

CONTRIBUTION OF THE CLOSED *d*-ELECTRON SHELL OF THE Tl⁺ ION TO CHEMICAL BOND

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A method that takes into account the influence of the crystal lattice field on the radial wave functions of an activator ion has been developed, with the electron density of lattice ions being approximated by a Gaussian distribution. The radial wave functions of a Tl⁺ ion embedded into KCl, KBr, and KI crystal lattices have been calculated. The results of calculations confirm the assumption made earlier about the existence of a new type of chemical bonds. These bonds are caused by a change of the self-energy of *d*-electrons, which belong to the activator ion's electron shell.

An assumption has been made in work [1], that the closed shell of *d*-electrons in a Hg-like $[nd^{10}(n+1)s^2]$ ion gives a certain contribution to the energy of a chemical bond. This additional energy of a chemical bond is caused by the environment-induced variation of the *d*-electron energy eigenvalue. The appearance of a chemical bond of such a type, i.e. a non-directed *d*-bond, can be considered as a process which consists of two stages. The first stage comprises a reduction of the distance between ions, e.g., Tl⁺ and Cl⁻, due to the Coulomb interaction. The second stage is a perturbation of the electron shell of each ion due to the influence on the neighbor ion. This perturbation results in a reduction of the self-energy of, mainly, *d*-electrons of the Hg-like ion, which strengthens, from the viewpoint of the general energy balance, the chemical bond between Tl⁺ and Cl⁻ ions.

The assumption concerning the existence of a non-directed *d*-bond, which hereafter is coined as isotropic *d*-bond, has arisen when studying the processes of formation of the complexes of Hg-like and halogen ions. Since the electron spectra of those complexes and alkali-halide crystals activated by Hg-like ions are practically identical, the early quantitative calculations of a change of the *d*-electron energy eigenvalue have been made for an activator ion embedded into the crystal lattice [2]. The thallium ion Tl⁺, which possesses the $5d^{10}6s^2$ external electron shell and is a typical representative of Hg-like ions, was selected as an activator.

In order to make allowance for the influence of the lattice field on the radial wave functions of an

activator ion, the model of a lattice of charged spheres (LCS) has been proposed in work [2]. This model takes into consideration both the lattice periodicity and that ions are non-point objects, which has not been accounted for in the previous model potentials of crystals [3]. The analysis of the results obtained from the calculations of the radial wave functions and electron energy eigenvalues of a Tl⁺ ion with the $5d^{10}6s^2$ configuration of the external electron shell in the field of KCl, KBr, and KI lattices has confirmed an assumption made in work [1] that, besides the electrostatic interaction energy, an additional binding energy, which arises due to a variation of the *d*-electron energy under the influence of lattice ions, has to be taken into account in the halide complexes of Hg-like ions.

It is known that the use of any model simplifies calculations but makes results dependent on the features of the model. In this connection, versatile estimations of the model under consideration should be applied. In particular, an attempt to estimate the energy of electron affinity to an alkali-halide crystal in the framework of the LCS model gave an unexpected result: the calculated value of the affinity energy had an opposite sign in comparison with the experimental one. In connection with this circumstance, two tasks arose. First, the LCS model has to be improved. Secondly, the calculations of wave functions have to be carried out making use of the amended model in order to check up, whether the conclusion [1, 2] about the existence of a non-directed *d*-bond is premature.

