

FRENKEL EXCITATIONS OF C_N (N=12,60) CLUSTERS

Stan F. Harlapenko, Slava V. Rotkin

*Ioffe Physico-Technical Institute, 26, Politechnicheskaya st.,
194021 St. Petersburg, Russia.* E-mail: rotkin@theory.ioffe.rssi.ru

Abstract

The simple Frenkel exciton model Hamiltonian is applied for calculation of spectrum of electron-hole excitations in carbon nanoclusters. The group-theoretical approach allows to find analytically mode frequencies as well as wavevectors of excitations.

PACS: 36.20.Kd, 36.40.+d, 36.20-r

Keywords: Frenkel exciton, carbon cluster, group theory

Introduction

The finite carbon nanoscale cluster electronic system stills to be a challenge to a theoretician. It has the intermediate scale: neither atomic nor 3D-bulk one, which troubles the typical many-body method application. There are some theoretical and experimental evidence that Coulomb interaction should be taken into account for these systems. Some interesting analytical results were obtained [1] for the fullerenes within SO(3) - spherical symmetry approximation - though the actual icosahedral symmetry group is much lower than the infinite full group of rotations. We note that the symmetry of the tight-binding (TB) one-electron Hamiltonian is high enough to obtain, for example, the spectrum within purely analytical method [2-4].

The high symmetry leads us to consider some simplified Coulomb Hamiltonian for C_{60} -like lattice of atoms possessing one electron-hole chargeless excitation per site. The Wigner-Eckart theorem allows to expand all operators into irreducible operator series for any lattice (here the icosahedral 60-membered lattice is considered). We write Hamiltonian in the standard secondary quantization (electron-hole) formalism. The next step is obvious – the multipole expansion in the first non-vanishing order for the electron-hole excitation is the dipole approximation. When considering only next-neighbor interaction, it is the simplest Frenkel-exciton Hamiltonian well known from organic insulator solid state theory. To be noted, the problem is easily solved numerically. Then we make use of TB dipole-dipole approximation. One can expect that a number of degrees of freedom is much larger than for translationally invariant systems, which makes analytical solution difficult if possible. Even so, we showed that the group-theoretical approach gives the exact result for some modes [5]. For example, we calculated analytically the triply-degenerate optically active excitons and non-degenerate excitations of C_{60} and modes of C_{12} (three are dipole active ones).

1. Symmetry classification

A number of carbon nanoclusters of high symmetry has been synthesized last years. Along with clusters of perfect geometrical shape a lot of less symmetrical closed (and even opened) macromolecules of carbon occur in the carbon soot. The main feature of these constructions is a three-coordinated network of carbon-carbon bonds that allows us treat them as graphite-like surfaces [6]. The most familiar C_{60} cluster has an icosahedral (Y_h) symmetry, being a perfect truncated icosahedron. This network (we will also call it the cluster lattice having in mind the correspondence to infinite lattice of 2D graphite sheet) can be obtained as some projection of triangular group (2,3,5). The notation reflects the symmetry of basic triangular patch of cluster which has to be rotated by all Y_h group elements to cover all the surface (see Ref. [7] for more details). Last number 5 in the notation shows that C_{60} has 5-fold axes (or 5-membered rings). One can consider polyhedrons with 3- and 4-fold axes which give more examples of carbon clusters with graphite-like curved surface. The first is

truncated tetrahedron which was considered theoretically as C_{12} . The last one represents the truncated cube and will not be considered below. It has only even-membered rings in the lattice that makes its symmetry slightly different.

We have to note that considered C_{12} and C_{60} clusters are the smallest representatives of truncated tetrahedron and icosahedron family which is formed by substitution of some graphite lattice fragment instead of single carbon atom in the same lattice (cf. Ref.[8]). The unified approach allows to calculate the TBA spectrum of these clusters. The matrix TBA Hamiltonian can be expanded in irreducible representation (IRR) space. The high symmetry results in essential simplification of secular equations, which are solved exactly for clusters with a simple lattice basis [2-4,7,8]. Let us consider the Hamiltonian symmetry of C_{12} cluster in more details.

