Introduction of spatial dispersion into the dielectric constant of a crystal in the spectral region of accidentally close exciton resonances

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The dielectric constant $\varepsilon(\omega, \mathbf{k})$ determined in the paper is intended for the description of strong spatial dispersion (SD) effects, particularly auxiliary light waves. The method described makes it possible, knowing ε and without taking SD into account, to determine, first, the dependences of the exciton energies and of the dipole-moment matrix elements on $\mathbf{s} = \mathbf{k}/|\mathbf{k}|$ without using exciton models. This cannot be done by a direct quantum-mechanical calculation. Second, it permits ε to be expressed with allowance for the SD if only the effective masses of the excitons are known. Crystals having various symmetries are considered.

We consider here only strong spatial-dispersion effects that are of importance in the theory of auxiliary light waves. We neglect throughout weak effects that necessitate relative corrections of order a/λ or $(a/\lambda)^2$ (where λ is the wavelength of the light and a is the lattice constant).

It is customary to express the macroscopic polarization $\mathbf{P}$ of a crystal in terms of the macrofield $\mathbf{E}$ by the formula

$$\mathbf{P}=\varkappa\mathbf{E}, \quad \varkappa(\omega, \mathbf{k})=[\varepsilon(\omega, \mathbf{k})-I]/4\pi, \quad \mathbf{E}, \mathbf{P}\propto e^{i(\mathbf{kr}-\omega t)}, \tag{1}$$

where $\varepsilon(\omega, \mathbf{k})$ is the dielectric tensor and I a unit tensor. In the standard quantum-mechanical calculation, however, $\mathbf{P}$ is expressed not in terms of $\mathbf{E}$ but in terms of its part of the electric field which perturbs the crystal[1]

$$\mathbf{E}_e=\mathbf{E}-\mathbf{E}', \tag{2}$$

where

$$\mathbf{E}'=-4\pi\overline{\mathbf{ss}}\mathbf{P}, \quad \mathbf{s}\equiv\mathbf{k}/|\mathbf{k}|. \tag{3}$$

A common superior bar above two vectors denotes here a dyad tensor: $(\overline{AB})_{xy}=A_xB_y$. Quantum-mechanical calculation yields

$$\mathbf{P}=\beta(\omega, \mathbf{k})\mathbf{E}_e. \tag{4}$$

An unique relation exists between the polarizabilities $\varkappa(\omega, \mathbf{k})$ and $\beta(\omega, \mathbf{k})$ and can be expressed by any one of three equivalent equations:

$$\varkappa=(I-4\pi\beta\overline{\mathbf{ss}})^{-1}\beta, \quad \beta=(I+4\pi\varkappa\overline{\mathbf{ss}})^{-1}\varkappa, \quad \text{[Refs. 1, 2]} \tag{5}$$

$$\varkappa=\left(I+\frac{4\pi\beta\overline{\mathbf{ss}}}{1-4\pi\langle\beta\rangle}\right)\beta, \quad \beta=\left(I-\frac{4\pi\varkappa\overline{\mathbf{ss}}}{1+4\pi\langle\varkappa\rangle}\right)\varkappa, \quad \text{[Refs. 1, 3]} \tag{6}$$

$$\beta^{-1}=\varkappa^{-1}+4\pi\overline{\mathbf{ss}}. \quad \text{[Refs. 1, 4]} \tag{7}$$

Here $\langle T\rangle\equiv(s, Ts)$, where T is a tensor of second rank.

It is shown in pp 120–123 or Ref. 1 that when spatial dispersion (SD) is introduced directly into the tensor $\varkappa$, one gets, generally speaking more new parameters than when it is introduced into the tensor β. The SD should therefore be introduced into the tensor β, and $\varkappa$ should next be expressed in terms of β using the exact equations (5)–(7). This is exactly how the tensors $\varkappa(\omega, \mathbf{k})$ were determined in Ref. 4 for crystals with different symmetries. Also considered in that reference are cases of degenerate excitons, when their degeneracy stems from the crystal symmetry. There exist, however, crystals with accidentally close exciton energy levels that become simultaneously resonant to the light and make a comparable contribution to the SD. This occurs, e.g., in crystalline PbI_2 (Ref. 5), ZnSe (Ref. 6), and others. We consider in this paper such accidentally close exciton levels, the SD is first introduced in β, and the corresponding $\varkappa$ are then determined using (5)–(7). Crystals with various symmetries are considered. No models are used for the exciton; all the result are obtained using a generalized definition of the exciton (see §3 of Ref. 1). We determine *in passim*, at $|\mathbf{k}|=0$, the dependences of the exiton energies and of the dipole-moment matrix elements on $\mathbf{s}$.

We consider first two nondegenerate randomly close exciton levels. All other more general cases will be subsequently reduced to this problem. Let β have the form 1

$$\beta(\omega, \mathbf{k})=\beta_0+\frac{V\overline{\mathbf{P}_1\mathbf{P}_1^*}}{\mathscr{E}_1(\mathbf{k})-\hbar\omega}+\frac{V\overline{\mathbf{P}_2\mathbf{P}_2^*}}{\mathscr{E}_2(\mathbf{k})-\hbar\omega}. \tag{8}$$

Here $\mathscr{E}_1(\mathbf{k})$ and $\mathscr{E}_2(\mathbf{k})$ are close energies of two excitons that became simultaneously resonant to the light $\mathbf{P}_l=\langle\Psi^0|\hat{\mathbf{P}}|\Psi_{lk}\rangle$, where Ψ^0 and Ψ_{ik} are the ground and exciton states of the crystal, $\hat{\mathbf{P}}$ is the specific polarization operator, $l=1, 2$; V is the volume of the main region of crystal cyclicity, β_0 is the "background" value of β, varies slowly with ω, and includes a contribution from the remaining excited states of the crystal. If this expression for β is substituted in the first equation of (6), we get

$$\varkappa=\varkappa_0+Q_+/(K_+(\mathbf{k})-\hbar\omega)+Q_-/(K_-(\mathbf{k})-\hbar\omega), \tag{9}$$

where

$$\varkappa_0=(I+4\pi\beta_0\overline{\mathbf{ss}}/(1-4\pi\langle\beta_0\rangle))\beta_0,$$
$$\beta_0=(I-4\pi\varkappa_0\overline{\mathbf{ss}}/\langle\varepsilon_0\rangle)\varkappa_0, \quad \varepsilon_0=I+4\pi\varkappa_0, \tag{10}$$

$$K_\pm=\frac{1}{2}\{\mathscr{E}_1-\Delta_1+\mathscr{E}_2-\Delta_2 \pm\{[(\mathscr{E}_1-\Delta_1)-(\mathscr{E}_2-\Delta_2)]^2+4\Delta_1\Delta_2\}^{1/2}\}, \tag{11}$$

$$\Delta_l=4\pi V\langle\varepsilon_0\rangle|(\mathbf{P}_l, \mathbf{s})|^2=\frac{4\pi V}{\langle\varepsilon_0\rangle}|(\tilde{\mathbf{P}}_l, \mathbf{s})|^2, \tag{12}$$

$$\tilde{\mathbf{P}}_l=\mathbf{P}_l+4\pi(\mathbf{P}_l, \mathbf{s})\varkappa_0\mathbf{s}, \quad \mathbf{P}_l=\tilde{\mathbf{P}}_l-\frac{4\pi}{\langle\varepsilon_0\rangle}(\tilde{\mathbf{P}}_l, \mathbf{s})\varkappa_0\mathbf{s}, \tag{13}$$