The LCS was simulated by hard spheres, the charges and radii of which were equal to those of corresponding ions, and the spatial arrangement corresponds to the lattice structure. The potential U_{si} inside every *i*-th sphere, without regard for the potential created by other charged spheres, was accepted constant and equal to the potential on its surface $U_{si} = \pm 1/r_i$, where r_i is the radius of the corresponding sphere, the plus and minus signs correspond to a cation and an anion, respectively (hereafter, the atomic system of units is used: $\hbar = 1$, $e = 1$, and $c = 1$). The potential $U_s(r)$ created by

those spheres periodically changes along each coordinate axis with a spatial frequency $k = \pi/a$, where $2a$ is the lattice constant. Taking only the first harmonic of the lattice potential into consideration and averaging over the sphere, we obtain

$$U_s^{\text{LCS}}(r) = U_{s0} \sin(\pi r \sqrt{3}/a) / (\pi r \sqrt{3}/a) + \langle U_s^{\text{LCS}} \rangle, \quad (1)$$

where

$$U_{s0} = (r_c^{-1} + r_a^{-1})/2 \quad (2)$$

is the amplitude of the variable component of the potential,

$$\langle U_s^{\text{LCS}} \rangle = (r_c^2 - r_a^2)/(r_c^3 + r_a^3) \quad (3)$$

is the value of the $U_s(r)$ potential averaged over the lattice volume, and r_c and r_a are the cation and anion radii, respectively.

Besides the potential $U_s(r)$, the potential $U_m(r)$ created in the center of every i -th sphere by all other lattice ions is to be included. At the lattice sites, it accepts the value of the Madelung potential U_{m0} . After carrying out the procedure similar to what has been applied to the $U_s(r)$ potential, we obtain

$$U_m(r) = U_{m0} \sin(\pi r \sqrt{3}/a) / (\pi r \sqrt{3}/a). \quad (4)$$

With both the components of the lattice potential being taken into account, its expression for a positive test charge can be written down as

$$U_{kr} = U_s(r) \text{St} - U_m(r), \quad (5)$$

where the step function $\text{St}(r) = \exp[-\log 2 e^{-2(r-r_i)}]$ was introduced into formula (5) to switch off the potential $U_s(r)$ in the region $r < r_i$, where it is rather a rough approximation ($r_i = 0.136$ nm is the radius of a thallium ion [4]).

At $r \rightarrow \infty$, the lattice potential calculated in the framework of the LCS model tends to the average bulk value $\langle U_s^{\text{LCS}} \rangle$. Therefore, for an electron, in view of the sign of its charge, its potential (5) in KCl, KBr, and KI lattices, according to Eq. (1), is positive if the vacuum energy level is accepted zero. From the physical point of view, the value of the crystal field potential at $r \rightarrow \infty$ must correspond to the value of the electron affinity energy χ taken with the negative sign. Although there exist crystals, for which the electron affinity energy is negative [5], but it is positive for the majority of crystals and in particular for KCl, KBr, and KI. In Table 1, experimental values of the electron affinity for the KCl, KBr, and KI lattices are confronted with the

corresponding values calculated in the framework of the LCS model. The tabular data testify to that not only a disagreement between experimental and theoretical values of the electron affinity takes place for each crystal, but also the directions of its variation in the series KCl \rightarrow KBr \rightarrow KI are different.

One of the reasons of this discrepancy is that, according to the LCS model, the potential inside every sphere is assumed constant. In essence, it means that the charge of every sphere is completely disposed on the surface of the latter, which does not correspond to the actual distribution of charge in ions.

An assumption about a Gaussian distribution of the electron density in ions is closer to the reality. To take this fact into consideration, we use the expressions

$$\rho_a(r) = \rho_{a0} \exp(-r^2 d/r_a) \quad (6)$$

and

$$\rho_c(r) = \rho_{c0} \exp(-r^2 d/r_c), \quad (7)$$

where ρ_{a0} and ρ_{c0} are the amplitudes of those distributions for an anion and a cation, respectively. The meaning of the parameter d will be disclosed below.

