the sum of (14) and (19). This Hamiltonian agrees with that of the phenomonological theory of the generalized nuclear model.

The introduction of auxiliary ("superfluous") variables leads to the necessity of applying subsidiary conditions to the wave function, and these can be written

$$\left(\rho_k - N^{-1/2} \sum_j \exp\{-i\,\mathbf{k}\mathbf{r}_j\}\right)\Phi = 0 \qquad (20)$$

for the first of the problems considered here (Sec. 3), and

$$\left[\alpha_{lm} - (4\pi/3N)\sum_j (r_j/R_0)^l Y_{lm}(\vartheta_j \varphi_j)\right]\Phi = 0 \qquad (21)$$

for the case of surface oscillations.

5. The special choices of the $\varphi_j(r_j)$ considered above can be generalized for other problems. The generalization consists of indicating a method for finding the $\varphi_j(r_j)$.

In solving boundary value problems the Schrödinger equation can be written in the hydrodynamic form

$$-E_j + \frac{1}{2M}(\nabla S_j)^2 - \frac{\hbar^2}{4M}\left[\frac{\Delta p_j}{p_j} - \frac{1}{2}\left(\frac{\Delta p_j}{p_j}\right)^2\right] = 0;$$

$$\frac{1}{M}\nabla(p_j \nabla S_j) = 0, \quad \varphi_j(r_j) = \sqrt{p_j}\exp(i/\hbar S_j).$$

This representation of the Schrödinger equation is convenient in that it is simple to formulate boundary conditions for it in analogy with hydrodynamics.

In the constant density case the S_j satisfy Laplace's equation. However this is not the only generalization. The $\varphi_j(r_j)$ can, for instance, be found from self-consistent field equations.

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Electrical, Optical and Elastic Properties of Diamond Type Crystals. I

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The energy of a homopolar crystal is expressed as a function of the displacements and of the dipole moments of the atoms. By means of a variational method, the relation between the displacements and the deformation of the electronic shells of the atoms is established and equations of motion are presented in which the displacements and dipole moment of the atoms play the role of generalized coordinates.

As was shown in a paper by one of the authors[1], Born's atomic theory[2] can be improved by taking into consideration the deformability of the atoms. In the foundation of a theory of the lattice one must assume an expression for the energy U in the form of a quadratic function of the displacements $\mathbf{u}_s^l$ and of the dipole moments $\mathbf{P}_s^l$ of all the atoms (l is the cell number and s the number of the atom in the cell). In the calculation of delay of interaction, one can consider optical, electrical and elastic properties of crystals from a single point of view. The explicit introduction of the quantities $\mathbf{P}_s^l$ is necessary also in the microscopic theory of localized electron states in a crystal[4].

While in ionic crystals the consideration of the deformability of the ions improves the quantitative agreement of theory with experiment[1], in homopolar crystals, where the dipole moments of the displacements $\mathbf{p}_s^l = e_s \mathbf{u}_s^l$ are absent ($e_s = 0$), such considerations lead to a series of qualitatively new consequences. Owing to the dependence of the exchange integrals on the dipole moments of the atoms, the displacements of the latter will lead to their polarization and conversely. Thus, inertial polarization can exist also in homopolar crystals. This permits one to examine the interaction of a nonpolar crystal with an electromagnetic field and, in particular, the lattice absorption which was experimentally observed by Lax and Burstein[5]. The explanation given in Ref. 5 for the lattice absorption (fractional division of charges during oscillations of the atoms) pertains only to secondary combination bands. Considerations of the role of impurity in the fundamental absorption are also inconclusive in view of the weak dependence of the absorption in diamond, Si and Ge on the character and quantity of the impurity. The present investigation permits one to predict the absorption correct as to order of magnitude (approximately λ/d times smaller than in ionic crystals) without the use of any free parameters.

Finally, the presence of inertial polarization leads to an interaction of current carriers with optical oscillations of the lattice. In homopolar crystals this must lead principally to the same, only quantitatively weaker, effects, examined by Pekar[6], as they occur in ionic crystals. In the present work, a method of examining that relation between the displacements and the polarization of the atoms is given. In the following works, it is applied to the study of various properties of crystals[7].