The TBA Hamiltonian has only two parameters to calculate the one-electron spectrum. There are a hopping integral t and the zero energy level (which is very naturally omitted in all expressions). The spin-orbit interaction will not be considered here, hence, the spin index will be omitted and spin degeneracy is implied. So far, at zero hopping $t = 0$ the level has 12-fold degeneracy. The hopping part of TBA Hamiltonian plays role of kinetic energy in Hubbard model. Let us consider non-zero hopping. We will distinguish between hopping along the bond belonging to triangular and hexagonal bond. The latter seems to be closer to pristine graphene. We will henceforward note two hopping parameters as t_3 and t . Substituting in Hamiltonian $t_3 = 0$ we get six non-connected pairs of sites. It is evident that two 6-fold energy levels appear. In the opposite limit of $t = 0$ we have four separate triangles with 4- and 8-fold levels.

At the intermediate hopping one has, in general, 5 levels labeled by tetrahedral symmetry. The degeneracy is 1, 3, 2, 3, 3 from the bottom to top. Three one-electron levels are occupied at half filling. Hence, $t = 0$ case gives the metallic ground state, which becomes "semiconducting" one at any small hopping parameter with a gap which is linear in t/t_3 at small t . We note that all these three cases are within a supersymmetry space of SO(4) problem. Let us consider the maximal 12-dimensional space of U(12) group (it corresponds to $t = t_3 = 0$). It can be restricted to SO(4) subgroup in two ways: [3/2,1] and [1/2,5/2] (here we use a standard notation of SO(4) IRR via two angular moments). However, the first representation has only half-integer SO(3) expansions. IRR [1/2,5/2] has three integer SO(3) representations: $|2\rangle + |3\rangle$, $|1\rangle + |4\rangle$ and $|0\rangle + |5\rangle$ (here bra-vectors give angular momentum IRRs of SO(3) group). The same time, the case $t_3 = 0$ can be presented as the SO(4) state [1/2,5/2] with $K_z^{(2)} = 0$. The reduction of symmetry to tetrahedral group results in the same set of IRRs for all these integer RRs, which correspond to finite hopping parameters. The case $t = 0$ is obtained as half-integer projection of SO(4) state. Of course, the one-electron level degeneracy does not deal with the real spectrum of the system, though classification in terms of hopping kinetic energy may occur useful.

In the next section we will consider Frenkel-exciton model as a solution for simplest Hubbard-like Hamiltonian for chargeless electron-hole excitation spectrum.

2. Frenkel-Exciton model

We suppose that initially the excitation is localized on a single atom. The electron and a hole on the same site possess a dipole moment, not a charge. Then the resulting excitation is formally an exciton of small radius, a Frenkel exciton [9]. Let us remind that in the Frenkel Hamiltonian we preserve, for chosen two-particle electron-hole state, only four terms – a kinetic energy of an electron, a kinetic energy of a hole, an electron-hole direct Coulomb interaction and an exchange one. The first non-vanishing term in the interaction is dipole-dipole one:

$$H_{\text{eff}} = \sum_{1,2} a_1^\dagger a_2 \mathcal{H}_{12}^e - \sum_{1,2} d_1^\dagger d_2 \mathcal{H}_{12}^h + \sum_{1,2,3,4} a_1^\dagger d_2^\dagger \mathcal{P}_{12}^\dagger \nabla \frac{1}{|R(1-2)|^3} d_3 a_4 \mathcal{P}_{34} (-\delta_{14} \delta_{32} + \delta_{12} \delta_{34}), \quad (1)$$

where the first sum is taken over electron states, the second is taken over hole states; \mathcal{H} represents the kinetic energy operator; \mathcal{P} is a dipole momentum matrix element, taken with the "bra" and "ket" vectors of chosen chargeless excitation on site; $|R(1-2)|$ is a distance between sites 1 and 2. Operator nabla appears from multipole expansion of Coulomb integral as the first dipole term.

