sec. V.

II. BRIEF SUMMARY OF THE TWO-DIMENSIONAL THOMAS-FERMI THEORY

The semiclassical TF statistical method is based on two assumptions: (i) a chemical potential equation for the fastest electron with Fermi momentum $p_F(\mathbf{r})$ and (ii) a phase-space argument relating $p_F(\mathbf{r})$ to the electron density $\rho(\mathbf{r})$. Assumption (i) corresponding to writing the chemical potential μ as the sum of the kinetic term $p_F^2/2m$, with m as the electron mass, and a one-body potential energy denoted below by $V(\mathbf{r})$ yields explicitly

$$\mu = \frac{p_F^2}{2m} + V(\mathbf{r}) \tag{1}$$

which is valid for general dimensionality D. However, D enters the phase-space considerations in (ii) above, since a cell of volume h^D can hold two electrons with opposed spin in the spin compensated ground state we consider throughout the present study. Thus in 2D, one has for an area Ω of coordinate space and a momentum space area πp_F^2, that the number of electrons per unit area, $\rho(\mathbf{r})$, is given by

$$\rho(\mathbf{r}) = \left(\frac{n_{el}}{\Omega}\right)_{\mathbf{r}} = \frac{2\pi p_F^2(\mathbf{r})}{h^2}, \tag{2}$$

the numerator of the final term being the spin occupancy two times the area of occupied momentum space, while the denominator is the size of the basic phase-space cell in 2D. Removing $p_F^2(\mathbf{r})$ from Eq. (1), in which μ is constant throughout the whole of the inhomogeneous electron distribution under discussion, using Eq. (2) yields

*Electronic address: amovilli@dcci.unipi.it
†Also at: Oxford University, Oxford, England.

$$\mu = \frac{h^2}{4\pi m}\rho(\mathbf{r}) + V(\mathbf{r}). \tag{3}$$

This is the basic TF equation yielding the areal density $\rho(\mathbf{r})$ in 2D from a given one body potential $V(\mathbf{r})$. As usual μ is determined by the normalization condition on $\rho(\mathbf{r})$.

We turn in the following section to apply this Euler Eq. (3) of the TF statistical method to planar ring clusters.

III. SELF CONSISTENT FIELD AND ITS CONSEQUENCES IN QUASI-2D RING CLUSTERS

As in the TF neutral atom, and in C_{60} in the March model [1,2,5], the chemical potential μ can be put to zero in the neutral ring clusters under discussion. Equation (3) can be combined with the 2D form of Poisson's equation of electrostatics to yield, in atomic units ($\hbar=1$, $m=1$, $q_e=-1$, and $4\pi\epsilon_0=1$), for the electrostatic potential V_{es},

$$V_{es}(r) = -\pi\rho(r), \tag{4}$$

where V_{es} satisfies

$$\frac{\partial^2 V_{es}}{\partial r^2} + \frac{1}{r}\frac{\partial V_{es}}{\partial r} = 4V_{es}. \tag{5}$$

Scaling r to s, via $s=2r$, the electrostatic potential can be obtained by solution of Eq. (5), for a line charge of radius R, and with $t=2R$ as

$$V_{es}(r) = -\lambda[K_0(t)\Theta(t-s)I_0(s) + I_0(t)\Theta(s-t)K_0(s)], \tag{6}$$

where the quantity $\lambda(>0)$ is to be obtained from the density normalization condition ($n_{el}=Nf$),

$$Nf = 2\pi\int_0^\infty \rho(r) r dr, \tag{7}$$

while $\Theta(x)$ is the Heaviside step function and $K_0(x)$ and $I_0(x)$ are modified Bessel functions [7]. From the Gauss theorem, we have additionally that

$$q(s) = \frac{s}{2}V'_{es}(s), \tag{8}$$

which means that $q(s)$, the total charge, must tend to 0 as $s\to\infty$ for a neutral system.