1. THE WAVE FUNCTION AND ENERGY OF THE ELECTRONS OF A CRYSTAL.

In the examination of the dynamics of the lattice, the motion of the nuclei and the electrons of the atoms are conveniently described in an adiabatic approximation. For the first step it is necessary to find the wave function of all the electrons under arbitrary (small displacements of the nuclei. This energy will play the role of the potential energy in the problem of the motion of the nuclei. In diamond type crystals, it is sufficient to consider only the four valence electrons of each atom, introducing the screened nuclear charge $z_s(\mathbf{r})$, where $z_s \to 4$ for $r \to \infty$.

In the Fock approximation we seek a wave function of the electrons in the form of products of functions of individual σ-bonds $\psi_{(pq)}$ (p and q are abbreviated notations of the numbers of atoms). Antisymmetrization is performed only over the strongly interacting electrons of a single bond:

$$\begin{aligned}\Psi_{(pq)} &= C_{(pq)}\,[\psi_{pq}(\mathbf{r}_{pq})\,\psi_{qp}(\mathbf{r}_{qp}) \\ &\quad + \psi_{pq}(\mathbf{r}_{qp})\,\psi_{qp}(\mathbf{r}_{pq})]\,\chi_a(\sigma_1,\sigma_2), \\ C_{(pq)} &= [2(1+|S_{pq}|^2)]^{-1/2}; \end{aligned} \tag{1}$$

S_{pq} is the nonorthogonality integral, Ψ_{pq} is the wave function of an electron $\mathbf{r}_{pq}$ in atom p which brings about its bond with atom q. The form of ψ_{pq} will be determined from a variational principle. Let $\overline{H}_{(pq)}$ denote the mean kinetic and potential energy of the electrons of the bond (pq), including their mutual interaction with the nuclei p and q, half the energy of interaction with the remaining electrons of the atoms p and q and one fourth of the energy of interaction with the nuclei of the nearest neighbors of p and q:

$$\begin{aligned}\overline{H}_{(pq)} &= 2|C_{(pq)}|^2 \Big\{ \int (\psi^*_{pq}(\mathbf{r}) \\ &\quad + S_{pq}\psi^*_{qp}(\mathbf{r}))\Big(-\frac{\hbar^2}{2m}\Delta_r - \frac{e^2 z_s(\mathbf{r}-\mathbf{R}_p)}{|\mathbf{r}-\mathbf{R}_p|} \\ &\quad + e^2 \sum_{q'}{}' \int \frac{|\psi_{pq'}(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}\,d\tau'\Big)\psi_{pq}(\mathbf{r})\,d\tau \\ &\quad + e^2 \sum_{q'}{}' \Big[(|C_{(pq')}|^2 - 1) \\ &\quad \times \int \frac{1}{|\mathbf{r}-\mathbf{r}'|}|\psi_{pq'}(\mathbf{r}')|^2(|\psi_{pq}(\mathbf{r})|^2 \\ &\quad + S_{pq}\psi^*_{qp}(\mathbf{r})\psi_{pq}(\mathbf{r}))\,d\tau\,d\tau' + |C_{(pq')}|^2 \\ &\quad \times \int \frac{1}{|\mathbf{r}-\mathbf{r}'|}(|\psi_{pq}(\mathbf{r})|^2 + S_{pq}\psi^*_{qp}(\mathbf{r})\,\psi_{pq}(\mathbf{r}) \\ &\quad + |\psi_{qp}(\mathbf{r})|^2 + S_{pq}\psi^*_{pq}(\mathbf{r})\,\psi_{qp}(\mathbf{r}))\,(|\psi_{q'p}(\mathbf{r}')|^2 \\ &\quad + S'_{qp}\psi^*_{pq'}(\mathbf{r}')\,\psi_{q'p}(\mathbf{r}') + |\psi_{pq'}(\mathbf{r}')|^2 \\ &\quad + S_{pq'}\psi^*_{q'p}(\mathbf{r}')\psi_{pq'}(\mathbf{r}'))\,d\tau\,d\tau' + \int \frac{1}{|\mathbf{r}-\mathbf{r}'|} \\ &\quad \times |\psi_{pq'}(\mathbf{r}')|^2\,(|\psi_{qp}(\mathbf{r})|^2 + S_{qp}\psi^*_{pq}(\mathbf{r}) \\ &\quad \times \psi_{qp}(\mathbf{r}))\,d\tau\,d\tau' - \int \frac{e^2 z_s(\mathbf{r}-\mathbf{R}_{q'})}{4|\mathbf{r}-\mathbf{R}_{q'}|}\,(|\psi_{qp}(\mathbf{r})|^2 \\ &\quad + |\psi_{pq}(\mathbf{r})|^2)\,d\tau\Big] - \int \frac{e^2 z_s(\mathbf{r}-\mathbf{R}_q)}{|\mathbf{r}-\mathbf{R}_q|}\,(|\psi_{pq}(\mathbf{r})|^2 \\ &\quad + S_{pq}\psi^*_{qp}(\mathbf{r})\cdot\psi_{pq}(\mathbf{r}))\,d\tau\Big\} + \{p \rightleftarrows q\} \\ &\quad + e^2 \int \frac{1}{|\mathbf{r}-\mathbf{r}'|}\,|\psi_{pq}(\mathbf{r})|^2\,|\psi_{qp}(\mathbf{r}')|^2\,d\tau\,d\tau' \\ &\quad + e^2 \int \frac{1}{(1+|S_{pq}|^2)\,|\mathbf{r}-\mathbf{r}'|}\,(\psi^*_{pq}(\mathbf{r})\,\psi^*_{qp}(\mathbf{r}')\,\psi_{pq} \\ &\quad \times (\mathbf{r}')\,\psi_{qp}(\mathbf{r}) - |S_{pq}|^2\,|\psi_{pq}(\mathbf{r})|^2\,|\psi_{qp}(\mathbf{r}')|^2) \\ &\quad \times d\tau\,d\tau' + \frac{16e^2}{|\mathbf{R}_q-\mathbf{R}_p|}. \end{aligned} \tag{2}$$

