FRENKEL-EXCITON IN FINITE-GROUP-LATTICE

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Frenkel Exciton model is solved for a single fullerene cluster, which icosahedral lattice has a very high symmetry. That allows to find analytically spectrum and dipole moments of 5 modes which are optically active.

The problem of many-body calculation is rarely solving in analytical expressions, especially for a finite electron system of the intermediate scale: neither atomic one nor 3D-bulk. The essential simplification can be obtained within Fourier-transformation approach, which is applicable to the system that is invariant relatively to translations. However, the Abel translation group has very high symmetry and holds not too often. We are interested in finite carbon nanoscale cluster electronic system. There are some theoretical and experimental evidence that Coulomb interaction should be taken into account. The paper is a step in this direction.

Some interesting analytical results were obtained for the fullerenes within SO(3) - spherical symmetry approximation. The SO(3) Coulomb interaction can be expanded into spherical harmonic series (multipole expansion). Though the actual icosahedral symmetry group is much lower than the infinite full group of rotations, we note that it is high enough to obtain, for example, the tight-binding (TB) one-electron spectrum within purely analytical method.

Here we will consider TB Coulomb Hamiltonian for C_{60}-like lattice of atoms possessing one electron-hole chargeless excitation. The Wigner-Ekkart theorem allows to expand all operators into irreducible operator series for any lattice (here the icosahedral 60-membered lattice is considered). We wrote Hamiltonian in the standard secondary quantization (electron-hole) formalism. Then we make use of TB approximation which simplifies the Coulomb interaction to Hubbard terms. The next step is obviouse - the multipole expansion in the first non-vanishing order for the electron-hole excitation is the dipole approximation. When considering only next-neighbour 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. The less evident step is to try the problem analytically. One can expect that a number of degrees of freedom is much larger than for translationaly invariant systems. Even so, the symmetry is high and group-theoretical approach gives the exact result for some modes. For example, we calculated analytically the triply-degenerate optically active excitons and non-degenerate excitatons.

Of course, this technique can be applied to any system, though the simplification

obtained is essentially depends on the degeneracy of one-electron levels (on the degree of symmetry). The lower symmetry, the larger secular equation occurs. Actually the icosahedral group, probably, is one of amusing examples, which provides the very variouse physics.

1. MODEL FORMULATION

One of most frequently used approximation for Coulomb Hamiltonian of highly degenerate system is the Hubbard model. In the paper we intend to consider an excitation in the lattice given by sixty carbon atom set of single C_{60} cluster. The excitation, which will be described, is a chargeless two-particle exciton on the lattice of carbon atoms of a single fullerene . 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 [1]. This is an excitation on a single cluster opposing to different computations of Frenkel exciton in 3D arrays of fullerenes. Starting with tight-binding lattice Hamiltonian, it seems to be very natural to consider also the nearest neighbor approximation for Coulomb interaction (similarly like it was done in the Hubbard model).

Let us remind the way leading to Frenkel exciton Hamiltonian. In the secondary quantization approach we preserve in the Coulomb Hamiltonian, for choosen 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. We suppose that the starting electron-hole excitation is chargeless and is localized on site. Then first non-vanishing term in the interaction is dipole-dipole one:

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

(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 choosen chargeless excitation on site; $|R(1-2)|$ is a distance between sites 1 and 2. The exact sense of notation of nabla operator will be given just after the next equation.

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:

$$H_{\text{FE}} = \sum_1 B_1^\dagger B_1 \left(\mathcal{H}_{12}^{eh} - W^{(\text{dir})}\right) + \sum_{1,2} B_1^\dagger B_2 \mathcal{P}^2 \nabla^2 \frac{1}{|R(1-2)|^3},$$

(2)

where a kinetic energy part and a direct Coulomb interaction are collected into first diagonal part of Hamiltonian. The off-diagonal part is given by exchange dipole-dipole interaction between sites 1 and 2, which is represented by well known expression:

$$\mathcal{P}^2\nabla^2\frac{1}{|R(1)-R(2)|^3} = \mathcal{P}_i(1)\mathcal{P}_j(2)\frac{\delta_{i,j}|R(1)-R(2)|^2 - (R(1)_i - R(2)_i)(R(1)_j - R(2)_j)}{|R(1)-R(2)|^5}$$
$$= \frac{1}{|R(1)-R(2)|^3}\tau_{ij}(\mathbf{R}(1)-\mathbf{R}(2)) \tag{3}$$

We will use the notation τ_{ij} for the angular part of dipole-dipole interaction operator henceforward.

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

2. GROUP-THEORETICAL APPROACH

All irreducible representations (IRs) of Y_h group are well known (one can follow one of approaches given in Refs. [2–5]). There are 10 IRs of dimensionality $1, 3, 3, 4, 5$. The harmonic analysis over the group lattice reduces any site-defined problem to 10 secular equations. The remaining task is to write an explicit form of given Hamiltonian and solve it for all IRs. The dynamical symmetry of Hamiltonian can results in more or less complicated secular equation for each of IRs. For example, one-electron tight-binding Hamiltonian has an analytical solution, owing to each IR has a secular equation of the same dimensionality as this IR matrix (that follows from the orthonormality relation for IR projection operators).

