Topical review
Order-of-magnitude estimates of the nonlinear optical susceptibility

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Abstract. We develop simple mathematical models that lead to order-of-magnitude predictions of the sizes of the electronic, nuclear, and electrostrictive contributions to the nonlinear optical susceptibility. We find that all three of these processes make comparable contributions to the third-order susceptibility, even though the optical-frequency linear susceptibility is dominated by the electronic response. We also find that when the mathematical expressions describing these contributions to the third-order susceptibility are written in terms of fundamental physical constants, they are identical to within numerical factors of the order of unity and are given in Gaussian units by $\chi^{(3)} = \hbar^8 / 8m^4 e^{10} = 4.25 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-2}$.

1. Introduction

The intent of the present paper is to provide simple order-of-magnitude estimates of the nonlinear optical response resulting from several different physical processes, namely, electronic polarization, nuclear (i.e. Raman) response, and electrostriction. Of course, the arguments leading to such predictions are well known for the case of the electronic response, dating back to the very earliest research papers on nonlinear optics [1]. However, arguments of this sort seem to be much less well established for the nuclear response and electrostriction. One of the motivations for the present paper is to develop mathematical descriptions for all three of these physical processes in a consistent manner, both to allow comparison of the nature of these processes and to make predictions of their expected strengths.

Another motivation for the present study is that several recent investigations have demonstrated that the contributions to the third-order susceptibility resulting from these physical processes often are of comparable size [2–8] and in special cases are in fact equal [9]. This conclusion at first sight appears surprising, because the three physical processes depend on different degrees of freedom of the material system. The intent of the present paper is to present an elementary mathematical description of these physical processes and to predict the sizes of their contributions to the nonlinear optical susceptibility in terms of fundamental physical constants. We find that in fact all three of these contributions depend in exactly the same manner on the fundamental physical constants, and that the magnitudes of these contributions are in fact equal to within numerical factors of the order of unity.

2. Electronic response

The linear optical properties of materials typically are dominated by the electronic contribution to the optical response. Moreover, since the electronic response is essentially instanteous, it is the dominant contribution to the nonlinear optical response when measured using ultrashort laser pulses. In this section, we present a simple description of these electronic properties.

Let us begin by estimating the optical properties of an atomic system. For simplicity, we model the system as a collection of hydrogen atoms. Of course, Schrödinger's equation can be solved exactly for the hydrogen atom, but for our present purposes it suffices to present an estimate of its electronic properties. We adopt the model shown in figure 1 (*a*), in which a nucleus of charge $+e$ is surrounded by an electron cloud of characteristic dimension a and total charge $-e$. We use the gaussian system of units in this paper. The appendix to this paper presents a brief description of how to express nonlinear optical quantities in different systems of units. The Hamiltonian of the system

$$H = -\frac{e^2}{r} + \frac{p^2}{2m} \tag{1}$$

can be estimated to order of magnitude by replacing r by the characteristic size a and by replacing p by $\hbar/a$, which follows from the Heisenberg uncertainty relation $\Delta x \Delta p \geq \frac{1}{2}\hbar$. One then finds that

$$H = -\frac{e^2}{a} + \frac{\hbar^2}{2ma^2}. \tag{2}$$

The value of a that minimizes this expression is found by setting $\mathrm{d}H/\mathrm{d}a = 0$, leading to the result

$$a_0 = \frac{\hbar^2}{me^2}, \tag{3}$$

which is the standard expression for the first Bohr radius. Numerically we find that $a_0 = 0.5\,\text{Å} = 0.5 \times 10^{-8}$ cm. When this expression is substituted back into
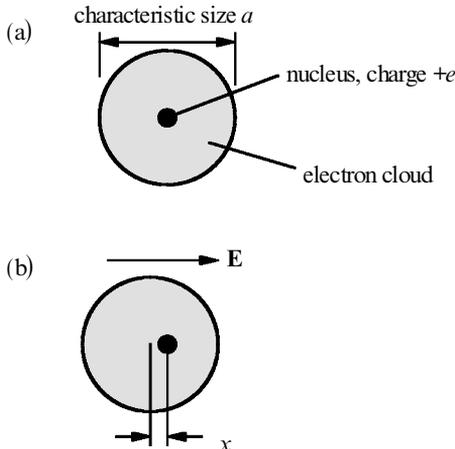