The symbol $\{p \rightleftarrows q\}$ denotes the addition of the entire preceeding expression in which p and q exchange places. We denote the sum of the interaction energies of the electrons of each pair of bonds (pq) and (rs) which do not have common atoms, by

$$\begin{aligned}\overline{H}_{(pq)(rs)} = & -e^2 \int \left(\frac{1}{|\mathbf{r}-\mathbf{R}_r|} + \frac{1}{|\mathbf{r}-\mathbf{R}_s|} \right) (|\psi_{pq}(\mathbf{r})|^2 \\ & + |\psi_{qp}(\mathbf{r})|^2)\, d\tau - e^2 \int \left(\frac{1}{|\mathbf{r}-\mathbf{R}_p|} + \frac{1}{|\mathbf{r}-\mathbf{R}_q|} \right) \\ & \times (|\psi_{rs}(\mathbf{r})|^2 + |\psi_{sr}(\mathbf{r})|^2)\, d\tau + \Big) \frac{e^2}{|\mathbf{R}_p - \mathbf{R}_s|} \\ & + \frac{e^2}{|\mathbf{R}_p - \mathbf{R}_r|} + \frac{e^2}{|\mathbf{R}_q - \mathbf{R}_s|} + \frac{e^2}{|\mathbf{R}_q - \mathbf{R}_r|} \\ & + \int \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} (|\psi_{pq}(\mathbf{r})|^2 \\ & \quad + |\psi_{qp}(\mathbf{r})|^2) \times (|\psi_{rs}(\mathbf{r}')|^2 + |\psi_{sr}(\mathbf{r}')|^2)\, d\tau\, d\tau'. \end{aligned} \tag{3}$$

Then

$$H = \sum_{(pq)} \overline{H}_{(pq)} + \sum_{(pq)(rs)}{}' \overline{H}_{(pq)(rs)}. \tag{4}$$

The overlap integrals, which are of the order of S_{pq}, are retained only in terms which contain the interaction of electrons of one atom or of one bond among themselves and with their nuclei.

