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Sum Rule Relating Optical Properties to the Charge Distribution*

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A sum rule is constructed which relates the third moment of the imaginary part of the dielectric function at zero wave vector to an integral of the product of the Laplacian of the crystal potential and the fluctuation of the electron density. This sum rule, though rigorous, will be of real use only when the real solid can be replaced by a solid of pseudoatoms having only valence electrons. A method is found for obtaining an "experimental" third moment from other known moments. In this approximation some of the recent empiricism about bonding in crystals can be given a more rigorous basis. A quantitative application of the theorem to the prediction of the dielectric constant of GaAs is sketched.

I. INTRODUCTION

The recent works of Phillips[1] and Van Vechten[1] have made extensive use of the optical dielectric constant due to electronic polarizability to aid in understanding covalent and ionic bonding in a wide class of materials. This theory is empiricism based on good physical notions, but has not been derived from the Schrödinger equation. More recently, Wemple and DiDomenico[2] have empirically found that the dispersion in $\epsilon_1(\omega)$ as a function of frequency shows a systematic correlation with crystal binding and coordination number. It is obvious that $\epsilon(\omega)$ contains information about the electronic wave function responsible for bonding. What is not clear from this empiricism is whether $\epsilon(\omega)$ directly relates to bonding, or whether wave functions are a necessary intermediate construct of a complete quantum-mechanical theory. In this paper we develop a theorem which provides a direct link between $\epsilon(\omega)$ and some physical quantities of relevance to bonding.

An exact sum rule relating an integral over the dielectric function at zero wave vector to the charge distribution within a unit cell is derived in Sec. II. While this theorem is exact, it is of real utility in understanding binding only if the atomic core is replaced by a pseudopotential (Sec. III). Silicon, for example, will be considered a four-electron atom. In Sec. IV the direct relation between the symmetric and antisymmetric charge distributions and potentials and the magnitude of the optical dielectric constant is demonstrated. A quantitative evaluation of the difference in dielectric constant between Ge and GaAs is obtained by using the theorem.

II. OPTICAL THEOREM

Consider a crystal having atoms a, b, $c, \ldots$ in a unit cell, producing (unscreened) central potentials V_a, V_b, $V_c, \ldots$. Let the crystal structure, for convenience, be cubic. The total Hamiltonian consists of these atomic potentials, electron-electron interactions, and the electron kinetic energy. The atomic potentials will be assumed to be continuous and finite. (The behavior of Coulomb potential at the origin can be included as a limiting case.) Let the crystal have N electrons of mass m in a volume Ω. The ordinary f-sum rule arises from the fact that at sufficiently high frequencies the electron charge density moves as a rigid unit in an applied uniform oscillating electric field $\vec{E}$. The equation of motion of the c.m. $\vec{x}$ of the electrons is then

$$Nm\ddot{\vec{x}}+N\overleftrightarrow{K}\cdot\vec{x}=Ne\vec{E}e^{i\omega t} \quad . \tag{1}$$

The term $N\overleftrightarrow{K}$ represents a restoring-force tensor on the rigid charge density motion due to the atomic potentials. Solving for $\vec{x}$ and multiplying by the charge density Ne/Ω to obtain the polarization density $\vec{P}$,

$$\vec{P}=(Ne^2/\Omega)(-m\omega^2\,\overleftrightarrow{I}+\overleftrightarrow{K})^{-1}\cdot\vec{E} \ . \tag{2}$$

At high frequencies, the dielectric tensor $\epsilon(\omega)$ is thus

$$\begin{aligned}\overleftrightarrow{\epsilon}(\omega)-\overleftrightarrow{I} &= \frac{4\pi Ne^2}{m\Omega}\left(-\omega^2\overleftrightarrow{I}+\frac{\overleftrightarrow{K}}{m}\right)^{-1}\\ &\approx \frac{4\pi Ne^2}{m\Omega}\left(\frac{-\overleftrightarrow{I}}{\omega^2}-\frac{\overleftrightarrow{K}}{m\omega^4}\right)\end{aligned} \tag{3}$$

and has only a real part.