The Frenkel exciton approximation consists in a substitution of exciton operator instead of pair of electron-hole operators $B_1 = d_1 a_1$ and in a subsequent linearization of this expression which leads to the follows:

$$H_{\text{FE}} = \sum_1 B_1^\dagger B_1 (\mathcal{H}_{12}^{eh} - W^{(\text{dir})}) + \sum_{1,2} B_1^\dagger B_2 \mathcal{P}_i(1) \mathcal{P}_j(2) \frac{\delta_{i,j} |\mathbf{R}(1) - \mathbf{R}(2)|^2 - 3(R(1)_i - R(2)_i)(R(1)_j - R(2)_j)}{|\mathbf{R}(1) - \mathbf{R}(2)|^5}, \quad (2)$$

where a kinetic energy part and a direct Coulomb interaction are collected into the first diagonal part of Hamiltonian. The off-diagonal part is given by exchange dipole-dipole interaction between sites 1 and 2.

So far the Frenkel exciton model is stated basing on two parameters $\mathcal{E} = (\mathcal{H}_{12}^{eh} - W^{(\text{dir})})$ and \mathcal{P}^2/b^3 , where $b \simeq 1.44\text{\AA}$ is the distance between nearest neighbors in C_{60} . The self energy \mathcal{E} simply shifts the energy zero level. Hence, we will drop it below when it will not cause misunderstanding.

3. Group-theoretical expansion

The harmonic analysis over the group lattice reduces any site-defined problem to ten secular equations for C_{60} (and four for C_{12}). Because of there are 10 IRRs of dimensionality 1, 3, 3, 4, 5 in Y_h (and 4 in $T-1, 1, 1, 3$). The remaining task is to write an explicit form of given Hamiltonian and solve it for all IRRs. We will present below the general consideration but will derive all expressions for C_{60} lattice, which is more complicated.

The Frenkel Hamiltonian for Y_h lattice of C_{60} cluster is given by the sum of dipole-dipole interaction terms over all 60×60 states:

$$\sum_{g \in Y, f \in \mathcal{F}} P_i^\dagger(g) \frac{1}{|R(f)|^3} \hat{\tau}_{ij}(g, fg) P_j(fg). \quad (3)$$

Here summation over $g \in Y$ is a summation over 60 sites of the C_{60} cluster surface, while summation over f is restricted by the model over a limited number of neighbors given by some set $\mathcal{F} \subset Y$ (or over a full unlimited set Y , then we will address it as a Hamiltonian of full dipole-dipole interaction). The dipole-dipole interaction between the nearest neighbors will be considered in the last part of the paper. Then the subset $\mathcal{F} \subset Y$ is given by 3 fixed elements for each site g (cf. Ref.[2]). P^\dagger and P are independent variables in the secondary quantization representation. In our old notation $P^\dagger(g_1) = \mathcal{P} B_1^\dagger$. We single out a distance dependent factor $1/|R(f)|^3$ from dipole-dipole interaction and collect an angle dependent remaining part, τ , as it is easily seen from Eq.(2). This τ is actually the traceless second-order tensor which is well-known from classical electric-multipole theory.

The operator $P_i^\dagger(g)$ creates an electron-hole pair on site \mathbf{g} . Here a vector \mathbf{g} is directed from the center of cluster, chosen as the global co-ordinate origin, to the site g . We will use below also the local co-ordinate system (LCS), which will be connected with each site $g \in Y$. The LCS on each site is directed so that any local axes in point $|g\rangle$ goes to $|fg\rangle$ LCS after the proper rotation $f \in Y$.

The operator $P_i^\dagger(g) = a_i^\dagger(g) d^\dagger(g)$ carries an index i connected with the spinor of the electron-hole excitation state.