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$$Q_{\pm}=\pm\frac{V}{\mathscr{L}_-}\Big[(\overline{\widetilde{\mathbf{P}}_1\widetilde{\mathbf{P}}_1}^{*}+\overline{\widetilde{\mathbf{P}}_2\widetilde{\mathbf{P}}_2}^{*})K_{\pm}-\mathscr{E}_1\overline{\widetilde{\mathbf{P}}_2\widetilde{\mathbf{P}}_2}^{*}-\mathscr{E}_2\overline{\widetilde{\mathbf{P}}_1\widetilde{\mathbf{P}}_1}^{*}+\frac{4\pi V}{\langle\varepsilon_0\rangle}\overline{\mathscr{P}\mathscr{P}}^{*}\Big],\quad(14)$$

where

$$\mathscr{P}=(\widetilde{\mathbf{P}}_2,\mathbf{s})\widetilde{\mathbf{P}}_1-(\widetilde{\mathbf{P}}_1,\mathbf{s})\widetilde{\mathbf{P}}_2,\quad \mathscr{L}_{\pm}=K_+\pm K_-.\quad(15)$$

If the two relations (11) are solved for $\mathscr{E}_1$ and $\mathscr{E}_2$, we get

$$\mathscr{E}_l=-\frac{1}{2}[\mathscr{L}_+ +2\Delta_l-(-1)^l(\mathscr{L}_-^2-4\Delta_1\Delta_2)^{1/2}],\quad l=1,2.\quad(16)$$

These levels are numberd such that $\mathscr{E}_1-\Delta_1>\mathscr{E}_2-\Delta_2$.

Combining (11) and (14) we easily express the energies of the Schrödinger excitons in terms of the parameters that enter in $\varkappa$, namely,

$$\mathscr{E}=\frac{1}{2}\Big\{\mathscr{L}_+ +\frac{4\pi}{\langle\varepsilon_0\rangle}\langle R_+\rangle \pm\Big[\Big(\mathscr{L}_-+\frac{4\pi}{\langle\varepsilon_0\rangle}\langle R_-\rangle\Big)^2+\frac{64\pi^2}{\langle\varepsilon_0\rangle^2}\langle Q_+\rangle\langle Q_-\rangle\Big]^{1/2}\Big\}.\quad(17)$$

Here

$$R_{\pm}=Q_+\pm Q_-.\quad(18)$$

All the foregoing equations are valid if $\mathbf{P}_l$ and $\widetilde{\mathbf{P}}_l$ depend on $\mathbf{k}$. If, however, this dependence (i.e., small spatial dispersion effects) is neglected it can be shown that $\mathbf{P}_l$ and $\widetilde{\mathbf{P}}_l$ can be chosen real, since the tensors β and $\varkappa$ must be symmetric (see Eq. (7.56) of Ref. 1). Equation (14) can then be written in simplified form:

$$Q_{\pm}=\tfrac{1}{2}V\{\overline{\widetilde{\mathbf{P}}_1\widetilde{\mathbf{P}}_1}+\overline{\widetilde{\mathbf{P}}_2\widetilde{\mathbf{P}}_2} \pm\mathscr{L}_-^{-1}[(\overline{\widetilde{\mathbf{P}}_1\widetilde{\mathbf{P}}_1}-\overline{\widetilde{\mathbf{P}}_2\widetilde{\mathbf{P}}_2})(\mathscr{L}_-^2-4\Delta_1\Delta_2)^{1/2} -2\Delta_1^{1/2}\Delta_2^{1/2}(\overline{\widetilde{\mathbf{P}}_1\widetilde{\mathbf{P}}_2}+\overline{\widetilde{\mathbf{P}}_2\widetilde{\mathbf{P}}_1})]\}.\quad(19)$$

In the derivation of this formula, the products $(\widetilde{\mathbf{P}}_l\cdot\mathbf{s})$ were expressed in terms of Δ_l from relations (12). To avoid uncertainties in sign, we agree to regard the products $(\mathbf{P}_l\cdot\mathbf{s})$ only as positive. This can always be achieved by choosing the sign of the Ψ function of the ground or excitonic state of the crystal. As a result, although (14) is invariant to the substitution $\widetilde{\mathbf{P}}_l\to-\widetilde{\mathbf{P}}_l$, Eq. (19) is no longer so.

Just as in Ref. 4, we start from a basic premise that the tensor $\varkappa$ does not depend on $\mathbf{s}$ if spatial dispersion is neglected, i.e., as $|\mathbf{k}|$ tends to zero.[1)] Since this should take place for different ω, each of the tensors $\varkappa_0$, Q_+, and Q_- in (9) must be independent of $\mathbf{s}$. These tensors are "numerical," since their principal axes should not depend on $\mathbf{s}$. As for the vectors $\widetilde{\mathbf{P}}_l$, they were likewise independent of $\mathbf{s}$ in Ref. 4, where accidentally close excitonic levels were not considered. In the present paper, however, such a dependence does occur and will be explicitly determined below.

We proceed now to a discussion of crystals with different symmetries.

§1. RHOMBIC-SYMMETRY CRYSTALS

We choose the axis x, y, and z along twofold crystal axes. Let $\mathbf{k}$ lie in the xz plane. It follows then from symmetry considerations that $\widetilde{\mathbf{P}}_l$ is either perpendicular to this plane or else lies in it.

1. If $\widetilde{\mathbf{P}}_1\|\widetilde{\mathbf{P}}_2\|y$, we have $\Delta_1=\Delta_2=0$, since $\mathbf{s}$ lies in the xz plane. We get from (19)

$$Q_+=V\overline{\widetilde{\mathbf{P}}_1\widetilde{\mathbf{P}}_1},\quad Q_-=V\overline{\widetilde{\mathbf{P}}_2\widetilde{\mathbf{P}}_2},$$

and from (11)

$$K_+=\mathscr{E}_1,\quad K_-=\mathscr{E}_2.$$

It follows from (13) that $\widetilde{\mathbf{P}}_l=\mathbf{P}_l$.

If we now take strong spatial-dispersion effects into account, we must take into account in the denominators of the fractions of the tensor (8) the dependence of $\mathscr{E}_l$ on $|\mathbf{k}|$, but in the numerators and in β_0 we must let, as before, $|\mathbf{k}|\to0$. From the exact Eqs. (13) it follows then that we must let $|\mathbf{k}|\to0$ also in $\widetilde{\mathbf{P}}_l$. The tensors $Q_{\pm}$ and $\varkappa_0$ thus remain the same as when spatial dispersion is neglected. It can be seen from (11) that if a dependence on $|\mathbf{k}|$ is introduced into $\mathscr{E}_1$ and $\mathscr{E}_2$, this dependence must also be introduced in $K_{\pm}$. As a result, the tensor (9) takes the form

$$\varkappa=\varkappa_0+V|\mathbf{P}_1|^2\overline{\mathbf{yy}}/(\mathscr{E}_1(\mathbf{k})-\hbar\omega)+V|\mathbf{P}_2|^2\overline{\mathbf{yy}}/(\mathscr{E}_2(\mathbf{k})-\hbar\omega).\quad(20)$$

Here and below $\mathbf{x}$, $\mathbf{y}$, and $\mathbf{z}$ are unit vectors along the axes x, y, and z.