If we are content to prove the theorem for cubic crystals, all tensor indices on K and ϵ can be omitted. We write the real part of $\epsilon(\omega)-1$ as the Kramers-Kronig integral over the imaginary part $\epsilon_2(\omega)$:

$$\epsilon_1(\omega)-1=\frac{2}{\pi}\int_0^\infty\frac{\omega'\epsilon_2(\omega')}{\omega'^2-\omega^2}\,d\omega' \quad . \tag{4}$$

The denominator can be expanded in powers of $(\omega'/\omega)^2$ for frequencies higher than any appreciable contribution to $\epsilon_2(\omega')$. Thus,

$$\begin{aligned}\epsilon_1(\omega)-1=(2/\pi)[&-(1/\omega^2)\int_0^\infty\omega'\epsilon_2(\omega')\,d\omega'\\ &-(1/\omega^4)\int_0^\infty\omega'^3\epsilon_2(\omega')\,d\omega'\cdots] \quad .\end{aligned} \tag{5}$$

Equating powers of ω^2 in (3) gives two relations: the usual f-sum rule

$$(2/\pi)\int_0^\infty\omega'\epsilon_2(\omega')\,d\omega'=4\pi Ne^2/m\Omega\equiv\omega_p^2 \tag{6}$$

and a new one determining K, namely,

$$(2/\pi)\int_0^\infty\omega'^3\epsilon_2(\omega')\,d\omega=\omega_p^2K/m \quad . \tag{7}$$

For the moment, the convergence of this integral will be presumed.

We now construct the meaning of K in terms of other quantities by examining the restoring force on a wave function moved rigidly in a crystal. The crystal will be chosen to be a long rod, and the electrons will be displaced parallel to the rod. In this case, there will be no macroscopic field built up by the displacement, and any restoring force will be due to K, not to depolarizing fields. Let the electron density $\rho(r)$ be rigidly moved along the bar by a small distance $\vec{a}$. The force on the center of mass of the electrons will then be

$$\vec{F}=\int_{\substack{\text{all}\\ \text{space}}}-e\sum_{\substack{\text{all atom types;}\\ \text{all cells } i}}-\vec{\nabla}_rV_b\,(\vec{r}-\vec{R}_{ib})\rho(\vec{r}-\vec{a})\,d^3r \quad , \tag{8}$$

where $\vec{R}_{ib}$ is the position of the atom of type b in cell i and e is the magnitude of the charge on the electron. Electron-electron interactions produce no force on the electron center of mass.

If $\rho(\vec{r})$ were a constant within the crystal, the only force would arise from the effect of the macroscopic field on the charge distribution. Since the macroscopic (average) field is unimportant in the presumed geometry, the uniform part of $\rho(\vec{r})$ can have no effect. If we write

$$\rho(\vec{r})=\bar{\rho}+\delta\rho(\vec{r}) \ ,$$

where $\bar{\rho}$ is the average electron density in the crystal and $\delta\rho(\vec{r})$ has a spatial average of zero, we can replace $\rho(\vec{r}-\vec{a})$ in (8) by $\delta\rho(\vec{r}-\vec{a})$. In a cubic crystal, the force $\vec{F}$ will necessarily be in the direction of the displacement $\vec{a}$, which is assumed to be the z direction. The force per unit displacement defines $-NK$. Expanding $\delta\rho(\vec{r}-\vec{a})$ in powers of $\vec{a}$, and using the periodicity of the crystal charge distribution, we find that

$$K=\frac{1}{n}\sum_{\substack{\text{all types of}\\ \text{atoms in a cell}}}e\int_{\substack{\text{all}\\ \text{space}}}\frac{\partial V_b(\vec{r})}{\partial z}\,\frac{\partial\delta\rho(\vec{r})}{\partial z}\,d^3r \quad . \tag{9}$$

The number of electrons per unit cell is denoted by n. For each integration in the sum, the atom position conveniently can be taken as the origin of coordinates. Since $\delta\rho(\vec{r})$ oscillates and V goes to zero at infinity, an integration by parts is legitimate, yielding

$$K=-\frac{1}{n}\sum_{\substack{\text{all types of}\\ \text{atoms in a cell}}}e\int_{\substack{\text{all}\\ \text{space}}}\frac{\partial^2V_b(r)}{\partial z^2}\,\delta\rho(\vec{r})\,d^3r \quad . \tag{10}$$