Let the total number of electrons be equal to N_a in an anion and to N_c in a cation. Then, the normalization relations for the electron densities $\rho_a(r)$ and $\rho_c(r)$ are

$$\int_0^{\infty} \exp(-r^2 d/r_a) dr = N_a, \quad (8)$$

and

$$\int_0^{\infty} \rho_{c0} \exp(-r^2 d/r_c) dr = N_c. \quad (9)$$

With the help of relations (8) and (9) and considering the constant d as a parameter, one can find the amplitude values ρ_{a0} and ρ_{c0} of the electron density distributions. The charge $Q_i(r)$ confined within the sphere of radius r can be found with the help of the formula

$$Q_i(r) = \int_0^r \rho_i(r) dr, \quad (10)$$

Table 1. Experimental χ_{exp} and theoretical χ_{LCS} , i.e. calculated in the framework of the LCS model, values (in eV units) of the electron affinity in KCl, KBr, and KI crystals

	KCl	KBr	KI
χ_{exp}	0.5 [6]	0.9 [7]	1.1 [8]
χ_{LCS}	-2.6	-3.1	-3.4

where the subscript i corresponds to either an anion or a cation.

The effective potential of the ion

$$U_i(r) = U_{1i}(r) + U_{2i}(r) \tag{11}$$

consists of two parts: the potential created by the nucleus

$$U_{1i}(r) = Z_i/r \tag{12}$$

and the effective potential of the electron density

$$U_{2i}(r) = \int_r^\infty Q_i(r)/r^2 dr. \tag{13}$$

Here, Z_i is the charge of the nucleus of the corresponding ion. Knowing the effective potential, one can calculate the function of the effective charge

$$Q_i^{\text{eff}}(r) = U_i(r)r. \tag{14}$$

The value of the effective potential, averaged over the ion volume, is equal to

$$\langle U_i \rangle = 3(4\pi r_i^2)^{-1} \int_0^{r_i} U_i(r)4\pi r^2 dr, \tag{15}$$

where r_i is the radius of the corresponding ion.

Knowing the average value of the effective potential for every ion, one can find its average value $\langle U \rangle$ over the volume of the whole crystal as

$$\langle U \rangle = (\langle U_c \rangle r_c^3 + \langle U_a \rangle r_a^3)/(r_c^3 + r_a^3), \tag{16}$$

where $\langle U_c \rangle$ and $\langle U_a \rangle$ are the average values of the effective potential inside an anion and a cation, respectively. By fitting the parameter d , the average value of the potential $\langle U \rangle$ can be made equal to the experimental value of the electron affinity in the corresponding crystal lattice χ_{exp} . In such a manner, one can remove the discrepancy between the calculated theoretically and measured experimentally values of the electron affinity, which appeared, as mentioned above, in the LCS model.

Knowing $\langle U \rangle$, we can determine the amplitude U_{G0} of the variable component of the lattice potential as a simple mean of deviations of the ion potentials averaged within the sphere from the average bulk value

$$U_{G0} = ((\langle U_c \rangle - \langle U \rangle) + (\langle U \rangle - \langle U_a \rangle))/2. \tag{17}$$

The obtained values $\langle U \rangle$ of the potential averaged over the lattice volume and the amplitude of its variable component U_{G0} should be substituted for $\langle U_s \rangle$ and

U_{s0} , respectively, in formula (1). Such an account of the lattice field eliminates the discrepancies between the theoretical and experimental data concerning the electron affinity energy.

Table 2 quotes the amplitude values of the variable component of the lattice field potential and its average value calculated in the framework of the proposed model with the Gaussian distribution of electron density (GDED) and, for comparison, the corresponding values obtained in the framework of the LCS model.

In order to estimate how close the distribution of the electron density of lattice ions obtained in the framework of the given model is to the real one, we compared the curve of the electron density distribution calculated for a Cl^- ion in this work with the curve obtained for the approximation, also by a Gaussian curve, of the electron density of a Cl^- ion according to the data of work [9]. Both plots practically coincide. Since we intend below to take into account only the first harmonic and to carry out averaging Eqs. (1) and (4) over the sphere, distributions (8) and (9) can be regarded as quite satisfactory.

