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A New Model of Onion-Like Fullerenes and Their Polymers*

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Abstract. A new approach to modelling chains of onion-like structures, based on a recently proposed realization of δ'-point interactions by chains of onion-like geometric scatterers, is developed and rigorous expressions for the effective masses of both electrons and holes in such structures are derived. The approach is applied to onion-like fulerene structures. Numerical analysis is performed and the values of the effective masses thus obtained are in agreement with experimental estimates for fullerene polymers. The drastic differences between these effective masses and those in chains comprising single atoms modelled by δ-point interactions is explained.

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The electronic band structure of chains of C_{60} molecules was usually computed either by using the first principle methods [1] or on the basis of semi-empirical models [2]. Relevant measurements confirmed the one-dimensional character of such structures [3]. It was also shown that when the distances between the fullerene chains in solids are sufficiently long their electronic structures remain definitely one-dimensional. The discovery of concentric-shelled nested fullerenes [4] and a range of fullerene-related graphitic onions [5-6] opened new challenging perspectives in this field, thus suggesting the need of new simple but still realistic one-dimensional models for chains of such onion-like clusters.

In this situation it is worth recollecting that Avron *et al.* [7] have recently raised a model of complicated "geometric scatterers in the form of onions" arranged in

*This work is dedicated to Professor Alexander Derzhanski, DSci, Corresponding Member of the Bulgarian Academy of Sciences, on the occasion of his 70-th anniversary.

a periodic chain. The relevant energy-band structure of this abstract construction approximates in certain limited cases that one of a periodic array of the somehow exotic δ'-point interactions [8]. There is little resemblance between this δ' interaction and what its name suggests, so that it should not be confused with the derivative of the Dirac δ-function [9]. Contrary to earlier somewhat controversial realizations [10-12], Avron's new realization of the δ'-point interaction is going to be considered as a new paradigm in mathematical physics [13], the only flaw in such an assertion being the lack of relevant application to a working model of real physical object.

In what follows, we show that it is possible to adapt Avron's abstract construction to model chains of concentric-shell onion-like fullerene-type structures with an eye to their electronic energy band characteristics. In support of our choice of the effective-mass approach, it should be noted that fullerene is known to bond covalently with itself in polymers [14], and some rough estimates for the effective masses of the carriers in solid C_{60} have already been given [15].

The best method for the discussion of periodic structures seems to be the transfer matrix approach [16-18]. As we have shown [19], the most general expression for the effective masses of the carriers at the edges of allowed energy bands may be given in the form

$$m^*_{k=0,\pi/a} = \mp\frac{\hbar^2}{a^2}\frac{d}{dE}\Big[\frac{1}{2}\mathrm{Tr}M(E)\Big], \tag{1}$$

provided the transfer-matrix $M(E)$ for the relevant structure with lattice constant a is well defined. Here $\hbar k$ is the electron crystal momentum and the simple roots of the equations $\mathrm{Tr}M(E) = \pm 2$ correspond to the energy-band edges.

For the periodic attractive δ-point interactions the transfer-matrix approach to the effective-mass notion was already developed in our papers [19-21].

For the case of periodic δ'-point interactions totally different picture emerges. One finds

$$\frac{1}{2}\mathrm{Tr}M(x) = \cos x - Bx\sin x, \tag{2}$$

where $x = a(2mE)^{1/2}/\hbar$ and B, a parameter characterizing the structure under consideration, is related to the "strength" β of the δ'-point scatterer and the lattice constant a by $B = \beta/2a$. From equations (1) and (2) we finally arrive at

$$\frac{m*}{m}\Big|_{k=0,\pi/a} = \pm\big[(1+B).x^{-1}.\sin x + B\cos x\big], \tag{3}$$

which defines the effective masses m^*_e of the electrons and m^*_h of the holes for the respective band edges (m is the free-electron mass).

Numerical analysis of equation (3) leads to the behaviour of the effective masses shown in Figure 1, which demonstrates the dependence of the effective masses (calculated for the first energy gap) on the value of B. It is seen that the well

known empirical relation $m_h^* > m_e^*$ is a rigorously obtained result for models comprising δ'-interactions. Recently, we have also derived an inequality of this type for models with δ-point interactions [21], however in the latter case the values of the corresponding effective masses differ by an order of magnitude, as is seen from a comparison of the present Figure 1 with Figures 1, 2 and 3 from [21]. What is more, for the simple but rigorously derived model with δ'-scatterers we are here dealing with, we get surprisingly good agreement with semi-empirical estimates for the effective masses of the carriers, as given by Saito & Oshiyama [15]. Namely, taking $m_e^*/m = 1.3$, we obtain from Figure 1 that $m_h^*/m = 2.4$, which is very close to the mean value of the relelvant effective masses of the heavy and light holes, *i.e.* $(3.4 + 1.5)/2 = 2.45$.