The Hamiltonian of general form the more complicated, the more equivalent IRs it is containing within. The group theory allows all of them to be mixed and the secular equation grows. We will show that for our Frenkel-Exciton Hamiltonian the result can be given in considerable expressions.

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

$$H = \sum_{g\in Y, f\in\mathcal{F}} P_i^\dagger(g)\frac{1}{|R(f)|^3}\hat{\tau}_{ij}(g, fg)P_j(fg). \tag{4}$$

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 lattice). $P^\dagger$ and P are independent variables in the secondary quantization representation. In our old notation $P^\dagger(g_1) = \mathcal{P}B_1^\dagger$. The

reason to single out a factor $1/|R(f)|^3$ from dipole-dipole interaction is that the remaining part, τ, is the angle dependent one but not distance dependent as it is easily seen from Eq.(3). This τ is actually the traceless second-order tensor which is well-known from classical electric-multipole theory.

We will apply the group-theoretical analysis to the Hamiltonian represented by Eq.(4). Let us first reduce the operator τ to most compact form. The operator $P_i^\dagger(g)$ creates an electron-hole pair on site **g**. Here a vector **g** is directed from the center of cluster, choosen 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. The optical transition should be between states of different symmetry. Hence, if a hole is single-component, then an elercton has three components transforming as a vector, the vector of a dipole moment of a transition $\mathcal{P}_i$, where $i = x, y, z$.

The term with τ has the simplest form in the LCS. The transformation to such a system is given by a vector rotation operator which changes the global axes to the local ones defined in the point **e**. We will often refer to this point on the fullerene sphere as a fundamental base of the group lattice (similar to Brave cell in solid).

The components of the electron-hole state transforms under this rotation as $P_i = D^{*(1)}_{ij}(g^{-1})P_j$, then in LCS the operator τ reads as follows:

$$\hat{D}^\dagger(g^{-1})\tau_{ij}(\mathbf{g}, \mathbf{fg})\hat{D}([fg]^{-1}) = D^{*(1)}_{ik}(g^{-1})\left(\delta_{k,n} - (\mathbf{g} - \mathbf{gf})_k(\mathbf{g} - \mathbf{gf})_n\right)D^{(1)}_{nj}([gf]^{-1}) =$$
$$(\delta_{k,n} - (\mathbf{e} - \mathbf{f})_k(\mathbf{e} - \mathbf{f})_n). \tag{5}$$

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.

Each function denoted over a group can be expanded using proper harmonics. One can do it for creation operators:

$$P_i^\dagger(g) = a_i^\dagger(g)d^\dagger(g) = D^{*(\alpha_1)}_{n_1 m_1}(g)a^\dagger_{i;\alpha_1,n_1 m_1}D^{*(\alpha_2)}_{n_2 m_2}(g)d^\dagger_{\alpha_2,n_2 m_2} =$$
$$C^{(\alpha_1 \alpha_2 \gamma)}_{n_1 m_1, n_2 m_2, k_1 k_2}a^\dagger_{i;\alpha_1,n_1 m_1}d^\dagger_{\alpha_2,n_2 m_2}D^{*(\gamma)}_{k_1 k_2}(g) \tag{6}$$

where Einstein notation for summation over repeated indices is used; all $D^{*(\beta)}_{st}(g)$ are the Wigner functions for IR β and the proper group rotation g. $C^{(\alpha_1 \alpha_2 \gamma)}_{n_1 m_1, n_2 m_2, k_1 k_2}$ is the Wigner coefficient given, for example, in [6]. Here we changed the co-ordinate basis to the symmetry adapted basis of IRs.

Last step is to come from two-particle state to an exciton state. For this purpose we collect terms with the proper symmetry in Eq.(6) and write finally:

$$P_i^\dagger(g) = C_{n_1 m_1, n_2 m_2, k_1 k_2}^{(\alpha_1 \alpha_2 \gamma)} a_{i;\alpha_1, n_1 m_1}^\dagger d_{\alpha_2, n_2 m_2}^\dagger D_{k_1 k_2}^{*(\gamma)}(g) = D_{k_1 k_2}^{*(\gamma)}(g) P_{i;k_1 k_2}^{\dagger(\gamma)} \qquad (7)$$

where $P_{i;k_1 k_2}^{\dagger(\gamma)}$ is the symmetry-adapted field operator (the creation operator in the subspace of definite IR) for the Frenkel exciton like $P_i^\dagger(g)$ is the field operator in the co-ordinate representation.