By supposition, the atomic (bare) potentials $V_b(\vec{r})$ are spherical. If each atom is at a site of cubic symmetry, this result simplifies to

$$K=-\frac{e}{3n}\sum_{\substack{\text{all atoms}\\ b \text{ in cell}}}\int_{\substack{\text{all}\\ \text{space}}}\delta\rho(\vec{r})\nabla^2V_b(\vec{r})\,d^3r \quad . \tag{11}$$

The optical theorem is the relation

$$\frac{2}{\pi}\int_0^\infty \omega^3\epsilon_2(\omega)\,d\omega = -\frac{\omega_p^3 e}{3mn}\sum_b \int_{\text{all space}} \delta\rho(\vec{r})\nabla^2 V_b(\vec{r})\,d^3r \ . \qquad (12)$$

It is valid in this form when all atoms are at sites of cubic or tetrahedral symmetry.

This theorem is particularly simple for potentials whose long-range part is $1/r$, for then $\nabla^2 V_b(\vec{r})$ vanishes except in the core. If, for example, it is applied to a possible pseudopotential for sodium

$$V(\vec{r}) = e/r, \quad r > b$$
$$V(\vec{r}) = e/b, \quad r < b \qquad (13)$$

then

$$\frac{2}{\pi}\int_0^\infty \omega^3\epsilon_2(\omega)\,d\omega = \frac{4\pi}{3}\,\frac{\omega_p^2 e^2}{m}\left(\frac{1}{4\pi}\int_{r=b}\delta\rho(\vec{r})\,d\Omega_r\right) \ ,$$

where the integration is carried out over a spherical surface of radius b. The average value of $\delta\rho(\vec{r})$ on this surface is in the parentheses. The weak optical absorption in sodium (i.e., the small integral) directly implies the smallness of the electron redistribution $\delta\rho(\vec{r})$.

This theorem can be easily generalized to slightly more complicated situations. First, it is true as it stands for cubic crystals even if each atom is not at a site of cubic symmetry. Second, if $\epsilon_\parallel$ and $\epsilon_\perp$ are the two dielectric functions of a uniaxial crystal, the theorem remains true with the replacement of $\epsilon_2(\omega)$ in (12) by $\frac{1}{3}[\epsilon_\parallel(\omega)+2\epsilon_\perp(\omega)]$.

The restoring-force constant K is related to the frequencies that the phonons would have if the electrons did not follow the lattice displacements. For such a hypothetical problem, the mean square phonon frequency in a cubic Bravais lattice will be given by

$$M\langle\omega^2\rangle_{\text{av}} = Z(\tfrac{1}{3}m\omega_p^2 + K) \ , \qquad (14)$$

where Z is the charge of the pseudoatom and M is the ion mass. The average is taken over all phonon polarizations and wave vectors.

A mathematical proof of theorem A which requires no insight will next be constructed. It has the advantage of being useful for nonlocal potentials as well as local ones. The Hamiltonian for the solid is

$$H = T_e + V_{ee} + V_{en} \ ,$$
$$T_e = \sum_{\text{electrons } i} \frac{p_i^2}{2m} \ ,$$
$$V_{ee} = \sum_{q\neq 0} \frac{2\pi e^2}{q^2\Omega}\,(\rho_q\rho_{-q} - N) \ , \qquad (15)$$
$$V_{eN} = -\frac{eN}{n\Omega}\,(NV_0 + \sum_{G\neq 0} V_G\rho_G) \ ,$$
$$V_G = \sum_b e^{i\vec{G}\cdot\vec{R}_b}\int_{\text{all space}} V_b(\vec{r})e^{i\vec{G}\cdot\vec{r}}\,d^3r \ .$$

Charge neutrality eliminates the Coulomb contribution to the zero wave-vector potential, but an explicit term may remain from a short-range deviation of $V_b(\vec{r})$ from a Coulomb potential.