A basic function of the present self consistent TF method for 2D ring clusters is then defined by $Q(s)=2q(s)/\lambda$. The merit of this definition is that $Q(s)$ no longer depends on normalization. It can be written, using Eqs. (6) and (8) as

$$Q(s) = -s[K_0(t)\Theta(t-s)I'_0(s) + I_0(t)\Theta(s-t)K'_0(s)]. \tag{9}$$

The jump (discontinuity due to line charge) at $s=t$ of Q, say ΔQ, is then given by

$$\Delta Q = t|I_0(t)K'_0(t) - K_0(t)I'_0(t)|, \tag{10}$$

where the right-hand side (rhs) of Eq. (10) contains the modulus of the Wronskian evaluated at t. Owing to the special form of the second order differential equation (5), the Wronskian is proportional to t^{-1} and, hence, ΔQ is constant. From (10) one finds $\Delta Q=1$. By the definition of Q this result leads to $\lambda=2Nf$, the jump of the function $q(s)$ being related to the total ring charge Nf. It is important to remark that, when t tends to 0, one recovers the two-dimensional TF model atom already discussed by Kventsel and Katriel [8].

Plots of scaled potential $v(s)=V_{es}(s)/\lambda$ and total charge $Q(s)$ are presented in Fig. 1 for various choices of scaled ring radii t.

A. Variational TF calculation of ring radii as a function of N

As already mentioned we follow the March model of C_{60} by using 2D TF theory variationally, based on the "line charge" circular density $\rho(r)$ given by Eq. (4). Then the energy $E_{TF}[\rho]$ in 2D is explicitly

$$E_{TF}[\rho] = \pi^2\int_0^\infty \rho(r)^2 r dr + 2\pi\int_0^\infty \rho(r)V_{lc}(r)r dr - \int \rho(r_1)\rho(r_2)\ln r_{12} d\mathbf{r}_1 d\mathbf{r}_2 + U_{nn}. \tag{11}$$

Here, V_{lc} is the confining potential due to the nuclear effective charges smeared on a circumference of radius R, namely

$$V_{lc}(r) = \begin{cases} 2Nf\ln R & (r\le R) \\ 2Nf\ln r & (r>R) \end{cases}. \tag{12}$$

As already emphasized, U_{nn} is to be treated using the discrete nuclei on rings, in order to calculate the equilibrium radius R_e given by the equilibrium condition

$$\left(\frac{\partial E_{TF}}{\partial R}\right)_{R_e} = 0. \tag{13}$$

Following the Hellmann-Feynman theorem, Eq. (13) is equivalent to the balance of the forces acting on nuclei if the electron density entering the energy has been obtained variationally. Using the TF density coming from the potential given by Eq. (6), the radial component of the electric field due to electrons and acting on the ring is

$$\mathcal{E}_e = -\frac{2Nf\chi(2R)}{R}, \tag{14}$$

where

$$\chi(t) = tK_0(t)I'_0(t) \tag{15}$$

is the fraction of electrons inside the circle of radius $t=2R$. Then, for a set of N equispaced point charges f lying on a circumference of radius R, the resultant electric field acting on one of such charges and due to the other $N-1$ has the radial component (still in 2D)