2. If $\widetilde{\mathbf{P}}_1\|y$ at $|\mathbf{k}|=0$ and $\widetilde{\mathbf{P}}_2$ lies in the xz plane, we have $\Delta_1=0$ and it follows from (19) that

$$Q_+=V\overline{\widetilde{\mathbf{P}}_1\widetilde{\mathbf{P}}_1},\quad Q_-=V\overline{\widetilde{\mathbf{P}}_2\widetilde{\mathbf{P}}_2}.$$

For the axes x, y, and z to the principal ones for the tensor Q_-, it is necessary that $\widetilde{\mathbf{P}}_2$ be directed along x or z. From (11) we obtain

$$K_+=\mathscr{E}_1,\quad K_-=\mathscr{E}_2-\Delta_2,$$

and from (13) it follows that $\mathbf{P}_1=\widetilde{\mathbf{P}}_1$, while $\mathbf{P}_2$ is in the xz plane. If $\widetilde{\mathbf{P}}_2\|z$, we get

$$\varkappa=\varkappa_0+V|\mathbf{P}_1|^2\overline{\mathbf{yy}}/(K_+(\mathbf{k})-\hbar\omega)+V|\widetilde{\mathbf{P}}_2|^2\overline{\mathbf{zz}}/(K_-(\mathbf{k})-\hbar\omega).\quad(21)$$

If $\widetilde{\mathbf{P}}_2$ is parallel to x, it is necessary to replace $\overline{\mathbf{zz}}$ in (21) by $\overline{\mathbf{xx}}$.

3. Let $\widetilde{\mathbf{P}}_1$ and $\widetilde{\mathbf{P}}_2$ be in the xz plane at $|\mathbf{k}|=0$. We determine the four scalar quantities $\widetilde{P}_{1x}$, $\widetilde{P}_{1z}$, $\widetilde{P}_{2x}$, and $\widetilde{\mathbf{P}}_{2z}$ and their dependences on s from the conditions $Q_{\pm xz}\equiv Q_{\pm zx}=0$, while $Q_{\pm xx}$ and $Q_{\pm zz}$ are constants independent of $\mathbf{s}$. Taking relations (18) into account, we can rewrite these conditions in the form of the following six equations. The condition $R_{\pm xz}=0$ leads to two equations:

$$\widetilde{P}_{1x}\widetilde{P}_{1z}+\widetilde{P}_{2x}\widetilde{P}_{2z}=0,\quad(22)$$

$$\widetilde{P}_{1x}\widetilde{P}_{1z}(\mathscr{L}_-^2-4\Delta_1\Delta_2)^{1/2}=\Delta_1^{1/2}\Delta_2^{1/2}(\widetilde{P}_{1x}\widetilde{P}_{2z}+\widetilde{P}_{2x}\widetilde{P}_{1z}).\quad(23)$$

From the conditions that $R_{\pm xx}$ and $R_{\pm xz}$ be independent of $\mathbf{s}$ we obtain the four equations

$$\widetilde{P}_{1x}^2+\widetilde{P}_{2x}^2=a^2,\quad(24)$$

$$(\widetilde{P}_{1x}^2-\widetilde{P}_{2x}^2)(\mathscr{L}_-^2-4\Delta_1\Delta_2)^{1/2}-4\Delta_1^{1/2}\Delta_2^{1/2}\widetilde{P}_{1x}\widetilde{P}_{2x}=f,\quad(25)$$

$$\widetilde{P}_{1z}^2+\widetilde{P}_{2z}^2=b^2,\quad(26)$$

$$(\widetilde{P}_{1z}^2-\widetilde{P}_{2z}^2)(\mathscr{L}_-^2-4\Delta_1\Delta_2)^{1/2}-4\Delta_1^{1/2}\Delta_2^{1/2}\widetilde{P}_{1z}\widetilde{P}_{2z}=g,\quad(27)$$

where a, b, f, and g are constants independent of s. The six equations with four unknowns can be satisfied, since the equations are not independent.

To classify the solutions it is convenient to start out

with Eq. (22). At least one projection of each of the vectors $\tilde{\mathbf{P}}_1$ and $\tilde{\mathbf{P}}_2$ must differ from zero, otherwise the corresponding exciton transition would be dipole-forbidden, a situation not considered in the present paper. The system (22)–(27) has solutions of the following three types:

(a) $\tilde{P}_{1x}\neq 0, \tilde{P}_{2x}\neq 0, \tilde{P}_{1z}=\tilde{P}_{2z}=0$. Equations (22), (23), (26), and (27) are then satisfied and it remains only to solve Eqs. (24) and (25). Since we agreed to choose the sign of P_l such that (P_l, s) is positive, the solution is

$$\tilde{P}_{1x}=2^{-1/2}[a^2\pm(a^4-D_x)^{1/2}]^{1/2}\ \mathrm{sign}\ s_x, \tag{28}$$

$$\tilde{P}_{2x}=2^{-1/2}[a^2\mp(a^4-D_x)^{1/2}]^{1/2}\ \mathrm{sign}\ s_x, \tag{29}$$

$$D_x=\frac{a^4\mathscr{L}_-^{-2}-f^2}{a^4\alpha_x^2+2f\alpha_x+\mathscr{L}_-^{-2}}, \qquad \alpha_x=\frac{4\pi V}{\langle\varepsilon_0\rangle}s_x^2. \tag{30}$$

From (9), (19), (24), and (25) we get

$$\varkappa=\varkappa_0+V(a^2+f/\mathscr{L}_-)\overline{\mathbf{xx}}/2[K_+(\mathbf{k})-\hbar\omega] +V(a^2-f/\mathscr{L}_-)\overline{\mathbf{xx}}/2[K_-(\mathbf{k})-\hbar\omega]. \tag{31}$$

The upper signs must be taken in (28) and (29) if $f>0$ (i.e., $Q_{+xx}>Q_{-xx}$), and the lower at $f<0$. In particular, if $\mathbf{s}\|z$, i.e., both excitons are transverse, $\Delta_1=\Delta_2=0$ and according to (25) we have $f/\mathscr{L}_-^2=\tilde{P}_{1x}^2-\tilde{P}_{2x}^2$ and

$$\varkappa=\varkappa_0+V\tilde{P}_{1x}^2\overline{\mathbf{xx}}/[K_+(\mathbf{k})-\hbar\omega]+V\tilde{P}_{2x}^2\overline{\mathbf{xx}}/[K_-(\mathbf{k})-\hbar\omega]. \tag{32}$$

(b) $\tilde{P}_{1z}\neq 0, \tilde{P}_{2z}\neq 0, \tilde{P}_{1x}=\tilde{P}_{2x}=0$. This case is perfectly analogous to the one just considered. In place of (24) and (25) we must now solve (26) and (27). The results are obtained by making the substitutions $a\to b$, $f\to g$, and $x\leftrightarrow z$ in Eqs. (28)–(32) and in the condition $\mathbf{s}\|z$.

