Bond-orbital theory of linear and nonlinear electronic response in ionic crystals. II. Nonlinear response

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A bond-orbital theory of linear electronic response set out in the preceding companion paper (I) is expanded to include nonlinear response. Attention is focused on the third-order susceptibility $\chi_{ijkl}^{(3)}$ (particularly as measured by the nonlinear refractive index n_2) in pretransition-metal halides and chalcogenides. Root-mean-square accuracy over 11 halides for relative n_2 values is about 9%, and points to an essential absence of local-field effects in bond-orbital response at least for halides. The latter conclusion enables us to make an absolute calibration for n_2—a question of some considerable controversy among different experimental groups.

I. INTRODUCTION

In the preceding paper[1] [referred to hereafter as I and its equations as Eq. (I1.1), etc.] a bond-orbital theory has been developed to describe linear electronic response in pretransition-metal halides and chalcogenides in the long-wavelength limit. In the present paper we formally extend this model to probe electronic nonlinear response in the same materials. Since all the relevant crystal structures contain a center of symmetry, the lowest-order nonzero electronic nonlinearity involves third-order susceptibility $\chi^{(3)}$, a fourth-rank tensor property which manifests itself experimentally in many ways including, for example, third-harmonic generation, three-and four-wave mixing, intensity modulation of refractive index, and the optical Kerr effect.[2,3]

Such a high-order effect is a rather extreme quantitative test of any model. For example, even if we assume a restriction to axially symmetric bonds (a condition which is immediately violated by any d- or f-electron contributions to bond orbitals) and to an essentially dispersionless low-frequency regime (for which Kleinman symmetry restrictions[4] apply) $\chi^{(3)}$ for a representative bond can still have as many as four independent components. Only one of these, albeit the dominant one, is directly derivable from the simplest bond-orbital representation as set out in I. In spite of this, we shall find that the ensuing bond-orbital computation for nonlinear refractive index gives relative values which, over those halides for which accurate experimental information is available, is accurate to better than $\pm 10\%$.

The theory of nonlinear response in solids can be discussed at various levels of sophistication, from the most formal and rigorous[5-7] (elucidating on the most general grounds what types of processes can contribute) to the more restricted and semiempirical (developed for predictive purposes concerning problems of practical interest).[8-14] Most work in the latter category concerns electronic response in the transparent frequency domain. Here only a small number of energy levels or bands are essential to the discussion—the others being far removed in energy. With the exception of the bond-orbital approach these theories are cast, almost universally, within the framework of anharmonic electronic oscillators—the electronic charges to be associated either with individual ions themselves[11,12] (introducing the concept of "ion hyperpolarizability") or with bond charges situated between ions.[9,10,13,14]

Although calculations of "ion hyperpolarizability" have now developed beyond the effective charge model,[15,16] the results for ionic crystals demonstrate the extreme sensitivity of the numerical findings to environment. They therefore confirm the original conjecture of Pantelides[17] that any separation of dielectric response into additive ionic constituents is of limited value since it obscures the dominantly interionic nature of the phenomenon. The bond-charge representation postulates the presence of a weakly bound well-localized bond charge positioned between cation and anion. Within this picture, both linear and nonlinear response is dominantly attributed to the perturbed motion of this charge via an association with the linear-response theory of Phillips and Van Vechten.[18,19]

The notion of a concentration of loosely bound charge located between ions is obviously most realistic for covalent systems, and consequently most work using this model has focussed on such systems and, in particular, upon calculations of $\chi^{(2)}$. In the context of ionic insulators the method appears to be least viable and what few estimates are available for $\chi^{(3)}$ for insulators using bond charge-methods (e.g., Ref. 14) are numerically far inferior to those of the present work.

In order to present as self-contained a paper as possible, we shall first restate the basic concepts of bond-orbital theory and, in particular, redefine the parameters which enter the equations of I for electronic linear response. Bond-orbital theory, in its simplest form, describes long-wavelength electronic response as the perturbation by an applied electric field of local bonding orbitals, each formed along a representative bond axis as a linear combination of unspecified atomic orbitals $|h_M\rangle$ and $|h_X\rangle$ centered on the cationic (M) and anionic (X) sites, respectively. Writing such a bond-orbital in the form

$$|b_0\rangle = u_M|h_M\rangle + u_X|h_X\rangle \ , \tag{1.1}$$

the coefficients u_M and u_X are determined first in the absence of applied field by minimizing the one-electron energy function $\langle b_0|\mathcal{H}_0|b_0\rangle/\langle b_0|b_0\rangle$ simultaneously with respect to u_M and u_X. Such a procedure (Sec. II of I) involves the intraorbital and interorbital matrix elements

$$\langle h_M|\mathcal{H}_0|h_M\rangle = -\langle h_X|\mathcal{H}_0|h_X\rangle = E_0 \tag{1.2}$$

and

$$\langle h_M|\mathcal{H}_0|h_X\rangle = -M \ , \tag{1.3}$$

where $\mathcal{H}_0$ is the one-electron Hamiltonian, as well as the overlap integral

$$S = \langle h_M|h_X\rangle \ . \tag{1.4}$$

If the minimization procedure is repeated in the presence of an applied external field E_x along the bond direction x, i.e.,

$$\mathcal{H} = \mathcal{H}_0 - efE_x \ , \tag{1.5}$$

where e is electronic charge and f a local-field factor, then the induced bond-orbital moment $\langle b|ex|b\rangle - \langle b_0|ex|b_0\rangle$, and hence electronic response, follows as a function of E_x^n to any required order of perturbation theory n. The only additional parameters which enter are the bond length d and the distance

$$x_0 = \frac{\langle h_M|x|h_X\rangle}{\langle h_M|h_X\rangle} \tag{1.6}$$

which would be equal to $d/2$ if $|h_X\rangle$ and $|h_M\rangle$ were identical orbitals, but which more generally differs from this value by an amount

$$\Delta/2 = (d/2) - x_0 \tag{1.7}$$

which can be empirically determined from measured linear-response trends in the form

$$\Delta/d = (d/2R_M)^{1/2} - 1 \tag{1.8}$$

in which R_M is cationic radius.

