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Generalized Solutions of the Quantum Chemistry Equations for Symmetric Systems. Some Applications

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Generalized Solutions of the Quantum Chemistry Equations for Symmetric Systems. Some Applications[#]

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Abstract

The conventional technique for solving the equations of quantum chemistry (of solid state) is extended unconventionally to the structures possessing certain symmetries. This proposal concerns changing the way for selection of the occupied orbitals, and allows revealing the unoccupied electronic states located lower than the ground–state Fermi level of a specific system. Such states can be treated as "spectral holes". Application of this technique, in particular, when calculating the electronic structure of the HTSC–compound $YBa_2Cu_3O_{7-\delta}$ ($0 \leq \delta \leq 1$) results in the following. The spectral holes of high spatial localization are found. These "spatial spectral holes" are located mainly at the p_y–orbitals of the apex oxygens. These orbitals overlap and form linear chains which are parallel to the known Cu(1)–O chains, disappearing when δ is close to 1. One can suppose that the linear chains of the overlapping hole states form a "superconducting channel". Some other parameters closely related to the critical characteristics of HTSC–materials are also calculated. The calculations show that "the superconducting channel" is broken when the oxygen chain atoms O(1) are removed ($\delta > 0$). One could easily connect the obtained results to the high–temperature superconductivity of Little's linear chains as well as Ginzburg's two–dimensional layers and even to BCS–model. It should be emphasized that the new approach in question has a general nature and therefore it could be applied to any symmetric quantum chemistry object.

Keywords. Quantum chemistry methods; electronic structure; spectral hole; symmetry properties; high–temperature superconductor; superconducting channel.

Abbreviations and notations

BCS, Bardeen–Cooper–Schrieffer	LCAO, linear combination of atomic orbitals
DOS, electronic density of states	MO, molecular orbital
GTO, Gaussian–type orbital	SCF, self–consistent field
HTSC, high–temperature superconductor	

1 INTRODUCTION

It is known that a majority of quantum chemistry problems implies solving a relevant Hartree–Fock equation or applying density functional theory. For the further statement it will be important only the fact that it is a nonlinear equation, which is solved by an iterative method. One feature of this procedure is of special interest. It concerns the selection of the occupied molecular (or solid

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state cluster) orbitals (MOs), being taken place at each iteration under the solving process.

In the Roothan method, as a result of constructing the required MOs as a certain linear combination of atomic orbitals, one obtains M molecular orbitals, where M is a dimension of the chosen multiatomic basis. In view of simplification, a spin–restricted case will be considered. In this case, $2N$ electrons of opposite spins will occupy N spatial MOs, where $N \leq M$. According to Slater, electrons are to be attributed to these molecular orbitals, and for the ground state one *naturally* takes the N molecular orbitals with the lowest energy [1]. Usually authors are not particularly interested in the relations between electrons and definite MOs, believing that there is no problem with their occupation. However, the problem exists, and is not as simple as it seems at first sight.

Let us consider a case in which the physical object in question can be related to a certain spatial group of symmetry. Evidently, this case does not considerably reduce a variety of the considered phenomena. Let the number of various irreducible representations of this group be equal to L. Then, each of MOs belongs to one of the L irreducible representations of the symmetry group. If m_i denotes the number of MOs that realize i–th irreducible representation, then we can write:

$$\sum_{i=1}^{L} m_i = M\,.$$

Let us note at once, that the set of numbers m_i is not changed from one iteration to another and depends only on the chosen basis and group of spatial symmetry for the object under consideration. It is clear, that in the final solution N occupied MOs also belong to these L (or less) irreducible representations, each involving n_i orbitals, so that:

$$\sum_{i=1}^{L} n_i = N \qquad (0 \leq n_i \leq m_i).$$

Further n_i isn't simply the number of occupied MOs among the total number of m_i referring to the i–th type of symmetry (irreducible representation). n_i is, by all means, the number of the lowest–energy MOs among the total number of m_i for the given symmetry type. Here, at each iteration step the selection of the n_i occupied orbitals of each type of symmetry (of the specified spatial group) corresponds to Slater's choice cited above. This selection is made *independently* of symmetry of the object in question. Such a selection of the occupied MOs, based only on its one–particle energies (to be more exact, the Fockian eigenvalues) but ignoring its symmetry (irreducible representations), seems quite reasonable. Lack of *physical* information on electrons in an object (only its total number N is known) speaks in favor of such a choice.