The transverse dielectric function for q in the z direction can be written

$$\epsilon_2(\omega, q) = (4\pi^2e^2/m^2\omega^2\Omega)\textstyle\sum_f |\langle 0|\sum_i p_{xi}e^{iqz_i}|f\rangle|^2$$
$$\times\,\delta(E_0 + \hbar\omega - E_f), \qquad (16)$$

where $|0\rangle$ and $|f\rangle$ are exact ground and excited states, respectively, of the many-electron system in the presence of the periodic potential. The optical dielectric function is the limit of this expression for $q \to 0$. Multiplying (16) by $2\omega^3/\pi$ and integrating, one obtains

$$(2/\pi)\int_0^\infty \omega^3\epsilon_2(\omega)\,d\omega = (8\pi e^2/m^2\hbar^2\Omega)$$
$$\times\,\langle 0|[\textstyle\sum_i p_{xi}e^{iqz_i}, H]\sum_j p_{xj}e^{-iqz_j}|0\rangle \qquad (17)$$

by using a commutator and closure. In the $q \to 0$ limit, the commutators of the sum

$$\textstyle\sum_i p_{xi}e^{iqz_i}$$

with the electron kinetic energy and with the electron-electron interaction vanish. The right-hand side is therefore

$$\frac{8\pi e^2}{m^2\hbar^2\Omega}\left\langle 0\left| -\frac{eN}{n\Omega}\sum_{G\neq 0}\left(\frac{\hbar}{i}\right)iG_x\sum_i e^{i\vec{G}\circ\vec{r}_i}V_G\sum_j\left(\frac{\hbar}{i}\right)\frac{\partial}{\partial x_j}\right|0\right\rangle \ . \qquad (18)$$

The bracket can be integrated by parts, yielding a term which is the negative of the present term and a new term in which the operators $\partial/\partial x_j$ act on the $e^{i\vec{G}\cdot\vec{r}_i}$ terms. The right-hand side of Eq. (17) is thus

$$\frac{4\pi e^2}{m^2\Omega}\left(\frac{eN}{n\Omega}\right)\left\langle 0\left|\sum_{G\neq 0}\sum_i V_G G_x^2 e^{i\vec{G}\cdot\vec{r}_i}\right|0\right\rangle \ . \qquad (19)$$

If the particle density is written as $\rho(\vec{r}) = \bar{\rho} + \delta\rho(\vec{r})$ as before, the expectation value in the above equation is

$$-\frac{\Omega}{3}\sum_{\substack{\text{atoms } b\\ \text{in a cell}}}\int_{\substack{\text{all}\\ \text{space}}}\delta\rho(\vec{r})\nabla^2 V_b(\vec{r})\,d^3r \ . \qquad (20)$$

The substitution of this result into Eq. (17) immediately yields (12), which proves the theorem.

A similar theorem, but relating an integral of the *total* charge density times $\nabla^2 V(\vec{r})$ to an integral over the atomic polarizability $\beta(\omega)$ can be demonstrated for atoms.[3] In this case, the polarizability integral required is

$$\int_0^\infty \omega^3 \beta_2(\omega)\, d\omega \ .$$

The convergence of such integrals depends on the nature of the potential. The Coulomb potential has a singularity at the origin which results in the asymptotic behavior $\beta_2(\omega) \sim \omega^{-4.5}$ for large ω. This form is characteristic of the r^{-1} singularity at the origin, and is expected for hydrogen metal also. Martin[4] points out that if the potential $V(r)$ is analytic, all moments of $\beta_2(\omega)$ or $\epsilon_2(\omega)$ will exist.

This method of proof may prove useful in working with nonlocal potentials. The theorem as written is valid only for local potentials.

