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Existence of a system of discrete volume-localized quantum levels for charged fullerenes

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In the framework of a simple physical model, we demonstrate the existence of a system of discrete short-lifetime quantum levels for electrons in the potential well of the self-consistent field of charged fullerenes and onionlike structures. For electrons, in the case of positively charged fullerenes and onionlike structures, combining analytic and numeric considerations, we find that the energy of the volume-localized levels ranges from 1 to 100 eV.

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I. INTRODUCTION

Fullerenes represent one of the allotropes of carbon, along with graphite, diamond, amorphous carbon, nanotubes, and graphene. Following earlier theoretical predictions, the first fullerene C_{60} molecule was experimentally discovered in the 1980s [1,2] as a nanometer-size hollow spherical structure of 60 carbon atoms located at the vertices of a truncated icosahedron. Subsequently, the production of fullerenes in large quantities was developed, and fullerene nanotubes and many other fullerenes were discovered, such as C_{20}, C_{70}, and even lager structures. This gave a start to explosive growth in research in the area of nanoscience, the historic development and the current status of which can be found in numerous reviews [3–7].

During recent times, the properties of charged fullerenes have been actively experimentally and theoretically investigated [8–28]. A considerable number of works are devoted to the study of their stability (lifetime), mechanisms for charging them, and decay [29].

The present paper is devoted to the discussion of the structure of the electronic spectrum of charged fullerenes. Simple models are used to show the existence of the volume-localized discrete quantum levels for the usual fullerene and for the onionlike structures [30]. Here we confine our attention to the case of positively charged fullerenes.

Basic notations are as follows: m_e and e are electron mass and the absolute value of electron charge, $\lambdabar_e = \frac{\hbar}{m_e c}$ is the electron Compton length, ε_0 is the electric constant of vacuum, $a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$ is the Bohr radius, and $\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c}$ is the fine-structure constant.

II. DISCRETE VOLUME-LOCALIZED LEVELS: QUALITATIVE PRELIMINARIES

As a preliminary step, let us formulate the corresponding quantum-mechanical spectral problem. With an account of the spherical symmetry of a fullerene, for the wave function we use the standard ansatz $\psi(r, \vartheta, \varphi) = R(r)Y_{lm}(\vartheta, \varphi)$, with the spherical harmonics Y_{lm}, and recast the spherically symmetric Schrödinger equation [31] into a second-order differential equation,

$$\frac{d^2\chi}{dr^2} - \frac{l(l+1)}{r^2}\chi + \frac{2m_e}{\hbar^2}[E - U(r)]\chi = 0 \tag{1}$$

for the function $\chi(r) = rR(r)$, $0 \leqslant r < \infty$, under the boundary conditions

$$\chi(0) = 0, \quad \chi(\infty) = 0. \tag{2}$$

The form of the solution is determined by the potential $U(r)$.

We will discuss the energy levels of an electron by starting with a simple model potential and then move on to a more complicated form of U. In the simplest model, one can describe a charged fullerene by the potential of a sphere with a constant surface charge density:

$$U(r) = -Z\,\Phi(r), \quad \Phi = \frac{e}{4\pi\varepsilon_0}\begin{cases} \frac{1}{R}, & r \leqslant R, \\ \frac{1}{r}, & r > R, \end{cases} \tag{3}$$

where $Z = Ne$ is a positive charge and $R = R_f$ is the fullerene radius. Our attention will be mainly confined to the C_{60} fullerene, where $R_f = 6.627a_0$.

A first very approximate estimate of the energy levels can be obtained by replacing (3) with a spherical rectangular well with the depth $U_0 = \frac{Ze}{4\pi\varepsilon_0 R_f}$. Inside such a well ($0 \leqslant r \leqslant R_f$), a non-normalized solution of the Schrödinger equation (1) is described by the spherical Bessel function $\chi = j_l(\xi r/R_f)$, which satisfies the boundary condition at zero, $\chi(0) = 0$, whereas outside the well ($R_f < r < \infty$) a solution that satisfies $\chi(\infty) = 0$ is given by the spherical Hankel function $\chi = h_l(i\eta r/R_f)$. The parameters η and ξ are algebraically related,

$$\xi^2 + \eta^2 = \frac{2m_e U_0 R_f^2}{\hbar^2} = 2\alpha\frac{Z}{e}\frac{R_f}{\lambdabar_e}, \tag{4}$$

and they determine discrete energy levels via

$$E = -\frac{\hbar^2\eta^2}{2m_e R_f^2} = -U_0 + \frac{\hbar^2\xi^2}{2m_e R_f^2}. \tag{5}$$

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The values of parameters η and ξ are fixed by the continuity condition of the wave function at $r = R_f$. For $l = 0$, this yields

$$\eta = -\,\xi \cot \xi. \tag{6}$$

It is worthwhile to notice that the right-hand side of (4) is essentially greater than 1, and already for a single charged C_{60}^{+1} we have $\frac{2m_e U_0 R_f^2}{\hbar^2} = 13.25$. As a result, for highly charged fullerenes ($Z \gtrsim 10e$) one can use an approximation of a very deep well $U_0 \gg \frac{\hbar^2}{2m_e R_f^2}$, deriving the energy levels from a condition of the vanishing of the wave function at the boundary: $j_l(\xi) = 0$.

The characteristic feature of the corresponding wave functions is that they obviously describe the volume-localized states which are basically confined to the central part of the potential, i.e., to the inner region of the fullerene $r \leqslant R_f$. The number of such states increases as the potential well becomes deeper, which happens when the charge Z of the fullerene grows.

An interesting issue is actually how high the value of an electric charge that a fullerene can carry is. In practice, one can multiply ionize C_{60} with the help of highly charged ions, fast electrons, or photons [7]. Experimentally, charged fullerenes in the range of $Z = 0, \ldots, 9e$ [13], and even up to $Z = 10e$ [11], were produced in collisions of a beam of C_{60} with a beam of highly ionized Xe atoms; such charged fullerenes are stable on a timescale of several microseconds. The highest value, $Z = 12e$, was observed for a charged fullerene (with the lifetime of the order of 1 μs) ionized by intense short infrared laser pulses [12]. The theoretic analysis of the Coulomb stability of highly charged fullerenes [14,15] predicted the limiting value $Z = 18e$ on the basis of a conducting sphere model, whereas the existence of $Z = 14e$ was established theoretically [16–19] by means of density functional theory (DFT). However, the predicted lifetime falls drastically, by ten orders, when Z increases from 11 to 14.