$$\mathcal{E}_n = \frac{(N-1)f}{R} \tag{16}$$

which can be used to establish the force balance equation

$$\mathcal{E}_e + \mathcal{E}_n = 0. \tag{17}$$

Combining Eqs. (14), (16), and (17) we get

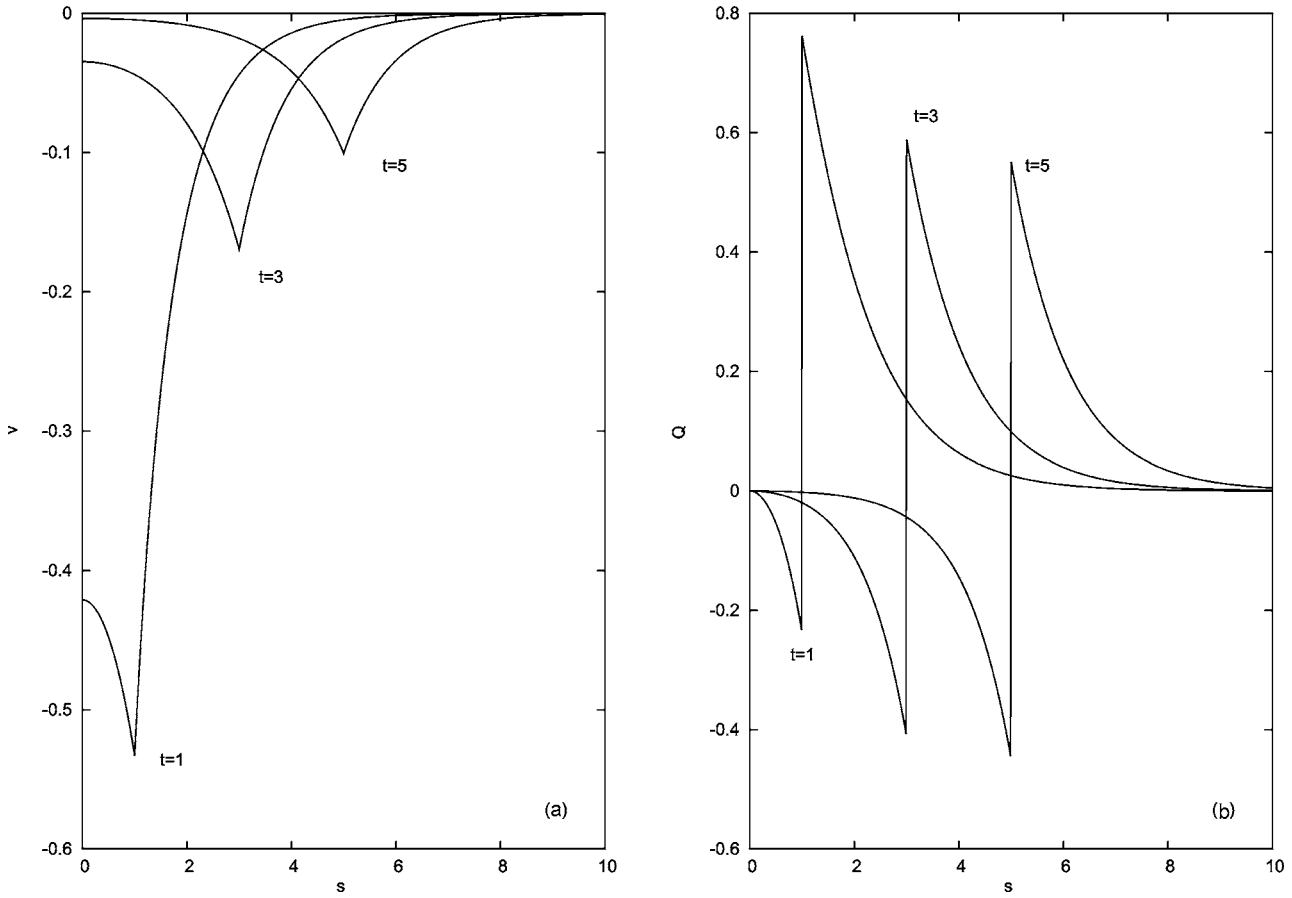

FIG. 1. Thomas-Fermi self consistent reduced potential (a) and charge (b) for a two-dimensional electron system, confined by a positive ring line charge, as a function of a properly scaled distance from the centre. Lengths (s and t) are in units of $2a_0$, Q is in units of Nf, the number of electrons in the ring, and v is in hartrees divided by $2Nf$ (see text for more details).

$$\chi(2R_e) = \frac{1}{2} - \frac{1}{2N}, \tag{18}$$

which can be solved to obtain R_e, the equilibrium radius in this model, as a function only of N, the number of atoms of the ring cluster.