III. PSEUDOATOM HYPOTHESIS

The theorem of Sec. II is correct for real solids. Useful application of the theorem as it stands is impossible, however, for the integrations involved extend over all frequencies, and must be carried out over a range of energies at least as large as several times the binding energy of the most tightly bound shell of electrons. Most of the contributions to the integral arise from core electrons whose contribution to chemical binding is in some sense small. One possible line of attack on the elimination of this large but chiefly irrelevant contribution to the integrals is to find theorems about the *difference* between such integrals for the solid and for isolated atoms. Such theorems could be useful if sufficiently good optical data were available to evaluate differences of these integrals carried out over all energies. This cannot be done with sufficient precision at present. A more useful line of approach is a pseudoatom hypothesis, in which the effect of the core electrons is replaced by an effective potential. Such a hypothesis is implicit in most of the connections between band-structure calculations and bonding. It is explicitly outlined in the following, because the choosing of pseudopotentials[5] has most often been done with band structure, not chemistry, in mind.

The pseudopotential approach[5] to wave functions in an atom or solid replaces all but the outer electrons by an effective potential. This effective potential can, for example, be chosen to have energy levels for a one-particle problem in agreement[6] with the measured term values of an atom or ion having one outer electron. The pseudo-wave-function is a smooth wave function, lacking the core wiggles of the true wave function.

In order for the optical theorem to be applicable, the electron-electron interactions must be a function only of the separation between the electrons. In most of space (i.e., outside the cores), the pseudo-wave-functions and the real wave functions are proportional to each other, and the electron-electron interactions can be correctly described in terms of a Coulomb interaction between the pseudo-wave-functions. Within the core region, the real and the pseudo-wave-functions differ. In the core, the description of the Coulomb interactions of electrons in terms of a Coulomb interaction between pseudo-wave-functions is not correct. This error will be important if the core volume is small.

For polyvalent atoms, the quantities most important to reproduce correctly are the charge distributions and excitation energies of the neutral and singly ionized (of either sign) atoms. These should be fit by making a many-electron calculation of the pseudoatom, including electron-electron interactions. The potential should contain as few unphysical kinks as possible, for they introduce high-momentum (and frequency) effects to both sides of (18). It two different pseudopotentials both give good pseudoatom properties, both should satisfy (18). The calculation of the experimental $\epsilon_2(\omega)$ will be more model sensitive for the potential having larger high-momentum components (see also Sec. IV). The potential which decreases the more rapidly for large momenta will be the more useful.

The pseudoatom hypothesis has two parts. First, it supposes that a central pseudopotential exists which will yield the correct charge distributions and low-lying excitations for pseudoatoms which match those of the true atom outside a (presumed small) core region. Second, it assumes that the conditions of the first supposition are sufficient to guarantee that the chemistry of solids made from pseudoatoms will closely resemble the chemistry of real solids. Chemists have recently begun investigating possible uses of pseudopotential methods for multielectron atoms and molecules.[7] Some problems of interest to molecular chemists involved small energy differences between dissimilar structures. The pseudoatom approach may not be sufficiently accurate for such problems. The first chemistry problem of solid-state physics, however, lies in understanding the total cohesive energy of a solid, and is much less subtle.

The size of the core will be the dominant factor in the accuracy of the pseudoatom point of view. Obviously, copper cannot be regarded as a one-electron pseudoatom, its 3*d* shell being large and loosely bound. On the other hand, sodium, carbon, and silicon should be representable as pseudoatoms with reasonable quantitative precision. For the remainder of the paper, we will assume the validity of the pseudoatom hypothesis, but will restrict considerations to cases in which the cores are small.

IV. APPLICATIONS

Phillips[1] and Van Vechten[1] have empirically demonstrated that there is a connection between an average frequency defined from the dielectric function and the degree of ionicity in a crystal bond. They have written the optical dielectric constant at low frequencies as

$$\epsilon_0 \equiv \epsilon_1(0) = 1 + \omega_p^2/\omega_g^2 \;, \quad \omega_p^2 = (4\pi e^2/m)(N/\Omega) \;, \tag{21}$$

where N/Ω is the number of valence electrons per unit volume (e.g., silicon has four electrons/atom). They have further split ω_g^2 into a homopolar (symmetric) part and an ionic (antisymmetric) part, and have shown the resulting empiricism to work well. Since $\epsilon_1(0)$ can be written in terms of a Kramers-Kronig integral on $\epsilon_2(\omega)$, their empirical result can be interpreted as the proposition: "There exists a squared frequency having a chemical interpretation and obtainable from $\epsilon_2(\omega)$. This squared frequency can be written as a sum of two terms, one relating to the symmetric part of the problem, and the other to the antisymmetric part." We will obtain such a result from the optical theorem.