III. ANALYTIC POTENTIAL FOR A CHARGED FULLERENE

The model above provides a rather simplified description in the sense that it does not take into account the actual physical structure of a fullerene. A more realistic potential $U(r)$ can be constructed in the framework of the jellium model [32–37] as a sum of the positive contribution of the carbon atom's nuclei located on the spherical surface of the fullerene radius R_f and the negative contribution of the electron clouds. The resulting potential is attractive, and it has a cusp-shaped form with clear localization in the thin spherical shell. For C_{60}, the corresponding Lorentz-bubble potential reads

$$U(r) = -\frac{\frac{\hbar^2}{m_e} V}{(r - R)^2 + d^2}, \tag{7}$$

where the parameter V determines the depth, d is the width, and R is the position. In the self-consistent spherical jellium model based on the Kohn-Sham equations, these parameters are fixed [37] to the values

$$V = 0.711, \qquad R = 6.627a_0, \qquad d = 0.610a_0. \tag{8}$$

TABLE I. Electron energy levels for model potential (7). Notation: n is the level number, l is the angular quantum number, and i is the radial quantum number.

n	l	i	E (a.u.)	n	l	i	E (a.u.)
1	0	1	−0.93858	7	6	1	−0.45503
2	1	1	−0.91502	8	7	1	−0.29839
3	2	1	−0.86809	9	8	1	−0.12197
4	3	1	−0.79812	10	0	2	−0.05641
5	4	1	−0.70558	11	1	2	−0.02985
6	5	1	−0.59101	12	2	2	−0.00130

In order to test the computational methods used in this paper, we found the energy levels E for different values of the angular quantum number l by integrating the Schrödinger equation (1) numerically. The results (see Table I) reproduce the findings of [37]. In contrast to the volume-localized feature of the wave functions for the model (3), the states for the potential (7) mostly have a typical surface-localized behavior. At the center of a fullerene, the value $U(0) = -0.016$ a.u. $= -0.44$ eV is only slightly below zero, and hence, only a few discrete levels with the negative energy higher than that value correspond to the volume-localized states.

Coming to the case of a charged fullerene, let us now modify the Lorentz-bubble potential (7) by including the contribution of the charged spherical surface (3). The generalization of the potential (7) for a charged fullerene model then reads

$$U(r) = -\frac{\frac{\hbar^2}{m_e} V}{(r - R)^2 + d^2} - Z\Phi(r), \tag{9}$$

where Z is the charge of the fullerene.

With such a modification, the central part of the potential deepens, so that $U(0) = -0.17$ a.u. $= -4.5$ eV already for $Z = 1e$, whereas $U(0) = -0.77$ a.u. $= -20.9$ eV for $Z = 5e$, and $U(0) = -1.52$ a.u. $= -41.5$ eV for $Z = 10e$. As a result, there are two types of wave functions for the modified potential (9): the lower-energy states are distinctly surface localized, whereas the higher-energy levels correspond to the volume-localized quantum states.

We find the discrete quantum energy levels of an electron in the potential (9) by integrating the Schrödinger equation (1) numerically. The corresponding results for different values of the fullerene charge Z are presented in Tables II–IV and Figs. 1–5. We limit ourselves to the first 12 eigenvalues.

TABLE II. Electron energy levels for charged fullerene potential (9) with $Z = 1e$. Notation: n is the level number, l is the angular quantum number, and i is the radial quantum number.

n	l	i	E (a.u.)	n	l	i	E (a.u.)
1	0	1	−1.08421	7	6	1	−0.59927
2	1	1	−1.06058	8	7	1	−0.44209
3	2	1	−1.01352	9	8	1	−0.26499
4	3	1	−0.94336	10	0	2	−0.18757
5	4	1	−0.85057	11	1	2	−0.14965
6	5	1	−0.73566	12	2	2	−0.10580

TABLE III. Energy levels for charged fullerene potential (9) with $Z = 5e$. Notation: n is the level number, l is the angular quantum number, and i is the radial quantum number.

n	l	i	E (a.u.)	n	l	i	E (a.u.)
1	0	1	−1.66770	7	6	1	−1.17767
2	1	1	−1.64384	8	7	1	−1.01862
3	2	1	−1.59630	9	8	1	−0.83915
4	3	1	−1.52544	10	0	2	−0.75648
5	4	1	−1.43170	11	1	2	−0.69300
6	5	1	−1.31558	12	9	1	−0.64014

It is known that for the choice of parameters (8), the depth of the potential well (7) is too large, and the calculated energy levels are not in agreement with the experimental value of the electron affinity 2.65 eV for C_{60}. This issue was discussed in [23,35–37] for different model potentials in order to bring theory to better agreement with experiment. By making use of the improved parameter set $V = 0.1104$, $R = 6.665a_0$, $d = 0.5a_0$, one finds an essentially shallower potential with a value at the center $U(0) = -0.0025$ a.u. that correctly reproduces the 2.65 eV detachment energy for the neutral C_{60} molecule [37]. For such an improved parameter choice, the central part of the potential (9) for charged fullerene is shifted to $U(0) = -1.5\,\text{a.u.} = -4.1\,\text{eV}$ for $Z = 1e$, to $U(0) = -0.75\,\text{a.u.} = -20.5\,\text{eV}$ for $Z = 5e$, and to $U(0) = -1.5\,\text{a.u.} = -40.8\,\text{eV}$ for $Z = 10e$. Notice that with an increase of the electric charge Z, the form of the model potential changes very little when the parameters (8) are replaced by an improved parameter set. As a result, the numerical analysis of the electronic spectrum for charged fullerenes with the improved set of parameters of the model potential confirms the existence of the volume-localized states, predicting slightly shifted theoretic values of the corresponding energy levels.

The spherically symmetric analytical model potential (9) can be compared with the result derived from DFT computations. Figure 6 shows the potential's behavior along the radial direction through the carbon atom ("atom" curve) and through the center between neighboring atoms ("middle" curve); averaging over the angles yields better agreement. Furthermore, one can directly confirm the existence of the volume-localized states by making use of the QUANTUM ESPRESSO package; the results of the corresponding DFT computations are presented in Fig. 7, and it is satisfactory to see the consistency with the results in Fig. 4 obtained in the framework of the model potential approach.

TABLE IV. Electron energy levels for charged fullerene potential (9) with $Z = 10e$. Notation: n is the level number, l is the angular quantum number, and i is the radial quantum number.

n	l	i	E (a.u.)	n	l	i	E (a.u.)
1	0	1	−2.39903	7	6	1	−1.90343
2	1	1	−2.37490	8	7	1	−1.74240
3	2	1	−2.32685	9	8	1	−1.56053
4	3	1	−2.25520	10	0	2	−1.49334
5	4	1	−2.16040	11	1	2	−1.41574
6	5	1	−2.04296	12	9	1	−1.35854

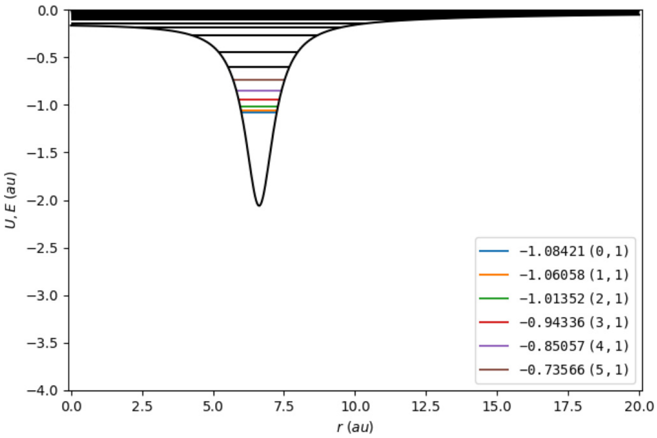

FIG. 1. Spectrum for charged fullerene potential (9) with $Z = 1e$.