In Fig. 2 we show the variation of the equilibrium radius with the number of ring atoms as it results from Eq. (18). From this plot one can see that R_e, in this model, tends rapidly to the limiting behavior, determined by the asymptotic forms of the modified Bessel functions, of about $N/4$ in atomic units. In the same figure we compare the equilibrium radii of this 2D model with realistic radii obtained from the DFT calculation on almost 2D ring clusters. This comparison will be discussed in the next section.

IV. CONSISTENCY OF THE 2D MARCH MODEL WITH REALISTIC PLANAR RING CLUSTERS

It is of interest now to compare the information that can be obtained from the model developed in the previous section with that arising from *ab initio* or DFT calculations on realistic planar ring clusters.

The prototype of such clusters could be rings of equispaced hydrogen atoms, $f=1$, constrained to lie on a circumference, while, in 2D, the analog of three-dimensional (3D) fullerenes are planar rings of N carbon atoms with N ranging from 14 to 22. The C rings of this size have been really produced in molecular beam experiments [9] and their stability has been discussed by Jones and Seifert [4]. Instead, the rings of hydrogen atoms considered here are only a theoretical construction that can be studied by standard methods for the electronic structure calculation.

In Fig. 2 we report the equilibrium radii of H and C clusters obtained from calculations performed at the B3LYP DFT level with basis sets flexible enough to give good constrained (circular) equilibrium geometries. For H rings we used even numbers of atoms ranging from 6 to 18, while for C rings we followed the study of Jones and Seifert [4] limiting attention to the three clusters C_{14}, C_{18}, and C_{22}. For C rings we made calculations on singlet states. For H clusters we considered singlet ground states when $N=4n+2$, n integer, and triplet states in the other cases.

From Fig. 2 is quite evident that in 2D the agreement between model equilibrium radii and radii of C ring clusters is not good as, instead, it happens in 3D for fullerenes. Some better consistency is instead observed between the model and our hypothetical H rings.

The existence of σ bonds in C rings modifies substantially the effective nuclear interaction from that expected in two dimensions. In order to overcome this inconsistency one can

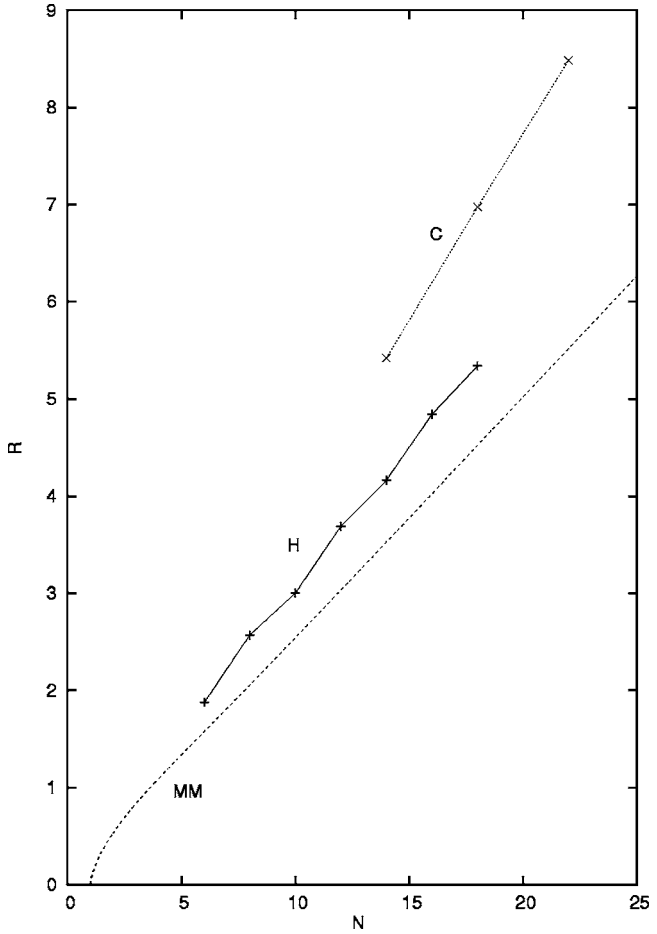

FIG. 2. Equilibrium radius as a function of the number of atoms of a ring cluster for the two dimensional March model of this work (MM) and for realistic H-ring (H) and C-ring (C) planar clusters. The radii are in atomic units.