(c) All the projections, or two unlike projections, of the vectors $\tilde{\mathbf{P}}_1$ and $\tilde{\mathbf{P}}_2$ differ from zero. In this case Eq. (22) can be written as the product of two unequal nonzero projections and expressed in the form

$$\tilde{P}_{2x}/\tilde{P}_{1x}=-\tilde{P}_{1z}/\tilde{P}_{2z}=\lambda. \tag{33}$$

Solving first the system of four equations (23), (24), (26), and (33) we obtain

$$\tilde{P}_{1x}=a/(1+\lambda^2)^{1/2};\ \tilde{P}_{1z}=-\lambda b/(1+\lambda^2)^{1/2};$$
$$\tilde{P}_{2x}=\lambda a/(1+\lambda^2)^{1/2};\ \tilde{P}_{2z}=b/(1+\lambda^2)^{1/2}. \tag{34}$$

Here λ can take one of the two values

$$\lambda=B_-/2A+(B_-^2/4A^2+1)^{1/2}, \quad B_-/A>0 \tag{35}$$

or

$$\lambda=B_+/2A-(B_+^2/4A^2+1)^{1/2}, \quad B_+/A>0, \tag{36}$$

where

$$A=abs_xs_z, \quad B_\pm=a^2s_x^2-b^2s_z^2\pm\langle\varepsilon_0\rangle\mathscr{L}_-/4\pi V. \tag{37}$$

The signs of a and b are chosen, depending on $\mathbf{s}$, such that the scalar products $(\tilde{\mathbf{P}}_l\cdot\mathbf{s})$ are positive. It can be shown that the solution of (34)–(37) satisfies also Eqs. (25) and (27).

Using the square root of (35), we get

$$\varkappa=\varkappa_0+Va^2\overline{xx}/[K_-(\mathbf{k})-\hbar\omega]+Vb^2\overline{zz}/[K_+(\mathbf{k})-\hbar\omega], \tag{38}$$

and using the square root in (36),

$$\varkappa=\varkappa_0+Va^2\overline{xx}/[K_+(\mathbf{k})-\hbar\omega]+Vb^2\overline{zz}/[K_-(\mathbf{k})-\hbar\omega]. \tag{39}$$

Thus, depending on the polarization of the considered pair of excitons, the tensor $\varkappa$ can be either of the type (20) and (31) when both fractions contribute to the same principal value of $\varkappa$, or of the type (21), (38), or (39) when the two fractions contribute to different principal values of $\varkappa$.

We have considered above the particular case when s lies in the xz plane. Since, however, the numerators of the fractions $Q_\pm$ do not depend on the direction of $\mathbf{s}$, they remain the same also at arbitrary direction of $\mathbf{s}$. To allow for large spatial-dispersion effects in the expressions obtained for $\varkappa$ it suffices to take into account in the denominators of the fractions the dependence of $K_\pm$ on $\mathbf{k}$ at arbitrary $\mathbf{k}$.

As for the directions and values obtained above for the vectors $\tilde{P}_l$ ($l=1,2$), particularly Eqs. (28), (29) and (34), they are valid, on the contrary, only if $\mathbf{s}$ lies in the xz plane, since the $\tilde{P}_l$ (in contrast to $Q_\pm$) depend on $\mathbf{s}$. The vectors $\mathbf{P}_l$ also depend on $\mathbf{s}$; they are expressed in terms of $\tilde{\mathbf{P}}_l$ by the second equation of (13), which is valid for arbitrary $\mathbf{s}$. It follows from it, in particular, that

$$(\tilde{\mathbf{P}}_l\mathbf{s})=(\mathbf{P}_l\mathbf{s})\langle\varepsilon_0\rangle. \tag{40}$$

If $\mathbf{s}$ and $\tilde{\mathbf{P}}_l$ are in the xz plane, the $\mathbf{P}_l$ are also in this plane.

We emphasize that by specifying the one definite initial tensor (8) we specify a definite pair of excitons with energies $\mathscr{E}_1$ and $\mathscr{E}_2$ and with vectors $\mathbf{P}_1$ and $\mathbf{P}_2$, i.e., $\tilde{\mathbf{P}}_1$ and $\tilde{\mathbf{P}}_2$. It can be seen from (17) and (34) that each of the roots λ, (35) and (36), defines its own pair of excitons with levels $\mathscr{E}_1$ and $\mathscr{E}_2$ and a pair of vectors $\tilde{\mathbf{P}}_1$ and $\tilde{\mathbf{P}}_2$. It is thus necessary to choose only the that of the two roots λ which determines just the initial exciton pair corresponding to the polarizability (8). If this pair of excitons has been theoretically calculated, the required root can be chosen to be the one that gives the correct sign of relations (33). If no such calculation was made but the experimental form of $\varkappa$ is known, the needed root λ can be determined using the inequality $K_+>K_-$, viz., if $\varkappa$ is given by (38), i.e., the larger of the $\mathbf{K}$ is under the dyad $\overline{\mathbf{zz}}$, then λ is given by (36). If is known, $\tilde{\mathbf{P}}_l$, $\mathbf{P}_l$, and Δ_l can be determined from (34), (13) and (12).

In (28) and (29), similarly, one must choose either only the upper or only the lower signs—those corresponding to the initial pair of excitons contained in (8). The upper signs must be chosen if calculation or experiment leads to $|\tilde{\mathbf{P}}_1|>|\tilde{\mathbf{P}}_2|$, and the lower in the opposite case. Since a change of s does not alte the choice of signs, this choice can be made at $\mathbf{s}\|z$, comparing (32) with experiment; this indicates which of the $|\tilde{\mathbf{P}}_l|$ is the larger.

If it is known from experiment that $\varkappa$ is of the form (20) or (21), the directions of $\tilde{\mathbf{P}}_l$ and $\mathbf{P}_l$ for $\mathbf{s}$ located in the xz plane are stipulated as in subsections 1 and 2 above.

§2. UNIAXIAL CRYSTALS

Let in this case the direction of $\mathbf{k}$ be arbitrary. We choose the z axis along the crystal $\mathbf{C}$ axis, the x axis in the ($\mathbf{C}$, $\mathbf{s}$) plane, and the y axis perpendicular to this plane. As $|\mathbf{k}|\to 0$ these axes are the principal axes of the tensor $\varkappa$. It follows from (7) that the y axis is also the principal axis of β, i.e., of β_0 and of the numerators of each fraction of an equation such as (8). When spatial dispersion is introduced in β, however, the

dependence on $\mathbf{k}$ is introduced only in the denominators of the fractions, while the numerators remain unchanged. The y axis remains therefore a principal axis of β also when spatial dispersion is taken into account. According to (7), however, it will be the principal axis of $\varkappa$ also when spatial dispersion is taken into account.

Since the y axis is a principal axis of the numerators of the fractions in β, the vectors $\mathbf{P}_l$ are either directed along y or lie in the xz plane. We separate in the right-hand side of an equation such as (8) those fractions that contain $\mathbf{P}_l \| y$ in the numerator, and designate their sum by the tensor $\beta^{(y)}$. The aggregate of the remaining terms of the right-hand side of (8) (including β_0) will be designated β', i.e.,

$$\beta = \beta' + \beta^{(y)}. \tag{41}$$

Since $\mathbf{s}\beta^{(y)} = \beta^{(y)}\mathbf{s} = 0$, substitution of (41) in the first equation of (6) gives

$$\varkappa = (I + 4\pi\beta'\overline{\mathbf{ss}}/(1 - 4\pi\langle\beta'\rangle)\beta' + \beta^{(y)} = \varkappa' + \beta^{(y)}. \tag{42}$$

The term $\beta^{(y)}$ is thus "transferred" to $\varkappa$ without changes, while the term β' enerates in $\varkappa$ a term of a type such as if there were no term $\beta^{(y)}$ in (41) at all.