The full parametrization therefore consists of two energies (M and E_0), two distances (d and Δ), and two dimensionless quantities (S and f). Of the four remaining "unknowns" [d is a measurable and Δ, via Eq. (1.8), follows from tabulated values of R_M] three can be deduced by fitting the theory to measured values of linear response alone if attention is given to bond summation and to frequency dependence on approach to the electronic long-wavelength limit (Sec. VII of I). In order to completely "close" the theory (in the sense of determining *all* parameters directly from observables) the final parameter, which we take to be the local-field factor f, requires one more observable. We choose this final observable to be the third-order nonlinear response $\chi^{(3)}$ which, as we shall see, will indicate that f probably does not differ appreciably from unity throughout, and certainly not for halides.

In the formal theoretical development of I, the energies M and E_0 of Eqs. (1.2) and (1.3) appear most naturally in combination with S in the forms

$$V_2 = M/(1-S^2) \tag{1.9}$$

and

$$V_3 = E_0/(1-S^2)^{1/2} \tag{1.10}$$

in terms of which it is convenient to define a dimensionless measure of covalency

$$\alpha = V_2/(V_2^2+V_3^2)^{1/2} \ . \tag{1.11}$$

In this notation, full covalency is represented by $\alpha=1$ (i.e., $E_0=0$) and is expected to be manifested in such sp^3-hybrid elemental crystals as Si and Ge. The most ionic crystals (i.e., the alkali halides) by contrast do not have $\alpha=0$, but rather $\alpha\approx S$ which is equivalent, in Eq. (1.1), to a bonding orbital with $u_M\approx 0$. From a practical point of view we therefore refer to the condition $\alpha=S$ as the "ionic" limit. It implies the presence of valence bands made up only of anionic orbital components.

II. NONLINEAR BOND-ORBITAL RESPONSE

Defining linear and nonlinear bond susceptibilities $\chi_b^{(n)}$, $n=1,2,3,\ldots$, from the induced bond-orbital moment in an applied field E_x parallel to the bond axis x in the manner of Eq. (I4.16) viz.,

$$\langle b|ex|b\rangle = const. + \sum_{n=1}^{\infty} \chi_b^{(n)} E_x^n \ , \tag{2.1}$$

it is possible to calculate each as a function of the bond-orbital parameters by combining Eqs. (I4.6), (I4.16), and (I4.10) to (I4.15). In this manner, after some algebraic manipulation, we obtain

$$\chi_b^{(1)} = \frac{e^2\alpha^3 f}{4a^2V_2}(d+g\Delta)^2 \ , \tag{2.2}$$

$$\chi_b^{(2)} = \frac{-3e^3\alpha^5 f^2}{16a^2V_2^2S}(d+g\Delta)^2(gd-\Delta S^2/a^2) \ , \tag{2.3}$$

$$\chi_b^{(3)} = \frac{e^4\alpha^5 f^3 d^2(d+g\Delta)^2 D}{32a^4V_2^3} \ . \tag{2.4}$$

in which a and g are defined as in I, viz.

$$a=(1-S^2)^{1/2}, \quad g=\frac{S(1-\alpha^2)^{1/2}}{\alpha(1-S^2)^{1/2}} \ , \tag{2.5}$$

and

$$D = 4-5\alpha^2-10g\alpha^2(\Delta/d)+(S/a)^2(5\alpha^2-1)(\Delta/d)^2 \ . \tag{2.6}$$

Since, for most materials, Δ/d is a small quantity [$\ll 1$ see Eq. (1.8)], the final term in Eq. (2.6) is usually small to the extent that it can be dropped from numerical work.

The macroscopic linear and nonlinear susceptibilities $\chi^{(n)}$, $n=1,2,3,\ldots$, which relate polarization $\mathbf{P}$ to applied field $\mathbf{E}$ in the manner

$$\mathbf{P} = \chi^{(1)}\cdot\mathbf{E} + \chi^{(2)}:\mathbf{E}^2 + \chi^{(3)}\vdots\mathbf{E}^3 + \cdots \ , \tag{2.7}$$

in which the dots imply tensorial contraction, have Cartesian representations $\chi_{ii}^{(1)}, \chi_{ijk}^{(2)}, \chi_{ijkl}^{(3)} \ldots$, which are related to the respective bond susceptibilities via the equations

$$\chi_{ii}^{(1)}=\sum_{b=1}^{m}\chi_b^{(1)}\beta_{ib}^2 G\ , \tag{2.8}$$

$$\chi_{ijk}^{(2)}=\sum_{b=1}^{m}\chi_b^{(2)}\beta_{ib}\beta_{jb}\beta_{kb}Gf\ , \tag{2.9}$$