The method of calculations of the radial wave functions was the same as that applied in work [2]. We calculated the radial wave functions of the ground $5d^{10}6s^2$ state for a monovalent thallium ion surrounded by one of the KCl, KBr, and KI lattices. For this purpose, we solved the system of Hartree equations which took into account the potential created by the lattice:

$$Z'_i = P_i^2, \tag{18}$$

$$Y' = (Y - Z + \sum h_i Z_i - 13)/r, \tag{19}$$

$$Y'_i = (Y_i - Z_i)/r, \tag{20}$$

$$W'_i = (\varepsilon_i + l_i(l_i + 1)/r^2 - 2(Y + Y_i - St)/r)P_i - 2U_{kr}P_i, \tag{21}$$

$$P'_i = W_i. \tag{22}$$

Table 2. The amplitude values U_{s0} of the variable component of the lattice field potential and the average values $\langle U \rangle$ of the latter, both in a.e.u., calculated for KCl, KBr and KI lattices in the framework of the GDED and LCS models

Value	Model	KCl	KBr	KI
U_{s0}	GDED	0.573	0.509	0.468
	LCS	0.345	0.333	0.321
$\langle U \rangle$	GDED	0.018	0.033	0.040
	LCS	-0.096	-0.112	-0.123

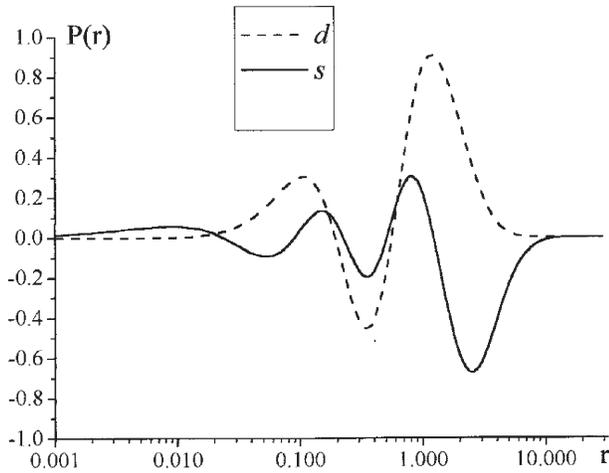


Fig. 1. The radial wave functions of d - and s -electrons of the ground $5d^{10}6s^2$ state of the Tl^+ ion surrounded by the KCl lattice

Here, the subscripts $i = 1, 2$ correspond to d - and s -electrons, respectively; l_i is the orbital quantum number ($l_1 = 2, l_2 = 0$); h_i is the number of electrons in the shell ($h_1 = 10, h_2 = 2$); ε_i is two times the eigenvalue of the electron energy; P_i is the radial wave function of the corresponding electron; Y_i and Z_i have the meaning of effective charges of the i -th electron shell for the field potential and strength, respectively; Y means the effective charge for the potential of the Tl^+ ion; and $Z + 13$ is the quantity calculated according to the data of work [10] and used for accounting the effective charge of the nucleus and the internal electrons of a thallium ion. The functions in Eqs. (18)–(22) correspond to the following boundary conditions: $Y(0) = 81, Y_i(0) = Z_i(0) = 0, Y(\infty) = Y_i(\infty) = Z_i(\infty) = 1, P_i(\infty) = P_i(0) = 0$. The radial wave function $P_i(r)$ has to possess $n_i - l_i - 1$ nodes in the region $0 < r < \infty$.

Potential (4) is created by all lattice ions, except for the nearest one. This expression takes also into account the potential created by the thallium ion at distances that exceed the radius of the latter r_i . Therefore, if $r > r_i$, the effective charge of the thallium ion should be reduced by one. This circumstance is taken into account by introducing the $St(r)$ function into Eq. (21).

The integration of the system of differential equations was carried out by the Torrance method [11], starting from large r 's, where the radial wave function can be approximated by an exponent.

The obtained radial wave functions are presented in Fig. 1. The energy eigenvalues are quoted in Table 3.