IV. ONIONLIKE FULLERENE

Onion (or onionlike) structures represent a highly interesting class of carbon systems which are obtained when fullerenes are concentrically enclosed one in another to form a double-, triple-, or, in general, multilayer object. Each (quasi)spherical layer is a fullerene (C_{60}, C_{240}, C_{540}, C_{960}, …), with the separation between shells equal to 0.335 nm, which is slightly larger than the distance between the planar layers in graphite crystals. The outer diameter of a typical 5–15-layer onion ranges between 4 and 10 nm, with the radius of the innermost layer equal to R_f; however, smaller and much larger onionlike structures are also observed. Following the first observation [38] of spherical multilayer structures, the concept of a "carbon onion" was coined in 1992 when the formation of the onionlike spherical particles was demonstrated by heating nanotubes with an electron beam [39–41]. Since then, the physical and chemical characteristics of carbon onions have been analyzed in numerous theoretical and experimental studies [42–45]; see the reviews in [46–54] for further information on the

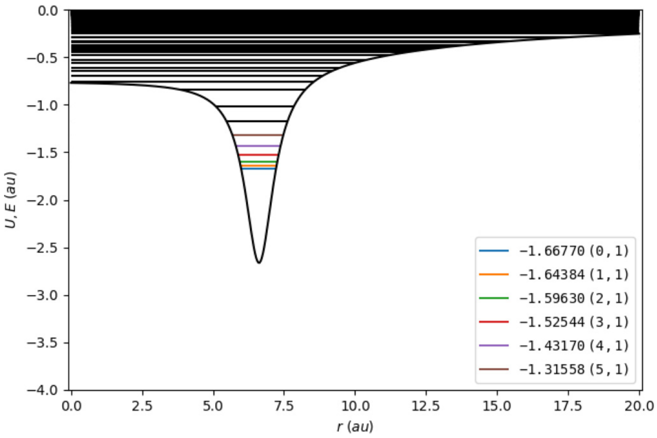

FIG. 2. Spectrum for charged fullerene potential (9) with $Z = 5e$.

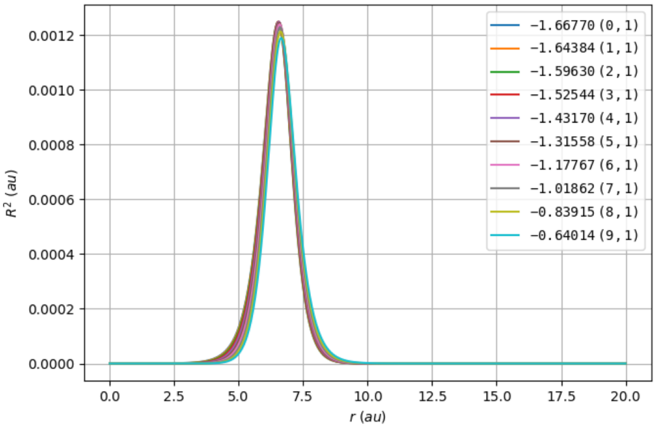

FIG. 3. Surface-localized wave functions for charged fullerene potential (9) with $Z = 5e$.

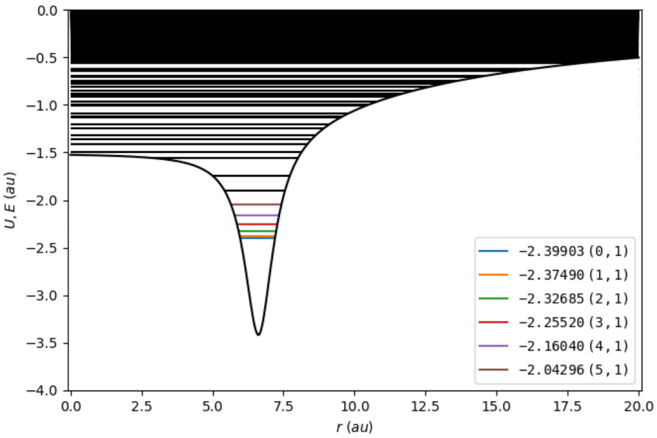

FIG. 5. Spectrum for charged fullerene potential (9) with $Z = 10e$.

production; geometrical, physical, and chemical properties; and applications of onionlike carbon structures.

In the context of the current investigation of the energy spectrum of charged carbon complexes, the onionlike structures are qualitatively different from the usual fullerenes in the sense that, in contrast to the latter case in which the electric charge is smeared only over the surface of the fullerene's hollow sphere, in the former case the electric charge is distributed in the volume of an onion sphere in its many internal layers.

Accordingly, in the simplest model for the study of discrete-volume levels of electrons in multilayer onionlike charged fullerenes (somewhat similar to the simplest model (5) and (6) of a rectangular spherical well for a fullerene), one can look for analytic estimates by assuming a homogeneous density when the charges of consecutive layers of the onion structure are proportional to the cube of the layer radius. In this case, the potential energy of an electron in an electrostatic field is as follows:

$$U(r) = -\frac{Ze}{4\pi\varepsilon_0}\begin{cases}\frac{1}{2R}\left(3-\frac{r^2}{R^2}\right), & r \leqslant R,\\ \frac{1}{r}, & r > R.\end{cases} \qquad (10)$$

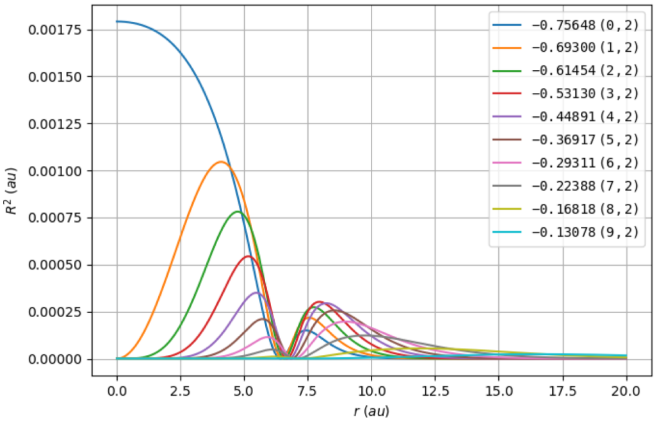

FIG. 4. Volume-localized wave functions for charged fullerene potential (9) with $Z = 5e$.