It follows from symmetry considerations that in a uniaxial crystal the exciton bands can be either nondegenerate or doubly degenerate. The degenerate bands are defined as those in which the $\mathscr{E}(\mathbf{k})$ coincide as $|\mathbf{k}| \to 0$ for the selected directions of $\mathbf{s}$.

At $\mathbf{k} \| z$ any direction in the plane xy should be principal for the tensor β also when spatial dispersion is taken into account. It follows therefore that a fraction containing $P_l \| y$ is either not contained at all in the right hand side of an equation such as (8), or is accompanied by a fraction having a denominator with exactly the same denominator and containing $|\mathbf{P}_l'| \| x$, where $|\mathbf{P}_l'| = |\mathbf{P}_l|$ (the exciton bands l and l' are mutually degenerate and are polarized in the xz plane at $\mathbf{k} \| z$). For the nondegenerate exciton l'' we have $\mathbf{P}_l'' \| z$ at $\mathbf{k} \| z$.

Two nondegenerate accidentally close exciton bands

If both bands are simultaneously at resonance with the light, β $(\omega, \mathbf{k})$ is given by Eq. (8). The vectors $\mathbf{P}_1$ and $\mathbf{P}_2$ are in the zx plane, for if either of these vectors were directed along the y axis the corresponding exciton would be doubly degenerate. The problem of determining $\varkappa$ when β is of this form was already solved above. Equations (8)–(19) and (22)–(27) remain in foce. Equations (22)–(27) were solved above, even though in the section devoted to rhombic crystals, without using the rhombic are any other symmetry of the crystal. It was shown that in the general case there are solutions of three types [(a), (b), and (c)]. If we now use the symmetry of the uniaxial crystal, i.e., stipulate $\varkappa_{xx} = \varkappa_{yy}$ as $|\mathbf{k}| \to 0$, the solutions (a) and (c) must be discarded. We are left with solution (b), which is obtained by making the substitutions $a \to b$, $f \to g$, $x \to z$ in Eqs. (28)–(31).

Nondegenerate band accidentally close to a pair of degenerate bands

In this case β takes the form

$$\beta = \beta_0 + V\overline{\mathbf{P}_1\mathbf{P}_1^*}/[\mathscr{E}_1(\mathbf{k}) - \hbar\omega] + V\overline{\mathbf{P}_2\mathbf{P}_2^*}/[\mathscr{E}_2(\mathbf{k}) - \hbar\omega] + V\overline{\mathbf{P}^{(y)}\mathbf{P}^{(y)*}}/[\mathscr{E}^{(y)}(\mathbf{k}) - \hbar\omega]. \tag{43}$$

The last term corresponds here to an exciton polarized along the y axis. Assume that the exciton bands $\mathscr{E}^{(y)}(\mathbf{k})$ and $\mathscr{E}_1(\mathbf{k})$ are mutually degenerate, and $\mathscr{E}_2(\mathbf{k})$ is nondegenerate. The last term is the above-mentioned tensor $\beta^{(y)}$, which is transferred to $\varkappa$ unchanged. The first three terms of the right-hand side of (43) constitute the tensor β', which has exactly the form (8). Therefore the calculation of $\varkappa'$ [of the first term of the right-hand side of (42)] coincides with the calculation above of $\varkappa$ from the first equation of (6). The vectors $\mathbf{P}_1$ and $\mathbf{P}_2$ lie again in the xz plane, and Eqs. (8)–(19) and (22)–(27) remain in force if β is replaced in them by β' and $\varkappa$ by $\varkappa'$. In view of the symmetry of the uniaxial crystal, the solutions (a) and (b) above must be discarded. The choice between the variants (38) and (39) in solution (c) can be made to satisfy the condition that at $\mathbf{k} \| z$ any direction in the xy plane should be principal for the tensor $\varkappa$. To this end it is necessary that the dyads $\overline{\mathbf{xx}}$ and $\overline{\mathbf{yy}}$ in the expression for $\varkappa$ enter with identical coefficients. Recognizing that according to (11) we have $K_+(\mathbf{k}) = \mathscr{E}_1(\mathbf{k}) = \mathscr{E}^{(y)}(\mathbf{k})$ at $\mathbf{k} \| z$, we must choose expression (39) for $\varkappa'$. As a result, the tensor $\varkappa$ takes for arbitrary $\mathbf{k}$ the form

$$\varkappa = \varkappa_0 + Va^2\overline{\mathbf{xx}}/[K_+(\mathbf{k}) - \hbar\omega] + Va^2\overline{\mathbf{yy}}/[\mathscr{E}^{(y)}(\mathbf{k}) - \hbar\omega] + Vb^2\overline{\mathbf{zz}}/[K_-(\mathbf{k}) - \hbar\omega], \quad a^2 = |\mathbf{P}^{(y)}|^2, \quad K_+(0) = \mathscr{E}^{(y)}(0). \tag{44}$$

This variant of the solution (c) corresponds to expression (36) for λ.

Exactly the same reasoning holds for the case when the bands $\mathscr{E}^{(y)}(\mathbf{k})$ and $\mathscr{E}_2(\mathbf{k})$ are mutually degenerate and $\mathscr{E}_1(\mathbf{k})$ is nondegenerate. We then obtain the expression for $\varkappa$ by interchanging $K_+(\mathbf{k})$ and $K_-(\mathbf{k})$ in (44). The corresponding value of λ is given by (35).

Accidentally close two pairs of degenerate exciton bands

One of the excitons of each pair should be polarized along the y axis, and the other in the xz plane. Let $\mathbf{P}_1$ and $\mathbf{P}_2$ lie in the xz plane, and $\mathbf{P}_3 \| \mathbf{P}_4 \| y$. Then

$$\beta' = \beta_0 + V\overline{\mathbf{P}_1\mathbf{P}_1^*}/[\mathscr{E}_1(\mathbf{k}) - \hbar\omega] + V\overline{\mathbf{P}_2\mathbf{P}_2^*}/[\mathscr{E}_2(\mathbf{k}) - \hbar\omega], \tag{45}$$

$$\beta^{(y)} = V\overline{\mathbf{P}_3\mathbf{P}_3^*}/[\mathscr{E}_3(\mathbf{k}) - \hbar\omega] + V\overline{\mathbf{P}_4\mathbf{P}_4^*}/[\mathscr{E}_4(\mathbf{k}) - \hbar\omega]. \tag{46}$$