Keeping in mind that the wave functions of the electrons which constitute the σ-bonds in the crystal ψ_{pq} are essentially different from the wave functions of isolated atoms, we use perturbation theory for calculation of the former, for close eigenvalues. For elements of the fourth group, the differences between the energies of s and p electrons with the same principal quantum number are of the order of the interaction energy between atoms. Therefore, on the incorporation of atoms into a crystal, there occurs a redistribution of electrons among levels and the formation of functions of σ-bonds.

Having denoted the energy levels of the valence electrons by $E_1 E_2 \ldots$, we can thus regard $\varepsilon^2 = (E_2 - E_1)/(E_5 - E_1)$ as a small expansion parameter. Obviously, S_{pq} and all the terms in $\overline{H}$ which contain products of functions with interchanged electrons must be regarded as quantities of the order of ε. We shall seek the wave function of the r-th electron of the bond (pq) in the form of a superposition of excited functions of the atom p:

$$\psi_{pq}(r) = \sum_{i=1}^{\infty} \gamma_{pqi} \psi_{pi}(\mathbf{r}), \tag{5}$$

and we expand the parameters γ_{pqi} in powers of ϵ:

$$\gamma_{pqi} = \gamma^{(0)}_{pqi} + \varepsilon^2 \gamma^{(2)}_{pqi} + \varepsilon^3 \gamma^{(3)}_{pqi} + \cdots \tag{6}$$

(the expansion of $\overline{H}$ must be begun from terms $\sim \epsilon^2$), wherein for $i \geqslant 5$, $\gamma^{(0)}_{pqi} = 0$. In order not to complicate the problem by the introduction of an endless chain of orthogonality conditions for the functions ψ_{pq} with different q's, we restrict the class of approximating functions with the hypothesis that $\gamma^{(0)}_{pqi} + \epsilon^2 \gamma^{(2)}_{pqi}$ does not depend on the displacements of the nuclei if $i \leqslant 4$.

We subject the parameters of the approximation γ_{pqi} to the orthogonality conditions

$$\sum_{i=1}^{\infty} \gamma^*_{pqi} \gamma_{pq'i} = \delta_{qq'},$$

i. e.,

$$\sum_{i=1}^{4} (\gamma^{(0)*}_{pqi} + \varepsilon^2 \gamma^{(2)*}_{pqi})(\gamma^{(0)}_{pq'i} + \varepsilon^2 \gamma^{(2)}_{pq'i}) = \delta_{qq'}, \tag{7}$$

$$\varepsilon^3 \sum_{i=1}^{4} (\gamma^{(0)*}_{pqi} \gamma^{(3)}_{pq'i} + \gamma^{(0)}_{pq'i} \gamma^{(3)*}_{pqi}) = 0, \tag{8}$$

$$\varepsilon^4 \sum_{i=1}^{4} (\gamma^{(0)*}_{pqi} \gamma^{(4)}_{pq'i} + \gamma^{(0)}_{pq'i} \gamma^{(4)*}_{pqi}) + \varepsilon^4 \sum_{i=5}^{\infty} \gamma^{(2)*}_{pqi} \gamma^{(2)}_{pq'i} = 0, \tag{9}$$

and in addition, as in Ref. 1, we simultaneously use the conservation of the dipole moments $\mathbf{P}_p$ of each atom.

$$-e \int \mathbf{r} \sum_q |\psi_{pq}(\mathbf{r}')|^2\, d\tau = \mathbf{P}_p = \text{const},$$

i. e., with accuracy to ϵ^2:

$$-e\varepsilon^2 \sum_q \sum_{j=1}^{4} \sum_{i=5}^{\infty} (\gamma^{(2)*}_{pqi} \gamma^{(0)}_{pqj} (i|x|j) + \text{complex conj.}) = P_{px}$$

We assume $\gamma^{(0)}_{pqi}$ and $\gamma^{(2)}_{pqi}$ for $i \leqslant 4$ known and the conditions Eq. (7) for undisplaced nuclei fulfilled. The conditions Eqs. (8) and (9) can be satisfied through the choice of $\gamma^{(3)}_{pqi}$ and $\gamma^{(4)}_{pqi}$. Their values are not important for us since the corresponding contribution to the Hamiltonian will be of the order of ϵ^5 or ϵ^6 and at the same time we retain terms no higher than ε^4.