Here Z is the total positive charge of an onion structure, and $R = R_{\mathrm{on}}$ is its outer radius. As the first step to understand the spectrum structure, we approximate the potential by extending the piece inside the sphere $r \leqslant R$ to all values of the radius:

$$U(r) = -U_0 + \tfrac{1}{2}\, m_e \omega^2 r^2, \qquad (11)$$

where we denoted

$$U_0 = \frac{3}{2}\frac{Ze}{4\pi\varepsilon_0 R_{\mathrm{on}}}, \qquad \omega = \sqrt{\frac{Ze}{4\pi\varepsilon_0 m_e R_{\mathrm{on}}^3}}. \qquad (12)$$

The maximal specific charge Z/N_{tot} of onionlike structures (where N_{tot} is the total number of atoms) before their decay would be smaller than that for C_{60}, but the absolute value of the charge can be much larger. Accordingly, the depth of the potential well U_0 of an electron in the field of a positively charged onion structure then can reach values of the order of 100 eV, thereby increasing the significance of the volume-localized quantum states. For the approximate potential (10), one can evaluate the energy spectrum analytically by making

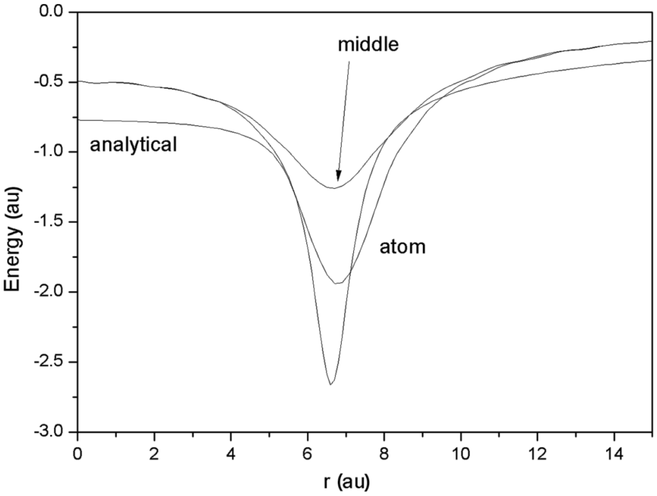

FIG. 6. Comparison of the analytical potential of the charged fullerene (9) for $Z = 5e$ with the DFT result: along the radial direction through the carbon atom ("atom" curve) and through the center between neighboring atoms ("middle" curve).

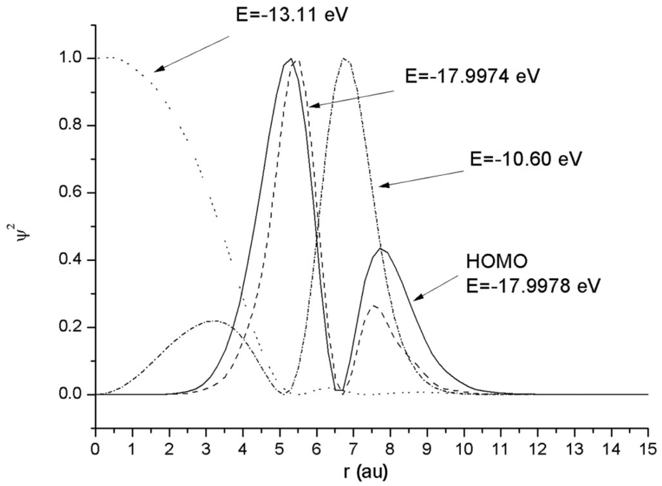

FIG. 7. Wave functions obtained with the help of the DFT computations for a charged C_{60} fullerene with $Z = 5e$: both the surface-localized (solid and dashed curves) and the volume-localized (dotted and dash-dotted curves) states are found. For convenience of comparison, the wave functions are shown by normalizing their maximal values to unity.

use of the well-known solution of the Schrödinger equation for the spherical oscillator [31]. For energy levels we find

$$E = E_0 + \hbar\omega(2i + l - 2), \tag{13}$$

$$E_0 = \frac{3}{2}\sqrt{\frac{Ze}{4\pi\varepsilon_0 R_{\text{on}}}}\left(\sqrt{\frac{\hbar^2}{m_e R_{\text{on}}^2}} - \sqrt{\frac{Ze}{4\pi\varepsilon_0 R_{\text{on}}}}\right), \tag{14}$$

whereas the wave functions of the corresponding stationary states are

$$\psi_{nlm} = \text{const}\, r^l \exp\left(-\frac{\lambda r^2}{2}\right) Y_{lm}(\theta, \varphi) \times {}_1F_1\left(1 - i, l + \frac{3}{2}, \lambda r^2\right), \tag{15}$$

where ${}_1F_1$ is the degenerate hypergeometric function,

$$\lambda = \frac{m_e\omega}{\hbar} = \sqrt{\frac{Ze\, m_e}{4\pi\varepsilon_0 \hbar^2 R_{\text{on}}^3}}, \tag{16}$$

the radial quantum number $i = 1, 2, \ldots$, the angular quantum number $l = 0, 1, 2, \ldots$, and $m = 0, \pm 1, \ldots, \pm l$.

As a particular application, let us consider a model of a five-layer charged onion fullerene with $Z = 55e$ and size $R_{\text{on}} = 5R_f$. The total charge arises from the assumption of the homogeneous distribution of the electric charge on the inner layers proportional to the second power radius of the layer. The corresponding energy levels (13) for such an onion model are presented in Table V. The well-known degeneracy properties of an oscillator spectrum are manifest. It is instructive to compare these analytic estimates with the results of the numeric integration of the Schrödinger equation for a five-layered onion structure which are given in Figs. 8–11 and in Tables VI and VII for different values of the positive charge of the layers.

TABLE V. Electron energy levels (13) for an onionlike fullerene potential (10) with $Z = 55$ and $R_{\text{on}} = 33.135a_0$. Notation: n is the level number, l is the angular quantum number, and i is the radial quantum number.

n	l	i	E (a.u.)	n	l	i	E (a.u.)
1	0	1	−2.48981	7	2	2	−2.45093
2	1	1	−2.41205	8	0	3	−2.37316
3	2	1	−2.33428	9	4	1	−2.29540
4	0	2	−2.25652	10	3	2	−2.21763
5	3	1	−2.17875	11	1	3	−2.13987
6	1	2	−2.10099	12	5	1	−2.06211

Theoretical analysis of the structure of discrete levels for electrons in the field of positively charged single- and multilayer fullerenes suggests the existence of a system of quantum transitions with the emission of photons within a wide range of energies that depends on the magnitude of the charge and the lifetime of the levels in the range from 21 ns to 21 fs.

In order to make estimates, let us recall that the characteristic lifetime for the spontaneous dipole transition is determined by the well-known expression for the photon emission rate

$$P_{\text{fi}} = \frac{\omega^3}{3\pi\varepsilon_0\hbar c^3}|d_{\text{fi}}|^2, \tag{17}$$

where ω is the emission frequency and d_{fi} is the matrix element of the dipole transition from an initial (i) to a final (f) state. One can roughly estimate the order of magnitude of d_{fi} for transitions between the volume-localized discrete levels as eR_f for charged fullerenes and as eR_{on} for onionlike structures. These processes may occur during pulse charging of fullerenes or in the process of irradiation of already charged fullerenes by a flow of electrons and ions. Experimental confirmation of the existence of volume-localized discrete levels is of great interest for experimental research and practical problems, including the development of new sources of coherent radiation in a wide range of wavelengths.