Below, we try to show that the simplest ordinary way of selection for occupied MOs isn't always valid. Further, we consider the opportunity for refinement (generalization) of the ordinary way of selection, as well as show a potential way to acquire required additional information. We will also consider the technique and the results of application of the proposed method to some HTSC materials.

2 MATERIALS AND METHODS

2.1 Unconventional Consideration of the Symmetry Properties

It should be noticed that the set of numbers m_i is constant for a specified problem in a chosen basis, whereas the set of numbers n_i can vary from one iteration to another in the solving process.

The *essence of approach* proposed herein consists in using the constant set of numbers n_i at each iteration step. Such a situation corresponds to a change of the way for selection of the occupied MOs. Instead of the standard selection of N lowest–energy MOs from their total number of M on each iteration, one should select the lowest energy n_i from m_i orbitals for each type of symmetry *separately*. At the same time, the numbers n_i, as well as the numbers m_i, do not change during the solving process. Thus, to solve the equation, instead of one parameter N (number of electrons) we should use L parameters represented by a set of numbers n_i.

Then at once two following questions are coming up:

1) In what way could one obtain the required splitting $\{n_i\}$ as on symmetry types for N electrons?
2) What could this result in?

It is possible, and rather simply to answer the first of the posed above questions, proceeding from mathematical (*computational*) reasons. For this purpose, at first, it is necessary *to solve our equation by a usual way*, *i.e.*, using the standard way for selection of the occupied MOs. At that, as it has been already mentioned above, the set of numbers n_i varies as a rule almost at each iteration. Above all, it is due to jumps between occupied orbitals of various types of symmetry near the Fermi level. Very often we encounter the troubles like that when solving the quantum chemistry equations for sufficiently complicated objects, such as, *e.g.*, Cu–O clusters in the HTSC compounds. Moreover, owing to the jumps mentioned above, it is impossible to achieve the desired convergence of the iterative procedure, despite all possible measures undertaken to avoid potential errors or inaccuracies of both physical and mathematical (computational) nature. However, at a definite stage of iteration process, these jumps occur in the frame of the assembly consisting of the nonvaried sets $\{\underline{n}_i\}$. Usually, this final assembly consists of two or three sets. One should use namely these sets $\{\underline{n}_i\}$, or possibly close to them, to solve our equation by means of the suggested above way for selection of the occupied MOs.

To answer the second of the questions posed above, first of all one should accentuate a fact of arising the following problem (*and*, *possibly*, *it is a solution of many problems*!). The point is that in this case not all of N electrons must occupy, by all means, the states with lowest energies. That is, some of the unoccupied $(M-N)$ orbitals may be located lower than the Fermi level.

It is easy to illustrate the mechanism of occurrence of such effect with the help of the simplified layout depicted in a Figure 1. For the sake of simplicity let us assume that we need to calculate an electronic structure for the quantum system containing 24 electrons which will occupy in spin–restricted case just 12 spatial MOs ($N = 12$). The total number of MOs is 17 ($M = 17$). Energy levels corresponding to the MOs with different types of symmetry are represented (for pictorial view) by different colours.