$$\chi_{ijkl}^{(3)}=\sum_{b=1}^{m}\chi_b^{(3)}\beta_{ib}\beta_{jb}\beta_{kb}\beta_{lb}Gf\ , \tag{2.10}$$

where there are m anion-cation bond axes b per anion (with direction cosines labeled by β_{ib}) and G is the electron "weighting" factor per bond ($2z/m$, $z=6$, see the Appendix of I) times the number of bonds per unit volume. Since, for a binary compound MX_n (M=metal, X=anion) the latter number is nN_0/V_M, where N_0 is Avogadro's number and V_M is molar volume, the general form for G can be expressed as

$$G=2znN_0/mV_M\ . \tag{2.11}$$

The presence of the local-field factor f in Eqs. (2.9) and (2.10) arises via interactions between nonlinear dipole moments at one ionic site and the linear dipole at another as set out by Armstrong *et al.*[5]

For crystals with a center of symmetry (which includes all of the compounds to be discussed in this paper) the second order-nonlinear susceptibility $\chi_{ijk}^{(2)}$ is zero on symmetry grounds. It follows that, in the context of binary insulators, the lowest-order nonlinearity is usually $\chi_{ijkl}^{(3)}$, involving third-order bond-orbital response $\chi_b^{(3)}$. In pursuing this third-order response we first note that $\chi_b^{(3)}$ can be directly related to $\chi_b^{(1)}$ via Eqs. (2.2) and (2.4) in the form

$$\chi_b^{(3)}=\left[\frac{e\alpha fd}{aV_2}\right]^2(D/8)\chi_b^{(1)}\ . \tag{2.12}$$

This can be simplified further by making use of the Sellmeier energy gap $E_s=2V_2/\alpha$ [see Eq. (I7.7)] to obtain

$$\chi_b^{(3)}=(efd/aE_s)^2(D/2)\chi_b^{(1)}\ . \tag{2.13}$$

III. THE THIRD-ORDER SUSCEPTIBILITY

Third-order optical nonlinear susceptibility $\chi_{ijkl}^{(3)}$ is most generally defined in Cartesian terms by introducing a frequency dependence e.g.,

$$P_i(t)=(1/2)[P_i(\omega)e^{-i\omega t}+P_i(-\omega)e^{i\omega t}]\ , \tag{3.1}$$

$$E_i(t)=(1/2)[E_i(\omega)e^{-i\omega t}+E_i(-\omega)e^{i\omega t}], \tag{3.2}$$

into the expansion of Eq. (2.7). In this manner the third-order Fourier component of polarization $P_i^{(3)}(\omega)$ becomes expressible as[2,3,20,21]

$$P_i^{(3)}(\omega)=\sigma\chi_{ijkl}^{(3)}(-\omega;\omega_1,\omega_2,\omega_3)E_j(\omega_1)E_k(\omega_2)E_l(\omega_3)\ , \tag{3.3}$$

where a repeated index summation over j, k, and l is implied, the frequencies satisfy the condition $\omega=\omega_1+\omega_2+\omega_3$, and σ is a degeneracy factor arising from the intrinsic permutation symmetry of the frequencies. These degeneracies are most easily calculated for the case of real-field amplitudes by expanding

$$P^{(3)}(\omega)=\chi^{(3)}[E_1\cos(\omega_1 t)+E_2\cos(\omega_2 t)+E_3\cos(\omega_3 t)]^3 \tag{3.4}$$

and suppressing the Cartesian component notation. In this manner we find terms in $E_i^3\cos(3\omega_i t)$, $i=1,2,3$, with $\sigma=\frac{1}{4}$ (defining third-harmonic generation), terms in $E_iE_j^2\cos(\omega_i t)$ with $\sigma=\frac{3}{2}$ (defining the optical Kerr effect), terms in $E_i^3\cos(\omega_i t)$ with $\sigma=\frac{3}{4}$ (describing self-induced refractive-index changes), and finally terms in $E_iE_j^2\cos(2\omega_j\pm\omega_i)t$ with $\sigma=\frac{3}{4}$ and in $E_iE_jE_k\cos(\omega_i\pm\omega_j\pm\omega_k)t$ with $\sigma=\frac{3}{2}$ defining, respectively, three-and four wave mixing. All these effects can obviously be incorporated into the general representation of Eq. (3.3). Note, however, that many authors *define* a frequency-dependent $\chi^{(3)}$ by setting $\sigma=1$ for the particular property under study, so that a check of definitions is essential when reading the literature.

For third-harmonic generation Eq. (3.3) takes on the form

$$P_i^{(3)}(3\omega)=\tfrac{1}{4}\chi_{ijkl}^{(3)}(-3\omega;\omega,\omega,\omega)E_j(\omega)E_k(\omega)E_l(\omega) \tag{3.5}$$

which experimentalists often reduce to a form

$$P_i^{(3)}(3\omega)=C_{ijkl}^{(3)}(\omega)E_j(\omega)E_k(\omega)E_l(\omega) \tag{3.6}$$

to define a "third-harmonic susceptibility tensor"

$$C_{ijkl}^{(3)}=\tfrac{1}{4}\chi_{ijkl}^{(3)}\ . \tag{3.7}$$

In principle, any of the above-defined third-order processes can be used to measure the relevant $\chi_{ijkl}^{(3)}$ or its $C_{ijkl}^{(3)}$ equivalent as defined in Eq. (3.7). In practice, one of the more common methods involves a measure of the mean field-intensity modulation of refractive index (n) via the index expansion