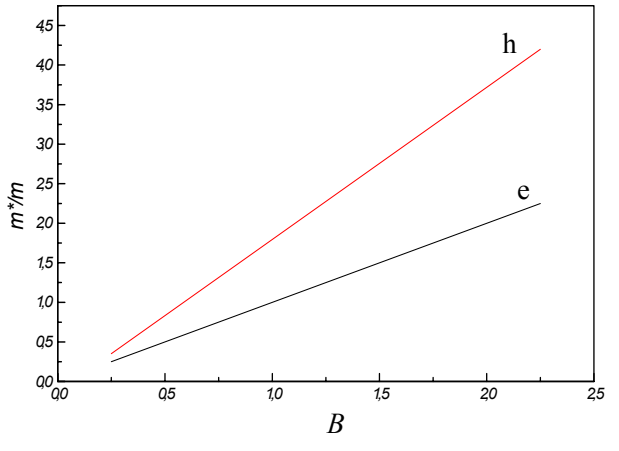

Figure 1. Effective masses of electrons and holes, calculated for different models characterised by the corresponding values of B.

The next question of interest is to clarify the possibility of using models with higher energy gaps. This might be essential *e.g.* for polymers comprising concentric-shell clusters of the type $Si_{60}@C_{60}$, see Gong and Zheng [22]. Figure 2 presents the effective masses of electrons and holes calculated for the first five energy gaps by a fixed *positive* value of B. Curiously enough, the essential characteristic feature of this type of model is that, *contrary* to the case of models with δ-function potentials, the effective mass of the *electrons* remains constant and is given by $m_e^*/m = B$ for *all* energy gaps. It is the effective mass of the holes that depends on the gap number n, and its value tends to m_e^* with increasing n.

Note that models with $B > 0$ correspond to energy-band pictures with $E > 0$ for all band edges. However, a physically meaningful situation may also arise for certain negative values of B, see [8]. For example, in the particular case $B = -0.5$, the effective mass of the *holes* takes the constant value $|B| = 0.5$,

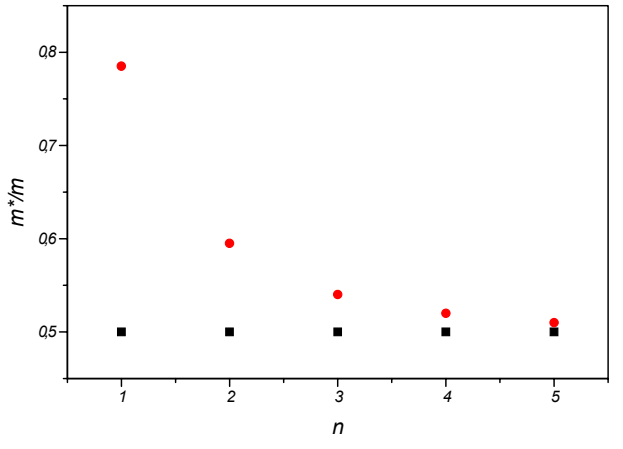

Figure 2. Effective masses of electrons (■) and holes (●) calculated for the first five energy gaps by $B = 0.50$.

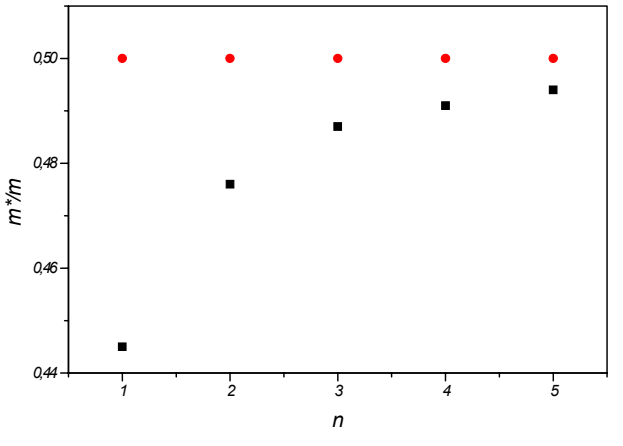

Figure 3. The same as in Figure 2 for the first five energy gaps by $B = -0.50$.

while the effective masses m_e^* of the electrons increase with n and tend to the value of m_h^*, compare Figures 2 and 3.

The demonstrated behavior of the effective masses is quite different from what is known for structures modelled by periodic δ-interactions. This difference corresponds to the difference in the energy-band pictures characterizing the two types of structures. In the case of periodic δ'-interactions the widths of the allowed bands remain approximately constant (their value being determined by the value of $|B|$), while the widths of the gaps increase with increasing n.

It should be noted that the new concentric-shell cluster $Si_{60}@C_{60}$ predicted re-

cently [22] offers new possibilities for the formation of the above considered fullerene-type polymers of concentric-shell onion-like clusters. Even chains of the recently discussed nested quasi-spherical fullerenes with additional heptagonal rings may be approached in a similar way due to the fact that, although the radii r_i in such quasi-spherical structures fluctuate, all fluctuations of r_i lie within a very small range [6].

Last but not least, as regards the complete theory of fullerene polymers in 3-dimensional Euclidean space, it is our feeling that the ordering of carbon atoms on 2-dimensional closed curved surfaces forming an onion-like fullerene-type structure, and the ordering of such clusters in a 1-dimensional chain of onion-like scatterers may be considered as one more example of *hierarchy*, *i.e.* different ordering schemes at different scales.

Of course, further work, both theoretical and experimental, is needed to clarify the limits of the proposed approach. We believe that the above introduced effective mass approach to structures modelled by chains of onion-like geometric scatterers is offers an attractive theoretical approach to the new field of onion-like fullerene-type polymers and their electrical properties.

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