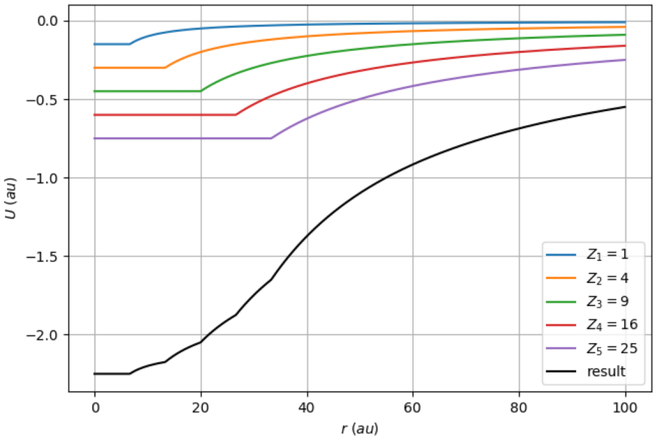

FIG. 8. Model of charged onionlike fullerene: contributions of layers and the resulting potential (19) with regular charge distribution (21).

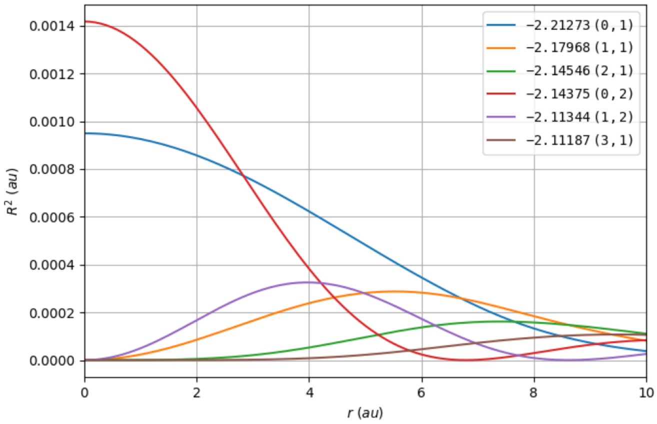

FIG. 9. Wave functions for charged onionlike fullerene model potential (19) with regular charge distribution (21).

Simple numeric estimates are straightforward. Substituting the approximation $|d_{\rm fi}| \sim eR_f$, we recast (17) into

$$P_{\rm fi} = \frac{4(6.627)^2}{3\alpha}\frac{c}{\bar{\lambda}_e}\left(\frac{\Delta E}{m_e c^2}\right)^3. \qquad (18)$$

Here we assumed $R_f = 6.627a_0$ for the radius of the fullerene. As a result, we find for different energy transitions $P_{\rm fi}(\Delta E = 1\,{\rm eV}) = 4.67 \times 10^7\,{\rm s}^{-1}$, $P_{\rm fi}(\Delta E = 10\,{\rm eV}) = 4.67 \times 10^{10}\,{\rm s}^{-1}$, $P_{\rm fi}(\Delta E = 100\,{\rm eV}) = 4.67 \times 10^{13}\,{\rm s}^{-1}$. More accurate estimates for transition rates in the system of discrete volume-localized levels of an electron in the field of a positively charged fullerene can be derived from the evaluation of the value $\langle er\rangle$ by making use of the wave functions of the spherical oscillator (15). The characteristic length of the exponential decay part of the wave function is then found as $1/\sqrt{\lambda} = (R_{\rm on}^3 a_0 e/Z)^{1/4}$.

To complete the discussion of the onionlike structures, it is important to analyze the possible values of Z for onion fullerenes. The corresponding experimental and theoretical results on the limiting values of the positive electric charge for ionized onionlike fullerenes are lacking. Nevertheless, one can make some simple estimates for the highest value of the charge by evaluating the critical value of the field strength on the outer spherical layer of an onion fullerene.

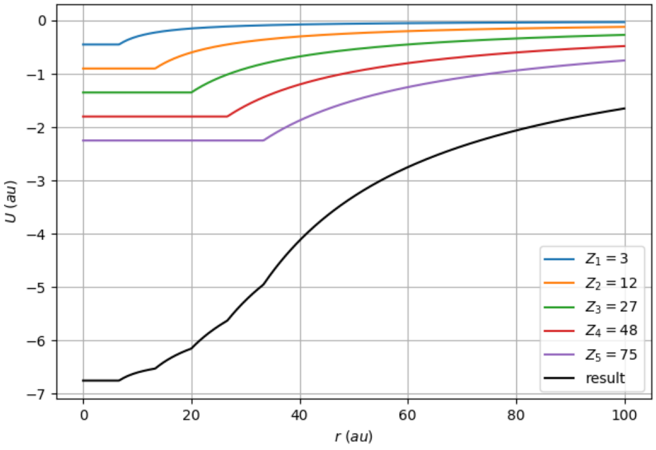

FIG. 10. Model of charged onionlike fullerene: contributions of layers and the resulting potential (19) with irregular charge distribution (22).

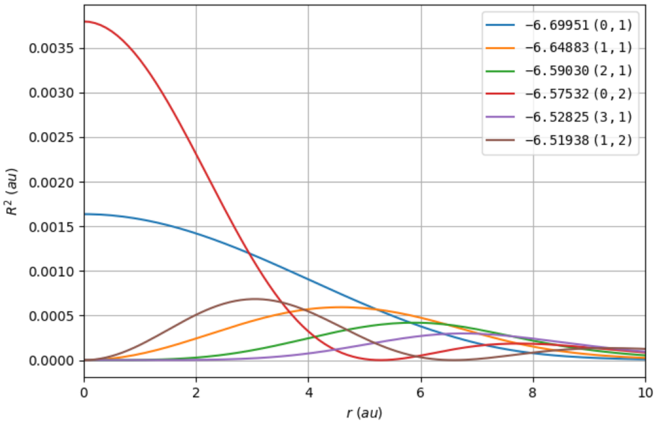

FIG. 11. Wave functions for charged onionlike fullerene model potential (19) with irregular charge distribution (22).

In order to do this, we start with the case of an ordinary fullerene and notice that, for a positive charge Z on it, the value of the electric field strength reads $\mathcal{E} = \frac{Z}{4\pi\varepsilon_0 R_f^2}$, evaluated at the spherical surface of a fullerene, before it becomes unstable due to the field ion emission. Taking $R_f = 6.627a_0$ and $Z = 12e$ in the fullerene C_{60}, we find for the field strength $\mathcal{E} = 1.38 \times 10^{11}$ V/m. This is smaller than the critical value (evaporation field) for the carbon $\mathcal{E}_{\rm max} = 1.48 \times 10^{11}$ V/m, above which the ion field emission starts [55,56]. One can reasonably assume that this field value should also not be exceeded for the onionlike structures.

We thus can formulate the simple criterion $\mathcal{E} \lesssim \mathcal{E}_{\rm max}$ for the stability of a charged multilayer onion fullerene, with the help of which we can derive a rough estimate of the corresponding maximal possible total positive charge $Z = Ne$. In particular, applying this scheme to the five-layer onion structure with $R_{\rm on} = 5R_f$ and $N = \sum_i N_i = 55$, we find $\mathcal{E} = 2.64 \times 10^{10}$ V/m, which is well below the threshold value. In a similar way, we can evaluate the limiting charge for onionlike structures with an arbitrary number of layers.