$$n=n_0+\tfrac{1}{2}n_2E(\omega)E(-\omega)\ . \tag{3.8}$$

Using the relevant terms of the general expansion Eq. (3.3), viz.,

$$P_i^{(3)}(\omega)=\tfrac{3}{4}\chi_{ijkl}^{(3)}(-\omega;\omega,\omega,-\omega)E_j(\omega)E_k(\omega)E_l(-\omega) \tag{3.9}$$

and recalling that $n^2=1+4\pi\chi$ (where n is refractive index) we readily deduce the relationship

$$n_2=3\pi\chi^{(3)}/n_0=12\pi C^{(3)}/n_0\ . \tag{3.10}$$

The appropriate tensor component (or components) to be used in Eq. (3.10) depends on the symmetry of the crystal under investigation and the direction of propagation and polarization of the light beam involved.[3,20] For the simplest case of a cubic material with a beam plane polarized along [100] and propagating along [001] Eq. (3.10) becomes

$$n_{2,1}=3\pi\chi_{1111}^{(3)}/n_0=12\pi C_{1111}^{(3)}/n_0\ . \tag{3.11}$$

We may now directly relate $C_{ijkl}^{(3)}$ with the bond-orbital theory of Sec. II by combining Eqs. (2.10), (2.11), (2.13), and (3.7). For a binary insulator MX_n we find the relationship

$$C^{(3)}_{ijkl}=\frac{DznN_0 f}{4V_M}\left[\frac{efd}{aE_s}\right]^2 \chi_b^{(1)}\langle \beta_{ib}\beta_{jb}\beta_{kb}\beta_{lb}\rangle \tag{3.12}$$

in which the angular brackets define an average over all bond directions b. Combining this form with Eq. (I4.20) which relates $\chi_b^{(1)}$ to linear dielectric response $\varepsilon=n_0^2$, we obtain a final form

$$C^{(3)}_{ijkl}=\frac{3Df^3}{32\pi}\left[\frac{ed}{aE_s}\right]^2 (n_0^2-1)\langle \beta_{ib}\beta_{jb}\beta_{kb}\beta_{lb}\rangle \ . \tag{3.13}$$

If d is expressed in Å and the Sellmeier gap E_s in eV, n_2 follows in esu by combining Eqs. (3.13) and (3.11) in the form

$$n_{2,1}=\frac{1.0\times 10^{-11} Df^3 d^2 (n_0^2-1)\langle \beta_{1b}^4\rangle}{n_0(1-S^2)E_s^2}\ \mathrm{cm}^3/\mathrm{erg}\ , \tag{3.14}$$

where we have used the definition $a^2=(1-S^2)$ of Eq. (2.5) and recognize that the final angular average will vary for different crystal structures. A conversion to the SI units of $\mathrm{m}^2/\mathrm{V}^2$ can be accomplished by noting that 1 $\mathrm{cm}^3/\mathrm{erg}\equiv 4\pi/(9\times 10^8)\ \mathrm{m}^2/\mathrm{V}^2$.

IV. COMPARISON WITH EXPERIMENT

The most frequent contact with experiment for third-order response occurs via measurement of the nonlinear refractive index n_2.[22–30] Firstly, we recognize that no frequency dependence has been built into the theory. Although this is by no means an essential restriction of the bond-orbital method (and frequency dependencies can readily be discussed), the present formalism should be completely adequate for comparison with experimental data obtained at frequencies large with respect to the highest phonon modes and small compared to the electronic band-gap frequencies. For the wide band-gap materials of interest in this paper (with Sellmeier gaps,[1] $E_s=\hbar\omega_s$, in the range 5–15 eV) frequencies of order $\omega_s/10$ to $\omega_s/20$ are adequate.

The primary difficulty confronting a direct comparison with experiment concerns absolute values. Thus, although a number of experimentalists essentially agree on relative values of n_2 (and claims of accuracies as high as ±5% for some halides have been made in this context by the most recent work),[30] a severe disagreement persists concerning calibration standards. Thus, for example, six reported measurements of ostensibly the same $\mathbf{n}_2$ value for CaF_2 (see Table III of Ref. 30) fairly uniformly span the range from $0.43\times(10^{-3})$ to 2.8×10^{-13} esu. So severe is this problem that we believe (see below) that the accuracy of bond-orbital theory is sufficient to narrow this range considerably.

A secondary difficulty in comparing theory [viz., Eq. (3.14)] with experiment involves an essential limitation of the theory itself. Thus, for cubic materials at frequencies well below the band gap (and isotropic materials more generally), there are only two independent components of the tensor $\chi^{(3)}$, namely $\chi^{(3)}_{1111}$ and $\chi^{(3)}_{1122}$. The problem is that whereas the ratio $\chi^{(3)}_{1122}/\chi^{(3)}_{1111}$ almost always occurs[30] within the *experimental* range 0.45 ± 0.15, within our bond-orbital picture, via Eq. (2.10), it is equal to $\langle\beta_{1b}^2\beta_{2b}^2\rangle/\langle\beta_{1b}^4\rangle$, which is readily seen to be equal to zero for cubic [001]-type bond axes of the kind possessed by the rocksalt crystal structure and equal to unity for the [111]-oriented bond axes of the fluorite or CsCl crystal structures.

Clearly the fault lies in the notion of a completely one-dimensional anion-cation orbital bond which ignores transverse response. Although the linear response of a bond-orbital is predominantly longitudinal,[31] as is directly apparent from measurements on layered structures like graphite,[32] important transverse terms can appear in higher-order bond nonlinearity.

