Clausius-Mosotti Equation for Anisotropic Crystals*

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THE well-known Clausius-Mosotti equation, $3(\epsilon-1)/(\epsilon+2)=4\pi\alpha N$, exhibits a relation between the dielectric constant ϵ of an isotropic substance, the polarizability α of its particles, and the number N of particles per unit volume. The equation can be generalized in such a way as to be applicable to anisotropic crystals.

Such directions are chosen for the coordinates x, y, z that the tensor of dielectric constant reduces to the diagonal ϵ_x, ϵ_y, ϵ_z. The tensor of polarizability of a particle is α_{xx}, α_{xy}, $\cdots\alpha_{zz}$. Then the Clausius-Mosotti equation can be written in two ways:

$$3(\epsilon_x-1)/(\epsilon_x+2)=4\pi\beta_x N, \tag{1}$$

$$\frac{\epsilon_x+2}{\epsilon_x-1}+\frac{\epsilon_y+2}{\epsilon_y-1}+\frac{\epsilon_z+2}{\epsilon_z-1}=\frac{9}{4\pi NA}. \tag{2}$$

In (1) x can be replaced by y or z. The meaning of the symbols is

$$1/\beta_x=A_x+(\alpha_{yy}\alpha_{zz}-\alpha_{yz}^2)/|\alpha_{ik}|,$$
$$3/A=(\alpha_{xx}\alpha_{yy}+\alpha_{xx}\alpha_{zz}+\alpha_{yy}\alpha_{zz}-\alpha_{xy}^2-\alpha_{xz}^2-\alpha_{yz}^2)/|\alpha_{ik}|.$$

$A_x=\Sigma_k(r_k^{-3}-3x_k^2r_k^{-5})$ can be computed if the structure of the crystal is known. r_k is the distance of the kth particle from one selected particle, $x_x=r_k\cos(\mathbf{x}, \mathbf{r}_k)$.

The necessary and sufficient condition for a dielectric to be isotropic is $A_x=0$.

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Electronic Structure of the Diamond Crystal

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THE author has investigated the energy band structure of diamond by means of Herring's orthogonalized plane wave method.[1] Some features of the present solution, shown in Fig. 1, differ significantly from previous results.[2-5]

The three lowest conduction bands are degenerate (state Γ_{15}) at the central point of the Brillouin zone ($\mathbf{k}=000$). Calculations based on the cellular method[2,3] and on the tight-binding approximation[4,5] indicate a nondegenerate lowest conduction band (eigenstate Γ_2') at $\mathbf{k}=000$. Of the four valence bands, three are degenerate (state Γ_{25}') and have negative curvature at $\mathbf{k}=000$. This agrees with Morita's result;[4] other investigators[2,5] found two of these bands to have zero curvature. One of the three lowest conduction bands has negative curvature at $\mathbf{k}=000$ in certain crystallographic directions (e.g., 100) due to the perturbing effect of the Γ_1 conduction band. The uppermost valence bands have greater negative curvature in these directions. Thus, it appears likely that the minimum separation between valence and conduction bands occurs at $\mathbf{k}=000$.

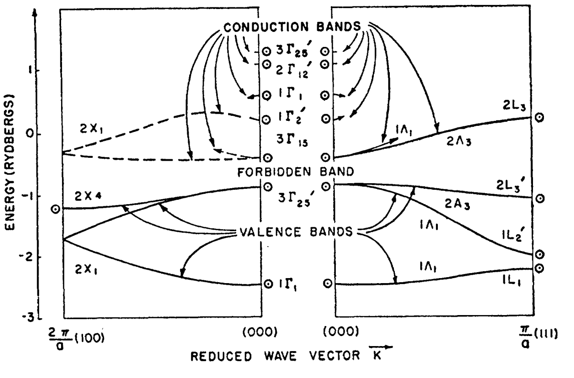

FIG. 1. Schematic of energy bands of diamond crystal in 100 and 111 directions. The notation follows references 11 and 12; for example, the symbol $3\Gamma_{15}$ indicates a threefold degenerate state of symmetry type Γ_{15}. The curves have horizontal slopes at points marked ⊙. Solutions at $2\pi(100)/a$ and at $\pi(111)/a$ are known with less precision than those at (000)

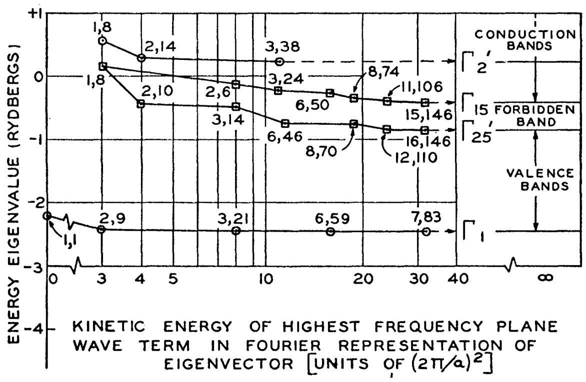

FIG. 2. Convergence of energy eigenvalues for reduced wave vector $\mathbf{k}=000$. Symmetry types Γ_{25}' and Γ_{15} are orthogonal to the core states; the types Γ_1 and Γ_2' must be orthogonalized to the core states. The symbol m, n indicates that an mth order secular determinant yields the eigensolution, which contains n plane wave terms.

