to the abscissa, thus indicating an $l=0$. However, the intensity is rather low and this result is not too certain.

We furthermore could obtain similar data for the levels of Al^{28} at 5.128 and 5.435 mev (curves *d* and *e* of Fig. 2). According to Ref. 4 there are some more levels in their vicinity which could not be resolved here. However, since according to the same work[4] the intensity of the groups we observed is almost an order of magnitude larger than that of the neighboring ones, the shape of the curves is mostly determined by these two groups. According to our estimates from Refs. 1, 7 as described above it seems likely that the transition to the level at 5.128 mev (curve *d*) involves an $l=3$, and hence the parity of this state would be odd while the spin could have a value between 0 and 6. Analogously, curve *e* indicates for the level at 5. 435 mev a transfer of $l=1$ and hence odd parity and a spin between 1 and 4.

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SOVIET PHYSICS JETP VOLUME 3, NUMBER 4 NOVEMBER, 1956

The Interaction of the States of Two Zones in the Single-electron Scheme

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(Submitted to JETP editor, November 15, 1954)
J. Exptl. Theoret. Phys. (U.S.S.R.) 30, 695-700 (April, 1956)

A generalization of the results of Bogoliubov [1] in the zone (single-electron) approximation is worked out for the case of the presence of an excited state. The expression obtained for the energy spectrum permits a direct judgment on the combination of two zone states.

1. INITIAL HAMILTONIAN OF THE PROBLEM

IN the well known investigations of Bogoliubov[1] on the theory of metals, the simplest case of *s* electrons was considered. The eigenfunction of the system of electrons in the crystal corresponding to this case was sought in the form of a linear combination of antisymmetrized products composed only of eigenfunctions of the lowest atomic energy level. Moreover, improvement of the accuracy of the method requires, as is well known, the consideration, along with the eigenfunctions, of the eigenfunctions of the succeeding energy levels, in particular when they are close to the ground state. Solution of a similar problem for the case of the excited state is also the purpose of the present research. In this case we limit ourselves only to the electron zone approximation, since calculation of the interaction of the electrons complicates all the considerations considerably, and requires independent consideration.

Following Bogoliubov, we consider the crystalline lattice with "frozen" positive ions, and limit ourselves to the case of monovalent metals. For such a crystalline lattice, the secular equations are written down in the monograph[1] cited above in the representation of second quantization and their detailed investigation is carried out for the case of the *s*-state. In this case the index $\lambda=(l,m)$ (the aggregate of orbital and magnetic quantum numbers) drops out everywhere in general in the Bogoliubov formula. If we calculate the *p*-state along with the *s*-state, then the index λ will have four values: (0,0), (1,1), (1,0), (1,-1), which naturally complicate all the calculations greatly. Therefore, it seems quite appropriate to consider initially the simplest possible case — nondegenerate *p*-states, i.e., to consider that the *p* electron of the free atom is described by one real eigenfunction, and not by three. In this case, let $\lambda=0$

everywhere characterize the s-state, and $\lambda=1$ the p-state. This assumption naturally simplifies the problem. For initial orientation, we find it appropriate to limit ourselves to the consideration of such an artificial case, which is a crude approximation to reality.

Thus in the approximations assumed above, the initial Hamiltonian of the problem in the representation of second quantization has the form (see Ref. 1, p. 128, Eq. 4.36);

$$H = U_0 + \Sigma L_e(f, \lambda;\ f', \lambda')\, \hat{a}^{+}_{f\lambda\sigma}\hat{a}_{f'\lambda'\sigma}. \tag{1.1}$$

Here summation is carried out over all indices; U_0 is the constant potential energy of electrostatic interaction of the ions; $f = (f^1, f^2, f^3)$ are the cartesian coordinates of the ion in the crystalline lattice; $\lambda = (0.1)$ are the indices which characterize the normal and excited states; $\sigma = (+1/2, -1/2)$ are the two possible values of the spin quantum number; $\hat{a}^{+}_{f\lambda\sigma}$, $\hat{a}_{f\lambda\sigma}$ are the Fermi amplitude operators;

$$L_e(f, \lambda;\ f', \lambda') = \int \theta_{f\lambda}(q)\left\{-\frac{h^2}{2\mu}\Delta_q + V(q)\right\}\theta_{f'\lambda'}(q)\,dq,$$