In principle, an axially symmetric bond along an x axis can have four independent third-order response elements as follows:

$$\chi^{(3)}_{xxxx}=A=\chi_b^{(3)} \text{ of Eq.(2.13)}\ , \tag{4.1}$$

$$\chi^{(3)}_{y(xxy)}=\chi^{(3)}_{z(xxz)}=B\ , \tag{4.2}$$

$$\chi^{(3)}_{x(xyy)}=\chi^{(3)}_{x(xzz)}=C\ , \tag{4.3}$$

$$\chi^{(3)}_{yyyy}=\chi^{(3)}_{zzzz}=\tfrac{1}{3}\chi^{(3)}_{y(zzy)}=\tfrac{1}{3}\chi^{(3)}_{z(yyz)} \tag{4.4}$$

which we may think of respectively as $\chi_{\parallel\parallel}$, $\chi_{\perp\parallel}$, $\chi_{\parallel\perp}$, and $\chi_{\perp\perp}$, in terms of components parallel (xx) or perpendicular (yy or zz) to the bond axes. Our numerical results (*a posteriori*) and the bond-orbital concept (*a priori*) point to the $\chi_{\parallel\parallel}$ component as being dominant. In addition, an examination of the possible perturbational coupling paths for transverse response suggest the likely relative transverse magnitudes $\chi_{\perp\parallel}>\chi_{\parallel\perp}>\chi_{\perp\perp}$. Neglecting the last, and defining $\chi_{\parallel\parallel}=A$, $\chi_{\perp\parallel}=B$, and $\chi_{\parallel\perp}=C$ from Eqs. (4.1)–(4.3), it is a simple exercise in coordinate transformation to compute the two independent cubic matrix elements $\chi^{(3)}_{1111}$ and $\chi^{(3)}_{1122}$ as functions of A, B, and C for the rocksalt (rs) and fluorite (fl) structures. We find, in particular, the ratios

$$\chi^{(3)}_{1122}/\chi^{(3)}_{1111}=(B+C)/A \quad (\text{rs})\ , \tag{4.5}$$

$$\chi^{(3)}_{1122}/\chi^{(3)}_{1111}=A/[A+6(B+C)] \quad (\text{fl})\ . \tag{4.6}$$

To this approximation, it follows that contact with bond-orbital theory (via $A=\chi_b^{(3)}$) can be made directly via $\chi^{(3)}_{1111}$ for rs-structures and via $\chi^{(3)}_{1122}$ for fl structures. In particular, nonlinear refractive index $n_{2,1}$ of Eq. (3.11) follows immediately from Eq. (3.14) in the form

$$n_{2,1}=\frac{100Df^3d^2(n_0^2-1)F}{n_0(1-S^2)E_s^2}\times 10^{-13}\ \mathrm{cm}^3/\mathrm{erg}\ , \tag{4.7}$$

where d is in Å, E_s in eV, and $F=\frac{1}{3}$ for rs structures. In Eq. (4.7), the parameter D is

$$D=4-5\alpha^2-10g\alpha^2(\Delta/d) \tag{4.8}$$

[from Eq. (2.6) neglecting the Δ^2 term], g is defined by Eq.

(2.5), Δ/d by Eq. (1.8), and the "covalency" parameter α [from Eq. (I6.7)] by

$$\alpha=(Z_X)^{1/2}S \tag{4.9}$$

with Z_X being the magnitude of the formal valence of the anion. If we now write the Sellmeier gap, from Eq. (I7.8) in the form

$$E_s=\frac{872fS^3}{\alpha d^{2.4}(1-S^2)}\ , \tag{4.10}$$

where d is in Å and E_s in eV, then the two equations (4.7) and (4.10) for the measurables $n_{2,1}$ and E_s respectively are cast solely in terms of linear refractive index n_0, bond length d (in Å), overlap parameter S, and local-field factor f. Since n_0 and d are directly measurable, these two equations now suffice for an unambiguous determination of S and f for the rocksalt structure ($F=\frac{1}{3}$).

This is extremely interesting since neither of these dimensionless quantities has previously been deduced from experiment to our knowledge. In fact, the question of the proper value to be taken for the local-field factor f in any context has been a vexed one, even for cubic materials. For the latter it is usually assumed to be between unity and the full "Lorentz" value $f_L=(n_0^2+2)/3$. In particular, unless $f=1$ its value should certainly be dependent on n_0 in some fashion.

For our initial comparison with experiment we use the *relative* $n_{2,1}$ measurements of Adair *et al.*[30] as given for seven rocksalt halides in Table IV of Ref. 30, since their claimed accuracy of better than ± 15 for relative values is the most accurate that we can find. As mentioned above, the experimental determination of an *absolute* n_2 scale is at present far from precise. To avoid bias we have chosen to compare theory with experiment both for the lowest (Adair *et al.*[30]) and highest (smith *et al.*[28]) scales adopted in the literature, the latter of which is some 6.5 times the former. In each case, however, we keep the *relative* values of Ref. 30.

Using these two sets of values we now compute, via Eqs. (4.7)–(4.10) the self-consistent values of f and S for these seven rocksalt-structured alkali halides. The values of n_0, d, and E_s required for the calculation are taken from Wemple.[33] In Fig. 1 we show the resulting f values for both limiting absolute n_2 scales together with the corresponding full Lorentzian local-field factors $f_L=(n_0^2+2)/3$. The important finding is that f is essentially constant as a function of n_0 within this set of halides regardless of the absolute scale of n_2 chosen although, of course, the actual (constant) value of f *is* a function of scale, rising from 0.63 ± 0.03 for the lower n_2 scale to 1.15 ± 0.05 for the upper.