Obviously, such a semiempirical estimate is very approximate and needs to be further refined on the basis of the microscopic calculations or the experimental measurements.

TABLE VI. Electron energy levels for charged onionlike fullerene model potential (19) with regular charge distribution (21). Notation: n is the level number, l is the angular quantum number, and i is the radial quantum number.

n	l	i	E (a.u.)	n	l	i	E (a.u.)
1	0	1	−2.21273	7	2	2	−2.08023
2	1	1	−2.17968	8	4	1	−2.07870
3	2	1	−2.14546	9	0	3	−2.07677
4	0	2	−2.14375	10	5	1	−2.04537
5	1	2	−2.11344	11	3	2	−2.04468
6	3	1	−2.11187	12	1	3	−2.04256

TABLE VII. Electron energy levels for charged onionlike fullerene model potential (19) with irregular charge distribution (22). Notation: n is the level number, l is the angular quantum number, and i is the radial quantum number.

n	l	i	E (a.u.)	n	l	i	E (a.u.)
1	0	1	−6.69951	7	2	2	−6.47005
2	1	1	−6.64883	8	0	3	−6.46943
3	2	1	−6.59030	9	4	1	−6.46691
4	0	2	−6.57532	10	3	2	−6.41962
5	3	1	−6.52825	11	1	3	−6.41376
6	1	2	−6.51938	12	5	1	−6.40848

V. NUMERIC ANALYSIS OF ONIONLIKE FULLERENE MODEL

The analytic model which we considered in the previous section treats a charged onion fullerene as a homogeneously charged solid sphere. In other words, in such an approach the internal structure is not taken into account. In order to improve the picture, we replace the model (10) with a potential that explicitly describes an onion fullerene as a multilayer structure with the concentric charged spheres enclosed in one another. For concreteness, let us consider a simple model of an onionlike fullerene with five layers. We construct the corresponding potential in the form of a superposition of the five Coulomb-like contributions (3) coming from each of the charged spherical shells:

$$U(r)=\sum_{k=1}^{5}U_k(r), \tag{19}$$

where

$$U_k(r)=-\frac{N_k e^2}{4\pi\varepsilon_0}\begin{cases}\frac{5}{kR_{\rm on}}, & r\leqslant \frac{k}{5}R_{\rm on},\\ \frac{1}{r}, & r>\frac{k}{5}R_{\rm on}.\end{cases} \tag{20}$$

Here $Z_k = N_k e$ is the charge on layer number $k = 1, 2, \dots, 5$. The choice of the values of the electric charge on shells is a highly nontrivial issue which basically should be determined by the physical procedure used to charge the layers. Below, we analyze the two options.

A. Regular charge distribution

Suppose one can arrange a charged onion structure in such a way that it closely reproduces a model of a uniformly charged solid sphere. We will call this a regular charge distribution. In this case, the values of the charge on the shells are proportional to the square of the layer's radius:

$$N_1=1,\ N_2=4,\ N_3=9,\ N_4=16,\ N_5=25. \tag{21}$$

The resulting potential $U(r)$ and its constituents (15) are shown in Fig. 8. The spectrum is presented in Fig. 9 and Table VI. The numerical computations should be compared to the estimates obtained on the basis of the analytical model which we studied in the previous section. The data in Tables V and VI are in very good agreement.

Although the total charge of such an onion fullerene $Z = 55e$ is large, the resulting specific charge (per total number of atoms) is actually smaller than that of the maximally charged C_{60}. Moreover, even with such a large total charge, this onion fullerene model satisfies the simple criterion of stability since the electric field on its boundary does not exceed the critical value for carbon.

B. Irregular charge distribution

Obviously, it is a highly nontrivial technical problem to produce a regularly charged onion fullerene. It is more likely that, in practice, in the course of an actual experimental laboratory setup, an onion structure can be charged in only an irregular way. In that case, one should expect to find that the charges on each shell would have more or less arbitrary values. In order to analyze the corresponding spectrum numerically, let us choose

$$N_1=3,\ N_2=12,\ N_3=27,\ N_4=48,\ N_5=75. \tag{22}$$

The resulting potential $U(r)$ and its constituents (15) are shown in Fig. 10. The spectrum is presented in Fig. 11, and the first energy eigenvalues for the irregular choice are listed in Table VII.

For such an irregularly charged onion fullerene, the total charge is $Z = 165e$, and the value of the electric field strength in the outer boundary $\mathcal{E} = 7.6\times10^{10}$ V/m is well below the stability limit. As a certain self-consistency test, one can verify that, keeping the same total charge, the mostly positive area is at the surface (the outmost shell) of an onionlike fullerene, which results in a shallower well with a smaller depth of the potential at the center.

VI. DISCUSSION AND CONCLUSION

In the framework of a simple physical model, we demonstrated the existence of a system of discrete short-lifetime quantum levels for electrons in the potential well of the self-consistent Coulomb field of charged fullerenes and onionlike structures. For electrons, in the case of positively charged fullerenes and onionlike structures, the energy of the volume-localized levels ranges from 1 to 100 eV.

We use an idealized spherically symmetric model potential in our study. As one knows, geometrically, a C_{60} fullerene is a truncated icosahedron with carbon atoms located in its 60 equivalent vertices. Such a geometrical shape is very close to a sphere, and it is possible to use the spherical harmonics to describe the electronic structure of a neutral C_{60} in terms of free electrons on a sphere of radius R. The corresponding symmetries of the icosahedron group are $\Gamma_{60} = A_g + T_{1g} + 2T_{1u} + T_{2g} + 2T_{2u} + 2G_g + 2G_u + 3H_g + 2H_u$, and with the help of a simple Hückel scheme one can calculate the eigenvalues and degeneracies of this system [57]. (In fact, the first such calculation by Bochvar and Gal'pern [58] predicted the existence of stable carbon structures with icosahedron geometry a decade before the experimental discovery of fullerenes.) The Hückel scheme calculation is perfectly consistent with the density functional theory computation [59] that explicitly demonstrates the correspondence of A_g, T_{1u}, H_g, $T_{2u}+G_u$ to $l = 0, 1, 2, 3$ ($1s$, $1p$, $1d$, $1f$) states, respectively; see also [60] for higher angular quantum numbers up to $l = 9$.

It is worthwhile to mention that the electronic structure of fullerenes (and, in general, interaction of electrons and photons with fullerenes and fullerenelike systems) is widely studied by means of simple model potentials. In particular, along with the square-well-type potentials one considers the Dirac bubble and Gaussian-type potentials and models the fullerene cage by a spherical jellium shell [61–68]. Previous discussions have mostly focused on neutral systems, whereas here we have analyzed the case of positively charged fullerenes and onionlike structures.

The results obtained provide a consistent qualitative picture both for the charged fullerenes and for the onionlike structures. In order to refine our very approximate findings, further investigation on the basis of the microscopic calculations, as well as the experimental measurements, is certainly needed.