Since the classification of electrons into *s*, *p* and *d* states is possible only for a spherically symmetrical field, we introduce (for each atom) the Hamiltonian of the zeroth approximation $\hat{H}^{(0)}$, identical, for all the valence electrons, with interaction potential energy.

$$\frac{3e^2}{4}\sum_{i=1}^{4}\int\frac{|\psi_{pi}(r')|^2\,d\tau'}{|\mathbf{r}-\mathbf{r}'|}$$

and we shall regard the ψ_{pi} $i=1, 2 \ldots \infty$ as its characteristic functions:

$$\hat{H}_p^{(0)}\psi_{pi} = E_i^0\psi_{pi}. \tag{11}$$

2. EXPANSION OF THE ENERGY OF THE ELECTRONS IN POWERS OF THE DIPOLE MOMENTS AND DISPLACEMENTS OF THE ATOMS

Substituting the expansions Eqs. (5) and (6) in the expression for the mean energy $\overline{H}$ [Eq. (2)], we transform that part of $\overline{H}$ which contains the dipole moments $\mathbf{P}_p$, i. e., the coefficients $\gamma_{pqi}^{(2)}$, $i \geqslant 5$, taking account of the orthogonality conditions and Eq. (11). Since the exchange integrals are of the order of ϵ^2, then with accuracy to ϵ^4:

$$\overline{H}(\gamma_{pqi}^{(2)}) = \varepsilon^4\sum_{p,\,q}\sum_{i=5}^{\infty}\{(E_i^0 - E_1^0)\,|\gamma_{pqi}^{(2)}|^2 + C_{pqi}\gamma_{pqi}^{*(2)} + C_{pqi}^*\gamma_{pqi}^{(2)}\}, \tag{12}$$

$$C_{pqi} = \sum_{j,k,m=1}^{4} B_{pqikjm}\gamma_{qpj}^{(0)*}\gamma_{pqm}^{(0)}\gamma_{qpk}^{(0)} + \frac{e^2}{\varepsilon^2}\sum_{j,k,m=1}^{4}\int\psi_{pi}^*(\mathbf{r})\,\psi_{pj}^*(\mathbf{r}') \times \frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi_{pm}(\mathbf{r})\,\psi_{pk}(\mathbf{r}')\,d\tau d\tau' \times\left(\frac{1}{4}\gamma_{pqm}^{(0)}\delta_{jk} - \gamma_{pqm}^{*(0)}\gamma_{pqj}^{(0)*}\gamma_{pqk}^{(0)}\right), \tag{13}$$

$$B_{pqikjm} = \frac{1}{\varepsilon^2}\Big\{S_{pqik}S_{pqjm}(E_k^0 + E_m^0 - 2E_1^0) + S_{qpjm}\int\frac{e^2z_э\psi_{qi}\psi_{qk}}{|\mathbf{r}-\mathbf{R}_p|}\,d\tau - S_{pqik}\int\frac{e^2z_э\psi_{pj}\psi_{pm}}{|\mathbf{r}-\mathbf{R}_q|}\,d\tau - e^2\int\frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi_{pi}^*(\mathbf{r})\,\psi_{qk}(\mathbf{r})\,\psi_{qj}^*(\mathbf{r}')\,\psi_{pm}(\mathbf{r}')\,d\tau\,d\tau'\Big\}.$$

$$S_{pqik} = \int\psi_{pi}^*\psi_{qk}\,d\tau. \tag{14}$$

Having multiplied Eqs. (10) by Lagrange multipliers μ_{px} and subtracted them from Eq. (12) we vary the obtained expression over $\gamma_{pqi}^{(2)}$. Then

$$\gamma_{pqi}^{(2)} = -\frac{C_{pqi} + \sum_{x}\sum_{j=1}^{4}\mu_{px}\gamma_{pqj}^{(0)}(i\,|\,x\,|\,j)\,e/\varepsilon^2}{E_i^0 - E_1^0}, \tag{15}$$