modify the U_{nn} term in the energy functional (11). Equation (11) with the variational density (4) becomes

$$E = \pi \int_0^\infty \rho(r) V_{lc}(r) r dr + U_{nn} \tag{19}$$

in which we have

$$\pi \int_0^\infty \rho(r) V_{lc}(r) r dr = N^2 f^2 \ln R + N^2 f^2 K_0(2R) I_0(2R) \tag{20}$$

and

$$U_{nn} = -N(N-1) f^2 \ln R + \frac{N^2 f^2}{2} A_N, \tag{21}$$

where $A_N = (1/N)\Sigma_{j=2}^N \ln 2(1-\cos\theta_{1j})$, θ_{1j} being the angle between nucleus 1, the ring centre and nucleus j. A_N does not depend on R. Now, to introduce some effect due to σ bonds, we propose to modify U_{nn} in the terms of order N, N being also the number of such bonds in C rings. σ bonds can be considered by including appropriate short ranged interactions acting between pairs of neighbor C atoms. Thus, we can write

$$U_{nn}^{(+\sigma)} = U_{nn} + \sum_{i=1}^{N} u(d_{i,i+1}) \tag{22}$$

where $u(d_{i,i+1})$ is the bond pair potential which depends on the distance $d_{i,i+1}$ between centres i and $i+1$ ($d_{N,N+1}=d_{N,1}$). In cumulenelike C rings the bond distances are all the same and, with the assumption $d_{i,i+1} \approx 2\pi R/N$, we have

$$U_{nn}^{(+\sigma)} = U_{nn} + Nu\left(\frac{2\pi R}{N}\right). \tag{23}$$

At this point, by writing

$$U_{nn}^{(+\sigma)} = -N^2 f^2 \ln R + Ng(R) \tag{24}$$

in which

$$g(R) = f^2 \ln R + \frac{f^2}{2} \sum_{j=2}^{N} \ln 2(1-\cos\theta_{1j}) + u\left(\frac{2\pi R}{N}\right), \tag{25}$$

the energy E takes the simple form

$$E = N^2 f^2 K_0(2R) I_0(2R) + Ng(R). \tag{26}$$

In the range of radii of C_N rings considered in this work, the modified Bessel function K_0 and I_0 can be substituted by their asymptotic expression. The product $K_0(t)I_0(t)$ in this regime is simply $1/2t$ with $t=2R$ in the present case. This fact, combined with the observation that the equilibrium radii are proportional to the number of atoms in the ring, suggests to maintain the $\ln R$ functional dependence in $g(R)$ of Eq. (26) in the region of the equilibrium geometries. Under these considerations we have

$$E(R) = \frac{N^2 f^2}{4R} + N(\alpha \ln R + \beta_N), \tag{27}$$

where β_N is a constant introduced to bring $E(R_{eq})$ to coincidence with that of calculated minimum. Here, we remark that the second term in the rhs of Eq. (27) corresponds to $Ng(R)$ of Eqs. (24) and (26). Equation (27) suggests that E/N could be written as a function of R/N in the more general form

$$\frac{E(R)}{N} = a\frac{N}{R} + b \ln\left(\frac{R}{N}\right) + c, \tag{28}$$

with a, b, and c related to f, α, and β_N through Eq. (27) above. Equation (28) is the analog of Eq. (9) of our previous work [6] on fullerenes in 3D.