Let the pair of bans $\mathscr{E}_1(\mathbf{k})$, $\mathscr{E}_3(\mathbf{k})$, and well as $\mathscr{E}_2(\mathbf{k})$, $\mathscr{E}_4(\mathbf{k})$ be mutually degenerate. Again β' is given by (8), and Eqs. (8)–(19) and (22)–(27) are valid if β and β' are replaced in them by $\varkappa$ and $\varkappa'$, respectively. Using the symmetry of a uniaxial crystal, a choice can be made between solutions (a), (b), and (c). To this end we consider the case $\mathbf{k} \| z$, when any direction in the xy plane should be a principal one for the tensor $\varkappa$ at all values of $|\mathbf{k}|$ and ω. Starting from this condition, it is easy to show that solutions (b) and (c) should be discarded, and $\varkappa'$ is given by Eq. (32) in which we have at all values of $|\mathbf{k}|$

$$K_+(\mathbf{k}) = \mathscr{E}_1(\mathbf{k}) = \mathscr{E}_3(\mathbf{k}), \quad K_-(\mathbf{k}) = \mathscr{E}_2(\mathbf{k}) = \mathscr{E}_4(\mathbf{k}), \quad \widetilde{\mathbf{P}}_1 \| \widetilde{\mathbf{P}}_2 \| x, \quad \widetilde{\mathbf{P}}_1^2 = |\mathbf{P}_3|^2, \quad \widetilde{\mathbf{P}}_2^2 = |\mathbf{P}_4|^2. \tag{47}$$

If we change over now to an arbitrary direction of $\mathbf{k}$, a generalization of (32) is then Eq. (31). We therefore obtain for $\varkappa$ ultimately

$$\varkappa=\varkappa_0+V|\mathbf{P}_3|^2\overline{\mathbf{xx}}/[K_+(\mathbf{k})-\hbar\omega]+V|\mathbf{P}_4|^2\overline{\mathbf{xx}}/[K_-(\mathbf{k})-\hbar\omega]$$
$$+V|\mathbf{P}_3|^2\overline{\mathbf{yy}}/[\mathscr{E}_3(\mathbf{k})-\hbar\omega]+V|\mathbf{P}_4|^2\overline{\mathbf{yy}}/[\mathscr{E}_4(\mathbf{k})-\hbar\omega], \quad (48)$$
$$a^2+f/\mathscr{L}_-=2|\mathbf{P}_3|^2, \quad a^2-f/\mathscr{L}_-=2|\mathbf{P}_4|^2.$$

If we let $|\mathbf{k}|\to 0$ at an arbitrary direction of $\mathbf{k}$, i.e., if we neglect spatial dispersion, the obtained $\varkappa$ should be independent of $\mathbf{s}$. Therefore $\mathbf{P}_3$, $\mathbf{P}_4$, $\mathscr{E}_3(0)$ and $\mathscr{E}_4(0)$ do not depend on $\mathbf{s}$. But it must be borne in mind here that when $\mathbf{s}$ is changed arbitrarily the directions of the x and y axes stipulated above also change in such a way that $\mathbf{s}$ remains all the time in the xz plane. The vectors $\mathbf{P}_3$ and $\mathbf{P}_4$ remain unchanged relative to this rotating coordinate system. From the condition $\varkappa_{xx}=\varkappa_{yy}$ we obtain $K_+(0)=\mathscr{E}_3(0)$, $K_-(0)=\mathscr{E}_4(0)$.

§3. CUBIC CRYSTALS

As $|\mathbf{k}|\to 0$ any direction is space is a principal one for the tensor $\varkappa$. Therefore, according to (7), a direction of $\mathbf{s}$ arbitrarily chosen in space is principal also for the tensor β at all ω. Consequently $\mathbf{s}$ is a principal direction for β_0 also for the numerators of all the fractions contained in β. If now $|\mathbf{k}|$ is made different from zero, i.e., if spatial dispersion is introduced, it suffices to make the change only in the denominators of the fractions and leave β_0 in the numerators of the fractions unchanged (neglecting small spatial-dispersion effects). As a result $\mathbf{s}$ remains the principal direction of β even when spatial dispersion is taken into account. We choose the z axis in the $\mathbf{s}$ direction. The two remaining principal axes of β will be then in the xy plane.

For $\mathbf{s}$ to be the principal direction of the tensor β, it is necessary that in an equation of type (8) the vectors $\mathbf{P}_l$ be directed either along s or in the xy plane. As shown in §15 of Pekar's book.[1] To satisfy the symmetry requirements in cubic crystals in the case of dipole-allowed excitons, the fractions in the expression for β can appear only in groups of three, and in each triad two exciton levels must be degenerate and the third must differ from them. The case of three fractions was considered in Ref. 4. We shall calculate here the value of $\varkappa$ when two exciton triads have accidentally close energies. Let the numbers of the first exiton triad be $l=1$, 2, and 3 and let the energy bands $\mathscr{E}_1(\mathbf{k})$ and $\mathscr{E}_2(\mathbf{k})$ be mutually degenerate. Next, let the second exciton triad be numbered $l=4$, 5, and 6 with the bands $\mathscr{E}_4(\mathbf{k})$ and $\mathscr{E}_5(\mathbf{k})$ mutually degenerate. We can then write for β:

$$\beta=\beta'+\beta^{(xy)},$$
$$\beta'=\beta_0+V\overline{\mathbf{P}_3\mathbf{P}_3^*}/[\mathscr{E}_3(\mathbf{k})-\hbar\omega]+V\overline{\mathbf{P}_6\mathbf{P}_6^*}/[\mathscr{E}_6(\mathbf{k})-\hbar\omega], \ \mathbf{P}_3\|\mathbf{P}_6\|\mathbf{s}, \quad (49)$$
$$\beta^{(xy)}=V\overline{\mathbf{P}_1\mathbf{P}_1^*}/[\mathscr{E}_1(\mathbf{k})-\hbar\omega]+V\overline{\mathbf{P}_2\mathbf{P}_2^*}/[\mathscr{E}_2(\mathbf{k})-\hbar\omega]$$
$$+V\overline{\mathbf{P}_4\mathbf{P}_4^*}/[\mathscr{E}_4(\mathbf{k})-\hbar\omega]$$
$$+V\overline{\mathbf{P}_5\mathbf{P}_5^*}/[\mathscr{E}_5(\mathbf{k})-\hbar\omega], \quad \mathbf{P}_1, \mathbf{P}_2, \mathbf{P}_4, \mathbf{P}_5\perp\mathbf{s}.$$

For the same reasons as in uniaxial crystals, the nondegenerate excitons must be polarized along the z axis, and the paired degenerated excitons polarized in the xy plane.

Since $\mathbf{s}\beta^{(xy)}=\beta^{(xy)}\mathbf{s}=0$, we easily obtain an equation similar to (42), in which $\beta^{(y)}$ is replaced by $\beta^{(xy)}$. As $|\mathbf{k}|\to 0$ any direction in the xy plane should be principal for $\varkappa$ and β. This means that

$$\mathbf{P}_1\perp\mathbf{P}_2, \ |\mathbf{P}_1|=|\mathbf{P}_2|, \ \mathbf{P}_4\perp\mathbf{P}_5, \ |\mathbf{P}_4|=|\mathbf{P}_5|. \quad (50)$$

Since the tensor $\beta^{(xy)}$ is transferred to $\varkappa$ without change it remains to calculate only $\varkappa'$ i.e., the first term in a formula of the type (42). A somewhat more general problem was solved in subsection 3 of §1 [case (b)]. There s could have an arbitrary direction in the xz plane and the exciton waves had a polarization $\mathbf{P}_l$ making an arbitrary angle with $\mathbf{s}$. In the case considered now, $\mathbf{P}_l$ and $\mathbf{s}$ are definitely directed along the z axis.