Experimental confirmation of the existence of volume-localized discrete levels would be of great interest for experimental research and practical problems, including the development of new sources of coherent radiation in a wide range of wavelengths.

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[1] W. H. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, C_{60}: Buckminsterfullerene, Nature (London) **318**, 162 (1985).

[2] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, Solid C_{60}: A new form of carbon, Nature (London) **347**, 354 (1990).

[3] A. V. Eletskii and B. M. Smirnov, Fullerenes and carbon structures, Phys. Usp. **38**, 935 (1995).

[4] A. Hirsch and M. Brettreich, *Fullerenes: Chemistry and Reactions* (Wiley-VCH, Weinheim, 2005).

[5] *Handbook of Nanophysics: Clusters and Fullerenes*, edited by K. D. Sattler (CRC Press, Boca Raton, FL, 2011).

[6] *Nanomaterials Handbook*, 2nd ed., edited by Yu. Gogotsi (CRC Press, Boca Raton, FL, 2017).

[7] E. E. B. Campbell, *Fullerene Collision Reactions* (Kluwer Academic, New York, 2004).

[8] P. P. Radi, M.-T. Hsu, M. E. Rincon, P. R. Kemper, and M. T. Bowers, On the structure, reactivity and relative stability of the large carbon cluster ions C_{62}^+, C_{60}^+ and C_{58}^+, Chem. Phys. Lett. **174**, 223 (1990).

[9] N. Troullier and J. L. Martins, Structural and electronic properties of C_{60}, Phys. Rev. B **46**, 1754 (1992).

[10] K. Yabana and G. F. Bertsch, Electronic structure of C_{60} in a spherical basis, Phys. Scr. **48**, 633 (1993).

[11] A. Brenac, F. Chandezon, H. Lebius, A. Pesnelle, S. Tomita, and B. A. Huber, Multifragmentation of highly charged C_{60} ions: Charge states and fragment energies, Phys. Scr. **T80B**, 195 (1999).

[12] V. R. Bhardwaj, P. B. Corkum, and D. M. Rayner, Internal Laser-Induced Dipole Force at Work in C_{60} Molecule, Phys. Rev. Lett. **91**, 203004 (2003).

[13] J. Jensen, H. Zettergren, H. T. Schmidt, H. Cederquist, S. Tomita, S. B. Nielsen, J. Rangama, P. Hvelplund, B. Manil, and B. A. Huber, Ionization of C_{70} and C_{60} molecules by slow highly charged ions: A comparison, Phys. Rev. A **69**, 053203 (2004).

[14] H. Zettergren, H. T. Schmidt, H. Cederquist, J. Jensen, S. Tomita, P. Hvelplund, H. Lebius, and B. A. Huber, Static over-the-barrier model for electron transfer between metallic spherical objects, Phys. Rev. A **66**, 032710 (2002).

[15] H. Zettergren, J. Jensen, H. T. Schmidt, and H. Cederquist, Electrostatic model calculations of fission barriers for fullerene ions, Eur. Phys. J. D **29**, 63 (2004).

[16] S. Díaz-Tendero, M. Alcamí, and F. Martín, Coulomb Stability Limit of Highly Charged C_{60}^{q+} Fullerenes, Phys. Rev. Lett. **95**, 013401 (2005).

[17] S. Díaz-Tendero, M. Alcamí, and F. Martín, Structure and electronic properties of highly charged C_{60} and C_{58} fullerenes, J. Chem. Phys. **123**, 184306 (2005).

[18] R. Sahnoun, K. Nakai, Y. Sato, H. Kono, Y. Fujimura, and M. Tanaka, Theoretical investigation of the stability of highly charged C_{60} molecules produced with intense near-infrared laser pulses, J. Chem. Phys. **125**, 184306 (2006).

[19] R. Sahnoun, K. Nakai, Y. Sato, H. Kono, Y. Fujimura, and M. Tanaka, Stability limit of highly charged C_{60} cations produced with an intense long-wavelength laser pulse: Calculation of electronic structures by DFT and wavepacket simulation, Chem. Phys. Lett. **430**, 167 (2006).

[20] G. S. Iroshnikov, Calculation of the cross section for charge transfer in fullerene-fullerene collisions, J. Exp. Theor. Phys. **103**, 707 (2006).

[21] G. S. Iroshnikov, Calculation of the cross section for charge transfer in $C_{70}^+ + C_{60}$ fullerene-fullerene collisions, J. Exp. Theor. Phys. **105**, 706 (2007).

[22] H. Kono, K. Nakai, and N. Niitsu, Ab initio molecular dynamics of highly charged fullerene cations in intense near-infrared laser fields, Proc. SPIE **6726**, 672606 (2007).

[23] M. E. Madjet, H. S. Chakraborty, J. M. Rost, and S. T. Manson, Photoionization of C_{60}: A model study, J. Phys. B **41**, 105101 (2008).

[24] E. M. Nascimento, F. V. Prudente, M. N. Guimarães, and A. M. Maniero, A study of the electron structure of endohedrally confined atoms using a model potential, J. Phys. B **44**, 015003 (2011).

[25] R. G. Polozkov, V. K. Ivanov, and A. V. Solov'yov, Photoionization of the fullerene ion C_{60}^+, J. Phys. B **38**, 4341 (2005).

[26] R. G. Polozkov, V. K. Ivanov, A. V. Verkhovtsev, A. V. Korol, and A. V. Solov'yov, New applications of the jellium model for the study of atomic clusters, J. Phys.: Conf. Ser. **438**, 012009 (2013).

[27] M. Lüders, A. Bordoni, N. Manini, A. Dal Corso, M. Fabrizio, and E. Tosatti, Coulomb couplings in positively charged fullerene, Philos. Mag. B **82**, 1611 (2009).

[28] D. Liu, N. Iwahara, and L. F. Chibotaru, Dynamical Jahn-Teller effect of fullerene anions, Phys. Rev. B **97**, 115412 (2018).

[29] Y. Wang, M. Alcamí, and F. Martín, Stability of charged fullerenes, in *Handbook of Nanophysics: Clusters and Fullerenes*, edited by K. D. Sattler (CRC Press, Boca Raton, FL, 2011), p. 25.

[30] R. V. Arutyunyan, Theoretical investigation of electronic properties of highly charged fullerenes, Nuclear Safety Institute, Report No. IBRAE-2018-08, 2018 (unpublished).

[31] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Nonrelativistic Theory*, 3rd ed. (Pergamon, Oxford, 1977).

[32] A. Rubio, J. A. Alonso, J. M. López, and M. J. Stott, Collective electronic excitations in metal coated C_{60}, Phys. Rev. B **49**, 17397 (1994).

[33] V. K. Ivanov, G. Yu. Kashenock, R. G. Polozkov, and A. V. Solov'yov, Photoionization cross sections of the fullerenes C_{20} and C_{60} calculated in a simple spherical model, J. Phys. B **34**, L669 (2001).