In Fig. 3 we show results for fitted scaled energies E/N obtained from Hartree-Fock (HF) and B3LYP DFT calculations performed on C_{14}, C_{18}, and C_{22} ring clusters. The three curves, in both the two plots of Fig. 3, look roughly identical apart for a small energy shift. Fitted parameters a, b, and c are given in Table I. These numerical results confirm some universality of Eq. (28). The value of a can also be used to estimate the number of electrons of each atom, namely f, involved in the TF model density (4). From Eq. (27) we can

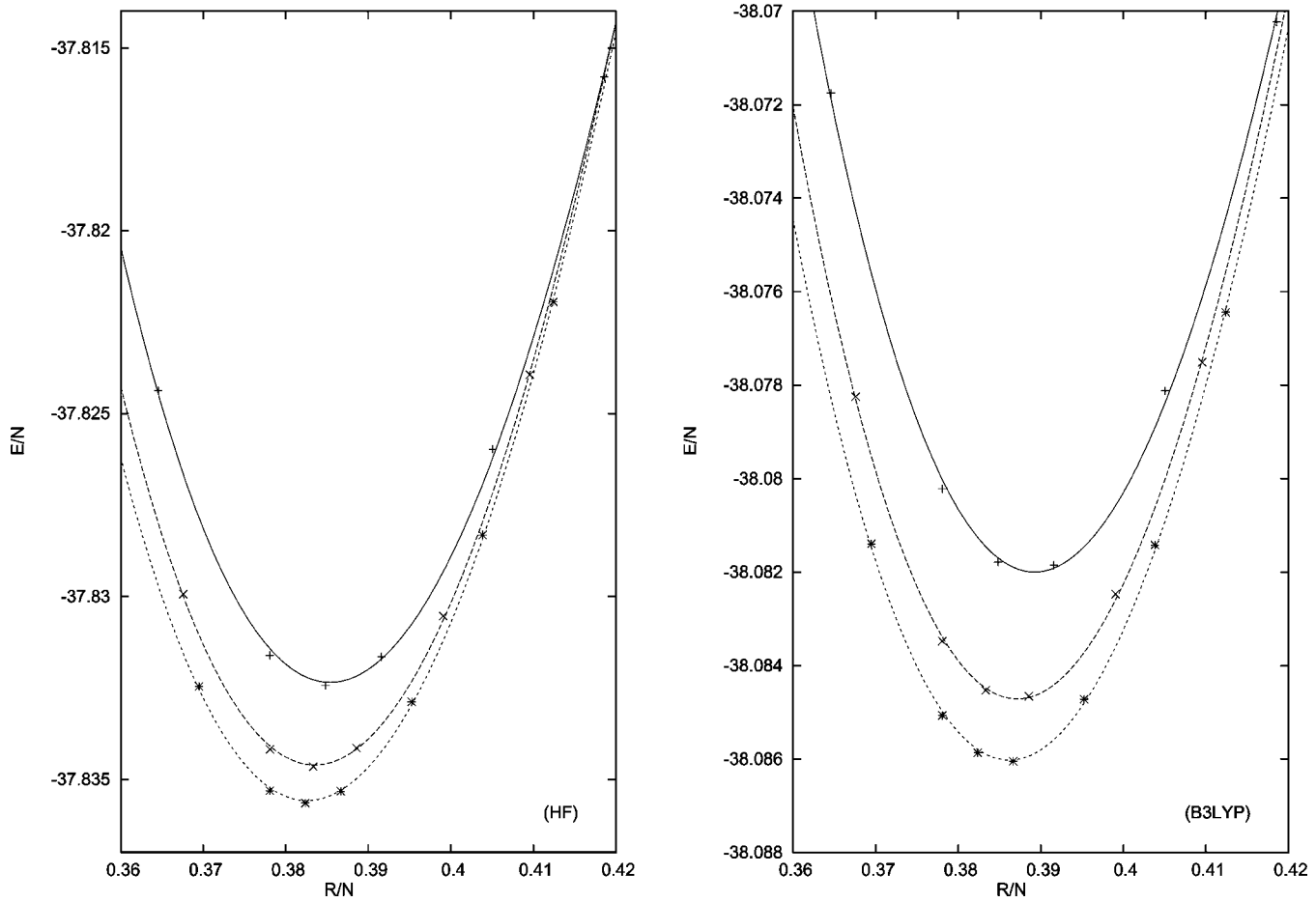

FIG. 3. Curves of scaled energies E/N against the scaled radius R/N, obtained at HF and DFT (B3LYP) level of calculation, for the three carbon rings C_{14} (upper curves), C_{18} (middle), and C_{22} (lower curves). Data are in atomic units.

write $f=2\sqrt{a}$, which tells us that this number is about 2.77 if the HF data are used or about 2.68 with B3LYP results.

Finally, with the parameters of Table I, we can calculate the frequency of the "breathing" symmetrical vibrational mode. The reduced mass for this motion is M/N where M is the mass of the carbon nucleus. By definition, the square of such angular frequency ω is given by

$$\omega^2 = \frac{N}{M}\left(\frac{\partial^2 E}{\partial R^2}\right)_{R_{eq}}, \tag{29}$$

where the energy E is the same as in Eq. (28) and plays the role of potential energy in the harmonic approximation for the study of the motion of nuclei in this case [10,11]. Combining Eqs. (28) and (29), we obtain

$$\omega = \sqrt{\frac{b^3}{a^2 M}}, \tag{30}$$

which is essentially a constant not depending on N. From the data of Table I we obtain $\bar{\nu}=\omega/2\pi c=1163$ cm^{-1} with B3LYP DFT and 1378 cm^{-1} at the HF level.

We conclude this section on connection with realistic systems by mentioning quantum rings. Quantum rings are artificial systems of confined electrons observed at the nanoscale in semiconductors. They originate from 2D quantum dots by

TABLE I. Parameters entering the definition of the scaled energy defined in Eq. (28) obtained from fitting of HF and B3LYP results of calculations performed on C_{14}, C_{18} and C_{22} ring clusters.