Consider a crystal of the zinc-blende structure as an example, having two kinds of atoms, I and II. If theorem (12) is divided by the f-sum rule (5), a squared frequency ω_a^2 is defined

$$\omega_a^2 \equiv \int_0^\infty \omega^3 \epsilon_2(\omega)\, d\omega \Big/ \int_0^\infty \omega \epsilon_2(\omega)\, d\omega = -\frac{e}{3mn} \int_{\substack{\text{all}\\ \text{space}}} \delta\rho(\vec{r}) \nabla^2 V_{\text{cell}}(\vec{r})\, d^3r \;. \tag{22}$$

The potential $V_{\text{cell}}(\vec{r})$ is the bare potential due to the two atoms I and II in one unit cell. While the integral is in principle over all space, $\nabla^2 V_{\text{cell}}$ vanishes except within the core regions of atoms I and II, for each has an r^{-1} potential outside its core. We define symmetric and antisymmetric charge distributions and potentials by picking an origin midway between the two atoms:

$$V_S = \tfrac{1}{2}[V_{\text{cell}}(\vec{r}) + V_{\text{cell}}(-\vec{r})] \;,$$
$$V_A = \tfrac{1}{2}[V_{\text{cell}}(\vec{r}) - V_{\text{cell}}(-\vec{r})] \;,$$
$$\delta\rho_S = \tfrac{1}{2}[\delta\rho(\vec{r}) + \delta\rho(-\vec{r})] \;,$$
$$\delta\rho_A = \tfrac{1}{2}[\delta\rho(\vec{r}) - \delta\rho(-\vec{r})] \;.$$

Then

$$\omega_a^2 = -\frac{e}{3mn}\left(\int_{\substack{\text{all}\\ \text{space}}} \nabla^2 V_s\, \delta\rho_s\, d^3r + \int_{\substack{\text{all}\\ \text{space}}} \nabla^2 V_A \delta\rho_A\, d^3r \right) \;. \tag{23}$$

Thus, this mean square frequency ω_a^2 determined from $\epsilon_2(\omega)$ is rigorously a sum of two terms, one arising from antisymmetric observables and the other from symmetric observables.

The frequency ω_a is not identically the same frequency as defined by Phillips and Van Vechten. From a theoretical viewpoint, the positive moments of $\epsilon_2(\omega)$, which do not give a heavy weighting to states near small band gaps, are a more satisfactory definition of an average appropriate to binding than is the static dielectric constant used by Phillips. From a pragmatic point of view, the "static" high-frequency dielectric constant and its frequency dependence are all that can be obtained easily from experiment. Thus, the moments

$$M_3 = (2/\pi) \int_0^\infty [\epsilon_2(\omega)/\omega^3]\, d\omega \;,$$
$$\epsilon_0 = (2/\pi) \int_0^\infty [\epsilon_2(\omega)/\omega]\, d\omega \;, \tag{24}$$
$$\text{and} \quad \omega_p^2 = (2/\pi) \int_0^\infty \omega \epsilon_2(\omega)\, d\omega$$

are generally known. The moment involved in (12) cannot be obtained from experimental data directly. Even worse, what is desired is not real experimental data for $\epsilon_2(\omega)$, but the data which would have been obtained if experiments were done on crystals of pseudoatoms. A high-frequency tail in $\epsilon_2(\omega)$ arises from the core "wiggles" of the valence band electrons in real experiments. These wave-function wiggles and concomitant tail in $\epsilon_2(\omega)$ are absent for pseudoatoms. At the same time, the static dielectric constant and low-frequency dispersion are virtually independent of the high-frequency tails.