Figure 1.   (*a*) Simple model of the hydrogen atom. (*b*) Displacement of the electron cloud in the presence of an applied static electric field.
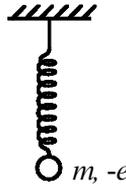
Figure 2. The Lorentz model of the atom. The atom is treated as a simple harmonic oscillator.

equation (2), one finds that the ground state energy of the hydrogen atom is given by

$$H_0 = \frac{-me^4}{2\hbar^2} = -\frac{1}{2}\frac{e^2}{a_0} \equiv -R, \tag{4}$$

where R is conventionally known as the Rydberg unit of energy and has the value $R = 13.6\,\mathrm{eV} = 2.17 \times 10^{-11}$ erg.

We next estimate the linear static polarizability of the atom. If an electric field E is applied to the atom (see figure $1(b)$) the electron cloud will be displaced slightly to the left by an amount $-x$, leading to a dipole moment of size $p = -ex$. (For simplicity and to very high accuracy, we are here considering the position of the nucleus to remain fixed. We examine the consequences of a nuclear motion in more detail in section 3.) To determine the displacement x, we note that the electron cloud will experience a force $-eE$ due to the applied field and a force of order of magnitude $e^2 x/a_0^3$ due to the field of the nucleus. This latter force is calculated by assuming that the electron cloud can be described by a uniform charge density $-e/\frac{4}{3}\pi a_0^3$ for $r \le a_0$ and zero charge density elsewhere, and performing an elementary calculation using Gauss's law. These two forces must be equal and opposite in equilibrium, leading to the result

$$x = -a_0^3 E/e. \tag{5}$$

Since $p = -ex$, and introducing the linear polarizability $\alpha(\text{electronic})$ defined by $p = \alpha(\text{electronic})E$, we find that

$$\alpha(\text{electronic}) = a_0^3. \tag{6}$$

For the hydrogen atom the quantum mechanical version of this problem can be solved exactly [10, 11] leading to the very similar result $\alpha(\text{electronic}) = (9/2)a_0^3$.

Expression (6) for the polarizability was derived for a static applied field, but is expected to be valid whenever the applied field frequency ω is much smaller than any atomic resonance frequency ω_0. In fact, this is not an unrealistic limit, because optical materials are often selected so that their absorption frequencies are far removed from the frequencies of the applied optical field. Under these circumstances, we can use equation (6) to estimate the linear refractive index n of the material. We make use of the standard relations $n = \epsilon^{1/2}$, where the dielectric constant is given by $\epsilon = 1 + 4\pi\chi^{(1)}$ and where (ignoring local field effects) $\chi^{(1)} = N\alpha(\text{electronic})$. We estimate the atomic number density as $N = 1/(2a_0)^3 = 8.44 \times 10^{23}$ cm^{-3}. We then find that $\epsilon \simeq 2.6$ and $n = 1.6$, in good agreement with typical values of the refractive index of bulk matter.

A very different model, the Lorentz model of the atom [12], is often used to estimate the near-resonance linear optical properties of an atomic system. Let us establish the connection of this model to the quasi-static model described above. The Lorentz model describes the atom as a harmonic oscillator of resonance frequency ω_0 and damping rate Γ as illustrated in figure 2. The equation of motion for the electron coordinate is then

$$m\ddot{x} = -kx - i\Gamma\dot{x} - eE(t), \tag{7}$$

where $k = m\omega_0^2$ is the effective spring constant of the oscillator. This equation can readily be solved for a field of the form $E(t) = E_0 \exp(-i\omega_0 t)$. One then finds that the induced dipole moment $p(t) = -ex(t)$ can be expressed as $p(t) = \alpha(\omega)E(t)$ where the polarizability $\alpha(\omega)$ is given by

$$\alpha(\omega) = \frac{e^2/m}{\omega_0^2 - \omega^2}, \tag{8}$$

which has the low frequency value $\alpha(\text{electronic}) = e^2/m\omega_0^2$. To order of magnitude, we can identify the resonance frequency ω_0 with $R/\hbar$, where $R = e^2/2a_0$ is the Rydberg constant introduced in equation (4). We thus find that $\alpha(\text{electronic}) = 4a_0^3$, in good order-of-magnitude agreement with our previous result (6).