where $q = (q^1, q^2, q^3)$ are the cartesian coordinates of the electron, $2\pi h$ is Planck's constant, μ is the mass of the electron, Δ is the Laplace operator, $V(q) = \sum_f U_f(q)$ is the periodic potential of the ionic lattice, $\theta_{f\lambda}(q) = \{\theta_{f0}(q), \theta_{f1}(q)\}$ are the orthonormalized atomic functions of the normal and excited states of the electron. The index e in $L_e(f\lambda; f'\lambda')$ denotes that to the potential of the ionic lattice is added the potential of the mean distribution of the charge of the electrons. Summation over f in (1.1) is extended over all fundamental directions of the crystal.

For what follows, it is appropriate to rewrite the Hamiltonian (1.1) differently, removing the sums over λ and λ' in it. Then the initial Hamiltonian is written in the following form:

$$\begin{aligned} H = U_0 &+ \sum_{f, f', \sigma} \{L_e(f0;\ f'0)\, \hat{a}^{+}_{f0\sigma}\hat{a}_{f'0\sigma} + L_e(f1; f'1)\, \hat{a}^{+}_{f1\sigma}\hat{a}_{f'1\sigma} \\ &+ L_e(f0;\ f'1)\, \hat{a}^{+}_{f0\sigma}\hat{a}_{f'1\sigma} + L_e(f1;\ f'0)\, \hat{a}^{+}_{f1\sigma}\hat{a}_{f'0\sigma}\}. \end{aligned} \tag{1.2}$$

Our problem now consists in the transformation of Eq. (1.2) to diagonal form.

2. DIAGONALIZATION OF THE HAMILTONIAN

The first step in the solution of the problem formulated in Sec. 1 consists in the transition from the operators $\hat{a}_{f0\sigma}$ and $\hat{a}_{f1\sigma}$ in (1.2) to the new Fermi operators $\hat{a}_{k0\sigma}$ and $\hat{a}_{k1\sigma}$. These new operators are related to the operators $\hat{a}_{f0\sigma}$ and $\hat{a}_{f1\sigma}$ by (see Ref. 1, p. 136):

$$\hat{a}_{f0\sigma} = N^{-1/2}\sum_k e^{i(kf)}\,\hat{a}_{k0\sigma};\quad \hat{a}_{k0\sigma} = N^{-1/2}\sum_f e^{-i(kf)}\hat{a}_{f0\sigma};$$
$$\hat{a}_{f1\sigma} = N^{-1/2}\sum_k e^{i(kf)}\hat{a}_{k1\sigma};\quad \hat{a}_{k1\sigma} = N^{-1/2}\sum_f e^{-i(kf)}\hat{a}_{f1\sigma}.$$

Making use of these relations, we obtain from (1.2):

$$\begin{aligned} H = U_0 + \sum_{k, \sigma} \{&W_{00}(k)\, \hat{a}^{+}_{k0\sigma}\hat{a}_{k0\sigma} \\ &+ W_{11}(k)\, \hat{a}^{+}_{k1\sigma}\hat{a}_{k1\sigma} + W_{01}(k)\, \hat{a}^{+}_{k0\sigma}\hat{a}_{k1\sigma} \\ &+ W_{10}(k)\, \hat{a}^{+}_{k1\sigma}\hat{a}_{k0\sigma}\}, \end{aligned} \tag{2.1}$$

where $(\lambda, \lambda' = 0,1)$

$$\begin{aligned} W_{\lambda\lambda'} &= \sum_f e^{-i(fk)} \int \theta_\lambda(q - f)\left\{-\frac{h^2}{2\mu}\Delta_q + V(q)\right\}\theta_{\lambda'}(q)\,dq \\ &= \sum_f e^{-i(fk)} L_e^{\lambda\lambda'}(f). \end{aligned} \tag{2.2}$$