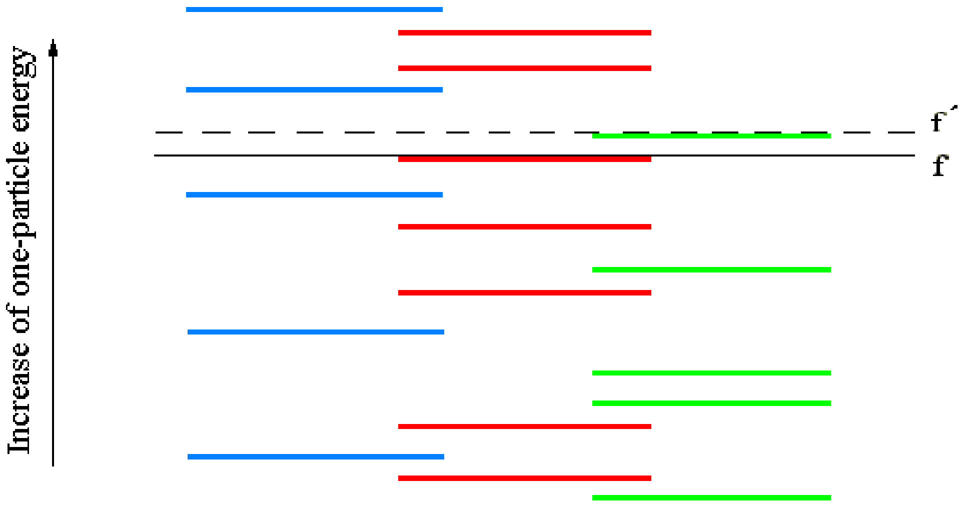

Figure 1. Scheme for the energy levels with different symmetry types and for formation of "spectral holes".

Let us assume that we occupy these MOs by conventional way, *i.e.* by selecting the 12 MOs with the lowest energy, and without taking the symmetry into account. Then these 12 occupied MOs will be split up onto 3 groups with different symmetry types: 3 blue, 5 red and 4 green. The occupied state with the highest energy (Fermi level f) will then be represented by the 5–th red level from the bottom.

Further let us assume that we want to occupy these 17 MOs by another (generalized) way described above. Then one could select for occupation, for example, only 2 blue, but 5 green levels and, of course, 5 red ones. Thus, it is easy to notice, that Fermi level will be displaced to the $f^{/}$ position, represented by the 5–th green level. At the same time, the 3–rd blue level will be unoccupied and will be located below the new Fermi level $f^{/}$. Let us call these unoccupied states, located below Fermi level, as "spectral holes" and denote their number amount as K. As it was already mentioned above, one could use several selected sets $\{\underline{n}_i\}$ to solve our quantum chemistry equation.

In principle, each of the tested sets can give rise to a certain solution. A solution with *a minimum* number of “spectral holes”, seemingly, corresponds to the ground state of a system. Ideally, the number of spectral holes equals zero. Then all electrons would occupy the states with lowest energy. The existence of this solution corresponds to the ordinary way which, *by definition*, can give *only* solutions with $K = 0$. Also it should be stressed that for a minimum basis set ($N = M$) one can obtain only the standard solution with $K = 0$.

It is clear, that if a solution with $K = 0$ does not exist for a physical object in question, any attempt to solve the relevant quantum chemistry equation by the standard method (*by definition*, with $K = 0$) will evidently give erroneous results. On the other hand, only when using the proposed above way for selection of the occupied MOs, it is possible to reveal the unoccupied states ("spectral holes"), which are located below Fermi level for the ground state of the system as a whole. It is quite possible, that namely these “spectral holes” will determine the main properties of the object under consideration.

For sake of simplicity, we treated the spin–restricted case. However, it can easily be proved that all said above is valid for a more general spin–polarized version of calculations. However, the situation is then more complicated because the population principle for the $N^{\uparrow}$ and $N^{\downarrow}$ orbitals that correspond to the opposite spin orientations must be considered separately, rather than the population principle for the $N^{\uparrow} = N^{\downarrow}$ orbitals in the spin–restricted case.

2.2 Technique for Calculation of the Electronic Structure of HTSC Matetials

Let us discuss the consequences of applying the technique described above to calculation of the electronic structure of the $YBa_2Cu_3O_7$ HTSC compound. The parameters for the crystal structure are taken from Ref. [2]. The Gaussian–type atomic orbitals (GTOs), which allow the accurate calculation of the multicenter integrals, have been used as basis functions. In particular, the following contracted basis sets of GTO as Cu[*7S/3P/2D*] and O[*3S/2P*] have been used for the atoms of copper and oxygen. These sets have been derived as a result of contraction of the (*14S9P6D*) GTO basis for the Cu (^{2}D) states by Wachters [3] complemented by the (*5d*) basis set with diffusion functions by Hay [4], and of the (*9S5P*) GTO basis for oxygen by Huzinaga [5].

A new version of the SCF LCAO–X_α method developed by the author in Ref. [6] has been used for the presented electronic structure calculations. This approach requires neither a choice of sample (spatial) points, which is needed in the X_α discrete variation method, nor the rough “muffin–tin” approximation, typical for the X_α scattered waves method. The largest Cu–O cluster of $YBa_2Cu_3O_7$, that is, the Cu_3O_{12} cluster (Figure 2), which conserves the most important structural features of the parent matrix, is chosen as a model one. The coordinates of all cluster atoms are taken in accordance with Ref. [2].