[34] V. K. Ivanov, G. Yu. Kashenock, R. G. Polozkov, and A. V. Solov'yov, Method for calculating photoionization cross sections of fullerenes in the local density and random phase approximations, J. Exp. Theor. Phys. **96**, 658 (2003).

[35] A. K. Belyaev, A. S. Tiukanov, A. I. Toropkin, V. K. Ivanov, R. G. Polozkov, and A. V. Solov'yov, Photoabsorption of the fullerene C_{60} and its positive ions, Phys. Scr. **80**, 048121 (2009).

[36] A. V. Verkhovtsev, R. G. Polozkov, V. K. Ivanov, A. V. Korol, and A. V. Solov'yov, Hybridization-related correction to the jellium model for fullerenes, J. Phys. B **45**, 215101 (2012).

[37] A. S. Baltenkov, S. T. Manson, and A. Z. Msezane, Jellium model potentials for the C_{60} molecule and the photoionization of endohedral atoms, $A@C_{60}$, J. Phys. B **48**, 185103 (2015).

[38] S. Iijima, Direct observation of the tetrahedral bonding in graphitized carbon black by HREM, J. Cryst. Growth **50**, 675 (1980).

[39] D. Ugarte, Curling and closure of graphitic networks under electron-beam irradiation, Nature (London) **359**, 707 (1992).

[40] D. Ugarte, How to fill or empty a graphitic onion, Chem. Phys. Lett. **209**, 99 (1993).

[41] D. Ugarte, Onion-like graphitic particles, Carbon **33**, 989 (1995).

[42] M. S. Zwanger, F. Banhart, and A. Seeger, Formation and decay of spherical concentric-shell carbon clusters, J. Cryst. Growth **163**, 445 (1996).

[43] S. Tomita, M. Fujii, S. Hayashi, and K. Yamamoto, Electron energy-loss spectroscopy of carbon onions, Chem. Phys. Lett. **305**, 225 (1999).

[44] A. V. Okotrub, L. G. Bulusheva, A. I. Romanenko, V. L. Kuznetsov, Yu. V. Butenko, C. Dong, Y. Ni, and M. I. Heggie, Probing the electronic state of onion-like carbon, AIP Conf. Proc. **591**, 349 (2002).

[45] V. D. Blank, V. D. Churkin, B. A. Kulnitskiy, I. A. Perezhogin, A. N. Kirichenko, S. V. Erohin, P. B. Sorokin, and M. Yu. Popov, Pressure-induced transformation of graphite and diamond to onions, Crystals **8**, 68 (2018).

[46] O. A. Shenderova, V. V. Zhirnov, and D. W. Brenner, Carbon nanostructures, Crit. Rev. Solid State Mater. Sci. **27**, 227 (2002).

[47] B.-S. Xu, Prospects and research progress in nano onion-like fullerenes, New Carbon Mater. **23**, 289 (2008).

[48] Y. V. Butenko, L. Šiller, and M. R. C. Hunt, Carbon onions, in *Handbook of Nanophysics: Clusters and Fullerenes*, edited by K. D. Sattler (CRC Press, Boca Raton, FL, 2011), p. 34.

[49] C. Chang, B. Patzer, and D. Sülzle, Onion-like inorganic fullerenes, in *Handbook of Nanophysics: Clusters and Fullerenes*, edited by K. D. Sattler (CRC Press, Boca Raton, FL, 2011), p. 51.

[50] C. He and N. Zhao, Production of carbon onions, in *Handbook of Nanophysics: Clusters and Fullerenes*, edited by K. D. Sattler (CRC Press, Boca Raton, FL, 2011), p. 24.

[51] J. Bartelmess and S. Giordani, Carbon nano-onions (multi-layer fullerenes): Chemistry and applications, Beilstein J. Nanotechnol. **5**, 1980 (2014).

[52] V. Georgakilas, J. A. Perman, J. Tucek, and R. Zboril, Broad family of carbon nanoallotropes: Classification, chemistry, and applications of fullerenes, carbon dots, nanotubes, graphene, nanodiamonds, and combined superstructures, Chem. Rev. **115**, 4744 (2015).

[53] O. Mykhailiv, H. Zubyk, and M. E. Plonska-Brzezinska, Carbon nano-onions: Unique carbon nanostructures with fascinating properties and their potential applications, Inorg. Chim. Acta **468**, 49 (2017).

[54] Y. V. Butenko, L. Šiller, and M. R. C. Hunt, Carbon onions, in *Nanomaterials Handbook*, edited by Yu. Gogotsi (CRC Press, Boca Raton, FL, 2017), p. 392.

[55] E. W. Müller, Field ionization and field ion microscopy, Adv. Electron. Electron Phys. **13**, 83 (1960).

[56] R. G. Forbes, Field electron and ion emission from charged surfaces: A strategic historical review of theoretical concepts, Ultramicroscopy **95**, 1 (2003).

[57] P. W. Fowler and J. Woolrich, π-Systems in three dimensions, Chem. Phys. Lett. **127**, 78 (1986).

[58] D. A. Bochvar and E. G. Gal'pern, On hypothetic systems: Carbon-dodehaedron s-icosahedron and carbon-s-icosahedron, Dokl. Akad. Nauk USSR **209**, 610 (1973).

[59] S. Saito, A. Oshiyama, and Y. Miyamoto, Electronic structures of fullerenes and fullerides, in *Computational Approaches in Condensed-Matter Physics*, edited by S. Miyashita, M. Imada, and H. Takayama (Springer, Berlin, 1992), p. 22.

[60] A. V. Verkhovtsev, A. V. Korol, and A. V. Solov'yov, Quantum and classical features of the photoionization spectrum of C_{60}, Phys. Rev. A **88**, 043201 (2013).

[61] W. Jaskólski, Confined many-electron systems, Phys. Rep. **271**, 1 (1996).

[62] L. L. Lohr and M. Blinder, Electron photodetachment from a Dirac bubble potential. A model for the fullerene negative ion C_{60}^-, Chem. Phys. Lett. **198**, 100 (1992).

[63] M. J. Puska and R. M. Nieminen, Photoabsorption of atoms inside C_{60}, Phys. Rev. A **47**, 1181 (1993).

[64] M. Ya. Amusia, A. S. Baltenkov, and B. G. Krakov, Photodetachment of negative C_{60}^- ions, Phys. Lett. A **243**, 99 (1998).

[65] J. P. Connerade, V. K. Dolmatov, P. A. Lakshmi, and S. T. Manson, Electron structure of endohedrally confined atoms: Atomic hydrogen in an attractive shell, J. Phys. B **32**, L239 (1999).

[66] J. P. Connerade, V. K. Dolmatov, and S. T. Manson, A unique situation for an endohedral metallofullerene, J. Phys. B **32**, L395 (1999).

[67] G. Schrange-Kashenock, $4d \rightarrow 4f$ resonance in photoabsorption of cerium ion Ce^{3+} and endohedral cerium in fullerene complex $Ce@C_{82}^{+}$, J. Phys. B **49**, 185002 (2016).

[68] Z. Felfli and A. Z. Msezane, Simple method for determining fullerene negative ion formation, Eur. Phys. J. D **72**, 78 (2018).