Method	Parameter	C_{14}	C_{18}	C_{22}
HF	a	1.93±0.03	1.94±0.02	1.90±0.02
	b	5.02±0.08	5.06±0.06	4.97±0.07
	c	−38.065±0.005	−38.045±0.004	−38.030±0.004
B3LYP	a	1.80±0.03	1.81±0.02	1.77±0.03
	b	4.62±0.08	4.67±0.07	4.57±0.07
	c	−38.343±0.005	−38.323±0.004	−38.308±0.004

depleting the central region of the disk and thereby forming a ring (see, for example, Ref. [12]). We do not enter into the details of the methods used to study such systems, but we say that the model developed in the present work in Secs. II and III can also be formulated in a context of a quantum ring. In order to do this, we need to introduce the effective mass of electrons and the relative dielectric constant of the medium in all expressions of the model. The effective mass m^* enters through the definition of the Fermi energy, while the medium dielectric constant ϵ through the Poisson equation. For this case, we get the following coupled equations in atomic units:

$$\mu = V + \frac{\pi\rho}{m^*} \qquad -\nabla^2 V = \frac{4\pi}{\epsilon}\rho. \tag{31}$$

Of course, some attention will need to be paid to the confinement. The choice of a background positive line charge potential is still valid but the total charge and the radius should be differently defined in terms of some other external parameter. One more important point concerns the effect of an applied magnetic field, but this needs an extension of the present model.

V. SUMMARY AND PROPOSED FUTURE DIRECTIONS

The selfconsistent potential $V_{es}(r)$ in the analog of the March model in 2D planar ring clusters has first been calculated analytically. It is given by Eq. (6) in terms of modified Bessel functions. The 2D TF energy functional is then shown to lead to the potential energy function in Eq. (28), where the energy per atom of the ring cluster of radius R depends on R/N. This is the 2D counterpart of our early scaling of potential energy in the 3D fullerenes. The breathing frequency of the planar ring clusters C_{14}, C_{18}, and C_{22} is thereby estimated.