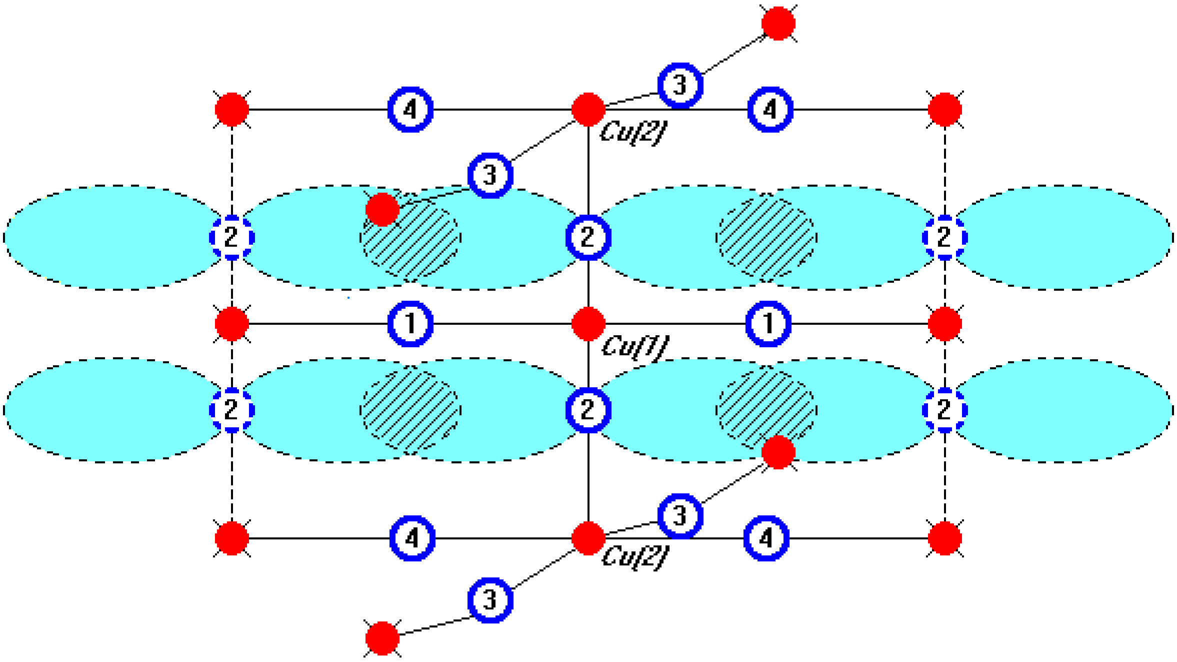

Figure 2. Structure of the extended cluster (Cu_3O_{12}+10$\underline{Cu}$). Numbers in the blue circles label the type of oxygen atoms, as in Ref. [2]. The crossed out red circles designate copper pseudoatoms. Neighbouring apex atoms O(2) (not included into the cluster), and linear chains of the hole states located mostly at p_y–orbitals of the apex atoms O(2) are designated by a dotted line.

This cluster is placed into an infinite medium of point charges representing the rest of the crystal lattice of $YBa_2Cu_3O_7$. The algorithms for treating the interaction between the cluster electronic states within the GTO basis and the infinite crystal lattice of point charges was presented by the author in Ref. [7]. It should be marked that the point charges of the Y, Ba, Cu or O atoms within the crystal lattice can be fractional. However, the number of electrons and the nuclear charges of the cluster atoms are integers. An entire physical system of cluster embedded into a crystal lattice of point charges should be electrically neutral. To follow this condition, a special "charge transfer" is placed between the cluster and each of 10 copper atoms that surround the cluster atoms along the continuations of the Cu–O bonds. Similar techniques were widely applied for appropriate boundary conditions with a cluster. A "valence" S–function is attributed to each of these 10 copper atoms denoted by the crossed out red circles in Figure 2. The S–functions complement this basis set, which consequently is increased from 192 to 202 functions. The potentials correspondent to the point charges of the two lattice atoms of $\underline{Cu}$ (1) and the eight lattice atoms of $\underline{Cu}$ (2) are replaced by appropriate pseudopotentials. A variation of the charges of the core electrons of the Cu–pseudoatoms and the exponents of "valence" S–functions allows "to pump" a required electron charge from the cluster to the buffer pseudoatoms of copper or vice versa. Let us recall that for the atoms of the Cu_3O_{12} cluster the basis sets are contracted GTOs mentioned above. This basis is complemented by the single (valence) S–functions centered at the 10 buffer pseudoatoms of copper.