We have already noted that for Coulomb potentials, $\epsilon_2(\omega)$ will fall off as $\omega^{-4.5}$ at high frequencies. The elementary pseudopotentials used have large wave-vector components which drop off more rapidly than those of a Coulomb potential. For example, the pseudopotential form (13) produces a high-frequency behavior $\omega^{-5.5}$, and a rounding of the corner in this potential will make the falloff even more rapid. For such pseudopotentials, the convergence of the moment of $\epsilon_2(\omega)$ used in (12) is fairly rapid, and the value of this moment is not critically sensitive to the exact form of $\epsilon_2(\omega)$. In this case, a model of $\epsilon_2(\omega)$ with parameters determined by the experimental moments ϵ_0, M_3, and the f-sum rule can be used to evaluate the experimental ω_a^2 appropriate to such pseudopotentials.

We take for illustration the model used by Wemple and DiDomenico[2]

$$\begin{aligned} &\epsilon_2(\omega) = (\pi/2)[\omega_p^2/\omega\omega_t(b-1)], && \omega_t \leqslant \omega \leqslant b\omega_t \\ &\epsilon_2(\omega) = 0, && \omega < \omega_t \text{ or } \omega > b\omega_t \;. \end{aligned} \tag{25}$$

The plasma frequency is determined by the electron density. The model obeys the f-sum rule (6) and contains two arbitrary parameters, an effective energy gap ω_t and a width $(b-1)\omega_t$ for $\epsilon_2(\omega)$. For this model the parameter ω_g^2 of (21) is $\omega_g^2 = b\omega_t^2$. The dispersion frequency ω_d^2 defined by Wemple and DiDomenico is

$$\epsilon_0^3/M_3 \equiv \omega_d^2 = (\omega_p^4/\omega_g^2)[3/(b+1+1/b)] \ , \qquad (26)$$

and the frequency ω_a^2 is given by

$$\omega_a^2 = \omega_g^2\left(\frac{b+1+1/b}{3}\right) \ . \qquad (27)$$

A typical value of b for a semiconductor is about 3, though b exhibits systematic trends in the Periodic Table. The parenthesis in (27) varies rather slowly with b, and is typically about 1.4 for group-IV semiconductors.

Thus, within a scale factor slightly greater than one, ω_a^2 can be identified with the parameter of ω_g^2 of Phillips and Van Vechten. Wemple and DiDomenico used the experimental dispersion frequencies ω_d^2 to classify binding. The success of this scheme may be directly connected to the intimate relation between ω_a^2 and ω_d^2, namely,

$$\omega_a^2 = \omega_p^4/\omega_d^2 \ . \qquad (28)$$

The use of ω_d^2 as the classification parameter contains the effects of the bandwidth of ω_a^2. This result is model dependent, but only weakly so.

Finally, we sketch a simple calculation which uses the optical theorem for quantitative prediction. Consider ω_a^2 for the compounds Ge, GaAs, and ZnSe. These three materials have very similar electron densities and similar symmetric potentials. The antisymmetric part of the potential vanishes in Ge and is expected to be approximately twice as great in ZnSe as in GaAs. As long as this potential can be considered small, $\delta\rho_A$ is proportional to the antisymmetric potential. Thus ω_a^2 should have an antisymmetric contribution four times as large for ZnSe as for GaAs. This relation is approximately obeyed in this sequence, as well as in the analogous sequences from the second and third rows of the Periodic Table.

The value of the increase in ω_a^2 for GaAs over Ge can be evaluated as follows: The smallest reciprocal-lattice vector is so large that the dielectric screening for such wavelengths is not appreciably affected by the small band gaps. To a good approximation, the antisymmetric charge distribution can be calculated from the linear response of a uniform electron gas to the antisymmetric potential. In this case

$$(\hbar^2\omega_a^2)_{\mathrm{GaAs}} - (\hbar^2\omega_a^2)_{\mathrm{Ge}} = (\hbar^2\Omega_{\mathrm{cell}}/96\pi m)\sum |V_{\vec{G}}|^2 |\vec{G}|^4 [1 - 1/\epsilon(G)] \ , \qquad (29)$$

where V_G is the antisymmetric electrostatic potential

$$V_G = (1/\Omega_{\mathrm{cell}}) \int_{\mathrm{cell}} e^{-i\vec{G}\cdot\vec{r}} V_A(\vec{r})\, d^3r$$

and $\epsilon(G)$ is the static dielectric function of the free-electron gas at wave vector G.