$$P_{px} = \varepsilon^2\left\{\mu_{px}\alpha_{px} + e\,\frac{C_{pqi}(j\,|\,x\,|\,i)\,\gamma_{pqj}^{(0)*} + C_{pqj}^*(i\,|\,x\,|\,j)\,\gamma_{pqj}^{(0)}}{E_i^0 - E_1^0}\right\}, \tag{16}$$

where

$$\alpha_{px} = 2e^2\sum_{j=1}^{4}\sum_{i=5}^{\infty}|(i\,|\,x\,|\,j)|^2/(E_i^0 - E_1^0)$$

is the polarizability of an atom along the *x* axis. Here we have supposed the functions ψ_{pj} chosen so that for any of the indices $j = 1 \ldots 4$; $i \geqslant 5$, $(i\,|x|\,j)$ is different from zero only for one of the three coordinates. In addition $\gamma_{pqj}^{(0)}$ are orthogonal over the indices *j*.

Expressing μ_{px} through P_{px} from Eq. (16) and substituting them in Eq. (15), we obtain for the part of the Hamiltonian which depends on $\mathbf{P}_p$:

$$\overline{H}(\gamma_{pqi}^{(2)}) = \sum_{p}\sum_{x}\left[\frac{1}{2\alpha_{px}}P_{px}^2 + \sum_{q}\frac{e\varepsilon^2}{\alpha_{px}}N_{pqx}P_{px}\right] + O(\varepsilon^4), \tag{17}$$

$$N_{pqx} = \sum_{j=1}^{4}\sum_{i=5}^{\infty}\frac{C_{pqi}^*\gamma_{pqj}^{(0)}(i\,|\,x\,|\,j) + C_{pqi}\gamma_{pqj}^{(0)*}(j\,|\,x\,|\,i)}{E_i^0 - E_1^0}. \tag{18}$$

The quantities $O(\epsilon^4)$ do not depend on P_{px} and can be discarded in comparison with the other terms of the same form which are of the order of ϵ^2. Analogously, for the part of $\overline{H}$ which does not depend on $\gamma_{pqi}^{(2)}$, we obtain

$$\overline{H}(\gamma_{pqj}^{(0)}) = \varepsilon^2\sum_{(pq)}\sum_{j,k,l,m=1}^{4}B_{pqjklm}\gamma_{pqj}^{(0)*}\gamma_{pqk}^{(0)}\gamma_{pql}^{(0)*}\gamma_{pqm}^{(0)}. \tag{19}$$

Finally, the sum of the integrals of Eq. (3) and of the Coulombic terms in Eq. (2) gives the dipole-dipole interaction. Thus,

$$H = \overline{H}\,(\gamma^{(2)}_{pqi}) + \overline{H}\,(\gamma^{(0)}_{pqj}) + \sum_{p,q}\left[\frac{\mathbf{P}_p\mathbf{P}_q}{R^3_{pq}} - 3\,\frac{(\mathbf{P}_p\mathbf{R}_{pq})\,(\mathbf{P}_q\mathbf{R}_{pq})}{|\,R_{pq}\,|^5}\right]. \tag{20}$$

The expansion of $\overline{H}$ in powers of the displacements $\mathbf{u}_p$ and of the dipole moments $\mathbf{P}_p$ of all the atoms is begun, obviously, from terms of the 2nd order, since $\overline{H}$ has a minimum for $\mathbf{u}_p = 0$, $\mathbf{P}_p = 0$.

In the expansion of the coefficients N_{pqx}, we notice that in the expression Eq. (18) quantities C_{pqi} $\gamma^{(0)}_{pqi}$ enter, which pertain only to a single bond pq in which the singled-out directions are those parallel to the vectors $\mathbf{R}_{pq}$ ($\gamma^{(0)}_{pqi}$ do not depend on the displacements). The vector $\mathbf{N}_{pq}$ will lie in the plain of the vectors $\mathbf{R}_{pq} = \mathbf{R}_p - \mathbf{R}_q$ and $\mathbf{u}_{pq} = \mathbf{u}_p - \mathbf{u}_q$ and will depend only on the components of $\mathbf{u}_{pq}$ parallel and perpendicular to $\mathbf{R}_{pq}$ which lie in the specified plane, i. e.,

$$\mathbf{N}_{pq} = \mathbf{N}_{pq}\,(\mathbf{r}_{pq}) + b'\,\mathbf{u}_{pq} + c'\,(\mathbf{u}_{pq}\mathbf{r}_{pq})\,\mathbf{r}_{pq}, \tag{21}$$

where b' and c' are constant coefficients.