To achieve a consistency between the charges of the cluster atoms and the lattice point charges, the following procedure is used. The lattice charges of Y and Ba are fixed. Certain initial charges at the atoms of Cu(1), Cu(2), O(1), O(2), O(3) and O(4) are chosen and the neutrality of the $YBa_2Cu_3O_7$ unit cell is conserved. Then, the Hartree–Fock–Slater equation is solved for the extended cluster (Cu_3O_{12} + 10$\underline{Cu}$) with the potential of the crystal lattice taken into account.

The procedure of self–consistency, by all means, begins with the spin–polarized version. Moreover, the initial density matrices for electrons (including its numbers) with the opposite spins are selected to be different. However, after several first iterations it becomes clear that the solution reduces to the spin–restricted case, making the situation much easier and accelerating the process of solving. Other authors dealt with the same effect in their quantum chemistry calculations (see, *e.g.*, Ref. [8,9]). It should be noted that the appropriate experimental data are quite contradictory. Some authors reveal the local magnetic moments at the Cu(1) atoms [10], whereas the others do not [11].

The obtained charges for the atoms of the main Cu_3O_{12} cluster are then used as the lattice charges when performing the next step of solving the Hartree–Fock–Slater equation. It should be noted that these cluster charges must be corrected before they are substituted into the lattice to keep the unit cell neutral. This procedure, which includes the above–mentioned "external" iterations, is repeated until a reasonable charge self–consistency is achieved (the relative inaccuracy is less than 1%). It should be noted that the results of the present procedure depend on the method and, to some extent, the accuracy of charge evaluation. The conventional Mulliken charges are only of a qualitative character. Therefore special algorithms have been constructed that make it possible to obtain more accurate estimates via analytical integration of both the one– and two–center electronic densities over a space around each cluster atom

3 RESULTS AND DISCUSSION

Electronic structure calculations have been performed for several of the most realistic combinations of charges, Z for the atoms of Y ($Z \leq +3$) and Ba ($Z \leq +2$). The results are presented in Tables 1 to 3 and Figure 3. In Table 1 the charges of copper and oxygen consistent with the lattice charges are presented for each considered combination of charges at the atoms of Y and Ba.

Table 1. Self–consistent charges (in a.u.) at the crystal lattice atoms of $YBa_2Cu_3O_7$

Y	3	2.5	2.5	2
Ba	2	2	1.75	1.75
Cu(1)	1.17	1.33	1.255	1.19
Cu(2)	1.25	1.46	1.42	1.35
O(1)	–1.48	–1.65	–1.485	–1.45
O(2)	–1.17	–1.15	–1.08	–1.08
O(3)	–1.735	–1.73	–1.645	–1.47
O(4)	–1.69	–1.67	–1.58	–1.42

The HTSC compound $YBa_2Cu_3O_7$ reveals for all considered charge distributions the presence of a single "spectral hole" ($K = 1$). This hole state possesses symmetry of the orbital (yz) of the central

Cu(1) cluster atom. The *y* and *z* axes are parallel to the **b** and **c** lattice vectors, respectively. As Table 2 demonstrates, this unoccupied orbital is strongly localized in an ordinary coordinate space. More than one–half of the corresponded charge originates from the p_y–orbitals of the apex O(2) atoms. The p_y–orbitals overlap and form (Figure 2) linear chains that are parallel to but not coincide with the known Cu(1)–O chains, which are missed in $YBa_2Cu_3O_6$. One can suppose that these linear chains of the overlapping hole states do form a "superconducting channel". It should be recalled that the high–temperature superconductivity in linear chains was predicted by Little [12] in 1964. Further, it should be noted that the above–mentioned "spectral holes", which are localized mostly on the p_y–orbitals of the O(2) atoms, are localized completely in the two–dimensional layers parallel to the (*yz*)–plane (see Table 2 and Figure 2). Here is useful to remember the works by Ginzburg [13] devoted to two–dimensional superconductivity. The existence of hole states from 2*p*–orbitals of "apex" oxygens was, in addition, revealed experimentally [14].