As to future directions, we already referred at the end of Sec. IV to a possible application of the present model to nanoscale quantum rings. Therefore, to conclude, we want to sketch briefly below how to eventually refine the 2D March model discussed fully above to take account of exchange, in what is essentially a local density (Dirac-Slater like) approximation. In 3D, the Slater $X\alpha$ method works as follows:

$$U_x = \frac{1}{2}\int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\rho(r_1)\rho(r_2)f_x(r_{12})}{r_{12}}$$

$$-1 = \int d\mathbf{r}_2 \rho(r_2) f_x(r_{12}),$$

$$f_x(r_{12}) \approx -1 (r_{12} \leqslant R) \approx 0 (r_{12} > R),$$

$$R = \left(\frac{3}{4\pi\rho}\right)^{1/3},$$

$$U_x \approx -2\pi \int d\mathbf{r}_1 \rho(r_1)^2 \int_0^R r_{12} dr_{12}$$

$$= -\pi \int d\mathbf{r}_1 \rho(r_1)^2 R^2$$

$$\approx -\left(\frac{3\pi^{1/2}}{4}\right)^{2/3} \int d\mathbf{r} \rho(r)^{4/3}. \tag{32}$$

The counterpart of the above argument in 2D goes as follows:

$$U_x = -\int d\mathbf{r}_1 \int d\mathbf{r}_2 \rho(r_1)\rho(r_2) f_x(r_{12}) \ln r_{12},$$

$$R = \left(\frac{1}{\pi\rho}\right)^{1/2},$$

$$U_x \approx 2\pi \int d\mathbf{r}_1 \rho(r_1)^2 \int_0^R r_{12} \ln r_{12} dr_{12}$$

$$= \frac{\pi}{2} \int d\mathbf{r}_1 \rho(r_1)^2 R^2 (2 \ln R - 1)$$

$$\approx -\frac{1}{2} \int d\mathbf{r} \rho(r)[1 + \ln(\pi\rho)]. \tag{33}$$

The final line of Eq. (33) prompt us to add that the exchange potential energy U_x in 2D contains a term which is reminiscent of the Shannon entropy, the latter having an integrand of the form $\rho \ln \rho$.

ACKNOWLEDGMENTS

C.A. acknowledges financial support from MIUR (PRIN 2004) and from the University of Pisa (Fondi di Ateneo 2005). N.H.M. wishes to acknowledge that his contribution to this work was made during a visit to Scuola Normale Superiore (Pisa) in 2006. He thanks Professor M. P. Tosi for very generous hospitality.

[1] D. P. Clougherty and X. Zhu, Phys. Rev. A **56**, 632 (1997).
[2] F. Despa, Phys. Rev. B **57**, 7335 (1998).
[3] C. Amovilli and N. H. March, Chem. Phys. Lett. **347**, 459 (2001).
[4] R. O. Jones and G. Seifert, Phys. Rev. Lett. **79**, 443 (1997).
[5] F. Siringo, G. Piccitto, and R. Pucci, Phys. Rev. A **46**, 4048 (1992).
[6] C. Amovilli, I. A. Howard, D. J. Klein, and N. H. March, Phys. Rev. A **66**, 013210 (2002).
[7] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (National Bureau of Standards, Washington D.C., 1964).
[8] G. F. Kventsel and J. Katriel, Phys. Rev. A **24**, 2299 (1981).
[9] S. J. La Placa, P. A. Roland, and J. Wynne, Chem. Phys. Lett. **190**, 163 (1992).
[10] N. H. March, Proc. Cambridge Philos. Soc. **43**, 665 (1952).
[11] H. C. Longuet-Higgins and D. A. Brown, J. Inorg. Nucl. Chem. **1**, 60 (1955).
[12] B. C. Lee and C. P. Lee, Nanotechnology **15**, 848 (2004).