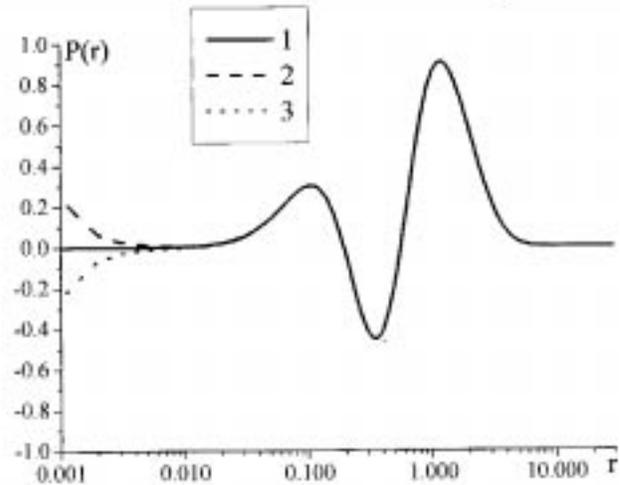


Fig. 2. Results of calculations of the radial wave functions of d -electrons for the energy value ε_d (1), $\varepsilon_d + 0.001$ (2), and $\varepsilon_d - 0.001$ (3); ε_d being the energy eigenvalue

Here, also for the sake of comparison, the energy eigenvalues of the radial wave functions calculated in the framework of the LCS model [2] are shown as well.

In Table 3, the electron energy eigenvalues of the thallium ion are displayed with an accuracy to three digits after the decimal point. Such an accuracy is necessary because the radial wave functions of the d -electron are very sensitive to relatively minor variations of the electron self-energy. As an example, the radial wave functions of d -electrons are depicted in Fig. 2 for the electron energy eigenvalues increased and reduced by 0.001 a.e.u. As is seen from these plots, even such a minor alteration in the energy eigenvalue results in violating the boundary conditions, which are the “criterion” that the solution is correct (it should be noted that the radial wave function of a d -electron is also sensitive to variations of the energy eigenvalues of s -electrons). Such a strong dependence of the wave function of the d -electron, which has a relatively large value of the orbital quantum number ($l = 2$), on small variations of electron energy eigenvalues correlates with the data of work [12].

Table 3. The energy eigenvalues for d - and s -electrons (ε_d and ε_s , respectively), the Madelung energy U_{m0} , and the “total” energy of the ion V calculated in the framework of the GDED and LCS models. All values are presented in a.e.u.

Quantity	GDED			LCS[2]		
	RCl	KBr	KI	KCl	KBr	KI
ε_d	1.328	1.349	1.367	1.226	1.234	1.260
ε_s	0.648	0.675	0.691	0.511	0.503	0.408
U_{m0}	0.295	0.281	0.265	0.295	0.281	0.265
V	7.583	7.701	7.791	6.935	6.954	6.977

An estimation of the contribution made by the closed d -shell to the chemical bond shows that this contribution modifies the self-energy value already in the second digit after the decimal point, so that such an accuracy can be adopted satisfactory in the framework of the Hartree model.

The radial wave functions, calculated in the GDED model, were compared with those calculated in the framework of the LCS model. It turned out that, in both cases, those functions are practically identical. Therefore, in this case, the conclusions made in work [2] about the form of the wave functions, in particular, about the compensation of the nepheloxetic effect, can be considered proper.

If the energy eigenvalues, calculated in the framework of both models, are confronted, one can see that the energy levels obtained in the GDED model are situated below the corresponding levels in the LCS model (see Table 3).

An increase, by the absolute value, of the d -electron energy eigenvalue with the anion radius, like what takes place in the LCS model, is preserved if the Gaussian distribution of the electron density is taken into account; it is also seen from Table 3. The behavior of the energy eigenvalue of an s -electron is quite different. According to the data of work [2], this value decreases as the anion radius grows, but if the Gaussian distribution of the electron density is taken into account, it increases together with the anion radius. So, a conclusion can be made that not only d -electrons contribute to the bond energy, but s -electrons too, although the contribution of the latter is considerably smaller.