To diagonalize Eq. (2.1), we turn to the method which has been applied recently in a number of researches.[2] For this purpose, we define the operators $\hat{b}_{k0\sigma}$ and $\hat{b}_{k1\sigma}$ by means of a canonical transformation [for the definition of S, see below, Eq. (2.7)]:

$$\begin{aligned} \hat{a}_{k0\sigma} &= e^{-iS}\hat{b}_{k0\sigma}e^{iS}; & \hat{a}^{+}_{k0\sigma} &= e^{-iS}\hat{b}^{+}_{k0\sigma}e^{iS}; \\ \hat{a}_{k1\sigma} &= e^{-iS}\hat{b}_{k1\sigma}e^{iS}; & \hat{a}^{+}_{k1\sigma} &= e^{-iS}\hat{b}^{+}_{k1\sigma}e^{iS}. \end{aligned} \tag{2.3}$$

Then the Hamiltonian (2.1) transforms into the Hamiltonian $\mathscr{H}$, so that

$$H = e^{-iS}\mathscr{H}e^{iS}, \tag{2.4}$$

$$\begin{aligned} \mathscr{H} = U_0 &+ \sum_{(k, \sigma)} \{W_{00}(k)\, \hat{b}^{+}_{k0\sigma}\hat{b}_{k0\sigma} + W_{11}(k)\, \hat{b}^{+}_{k1\sigma}\hat{b}_{k1\sigma} \\ &+ W_{01}(k)\, \hat{b}^{+}_{k0\sigma}\hat{b}_{k1\sigma} + W_{10}(k)\, \hat{b}^{+}_{k1\sigma}\hat{b}_{k0\sigma}\}. \end{aligned} \tag{2.5}$$

Further, we represent (2.4) in the form of an infinite series

$$H = \mathcal{H} - \frac{i}{1!}[S, \mathcal{H}] - \frac{1}{2!}[S,[S,\mathcal{H}]] + \frac{i}{3!}[S,[S,[S,\mathcal{H}]]] + \frac{1}{4!}[S,[S,[S,[S,\mathcal{H}]]]] + \ldots, \tag{2.6}$$

where S is a generating function which we define in the following fashion:

$$S = i\sum_k \{\Phi_1(k)\, \hat{b}^+_{k1\sigma}\hat{b}_{k0\sigma} + \Phi_2(k)\hat{b}^+_{k0\sigma}\hat{b}_{k1\sigma}\}, \tag{2.7}$$

where the coefficients $\Phi, (k)$ and $\Phi_2(k)$ are primitive unknown functions of the propagation vector k.

With the help of lengthy, but elementary, calculations, it is now easy to find all the expressions entering successively into Eq. (2.6). Below we write the result of the appropriate series of calculations:

$$\begin{aligned} H = U_0 + \sum_k \{W_{00}(k) & \\ - (W_{01}(k)\Phi_1(k) - W_{10}(k)\Phi_2(k))\Lambda_1(k) & \\ + 2(W_{00}(k) - W_{11}(k))\Phi_1(k)\Phi_2(k)\Lambda_2(k)\}\, \hat{b}^+_{k0\sigma}\hat{b}_{k0\sigma} & \\ + \sum_k \{W_{11}(k) & \\ + (W_{01}(k)\Phi_1(k) - W_{10}(k)\Phi_2(k))\Lambda_1(k) & \\ - 2(W_{00}(k) - W_{11}(k))\Phi_1(k)\Phi_2(k)\cdot\Lambda_2(k)\}\, \hat{b}^+_{k1\sigma}\hat{b}_{k1\sigma} & \\ + \sum_k \{W_{10}(k) & \\ - 2(W_{01}(k)\Phi_1(k) - W_{10}(k)\Phi_2(k))\Phi_1(k)\Lambda_1(k) & \\ + (W_{00}(k) - W_{11}(k))\Phi_1(k)\Lambda_1(k)\}\, \hat{b}^+_{k1\sigma}\hat{b}_{k0\sigma} & \\ + \sum_k \{W_{01}(k) & \\ + 2(W_{01}(k)\Phi_1(k) - W_{10}(k)\Phi_2(k))\Phi_2(k)\Lambda_2(k) & \\ - (W_{00}(k) - W_{11}(k))\Phi_2(k)\Lambda_1(k)\}\, \hat{b}^+_{k0\sigma}\hat{b}_{k1\sigma}, & \end{aligned} \tag{2.8}$$