Let us give now the Frenkel Exciton Hamiltonian in the simplest notation:

$$\sum_{\alpha \in \{\text{RGR} \times \text{T}_1\}} \sum_{m, n; m_1, n_1 \in \alpha} P_{i, \alpha, m, n}^\dagger \frac{\tau_{ij}^{(\text{LCS})}(f)}{|R(f)|^3} D_{m_1 k}^{(\alpha)}(f) P_{j, \alpha, m_1, n_1} \delta_{n, n_1} \delta_{m, k}. \quad (4)$$

where the summation is taken over all indices m, n belonging to the IRR α containing in the direct product of vector representation T_1 and the full dynamical group of the TB Hamiltonian symmetry, given by the regular representation of Y group (RGR). $P_{i,\alpha,m,n}^\dagger$ is the creation operator of electron-hole excitation of α IRR (more details are in Ref.[5]). For the sake of clarity we suppose here all bonds to be equal b , the energy scale is given by dipole matrix element \mathcal{P}^2/b^3 . $D_{m_1k}^{(\alpha)}(f)$, as usual, is the rotation matrix for IRR α . The dipole-dipole interaction in LCS reads as:

$$\tau_{ij}^{(\text{LCS})}(f) = D_{ij}^{(T_1)}(f) - 3(\mathbf{e} - \mathbf{f})_i(\mathbf{f}^{-1} - \mathbf{e})_j. \quad (5)$$

It is seen that Frenkel exciton Hamiltonian is reduced to secular equations for each IRR of the following form:

$$\tau_{ij}^{(\text{LCS})}(f) \otimes D_{m_1k}^{(\alpha)}(f). \quad (6)$$

This is blockmatrix of dimensionality $3 \times d$, where $d = [\alpha]$ is the dimensionality of α IRR vector. For nondegenerate mode $\alpha = A$, it is 3-row matrix. The resulting three full symmetry A -modes has different energies, depending on the local symmetry of a mode. There are five triply degenerate dipole-active modes in the Frenkel Exciton Hamiltonian as it follows from group theory. Our model allows to obtain analytically the mode frequencies as well as the wavevectors for C_{60} and more easily for C_{12} cluster.

SUMMARY

We present a Frenkel exciton model for calculation of optical response of carbon nanoclusters of high symmetry. The model Hamiltonian includes a dipole-dipole interaction between electron-hole chargeless excitations. The nearest-neighbor approximation has been used for simplicity of derivation, though the generalization for full dipole interaction is straightforward. The group expansion of the problem is described. The analytical expression will be presented elsewhere for mode frequency and the corresponding wavevectors as a solution of secular equation of much smaller dimensionality than before expansion. This approach seems to be promising for different lattice problems defined for graphite-like cluster surfaces.

Acknowledgments: This work was partially supported by program 'Fullerenes and Atomic Clusters' project no. 98062, RFBR Grant no. 96-02-17926 and grant no. 1-001 of Russian Programm "Physics of solid state nanostructures".

- [1] A. Auerbach et.al., Phys.Rev.Lett. 72, 2931, 1994.
- [2] R.Friedberg et.al., Phys.Rev. B46, 14150, 1992.
- [3] Samuel S., Int.J. Mod.Phys. B, vol. 7, N 22, pp. 3877-3897, 1993.
- [4] Tang Au Chin, Huang Fu Quiang, Chem.Phys.Lett. 245, 561-565, 1995.
- [5] S.F. Harlapenko, S.V. Rotkin, The 193th Meeting of the Electrochemical Society; Fullerenes: chemistry, physics and new directions XI. May 3-8, 1998; San Diego, CA.
- [6] V.V. Rotkin, PhD. thesis, St.Petersburg, Russia, 1997, 142 pages (Russian).
- [7] Rasetti M., Zecchina R. Physica A 199, 539-570, 1993.
- [8] Tang Au Chin et.al., Chem.Phys.Lett. 227, 579-587, 1994.
- [9] Ja.I.Frenkel, Phys.Rev. 37, 17, 1931. Ja.I.Frenkel, Phys.Rev. 37, 1276, 1931.