To rewrite Eqs. (8)–(19) and (22)–(27) in our notation, we must introduce the following changes:

$$\beta\to\beta', \ \varkappa\to\varkappa', \ \mathbf{P}_1, \widetilde{\mathbf{P}}_1\to\mathbf{P}_3, \widetilde{\mathbf{P}}_3, \ \mathbf{P}_2, \widetilde{\mathbf{P}}_2\to\mathbf{P}_6, \widetilde{\mathbf{P}}_6,$$
$$\mathscr{E}_1(\mathbf{k})\to\mathscr{E}_3(\mathbf{k}), \ \mathscr{E}_2(\mathbf{k})\to\mathscr{E}_6(\mathbf{k}), \ \Delta_1\to\Delta_3, \ \Delta_2\to\Delta_6.$$

As a result we get

$$\varkappa'=\varkappa_0+V(b^2+g/\mathscr{L}_-)\overline{\mathbf{zz}}/2[K_+(\mathbf{k})-\hbar\omega]$$
$$+V(b^2-g/\mathscr{L}_-)\overline{\mathbf{zz}}/2[K_-(\mathbf{k})-\hbar\omega], \quad (51)$$
$$b^2=\tilde{P}_3^2+\tilde{P}_6^2, \ g=(\tilde{P}_3^2-\tilde{P}_6^2)(\mathscr{L}_-^{-2}-4\Delta_3\Delta_6)^{1/2}-4\Delta_3^{1/2}\Delta_6^{1/2}\tilde{P}_3\tilde{P}_6. \quad (52)$$

It was assumed above in accord with (16) that $\mathscr{E}_1-\Delta_1>\mathscr{E}_2-\Delta_2$. Now this means that $\mathscr{E}_3-\Delta_3>\mathscr{E}_6-\Delta_6$.

The polarizability $\varkappa$ is equal to the sum of the tensors (51) and $\beta^{(xy)}$. It must be stipulated that $\varkappa_{xx}=\varkappa_{yy}=\varkappa_{zz}$ as $|\mathbf{k}|\to 0$ for all ω. Hence

$$K_+(0)=\mathscr{E}_1(0)=\mathscr{E}_2(0), \ K_-(0)=\mathscr{E}_4(0)=\mathscr{E}_5(0),$$
$$b^2+g/\mathscr{L}_-=2|\mathbf{P}_1|^2, \quad b^2-g/\mathscr{L}_-=2|\mathbf{P}_4|^2. \quad (53)$$

We ultimately obtain then for $|\mathbf{k}|\neq 0$

$$\varkappa=\varkappa_0+V\overline{\mathbf{P}_1\mathbf{P}_1^*}/[\mathscr{E}_1(\mathbf{k})-\hbar\omega]$$
$$+V\overline{\mathbf{P}_2\mathbf{P}_2^*}/[\mathscr{E}_2(\mathbf{k})-\hbar\omega]+V\overline{\mathbf{P}_4\mathbf{P}_4^*}/[\mathscr{E}_4(\mathbf{k})-\hbar\omega]$$
$$+V\overline{\mathbf{P}_5\mathbf{P}_5^*}/[\mathscr{E}_5(\mathbf{k})-\hbar\omega] \quad (54)$$
$$+V|\mathbf{P}_1|^2\overline{\mathbf{zz}}/[K_+(\mathbf{k})-\hbar\omega]+V|\mathbf{P}_4|^2\overline{\mathbf{zz}}/[K_-(\mathbf{k})-\hbar\omega].$$

At arbitrary direction of s the directions of the vectors $\mathbf{P}_1$, $\mathbf{P}_3$, $\mathbf{P}_4$, and $\mathbf{P}_5$ are restricted only by the last equation of (49) and by Eq. (50), and cannot be determined more accurately from symmetry considerations. To determine the directions of $\mathbf{P}_1$ and $\mathbf{P}_2$ we must consider the problem of degenerate excitons with $l=1$ and 2 quantum-mechanically and solve the two-dimensional secular equation that determines the correct linear combinations of the zeroth-approximation wave functions. The small parameter must be taken here to be $|\mathbf{k}|$, which is set equal to zero in the zeroth approximation. The directions of the vectors $\mathbf{P}_4$ and $\mathbf{P}_5$ are similarly determined by a quantum-mechanical analysis of the degenerate excitons with $l=4$ and 5.

In the important particular cases when $\mathbf{s}$ lies in one of the mirror-symmetry planes of the crystal, the vectors $\mathbf{P}_1$, $\mathbf{P}_2$, $\mathbf{P}_4$, and $\mathbf{P}_5$ must be so directed that two are perpendicular to the symmetry plane and two lie in this plane. Let $\mathbf{P}_1$ and $\mathbf{P}_4$ lie in this plane and let $\mathbf{P}_2$ and $\mathbf{P}_5$ be perpendicular to it. We choose the x axis in the direction of the vectors $\mathbf{P}_1$ and

$\mathbf{P}_4$. The y axis is then along the vectors $\mathbf{P}_2$ and $\mathbf{P}_5$. Taking (5) into account we have then

$$\overline{\mathbf{P}_1\mathbf{P}_1^*}=|\mathbf{P}_1|^2\overline{\mathbf{xx}},\quad \overline{\mathbf{P}_2\mathbf{P}_2^*}=|\mathbf{P}_1|^2\overline{\mathbf{yy}},$$
$$\overline{\mathbf{P}_4\mathbf{P}_4^*}=|\mathbf{P}_4|^2\overline{\mathbf{xx}},\quad \overline{\mathbf{P}_5\mathbf{P}_5}=|\mathbf{P}_4|^2\overline{\mathbf{yy}}. \tag{55}$$

These expressions must be substituted in the numerators of the first four fractions in (54). The principal axes of $\varkappa$ are thus determined without solving the secular equations.

If the **s** unit vector is directed along one of the fourfold or threefold axes. Then the equality of the energies $\mathscr{E}_1(\mathbf{k})$ and $\mathscr{E}_2(\mathbf{k})$, as well a of $\mathscr{E}_4(\mathbf{k})$ and $\mathscr{E}_5(\mathbf{k})$ is preserved for any $|\mathbf{k}|$. In this case the pairs of mutually orthogonal vectors $\mathbf{P}_1$ and $\mathbf{P}_2$ or $\mathbf{P}_4$ and $\mathbf{P}_5$ can be oriented arbitrarily in a plane perpendicular to **s**. In this case, too, we obtain Eqs. (55), but the coordinate axes x and y can be arbitrarily chosen in plane perpendicular to **s**.

We show now that if the number of fractions in expression (29) for β were not six but less, the symmetry requirement would be satisfied only by eliminating an antire triad of fractions corresponding either to the excitons with $l=1,2,4$ or with $l=4,5,6$. Let us attempt, for example, not to introduce the exciton with $l=6$. The formulas for this case can be easily obtained by putting everywhere above $\mathbf{P}_6=0$. Then $\widehat{\mathbf{P}}_6=\varepsilon_0\mathbf{P}_6=0$ according to the first equation of (13), and $\Delta_6=0$ according to (12). We then obtain from (52)

$$b^2-g/\mathscr{L}_-=0. \tag{56}$$

Equations (5) and the last equation of (53) yield then $\mathbf{P}_4=\mathbf{P}_5=0$. Thus the excitons $l=4$ and 5 vanish in the expression (49) for β together with the exciton $l=6$.