where $\Lambda_1(k)$ and $\Lambda_2(k)$ are given by

$$\begin{gathered} \Lambda_1(k) = 1 + \sum_{n=1}^{\infty} \frac{(4\Phi_1(k)\Phi_2(k))^n}{(2n+1)!} = \frac{\operatorname{sh} 2\sqrt{\Phi_1(k)\Phi_2(k)}}{2\sqrt{\Phi_1(k)\Phi_2(k)}}; \\ \Lambda_2(k) = \frac{1}{2} + \sum_{n=1}^{\infty} \frac{(4\Phi_1(k)\Phi_2(k))^n}{(2n+2)!} = \frac{\operatorname{ch} 2\sqrt{\Phi_1(k)\Phi_2(k)} - 1}{4\Phi_1(k)\Phi_2(k)}. \end{gathered} \tag{2.9}$$

If we substitute Eq. (2.9) in (2.8) and set the curly brackets equal to zero (which stand in front of the nondiagonal products of operators $b_{k\lambda\sigma}$), then it is not difficult to show that

$$\begin{gathered} \Phi_2(k) = -\frac{W_{01}(k)}{W_{10}(k)}\Phi_1(k); \\ \operatorname{tg} 2\Phi_1(k)\sqrt{\frac{W_{01}(k)}{W_{10}(k)}} = -\frac{2\sqrt{W_{10}(k)W_{01}(k)}}{W_{00}(k) - W_{11}(k)}, \end{gathered} \tag{2.10}$$

and the terms remaining in Eq. (2.8) in this case yield

$$\begin{aligned} H = U_0 + & \\ \frac{1}{2}\sum_{k,\sigma}\{W_{00}(k) + W_{11}(k) + [(W_{00}(k) - W_{11}(k))^2 & \\ + 4W_{01}(k)W_{10}(k)]^{1/2}\}\, \hat{b}^+_{k0\sigma}\hat{b}_{k0\sigma} & \\ + \frac{1}{2}\sum_{k,\sigma}\{W_{00}(k) + W_{11}(k) & \\ - [(W_{00}(k) - W_{11}(k))^2 & \\ + 4W_{01}(k)W_{10}(k)]^{1/2}\}\, \hat{b}^+_{k1\sigma}\hat{b}_{k1\sigma}. & \end{aligned} \tag{2.11}$$

Thus the energetic spectrum of the system under investigation will be

$$\begin{aligned} E = U_0 + & \\ \frac{1}{2}\sum_{k,\sigma}\{W_{00}(k) + W_{11}(k) + [(W_{00}(k) - W_{11}(k))^2 & \\ + 4W_{01}(k)W_{10}(k)]^{1/2}\}\, n_{k0\sigma} & \\ + \frac{1}{2}\sum_{k,\sigma}\{W_{00}(k) + W_{11}(k) & \\ - [(W_{00}(k) - W_{11}(k))^2 & \\ + 4W_{01}(k)W_{10}(k)]^{1/2}\}\, n_{k1\sigma}, & \\ n_{k1\sigma},\quad n_{k0\sigma} = 0,1; \quad \sum_{k,\sigma}(n_{k0\sigma} + n_{k1\sigma}) = N, & \end{aligned} \tag{2.12}$$

and the generating function is

$$S = \frac{i}{2}\sum_k \arccos \frac{W_{00}(k) - W_{11}(k)}{[(W_{00}(k) - W_{11}(k))^2 + 4W_{01}(k)W_{10}(k)]^{1/2}} \times \left\{\sqrt{\frac{W_{10}(k)}{W_{01}(k)}}\,\hat{b}^+_{k1\sigma}\hat{b}_{k0\sigma} - \sqrt{\frac{W_{01}(k)}{W_{10}(k)}}\,\hat{b}^+_{k0\sigma}\hat{b}_{k1\sigma}\right\}.$$