Since any local-field deviation of f from unity should be monotonically dependent upon n_0 in an isostructural cubic series, the conclusion to be drawn from Fig. 1 is that the correct value of f is probably close to unity. This essential absence of a local-field correction within the bond-orbital framework is presumably due to the extended nature of the wave functions involved in the bonding. Putting $f=1$ in Eqs. (4.7) and (4.10) we may now readily calculate self-consistent values of S and $n_{2,1}$ for

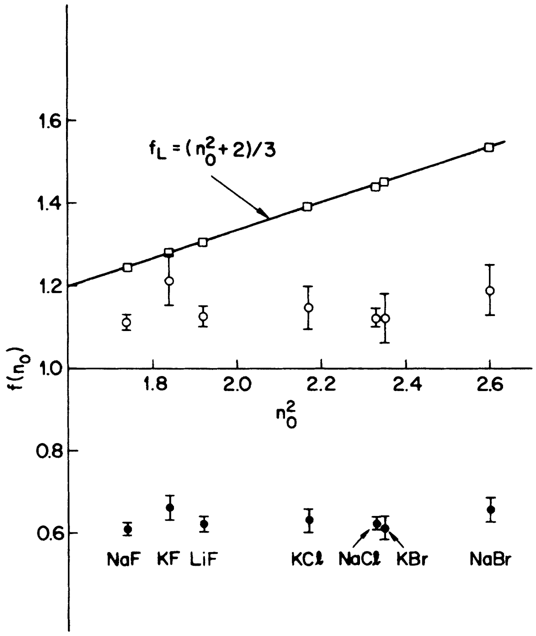

FIG. 1. The local-field factor f deduced as a function of n_0^2 for a series of alkali halides by comparison of the theory of Eqs. (4.7)–(4.10) with the *relative* $n_{2,1}$ measurements of Adair *et al.* (Ref. 30) using both the smallest (Ref. 30) (solid circles) and largest (Ref. 28) (open circles) *absolute* nonlinear refractive-index calibrations found in the literature. The bars indicate the accuracy of the experimental data (as estimated in Ref. 30) and the open squares mark the Lorentz local-field values $f_L=(n_0^2+2)/3$ for the same set of halides.

all the rocksalt-structured halides, most of which have yet to be probed experimentally. The detailed results are given in Table I. For the seven samples measured by Adair *et al.*[30] the relative values given by theory (Table I) agree with experiment to an accuracy $\approx\pm8\%$. To our knowledge this accuracy exceeds that of any other empiric relationship predicting n_2 for insulators, the most commonly used of which is that of Boling *et al.*[12,30] The absolute values, on the other hand, exceed those of Ref. 30 by a factor of 4.3 (using a geometric average) and agree fairly closely with the absolute scale adopted by Levensen,[26] who used a calcite reference standard with $n_{2,1}\approx3.2\times10^{-13}$ cm^3/erg.

It is now a straightforward exercise to proceed to the rocksalt-structured chalcogenides, if we again write $f=1$ and use the sequence of Eqs. (4.7)–(4.10). The essential difference is that for these, with an anion valence $Z_X=2$, the covalency parameter is $\alpha=\sqrt{2}S$ in place of the $\alpha=S$ equivalent for halides. The self-consistent findings for $n_{2,1}$ and S are given Table II.

Experimental data for members of the series is scant. Only Adair *et al.*[30] report any measurements, giving values for MgO, CaO, and SrO. If we maintain the absolute scale for $n_{2,1}$ determined by the $f=1$ choice for halides, and retain Adair's relative values from halides to oxides, then the measured values are about a factor 2 larger than the theoretical predictions of Table II. This could be marginal evidence for the existence of a local-

TABLE I. Calculated values of overlap S and nonlinear refractive index $n_{2,1}$ from the theory of Sec. IV—Eqs. (4.7)–(4.10)—for the rocksalt-structured alkali halides i.e., $F=\frac{1}{3}$. Local-field parameter f has been set equal to unity (see text) and experimental values for linear refractive index n_0, bond length d, and Sellmeier gap E_s have been taken from the literature (Ref. 33). Also shown for completeness are the parameters d of Eq. (4.8) and Δ/d of Eq. (1.8).

Crystal (Units)	n_0^2	d (Å)	E_s (eV)	Δ/d	D	S	$n_{2,1}$ (10^{-13} cm^3/erg)
CsCl	2.30	3.57	10.6	0.03	2.91	0.45	11.9
CsBr	2.43	3.71	9.4	0.05	2.90	0.45	17.3
CsI	2.63	3.95	7.7	0.08	2.88	0.44	31.5
RbF	1.93	2.82	14.5	−0.02	3.20	0.41	3.2
RbCl	2.17	3.29	10.4	0.05	3.05	0.41	9.8
RbBr	2.34	3.43	9.3	0.08	3.01	0.41	14.4
RbI	2.59	3.67	7.8	0.11	2.97	0.41	26.1
KF	1.84	2.67	14.7	0.00	3.24	0.39	2.60
KCl	2.17	3.15	10.5	0.09	3.06	0.40	8.7
KBr	2.35	3.30	9.2	0.11	3.05	0.39	13.7
KI	2.63	3.53	7.6	0.15	3.01	0.39	25.7
NaF	1.74	2.31	15.1	0.10	3.31	0.34	1.64
NaCl	2.33	2.81	10.5	0.22	3.10	0.35	7.4
NaBr	2.60	2.99	9.1	0.25	3.05	0.35	12.5
NaI	2.98	3.24	7.4	0.31	2.99	0.35	25.0
LiF	1.92	2.01	16.5	0.29	3.27	0.30	1.18
LiCl	2.68	2.57	11.0	0.46	2.96	0.33	6.2
LiBr	3.00	2.75	9.5	0.51	2.89	0.33	10.5
LiI	3.4	3.00	8.0	0.58	2.77	0.34	19.1