That the lowest conduction bands of diamond are degenerate and have nonspherical energy surfaces is particularly interesting in view of ingenious attempts[6,7] to account for the large anisotropic magneto resistance and the anomalous mobility effects observed in germanium. The first effect is interpreted in terms of nonspherical energy surfaces at the bottom of the lowest conduction band, and the second, by postulating that they are re-entrant. Degeneracy is sufficient to account for the former and is necessary for the latter. An investigation of the germanium crystal, just completed, indicates an energy band structure similar to that of diamond. The results will be submitted for publication shortly, as will a more detailed account of the diamond analysis.

The method of orthogonalized plane waves, successfully applied to metallic beryllium[8] and lithium,[9,10] appears to be suitable for diamond-type crystals as well. The precision of the method is dependent upon (1) the accuracy of the assumed potential, (2) the accuracy of the assumed core eigenstates, and (3) the number of terms admitted to the Fourier representations of the crystal wave functions. The Rayleigh-Ritz variational method is used to determine the crystal eigensolutions. Group theory is employed to simplify the computations.[11,12]

The present solution appears to be more reliable than previous investigations: cellular studies,[2,3,13] though useful qualitatively, are unsatisfactory quantitatively;[14] the approximation of tight binding[4,5] is inappropriate for valence and conduction states.

The Coulomb potential and the core eigenstates were obtained from a crystal model consisting of isolated carbon atoms in the $(1s)^2(2s)^1(2p)^3\ {}^5S_2$ state[15] arranged in the form of a diamond lattice. Slater's free-electron approximation[16] was used to represent the exchange potential. The orthogonalization procedure hastened convergence, as is shown in Fig. 2. The eigensolutions automatically orthogonal to the core states approached stable forms slowly as terms were added to the Fourier expansions; the others converged more rapidly, but not so rapidly as corresponding metallic solutions.[8-10] The high order secular equations were solved with the aid of IBM calculating machines at the Watson Scientific Computing Laboratory at Columbia University.

The energy gap remains close to 6 ev over a wide range of solutions. Fluctuations about this value are no longer than uncertainties in the assumed potential. Measurements[17,18] of the ultraviolet absorption of diamond indicate an energy gap of at least 5.5 ev. The calculated width of the valence band 22 ev is consistent with interpretations[19,20] of soft x-ray emission spectra from diamond.

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Bound States and the Interaction Representation

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IN a recent article[1] the temporal development of the state vectors of the free and bound states has been derived from the time-independent formulation of quantum theory. According to this mathematical treatment the transformation operator $W_+(t)$ is non-unitary. On the other hand, it has been observed in Sec. IV of reference 1 that application of an iteration process leads to the conclusion that $W_+(t)$ is unitary. In the present note we shall clarify this apparent inconsistency.

From Eqs. (53) and (36) of reference 1 we see that the integral equations,

$$X(t)=1-i\int_{-\infty}^{t}[H_1(t'),X(t')]dt', \tag{1}$$

$$Y(t)=-i\int_{-\infty}^{t}[H_1(t'),Y(t')]dt', \tag{2}$$

are satisfied by

$$X(t)=W_+(t)W_+{}^\dagger(t)=\int\Psi_{+\lambda}(t)\Psi_{+\lambda}{}^\dagger(t)d\lambda, \tag{3}$$

$$Y(t)=\Sigma_s\Psi_s(t)\Psi_s{}^\dagger(t). \tag{4}$$

However, Eqs. (1) and (2) have also the solutions

$$X(t)=1, \tag{5}$$

$$Y(t)=0. \tag{6}$$

The iteration process described in Sec. IV of reference 1 leads to Eqs. (5) and (6), but not to Eqs. (3) and (4). One cannot, therefore, draw any conclusion about the product $W_+(t)W_+{}^\dagger(t)$ by means of the iteration process we have considered.

The fact that iteration of Eqs. (1) and (2) does not lead to the solutions given by Eqs. (3) and (4) indicates that these solutions cannot be expanded into power series that satisfy the convergence requirements for the validity of the iteration process. Consider, for example, the wave functions $\Psi_s(\mathbf{p})$ of the bound states of the hydrogen atom in the momentum representation. These wave functions contain the factors $[(nap/\hbar)^2+1]^{-1}$, where $n=1,2,\cdots$, $a=\hbar^2/me^2$, and $p=|\mathbf{p}|$. Expansion of $\Psi_s(\mathbf{p})$ in powers of e involves the power-series expansion

$$[1+(\hbar/nap)^2]^{-1}=1-(\hbar/nap)^2+\cdots,$$

which diverges when $p<\hbar/na$. Similarly, the power-series expansion of the sum $\Sigma_s\Psi_s(\mathbf{p})\Psi_s{}^*(\mathbf{p}')$ diverges for small p and p'.