We attempt now to use the expression for β without introducing the exciton with $l=4$, i.e., we put $\mathbf{P}_4=0$ in the equations. Then $\mathbf{P}_5=0$ according to (50) and from the last equation of (53) we obtain (56). It follows from the latter that[2)] $\widetilde{\mathbf{P}}_6=0$, and hence $\mathbf{P}_6=0$. Thus, with vanishing of the exciton $l=4$ in (49), the excitons $l=5$ and 6 also vanish. A similar result is obtained if we try to put $\mathbf{P}_5=0$. The foregoing confirms a statement made in Ref. 4, that in the case of dipole-allowed excitons the fractions in the expression for β can appear only in groups of three, and two band excitons are degenerate within each triad.

Spatial dispersion has thus been introduced in the tensor $\varkappa$, and hence in the dielectric constant at accidentally close excitonic resonances in crystals of varying symmetry. The use of $\varkappa$ is in many cases more convenient than the use of β to calculate the refractive indices of light waves in excitonic resonance regions.

§4. DETERMINATION OF THE DEPENDENCES OF $\mathscr{E}_l$ AND $\mathbf{P}_l$ ON s BY MACROELECTRODYNAMICS METHODS

The exciton energies and polarizations and their dependences on the quasimomentum directions are usually determined by solving the Schrödinger equation for the crystal; this can be done only approximately and by using actual models of the exciton. The theory developed makes it possible to determine these dependences without solving the Schrödinger equation and without introducing an exciton model, but using only a general quantum-mechanical method of calculating β, which leads to equations similar to (8) (Ref. 1), provided that β_0 can be regarded as independent of ω, i.e., if the aggregate of the considered close exciton bands is far enough from the remaining excited levels of the crystal.

It is useful to recall further that Eqs. (1)–(18) are valid for **k** that is arbitrary but is small enough for macroelectrodynamics to be valid. An approximation was used in the remaining equations, viz., $|\mathbf{k}|\to 0$ in the expression for β in the numerators of the fractions. In §1 the direction of **s** was restricted to the mirror-symmetry plane xz of a rhombic crystal. In §§2 and 3 the direction of **s** is arbitrary.

We illustrate the macroelectrodynamic method using as an example uniaxial crystals. The reader is assumed to know the general form of the tensor $\varkappa$ with neglect of spatial dispersion.

If $\varkappa$ contains two resonant fractions whose numerators include the dyad $\overline{\mathbf{zz}}$, this is the case of two close nondegenerate excitonic bands. In this case, as shown above, the solution (b) of §1 is realized, i.e., $\widetilde{\mathbf{P}}_1\|\widetilde{\mathbf{P}}_2\|z$. Then, according to the second equation of (13), the dependence of each of the two excitons on s is given by

$$P_{lz}/P_{lx}=-(\varepsilon_{0xx}s_x^2+s_z^2)/(\varepsilon_{0xx}-1)s_xs_z,\quad l=1,\ 2. \tag{57}$$

The dependence of the energy of these excitons on s as $|\mathbf{k}|\to 0$ is determined by Eq. (16) or (17) if we let in them $|\mathbf{k}|\to 0$. The parameters that enter in $\varkappa$, i.e., $K_\pm(0)$, $Q_\pm(0)$, and $\varkappa_0$, are independent of **s** and can therefore be calculated or measured by choosing a convenient direction (that simplifies the problem) of **s**. The equations obtained from (28)–(31) by making the substitutions $q\to b$, $f\to g$, $x\leftrightarrow z$ are also valid.

If $\varkappa$ contains three fraction terms, it can be only of the form (44) or expressed by an equation obtained from (44) by the interchange $K_+(\mathbf{k})\leftrightarrow\mathbf{K}_-(\mathbf{k})$. Let us consider the first of these cases, which is described above in the section in which a nondegenerate band is accidentally close to a pair of degenerate exciton bands. The energy band $\mathscr{E}^{(\nu)}(\mathbf{k})$ corresponds to an exciton that is transverse at any direction of **s**. The energy $\mathscr{E}^{(\nu)}(0)$ does not depend on **s**. As we have shown, the solution (c) of §1 is realized and the value of λ is determined by Eq. (36). The vectors $\widetilde{\mathbf{P}}_l$ are determined by Eqs. (34) and depend on **s**. Here a and b are parameters that are independent of **s** and enter in (44). The **s**-dependence of the exciton polarizations $\mathbf{P}_l$ with $l=1$ and 2 is determined by the second equation of (13), in which we must substitute the now known $\widetilde{\mathbf{P}}_l$. The dependence of the exciton energy $\mathscr{E}_1(0)$ or $\mathscr{E}_2(0)$ on **s** is determined by Eq. (16) or (17), in which $K_\pm(0)$, $Q_\pm$, and $\varkappa_0$ do not depend on **s** and are known from the expression for $\varkappa$ in the absence of spatial dispersion.

If $\varkappa$ contains four fraction terms, it can have only the form (48); this corresponds to accidentally close two pairs of degenerate exciton bands. As we have shown, excitons with $l=3$ and 4 are transverse at any direction of s and at $\mathbf{P}_3\|\mathbf{P}_4\|y$. The energies $\mathscr{E}_3(0)$ and $\mathscr{E}_4(0)$ do not depend on **s**. The remaining two excitons with $l=1$ and 2 are described by solution (a) of §1. They have $\widetilde{\mathbf{P}}_1\|\widetilde{\mathbf{P}}_2\|x$, and for their polarization we easily obtain from the second equation of (13)

$$\frac{P_{lx}}{P_{lz}}=-\frac{\varepsilon_{0zz}s_z^2+s_x^2}{(\varepsilon_{0zz}-1)s_xs_z}. \tag{58}$$

These excitons satisfy Eqs. (28)–(32). The dependences of the energies $\mathscr{E}_1(0)$ and $\mathscr{E}_2(0)$ on **s** are determined by Eq. (16) or (17).

We can similarly determine the **s**-dependences of the energy limits of the excitons and their polarizations for crystals with other symetries. In cubic crystals, the choice of the direction of s was also arbitrary. In rhombic crystals (in §1), however, it was assumed that **s** lies in the mirror symmetry xz. The dependences of the polarizations of $\mathbf{P}_l$ and $\tilde{\mathbf{P}}_l$ with $l = 1$ and 2 and of the energies Δ_l and $\mathscr{E}_l(0)$ on **s** can therefore be determined from Eq. (16) only for the indicated particular directions of **s**. In the limit as $|\mathbf{k}| \to 0$, however, for particular directions of **s** the tensor $\varkappa$ determined in §1 does not depend on **s**. In particular, $K_{\pm}(0)$, $Q_{\pm}$, and $\varkappa_0$ do not depend on **s**. Equation (17) permits therefore the s-dependence of the energy to be determined for arbitrary direction of **s**.

[1)]At $|\mathbf{k}| = 0$ the field **E** ceases to depend on **s**. If the tensor $\varkappa$ were then dependent on **s**, this would mean that an infinite manifold of different polarizations **P** corresponds to the same spatially homogeneous field **E**.

[2)]$\tilde{P}_6 = 0$ is the only root of Eq. (56). This can be seen from the fact that according to Eqs. (53) b^2 increases and $g/\mathscr{L}_-$ decreases when $\tilde{\mathbf{P}}_6$ becomes different from zero.

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