field factor $f \approx 2^{1/3} \approx 1.25$ in these more polarizable systems, but it may equally well be a reflection of the fact that bond-orbital contributions lose their independence for highly coordinated systems as we move away from the ionic limit (see the Appendix of I).

Turning to the [111]-bonded cubic crystals we expect, via Eq. (4.6), to make contact between experiment and bond-orbital theory via $\chi^{(3)}_{1122}$. Experimentally, this tensor component can be determined from n_2 measurements by combining findings on linear and circularly polarized light[3,20] or by variation of the propagation direction of linearly polarized light alone.[30] Thus, if R is the ratio $\chi^{(3)}_{1(122)}/\chi^{(3)}_{1111}$ for these materials, then the principal nonlinear refractive index $n_{2,1}$ can again be cast in the form of Eqs. (4.7), but now where

$$F=\langle \beta_{1b}^4 \rangle /R = 1/(9R) . \tag{4.11}$$

A number of experimental results for R are available for the fluorites CaF_2, SrF_2, and BaF_2 (Refs. 29 and 30) with findings scattered generally in the range $0.4<R<0.7$. Correspondingly we anticipate, from Eq. (4.11), F values

TABLE II. As in Table I, but for the rocksalt-structured chalcogenides; $f=1$, and $F=\frac{1}{3}$.

Crystal (Units)	n_0^2	d (Å)	E_s (eV)	Δ/d	D	S	$n_{2,1}$ (10^{-13}cm^3/erg)
BaO	3.68	2.76	7.1	0.01	2.82	0.34	22.5
BaS	4.26	3.19	6.3	0.09	2.42	0.38	38.0
BaSe	4.48	3.30	5.3	0.11	2.50	0.36	61.3
BaTe	4.71	3.49	4.2	0.14	2.58	0.35	115.0
SrO	3.35	2.58	8.3	0.07	2.74	0.34	12.8
SrS	4.09	3.01	6.6	0.15	2.43	0.36	29.7
SrSe	4.33	3.12	5.4	0.17	2.55	0.34	51.5
SrTe	4.91	3.24	4.9	0.20	2.51	0.34	73.2
CaO	3.27	2.41	9.9	0.10	2.68	0.34	7.5
CaS	4.24	2.85	6.9	0.20	2.47	0.35	25.1
CaSe	4.58	2.96	5.6	0.22	2.59	0.33	45.3
MgO	2.95	2.10	11.4	0.27	2.66	0.31	3.8
MgS	4.84	2.60	7.6	0.41	2.32	0.33	17.7
MgSe	5.28	2.73	7.0	0.45	2.21	0.34	23.5

TABLE III. As in Table I, but for the CsCl (sc) and fluorite (fl) structured halides (i.e., with ⟨111⟩ bond coordination); $f=1, F=1/(9R)=0.27$, see text.

Crystal (Units)	n_2^0	d (Å)	E_s (eV)	Δ/d	D	S	$n_{2,1}$ (10^{-13} cm^3/erg)
CsF (sc)	2.15	3.00	14.3	−0.06	3.18	0.43	3.64
CsCl (sc)	2.63	3.57	10.4	0.03	2.93	0.45	11.7
CsBr (sc)	2.79	3.71	9.3	0.05	2.91	0.45	16.7
CsI (sc)	3.03	3.95	7.7	0.08	2.88	0.44	29.6
CaF_2 (fl)	2.04	2.37	15.7	0.09	3.26	0.35	1.67
SrF_2 (fl)	2.06	2.51	14.7	0.05	3.27	0.36	2.19
BaF_2 (fl)	2.15	2.69	13.8	0.00	3.27	0.38	3.08

in the range 0.22 ± 0.06 for use in Eq. (4.7).

Using the theoretical equations [(4.7)–(4.10)], the closest agreement between theory and experiment for Adair's[30] (rescaled) $n_{2,1}$ findings for CaF_2 (viz., 1.85), SrF_2 (2.15), and BaF_2 (2.18), in units of 10^{-13} cm^3/erg, obtains for an F value of 0.27. Adopting this value we now calculate $n_{2,1}$ and S for the pretransition-metal fluorites and CsCl-structured alkali halides. The results are shown in Table III. To our knowledge, no experimental information is available for the CsCl-structured halides.