In principle, the values of V_G should be directly obtainable from the pseudoatom potentials of Ge, Ga, and As. We have not yet computed these, and reliable values are available from the literature only for Ge. This difficulty can be circumvented by using the antisymmetric pseudopotential coefficients determined by Cohen and Bergstresser[8] for GaAs. Their numbers for V_G can be directly used by correcting them for the *lack* of screening [the bare potential is wanted in (29)] and for the structure factor present in their definition. Table I shows the results of this calculation. The value for the difference of $(\hbar\omega_a)^2$ obtained is 14.5(eV^2). The contributions of the first and second reciprocal-lattice vectors are almost equal, and that of the third reciprocal-lattice vector negligible. For comparison, the experimental value is 12.2(eV^2) if b is chosen as 3 for both Ge and GaAs, and 13.5(eV^2) if $(\hbar\omega_a)^2$ is evaluated by using (29). The theoretical value reproduces the difference in dielectric constant between Ge and GaAs with this same precision, about 20%. Better suppositions about the magnitude of the pseudopotential would be necessary to claim a theoretical accuracy as good as this agreement indicates. A better approximation than the Hartree dielectric function may also be needed.

V. CONCLUSION

A theorem was proved relating the third moment of $\epsilon_2(\omega)$ to an integral over a product of the electron density and the Laplacian of the bare crystal potential. This theorem relates average optical properties directly to quantities of relevance to bonding. This theorem cannot be effectively used unless the core electrons are eliminated from the problem, and the atoms thus replaced by pseudoatoms. The problem of obtaining an experimental value of the third moment for a crystal of pseudoatoms from experimental data on a real crystal has been solved for semiconductors by noting that for the pseudopotentials generally used in band-structure calculations the third moment integral would converge fairly rapidly. The third moment for use with such potentials can therefore be extrapolated from a model of $\epsilon_2(\omega)$ chosen to fit the experimental first, minus first, and minus third moments. The rapid convergence means the extrapolated value of the third moment is not critically dependent on the model.

The theorem and the third-moment extrapolation

TABLE I. Contribution of the antisymmetric potential to the calculation of $(\hbar\omega_a)^2$. Only these first three reciprocal-lattice vectors are included.

V_3	V_4	V_{11}	
0.95	0.68	0.14	Cohen and Bergstresser (Ref. 8) (eV)
1.34	1.15	0.11	Corrected for screening and structure factor (eV)
7.8	6.3	0.4	Contribution to $(\hbar\omega_a)^2$ $(\mathrm{eV})^2$

provide a direct understanding of two empirical results. First, the division by Phillips of the average squared energy gap E_g^2 (defined through the high-frequency dielectric constant) into a homopolar and an ionic part is given a solid justification without the necessity of investigating any details of band structure. Second, the parameter ϵ_d^2 used by Wemple and DiDomenico to classify crystal binding is found to have a direct relation to the third moment of $\epsilon_2(\omega)$. This parameter may therefore be somewhat more closely related to parameters of relevance to binding that is E_g^2.

If atomic pseudopotentials suitable for chemical considerations can be found, it should be possible to use the present theorem as an aid to the quantitative understanding of crystal binding. Most evaluations of atomic pseudopotentials to date have relied heavily on the energy levels (and not on the charge distributions) of systems such as Ge^{+++}. A pseudopotential based on the energy and the charge distribution of neutral Ge would be more relevant for pseudoatom chemistry. A numerical application of the theorem was given to predict the charge of ϵ_0 from Ge to GaAs. This calculation was based on a band-structure estimate of the antisymmetric potential. The difference in dielectric constant $\epsilon_{\mathrm{Ge}} - \epsilon_{\mathrm{GaAs}}$ inferred from this calculation is in reasonable accord with experiment. To the extent that linear dielectric response can be used to treat the antisymmetric charge distribution, it should be possible to predict such differences in many compound semiconductors. The *potential* dependence of the third-moment extrapolation must be examined in detail in order to accomplish this. Until further work is done on this extrapolation and on pseudoatom pseudopotentials, the above numerical calculation can only be regarded as suggestive that the method may be quantitatively useful.

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