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Charge Independence and Multiple Pion Production*

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SEVERAL authors have recently discussed the role of charge independence in processes involving pions and nucleons.[1] We have explored the consequences of charge independence for multiple pion products in nucleon-nucleon and in pion-nucleon collisions. Before presenting our results,[2] we wish to call attention to a point which has been overlooked in previous treatments of single pion production in nucleon-nucleon collisions and leads to an additional relation among the differential cross sections.

Let us denote by $\sigma(\nu_1\nu_2\rightarrow\nu_1'\nu_2'\pi^i)$ the differential cross section for the production of a pion $\pi^i(i=+,-,0)$ in a collision of two nucleons ν_1 and ν_2 ($\nu=p$ or n), which are transformed into two nucleons ν_1' and $\nu_2'(\nu'=p$ or $n)$, respectively. As the differential cross section refers the direction of motion of the outgoing pion to the direction of motion of the incident nucleons, and as all nucleon charges are specified, it follows that in general $\sigma(\nu_1\nu_2\rightarrow\nu_1'\nu_2'\pi^i)$ is distinct from $\sigma(\nu_2\nu_1\rightarrow\nu_1'\nu_2'\pi^i)$ [or from $\sigma(\nu_1\nu_2\rightarrow\nu_2'\nu_1'\pi^i)$] if the initial (or final) nucleons have different charges. If charge symmetry is taken into account, the number of distinct differential cross sections for single pion production reduces to seven which can be written in the form:

$$\begin{aligned}
\sigma(np\rightarrow nn\pi^+)&=|F_0/\sqrt{6}-F_1'/2|^2,\\
\sigma(np\rightarrow np\pi^0)&=|F_0/2\sqrt{3}+F_1/2|^2,\\
\sigma(np\rightarrow pn\pi^0)&=|F_0/2\sqrt{3}-F_1/2|^2,\\
\sigma(pn\rightarrow nn\pi^+)&=|F_0/\sqrt{6}+F_1'/2|^2,\\
\sigma(pp\rightarrow np\pi^+)&=|F_1/\sqrt{2}+F_1'/2|^2,\\
\sigma(pp\rightarrow pn\pi^+)&=|-F_1/\sqrt{2}+F_1'/2|^2,\\
\sigma(pp\rightarrow pp\pi^0)&=|F_1'/\sqrt{2}|^2,
\end{aligned}$$

where F_0 is the isotopic singlet amplitude and F_1, F_1' are the two isotopic triplet amplitudes. Thus, the seven cross sections depend on the three absolute values and the two relative phases of these amplitudes. Hence, there exist two relations among the σ's as a consequence of charge independence. One of these is linear:

$$\sigma_1{}^+ + \sigma_3{}^+ = 2(\sigma_2{}^+ + \sigma_4); \tag{1}$$

the other is essentially a phase relationship:

$$\cos^{-1}\{\sigma_3{}^-/2[(\sigma_3{}^+-\sigma_4)\sigma_4]^{\frac{1}{2}}\}+\cos^{-1}\{\sigma_1{}^-/2[(\sigma_1{}^+-\sigma_4)\sigma_4]^{\frac{1}{2}}\} =\cos^{-1}\{\sigma_2{}^-/[(\sigma_1{}^+-\sigma_4)(\sigma_3{}^+-\sigma_4)]^{\frac{1}{2}}\}. \tag{2}$$

Here we have set

$$\begin{aligned}
\sigma_1{}^\pm&=\sigma(np\rightarrow nn\pi^+)\pm\sigma(pn\rightarrow nn\pi^+),\\
\sigma_2{}^\pm&=\sigma(np\rightarrow np\pi^0)\pm\sigma(np\rightarrow pn\pi^0),\\
\sigma_3{}^\pm&=\sigma(pp\rightarrow pn\pi^+)\pm\sigma(pp\rightarrow np\pi^+),\\
\sigma_4&=\sigma(pp\rightarrow pp\pi^0).
\end{aligned}$$

Relation (2) can only be obtained by distinguishing between $\sigma(np\rightarrow nn\pi^+)$ .and $\sigma(pn\rightarrow nn\pi^+)$, etc. Messiah[1] [see his Eq. (10)] and Luttinger[1] [see his Eq. (2)] do not make this distinction, so that their relation is only valid in so far as *total* cross sections are concerned.

The above considerations can be generalized to multiple pion production in nucleon-nucleon collisions; as the number k of pions increases, both the number S_k of distinct cross sections (in the