Finally, if we now look with the hindsight of Tables I–III back to Eq. (4.7) for $n_{2,1}$, we notice that the factor $DF/(1-S^2)$ rarely strays outside the range 1.1 ± 0.15. It follows that an extremely simple explicit expression for nonlinear refractive index $n_{2,1}$ can now be written which possesses an accuracy only slightly less than that of the full formalism of Eqs. (4.7)–(4.10): it is

$$n_{2,1}=\frac{110f^3(n_0^2-1)d^2}{n_0E_s^2}\times10^{-13}\ \mathrm{cm^3/erg}\ . \tag{4.12}$$

Since we believe that $f^3\approx1$ for halides, and have some preliminary evidence that f^3 may be larger (≈2) for chalcogenides, we can now tentatively combine these in the form $f^3=Z_X$, leading to a final expression

$$n_{2,1}=\frac{110Z_X(n_0^2-1)d^2}{n_0E_s^2}\times10^{-13}\ \mathrm{cm^3/erg}\ , \tag{4.13}$$

in which bond length d is in Å and Sellmeier energy E_s in eV.

We compare the accuracy of this expression with that of the full theory of Eqs. (4.7)–(4.10), and also with the often-used empirical expression of Boling *et al.*[12] and the experimental measurements of Adair *et al.*[20] in Table IV for 11 halides. Experimental data on chalcogenides are not yet sufficient to make any parallel comparison for these meaningful at the present time.

V. SUMMARY

The bond-orbital theory of I (Ref. 1) for linear electronic response in pretransition-metal halides, and chalcogenides has been expanded to include nonlinear response and, in particular, to calculate the third-order electronic susceptibility $\chi^{(3)}_{ijkl}$. Contact with experiment has been made via the nonlinear refractive index n_2. Since the linear theory alone is sufficient to empirically determine all the parameters appearing in the simplest bond-orbital representation except one, the nonlinear

TABLE IV. A comparison of the *relative* $n_{2,1}$ values between experiment (Ref. 30), the full theoretical results of Tables I and III (labeled A), the approximate representation of Eq. (4.13) (labeled B), and the theoretical expression proposed by Boling *et al.* (Ref. 12) as computed by Adair *et al.* (Ref. 30). All columns are normalized such that the product of the 11 components in each is equal to unity.

	Expt. (Ref. 30)	A	(% error)	B	(% error)	Boling (Ref. 12)	(% error)
LiF	0.33	0.35	(+6)	0.34	(+3)	0.46	(+39)
NaF	0.43	0.48	(+12)	0.45	(+5)	0.44	(+2)
KF	0.95	0.77	(−19)	0.70	(−26)	0.41	(−57)
NaCl	2.02	2.18	(+8)	2.13	(+5)	2.62	(+30)
KCl	2.55	2.56	(+0)	2.43	(−5)	2.11	(−17)
NaBr	4.14	3.68	(−11)	3.65	(−12)	5.45	(+32)
KBr	3.72	4.03	(+8)	3.86	(+4)	3.92	(+5)
MgF_2	0.32	0.33[a]	(+3)	0.31	(−3)	0.39	(+22)
CaF_2	0.54	0.49	(−9)	0.57	(+6)	0.56	(+4)
SrF_2	0.63	0.64	(+2)	0.73	(+16)	0.57	(−10)
BaF_2	0.85	0.91	(+7)	1.01	(+19)	0.80	(−6)
rms ERRORS			(9%)		(12%)		(26%)

[a]Assuming $F=\frac{1}{3}$ in Eq. (4.7).

response (and in particular n_2) is used to focus self-consistently upon this final parameter–the local-field factor f.

Unfortunately, although different experimentalists largely agree as to the *relative* n_2 values among the relevant materials studied, they use absolute calibrations which differ by up to a factor of 6. This degree of confusion enables us only to compute upper and lower bounds on f equal to 0.63 and 1.15, respectively. However, focusing only on *relative* n_2 values, the theoretical interpretation for a series of rocksalt alkali halides establishes clearly that f is independent of linear refractive index n_0. Since any local-field enhancement or shielding (represented by values $f \neq 1$) should certainly correlate with n_0 in some manner [e.g., the Lorentzian local-field factor $f_L = (n_0^2+2)/3$] we infer that f must be effectively equal to 1, at least for halides. The lack of local-field effects within the present framework presumably reflects the extended nature of the orbitals involved in the bond-orbital description, the Lorentz condition arising only in the limit of point dipoles. Putting $f=1$ enables us to locate an absolute n_2 calibration. It is close to the calcite "standard" $n_{2,1} = (3.2 \pm 0.4) \times 10^{-13}$ cm^3/erg used by Levenson and co-workers.[25–27]

With $f=1$ we have calculated $n_{2,1}$ (the n_2 value for light propagating along [001] and plane polarized along [100]) which is a measure of $\chi^{(3)}_{1111}$, for a wide selection of cubic halides and chalcogenides in Tables I–III. A direct comparison of theory with experiment for relative $n_{2,1}$ values over 11 halides (Table IV) shows a rms accuracy of 9%. In particular, a very simple (if approximate) proportionality

$$n_{2,1} \sim (n_0^2 - 1) d^2 / (n_0 E_s^2) \tag{5.1}$$

is noted, where d is bond length and E_s is the Sellmeier energy gap [observable from the long-wavelength electronic frequency dependence of linear response in the form $n_0^2 - 1 \sim (E_s^2 - \hbar^2\omega^2)^{-1}$] and found to be only slightly less accurate (rms 12%) than the full theory over these same halides (Table IV).

Experimental data for pretransition-metal oxides is scant and for the remaining chalcogenides virtually nonexistent. However, the few n_2 measurements for oxides (relative to halides) which are available suggest that the local-field factor f for these generally more polarizable materials may be slightly larger that unity, although this finding is hardly more than speculative at the present time.

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