The total bond energy consists of two components. One of them is caused by electrostatic interaction of a thallium ion with lattice ions and can be accepted equal to the Madelung energy U_{m0} . The second component stems from the energy variation of electrons of the external shell. Therefore, the energy balance connected to the formation of new complexes can be estimated by the variation of the total ion energy

$$V = E + U_{m0}, \quad (23)$$

where $2E = 10\varepsilon_d + 2\varepsilon_s$ is the energy of the electron shell calculated according to Koopman's theorem [12].

Thus, the account of the Gaussian distribution of the electron density in the lattice ions allows the discrepancies with experimental data, which exist in the LCS model, to be eliminated. The energy eigenvalues of d - and s -electrons, calculated within the framework of the GDED model, are larger by their absolute values

than the corresponding values obtained in the LCS model. Nevertheless, the assumption about the existence of an isotropic d -bond is confirmed in both models. The radial functions calculated in the framework of both methods practically coincide. Therefore, we may assert that the principal conclusions made on the basis of LCS calculations remain valid. Moreover, they find another sound confirmation in the GDED model.

1. *Belyi M.U., Okhrimenko B.A.* // Zh. Prikl. Spekr. — 1984. — **40**, N 4. — P. 648–652.
2. *Belyi M.U., Okhrimenko B.A.* // Izv. Vyssh. Ucheb. Zaved., Fiz. — 1995. — **38**, N 2. — P. 42–47.
3. *Kaminskii A.A., Aminov L.K., Ermolaev V.L. et al.* Physics and Spectroscopy of Laser Crystals and Molecules. — Moscow: Nauka, 1986 (in Russian).
4. *Chemist's Handbook*. Vol.1. — Leningrad: Gos. Nauch. Tekh. Izd. Khim. Liter., 1963 (in Russian).
5. *Bell R. L.* Negative Electron Affinity Devices. — Oxford: Clarendon Press, 1973.
6. *Pisani M.N., Hamill W.H.* // J. Appl. Phys. — 1980. — **51**, N 3. — P. 1569.
7. *Sasaki T., Iguchi Y., Sugawara H. et al.* // J. Phys. Soc. Jpn. — 1971. — **30**, N 2. — P. 580.
8. *Physical Constants. A Handbook* / Ed. by I.S. Grigoryev, E.Z. Meilikhov. — Moscow: Energoatomizdat, 1991 (in Russian).
9. *Froese Fischer C.* // Atom. Data — 1972. — **4**, N 4. — P. 301–399.
10. *Douglas A.S., Hartree D.R., Runciman W.A.* // Proc. Cambr. Soc. — 1955. — **51**, N 4. — P. 486–503.
11. *Hartree D.R.* The Calculation of Atomic Structures. — New York: John Wiley and Sons, 1957.
12. *Bethe H.A.* Intermediate Quantum Mechanics. — New York: Benjamin, 1964.

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ВНЕСОК ЗАМКНЕНОЇ ОБОЛОНКИ d -ЕЛЕКТРОНІВ ІОНА ТАЛІУ У ХІМІЧНИЙ ЗВ'ЯЗОК

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Резюме

Розроблено метод врахування впливу поля кристалічної ґратки на радіальні хвильові функції активаторного іона. У запропонованому методі використано наближення гауссового розподілу електронної густини іонів ґратки. Розраховано радіальні хвильові функції іона Tl^{+} , введеного в кристалічні ґратки KCl , KBr та KI . Результати розрахунків підтверджують висловлене раніше припущення про існування нового типу хімічного зв'язку. Цей зв'язок зумовлений зміною власного значення енергії d -електронів замкненої електронної оболонки активаторного іона.