3. CRITIQUE OF THE RESULTS

The quantities $W_{\lambda\lambda'}(k)$ by which the energy spectrum (2.12) is given, can be given a graphic physical interpretation. With this purpose we must first transform $W_{\lambda\lambda'}(k)$. In the Eqs. (2.2) for $W_{\lambda\lambda'}(k)$, it is appropriate to go from the orthonormal atomic functions $\theta_{f\lambda}(q)$ to the ordinary atomic functions $\varphi_{f\lambda}(q)$. The general method of such a transformation was developed by Bogoliubov[1], and can be reproduced without difficulty in our case. Therefore we give below the explicit equations for the quantities under consideration up to first order of smallness inclusively, not basing any conclusion on them:

$$W_{00}(k) = E_0 + \int \varphi_0^2(q)\,[V(q) - U(q)]\,dq + \sum_{f\neq 0} A_{00}(f)\, e^{-i(fk)}; \tag{3.1}$$

$$W_{11}(k) = E_0 + \Delta E + \int \varphi_1^2(q)\,[V(q) - U(q)]\,dq + \sum_{f\neq 0} A_{11}(f)\, e^{-i(fk)};$$

$$W_{01}(k) = \int \varphi_0(q)\,\varphi_1(q)\,[V(q) - U(q)]\,dq + \sum_{f\neq 0} A_{01}(f)\, e^{-i(fk)};$$

$$W_{10}(k) = \int \varphi_1(q)\,\varphi_0(q)\,[V(q) - U(q)]\,dq + \sum_{f\neq 0} A_{10}(f)\, e^{-i(fk)},$$

where E_0 is the energy of the s-electron in the isolated atom, ΔE is the perturbation energy of the electron in the isolated atom;

$$\begin{aligned}
A_{00}(f) &= \tfrac{1}{2}\int\Big\{\Big[V(q) - U(q-f) - \int \varphi_0^2(q_1 - f)\,(V(q_1) - U(q_1 - f)\,dq_1\Big] \\
&\quad + \Big[V(q) - U(q) - \int \varphi_0^2(q_1)\,(V(q_1) - U(q_1))\,dq_1\Big]\Big\}\,\varphi_0(q)\,\varphi_0(q-f)\,dq; \\
A_{11}(f) &= \tfrac{1}{2}\int\Big\{\Big[\Delta E + V(q) - U(q-f) - \int \varphi_1^2(q_1 - f)\,(\Delta E + V(q_1) \\
&\quad - U(q_1 - f))\,dq_1\Big] + \Big[\Delta E + V(q) - U(q) - \int \varphi_1^2(q_1)\,(\Delta E + V(q_1) \\
&\quad - U(q_1))\,dq_1\Big]\Big\}\,\varphi_1(q)\,\varphi_1(q-f)\,dq; \\
A_{01}(f) &= \int [\Delta E + V(q) - U(q-f)]\,\varphi_0(q)\,\varphi_1(q-f)\,dq - \tfrac{1}{2}\Big\{\int \varphi_0^2(q)\,[V(q) \\
&\quad - U(q)]\,dq + \int \varphi_1^2(q-f)\,[\Delta E + V(q) - U(q-f)]\,dq\Big\}\int \varphi_0(q)\,\varphi_1(q-f)\,dq; \\
A_{10}(f) &= \int [V(q) - U(q-f)]\,\varphi_1(q)\,\varphi_0(q-f)\,dq - \tfrac{1}{2}\Big\{\int \varphi_0^2(q-f)\,[V(q) \\
&\quad - U(q-f)]\,dq + \int \varphi_1^2(q)\,[\Delta E + V(q) - U(q)]\,dq\Big\}\int \varphi_1(q)\,\varphi_0(q-f)\,dq.
\end{aligned} \tag{3.2}$$

Furthermore, if we limit our consideration, for example, to the case of a simple cubic lattice, then in place of Eq. (3.1) we will have:

$$W_{00}(k) = E_0 + C_0 + 2A_{00}\,(\cos ak^x + \cos ak^y + \cos ak^z); \tag{3.3}$$

$$W_{11}(k) = E_0 + \Delta E + C_1 + 2A_{11}\,(\cos ak^x + \cos ak^y + \cos ak^z);$$

$$W_{01}(k) = B + 2A_{01}\,(\cos ak^x + \cos ak^y + \cos ak^z);$$

$$W_{10}(k) = B + 2A_{10}\,(\cos ak^x + \cos ak^y + \cos ak^z).$$

Here a is the cubic lattice constant;

$$C_0 = \int \varphi_0^2(q)\,[V(q) - U(q)]\,dq; \qquad (3.4)$$

$$C_1 = \int \varphi_1^2(q)\,[V(q) - U(q)]\,dq;$$

$$B = \int \varphi_0(q)\,\varphi_1(q)\,[V(q) - U(q)]\,dq.$$

Thus, as might be expected, the s level E_0 of the isolated atom in the crystalline lattice is displaced by a quantity C_0 and split into a band, the width of which is determined by the value of the transfer integral A_{00}. Analogously, the perturbed p-level $(E_0 + \Delta E)$ of the isolated atom is shifted in the crystalline lattice by the value C_1 and splits into a band whose width is determined by the transfer integral A_{11}. $W_{00}(k)$ and $W_{11}(k)$ are respectively the energies of the s- and p-electrons in the crystalline lattice.