Table 2. Localization of "spectral holes" (in %) on atomic orbitals of the standard cluster (Cu_3O_{12} +10*Cu*) in the crystal lattice of $YBa_2Cu_3O_7$

Z(Y)	Z(Ba)	Cu(1) yz	Cu(2) yz	O(1) z	O(2) y	O(4) z
3	2	4	1	33	58	4
2.5	2	3	1	24	49	23
2.5	1.75	4	0	31	59	6
2	1.75	4	0	30	60	6

Table 3. The depth E of the hole state (below the Fermi level) and the width Δ of the energy gap (in eV) for the standard cluster in HTSC compound $YBa_2Cu_3O_7$

Z(Ba)	Z(Ba)	E	Δ
3	2	0.64	0.10
2.5	2	0.50	0.20
2.5	1.75	0.30	0.21
2	1.75	0.18	0.15

Table 4. Localization of the "spectral holes" (in %) on the atomic orbitals of the defect cluster (Cu_3O_{10} + 10*Cu*) in the crystal lattice of $YBa_2Cu_3O_7$

Z(Y)	Z(Ba)	Cu(1) xz	Cu(2) xz	O(2) x	O(3) z	O(4) x
3	2	17	7	46	29	1
2.5	2	11	4	35	37	13
2.5	1.75	18	1	57	23	1
2	1.75	16	2	53	28	1

Besides the extent of localization in the "channel" (see Table 2), the depth of "spectral hole" (energy below the Fermi level) can play a significant role in the phenomenon of HTSC. The data are presented in Table 3. One can assume that both parameters are closely related to the critical characteristics of the HTSC materials.

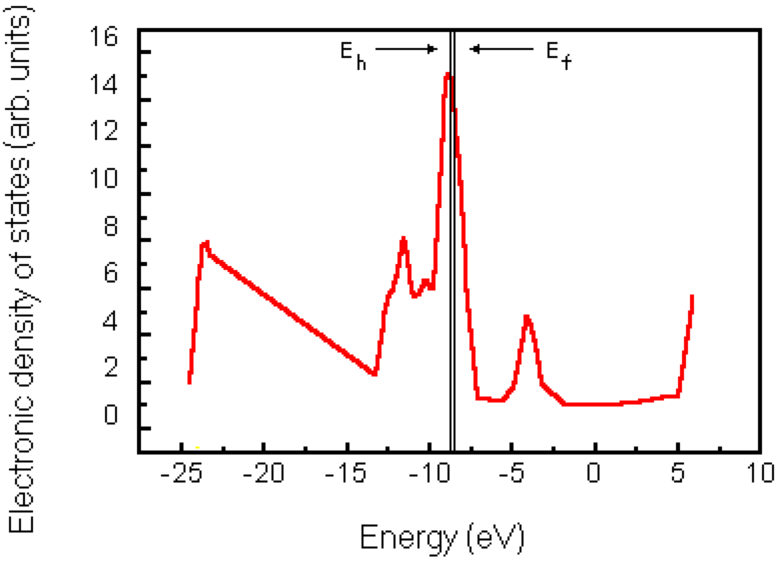

Figure 3. The electronic density of states (DOS) for the standard cluster (Cu_3O_{12} + 10<u>*Cu*</u>) in the crystal lattice of $YBa_2Cu_3O_7$ for Z(Y)=2.5 and Z(Ba)=1.75.