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

$$H = \sum_{\alpha \in \{\mathrm{RGR} \times \mathrm{T}_1\}} \sum_{m,n;m_1,n_1 \in \alpha} P_{i,\alpha,m,n}^\dagger \frac{\tau_{ij}^{(\mathrm{LCS})}(f)}{|R(f)|^3} D_{m_1 k}^{(\alpha)}(f) P_{j,\alpha,m_1,n_1} \delta_{n,n_1} \delta_{m,k}. \qquad (8)$$

where the summation is taken over all indices m, n belonging to the IR 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). When we suppose all bonds to be equal, the second term gives us the energy scale together with the dipole matrix element as $\mathcal{P}^2/b^3$. $D_{m_1 k}^{(\alpha)}(f)$ as usual is the rotation matrix for IR α. The dipole-dipole interaction in LCS reads as:

$$\tau_{ij}^{(\mathrm{LCS})}(f) = D_{ij}^{(T_1)}(f) - 3(\mathbf{e} - \mathbf{f})_i (\mathbf{f}^{-1} - \mathbf{e})_j. \qquad (9)$$

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

$$\tau_{ij}^{(\mathrm{LCS})}(f) \otimes D_{m_1 k}^{(\alpha)}(f). \qquad (10)$$

This is blockmatrix of dimensionality $d \times 3$, where $d = [\alpha]$ is the dimensionality of α IR 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. Next figure shows the symmetry of the mode of highest energy.
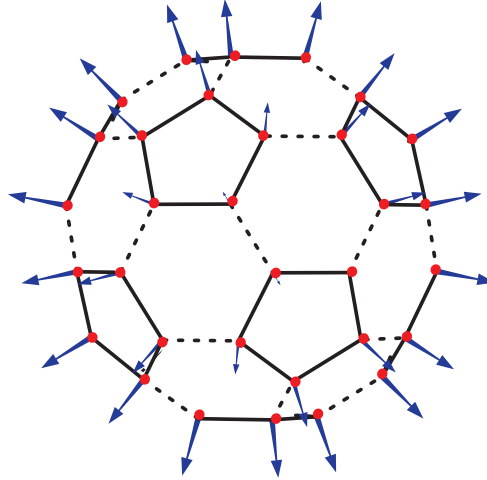

FIG. 1. The symmetry of the mode with the highest energy is a full icosahedral symmetry A_g. This is one from 3 non-degenerate modes of C_{60}. It is optically non-active.

There are five triply degenerate dipole-active modes in the Frenkel Exciton Hamiltonian as it follows from group theory. We will present below very characteristic shape of wafe-function of some of them.
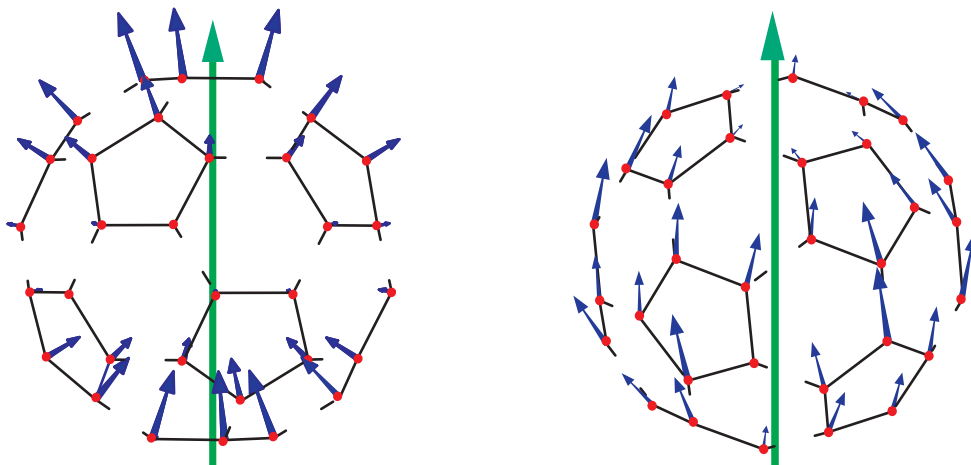

FIG. 2. Two of 5 dipole modes of the Frenkel Exciton Hamiltonian of C_{60}. Left: the lowermost dipole mode which has the largest dipole momentum (shown as a global vector). It is the direct product of p-type wave-function and the mode shown in Fig.1. Right: the mode which is the cross product of p-function and triply-degenerate vector mode of TBA fullerene Hamiltonian.

SUMMARY

We suggested and solved the Frenkel Exciton model for calculation of the electron-hole two-particle excitation spectrum on the single fullerene cluster. The spectrum was obtained using two phenomenological parameters to be taken from experiment. Frequencies and dipole moments of five optically active dipole modes were found analytically as well as three non-degenerate states of full icosahedral symmetry. We used nearest-neghbour for the sake of clarity, but the full dipole Hamiltonian will be shown to shift the considered modes slightly.

ACKNOWLEDGMENTS

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