It is evident that the energy spectrum of the system will be determined only by the energies $W_{00}(k)$ and $W_{11}(k)$ if we neglect the integrals $L_e(f0; f'1)$ and $L(f1; f'0)$ in Eq. (1.2). Actually,

$$E = U_0 + \sum_{k,\sigma} (W_{00}(k)\, n_{k0\sigma} + W_{11}(k)\, n_{k1\sigma}), \qquad (3.5)$$

$$n_{k0\sigma},\ n_{k1\sigma} = 0, 1; \quad \sum_{k,\sigma} (n_{k0\sigma} + n_{k1\sigma}) = N,$$

i.e., the energy spectrum of the system in this case is composed additively of $W_{00}(k)$ and $W_{11}(k)$ taken with corresponding coefficients (occupation numbers). If the integrals $L_e(f0; f'1)$ and $L_e(f1; f'0)$ are considered as small quantities, then we can expand the square root in Eq. (2.12) in a series and restrict ourselves to the second terms of the expansion. In this case we have

$$E = U_0 + \sum_{k,\sigma} \left\{ W_{00}(k) + \frac{W_{01}(k)\, W_{10}(k)}{W_{00}(k) - W_{11}(k)} \right\} n_{k0\sigma}$$

$$+ \sum_{k,\sigma} \left\{ W_{11}(k) - \frac{W_{01}(k)\, W_{10}(k)}{W_{00}(k) - W_{11}(k)} \right\} n_{k1\sigma}, \qquad (3.6)$$

$$n_{k0\sigma},\ n_{k1\sigma} = 0, 1; \quad \sum_{k,\sigma} (n_{k0\sigma} + n_{k1\sigma}) = N.$$

Comparing (3.5) with (3.6), we conclude that in the latter case the energies of the s-and p-electrons in the crystal are changed by $W_{01}(k)\, W_{10}(k) / [W_{00}(k) - W_{11}(k)]$. This correction depends on the integrals $W_{01}(k)$ and $W_{10}(k)$. The latter in turn, in agreement with Eq. (3.3), contain the energy of transfer of the electron from the normal to the excited state at its lattice point (integral B) and the integral A_{01} and A_{10} for transitions between neighboring atoms are of the same type. Consequently, the matrix elements $W_{01}(k)$ and $W_{10}(k)$ can be treated as the energy of the "excited" and "bound" electron in the lattice.

In the general case, when the integrals $L_e(f0; f'1)$ and $L_e(f1; f'0)$ are not small, the energy spectrum of the electrons in the crystalline lattice is given by Eq. (2.12). In this case, the combination of the s- and p-states is essentially established, and we cannot neglect the energies $W_{01}(k)$ and $W_{10}(k)$ in comparison with the energies $W_{00}(k)$ and $W_{11}(k)$. Such is evidently the case, for example, in bivalent metals (alkali earths)[3] and must be taken into account in the construction of a theory of their electrical conductivity. The first case of the overlapping of the bands was considered by Blokhintsev.[4] He performed an attempt at the approximation treatment of the combination of of the s-state with degenerate p-states and obtained a series of interesting, but only qualitative results.

Finally, it seems appropriate to emphasize that in the ordinary treatment of the approximation of strong coupling in the zone theory interaction of the states of the s- and p-zones in the zeroth approximation does not in general enter into the theory at all. It appears only upon the introduction of additional, in considerable degree artificial, assumptions. In our case, the necessity for this is lacking. The interaction of the zones enters into the theory in zeroth approximation (through the quantities W_{10} and W_{01}) as a consequence of the strict treatment of the zone approximation with the help of the apparatus of second quantization.

In conclusion, the authors consider it their pleasant duty to express their gratitude to Prof. S. V. Vonsovskii for a series of critical discussions.

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