Applying analogous considerations to the coefficients B_{pqiklm}, we can conclude that each term in the sum over all bonds (pq) in Eq. (19) will depend only on $\mathbf{u}_{pq\,\parallel}$ and $\mathbf{u}_{pq\,\perp}$. However, in the corresponding quadratic form, the cross term must be absent, since in the absence of the components $\mathbf{u}_{pq\,\perp}$, the force in the direction perpendicular to $\mathbf{r}_{pq}$ must also be absent. Then

$$\overline{H}\,(\gamma^{(0)}_{pqj}) = \sum_{(pq)} [d_p\,(\mathbf{u}_{pq}\mathbf{r}_{pq})^2 + g_p\mathbf{u}^2_{pq}]. \tag{22}$$

Converting to the usual notation of Born $\mathbf{r}^l_s$, $\mathbf{u}^l_s$, $\mathbf{P}^l_s$ and gathering all the terms, for a binary crystal we obtain:

$$U = \overline{H} = \sum_{l}\sum_{l'}\{d_p\,(\mathbf{u}^{ll'}_{12}\mathbf{r}^{ll'}_{12})^2 + g_p\,(\mathbf{u}^{ll'}_{12})^2 + b_p\mathbf{P}^{ll'}_{12}\mathbf{u}^{ll'}_{12} + c_p\,(\mathbf{P}^{ll'}_{12}\mathbf{r}^{ll'}_{12})(\mathbf{u}^{ll'}_{12}\mathbf{r}^{ll'}_{12})\} + \frac{1}{2\alpha}\sum_{ls}\mathbf{P}^{l2}_s - \frac{1}{2}\sum_{sl}\mathbf{P}^l_s\mathbf{E}^l_s, \tag{23}$$

where

$$\mathbf{E}^l_s = \sum_{l's'}\,[3\,(\mathbf{P}^{l'}_{s'}\mathbf{r}^{ll'}_{ss'})\,\mathbf{r}^{ll'}_{ss'}/|\mathbf{r}^{ll'}_{ss'}|^5 - \mathbf{P}^{l'}_{s'}/|\,\mathbf{r}^{ll'}_{ss'}|^3] \tag{24}$$

is the field established at the point $\mathbf{r}^l_s$ by all the dipoles $\mathbf{P}^{l'}_{s'}$. In the expression in Eq. (23) the first item is of the order of ϵ^2, while the remaining three are of order ϵ^4. Retention of the latter with simultaneous rejection of the terms $\sim\epsilon^4$ in $\overline{H}\,(\gamma^{(0)}_{pqj})$ has the justification that the dependence of the energy on $\mathbf{P}^l_s$ leads to qualitatively new consequences at the same time that retention of terms $\sim\epsilon^4$ in $\overline{H}(\gamma^{(0)}_{pqj})$ would lead merely to some other value of the parameters d_p, g_p, which will all be determined equally from experiment. Since ϵ practically is very small (the binding energy is comparable with the ionization energy), the calculation of $\mathbf{P}^l_s$ leads to consequences which are easily observable experimentally.

In comparison with the theory of ionic crystals[1], here there are four interaction parameters d_p, g_p, b_p, c_p, instead of three G, g, h. This is connected with giving up a hypothesis of central forces. These parameters must be determined from experiment since they cannot, in view of the inadequacy of our knowledge of the form of the functions ψ_{pi}, be successfully calculated.

Using Eq. (23) we write down the equations of motion:

$$m_s\ddot{u}^l_{sx} = -\,\partial U\,(u,\,P)/\partial u^l_{sx};\;\; 0 = -\,\partial U\,(u,\,P)/\partial P^l_{sx}. \tag{25}$$

The second group of equations also gives the sought relation of the polarization of the atoms with their displacements. It stipulates those effects referred to in the introduction and it is examined in the following article[7].

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