The electronic density of states (DOS) has been obtained by means of a Gaussian smearing with a broadening of $\underline{\Delta}$ = 0.5 eV. Because these DOSs are qualitatively the same for all specified charge distributions, only the part near the Fermi energy is depicted in Figure 3 for Z(Y) = 2.5 and Z(Ba) = 1.75. The DOS shows that the Fermi level falls in the upper part of the valence bands, corresponding to semiconductors. The unoccupied state with the energy of E_h (Table 3) lies by 0.24 eV lower than the Fermi energy E_f. For ordinary semiconductors, a hole appears as a result of an electron excitation (*e.g.*, by an electric field) into a conduction band above the Fermi level. However, a hole here occurred in the *ground* (nonexcited) state of the electronic system and is strongly localized in space. It should be noted that this “spectral hole” in the ground state of the system can be characterized by the presence of a gap in an energy spectrum. Let us enumerate all *M* states of the calculated spectrum in order of increasing energy. Then, the hole state with energy E_h acquires number *i* ($E_i = E_h$). The value of $\Delta = (E_{i+1} - E_{i-1})$ can be considered as an energy gap in a valence band. These parameters are also presented in Table 3. If one takes into account the BCS relation to be Δ / k_BT_c = const and adopt $\Delta \approx 0.003$ eV for the best superconductors (non–high–temperature ones), then the values of Δ presented in Table 3 correspond to increasing T_c by a factor of 30 – 70.

The well–known situation when the lattice of $YBa_2Cu_3O_7$ easily loses the chain oxygen O(1) has been simulated with a cluster. For this purpose, the nuclei and the atomic orbitals of the two O(1) atoms have been removed from the extended cluster (Cu_3O_{12} + 10<u>*Cu*</u>) and the number of electron pairs in the system has been reduced by 8. The charge distribution which represents the rest of the lattice has been left the same as in the nondefect cluster for $YBa_2Cu_3O_7$. The whole system (lattice + cluster) has remained electrically neutral. The solutions of the relevant equations for all (four) examined charge distributions showed again a single "spectral hole" ($K = 1$). However, as Table 4 demonstrates, its symmetry and localization have changed substantially. In this case, the hole state has acquired symmetry of the (xz)–orbital of the central Cu(1) atom with a predominant localization at the p_x–orbitals of the apex oxygen atoms O(2). It should be noted that the spectral hole now is localized mostly at the O(3) and Cu(1) atoms. In general, one can conclude that a removal of the chain O(1) atoms causes the hole state to delocalize to some extent and to turn by 90° and therefore break "the superconducting channel". Another interpretation of the loss of superconductivity properties is also possible. It is simply related to a loss of two–dimensionality for "spectral holes" in the last case.

4 CONCLUSIONS

The proposed algorithm for solving the quantum chemistry equation consists of the following:

1. First, we solve the equation following the ordinary way, selecting occupied orbitals by the lowest Fockian eigenvalues and disregarding the type of irreducible representation of the point symmetry group.

2. If the iteration procedure of solving is convergent, and jumps between different symmetry orbitals are absent, then we obtain ordinary solution without "spectral holes" ($K = 0$).

3. Otherwise, we find the final assembly of sets $\{\underline{n_i}\}$ from the latter iteration. Then, we solve successively the equation for each set $\{n_i\}$, choosing n_i the lowest–energy orbitals among m_i for every symmetry type *separately*.

4. Among the obtained solutions, the solution with minimal number of "spectral holes" is chosen. The chosen solution corresponds to the ground state of the system under consideration.

It should be stressed that the essence of the proposed technique consists, finally, in changing the way for selection of the occupied orbitals. As a result, unoccupied electronic states located below the Fermi level ("spectral holes") have been explicitly obtained for the ground state of a quantum system.

With the proposed technique the electronic structure calculations have been performed both for the extended cluster ($Cu_3O_{12} + 10\underline{Cu}$) and the defect cluster ($Cu_3O_{10} + 10\underline{Cu}$) in the lattice of point charges representing the rest of the $YBa_2Cu_3O_7$ crystal. For all considered charge distributions, a solution with one "spectral hole", which strongly localized in the ordinary space, has been found. For the cluster of the HTSC compound $YBa_2Cu_3O_7$, this hole state is mainly localized in the p_y–orbitals of apex O(2). By overlapping these orbitals form linear chains that can be considered as a "superconducting channel".

When the chain oxygens O(1) are removed (defect cluster), the hole state is more delocalized and turned by 90°, breaking the "superconducting channel" as expected. Also, a set of the parameters, assumed to be closely related to the critical characteristics of HTSC materials, has been calculated.

The relationship between the obtained results and the BCS theory, as well as the linear superconductivity by Little and two–dimensional superconductivity by Ginzburg, is pointed out.

It should be emphasized once more that the approach described above has a general nature and therefore it could be applied to any symmetric quantum chemistry object.

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