We next generalize this treatment by allowing the optical response to be nonlinear. We assume that the atomic dipole can be expanded in a power series in the applied field as

$$p(t) = \alpha E(t) + \beta E^2(t) + \gamma E^3(t) + \cdots$$

$$= p^{(1)}(t) + p^{(2)}(t) + p^{(3)}(t) + \cdots. \tag{9}$$

We assume that the local environment is not necessarily centrosymmetric, and thus we allow even powers of $E(t)$ as well as odd powers to appear in these expressions. We also assume that the conditions are quasi-static, that is, $E(t)$ and $p(t)$ are allowed to vary in time, but only at frequencies much smaller than the resonance frequency of the atomic system.

We can estimate the size of the nonlinear coefficients β and γ by means of a well-known argument [1]. We assume that the nonlinear response will become comparable to the linear response for applied field strengths E comparable to the atomic field strength $E_{\text{at}} = e/a_0^2$. Note that $E_{\text{at}} = m^2 e^5/\hbar^4 \approx 1.9 \times 10^7$ s V cm^{-1} = 5.7×10^{11} V m^{-1}. We thus predict that, to order of magnitude,

$$\beta = \alpha(\text{electronic})/E_{\text{at}} = a_0^5/e = \hbar^{10}/m^5 e^6 = 8.63 \times 10^{-33} \text{ cm}^4 \text{ s}^{-1} \text{ V}^{-1}, \tag{10a}$$

$$\gamma = \alpha(\text{electronic})/E_{\text{at}}^2 = a_0^7/e^2 = \hbar^{14}/m^7 e^{16} = 5.03 \times 10^{-40} \text{ cm}^5 \text{ s}^{-1} \text{ V}^{-2}. \tag{10b}$$

We have written these results both in terms of a_0 to suggest how rapidly the nonlinear coefficient increases with the linear dimensions of the atom and in terms of fundamental physical constants to show this dependence. The nature of optical nonlinearities can also be understood by noting that equations (9) and (10) can be combined to give the following results, valid to order of magnitude

$$p^{(1)} = -ea_0 \left(\frac{E}{E_{at}} \right), \tag{11 a}$$

$$p^{(2)} = -ea_0 \left(\frac{E}{E_{at}} \right)^2, \tag{11 b}$$

$$p^{(3)} = -ea_0 \left(\frac{E}{E_{at}} \right)^3. \tag{11 c}$$

Often the nonlinear optical properties of materials are described in terms of nth order susceptibilities $\chi^{(n)}$, which are defined by the equation

$$P(t) = \chi^{(1)} E(t) + \chi^{(2)} E^2(t) + \chi^{(3)} E^3(t) + \cdots, \tag{12}$$

where the polarization is defined by $P(t) = Np(t)$ and where as above we assume that $E(t)$ varies slowly compared to the inverse of the atomic resonance frequency. We then find that, to order of magnitude,

$$\chi^{(1)} = N\alpha = Na_0^3 = \tfrac{1}{8}, \tag{13 a}$$

$$\begin{aligned} \chi^{(2)} = N\beta = Na_0^5/e &= a_0^2/8e \\ &= \hbar^4/8m^2e^5 = 7.29 \times 10^{-9}\ \mathrm{cm\,s^{-1}\,V^{-1}}, \end{aligned} \tag{13 b}$$

$$\begin{aligned} \chi^{(3)} = N\gamma = Na_0^7/e^2 &= a_0^4/8e^2 \\ &= \hbar^8/8m^4e^{10} = 4.25 \times 10^{-16}\ \mathrm{cm^2\,s^{-1}\,V^{-2}}, \end{aligned} \tag{13 c}$$

where as above we have set N equal to $(2a_0)^{-3} = 8.44 \times 10^{23}\ \mathrm{cm^{-3}}$. We have written each of these results in several different forms to display the functional dependences on the various parameters of the problem and to provide numerical estimates of their values.

As a test of the validity of the simple model just presented, we recall that the hyperpolarizability of a radiatively broadened atom in the two-level approximation is given for near-resonant excitation by ([13], equation (5.3.37))

$$\gamma = \frac{2}{3} \frac{|\mu|^4}{\hbar^3 (\omega - \omega_0)^3}, \tag{14}$$

where μ is the transition dipole moment, ω is the optical frequency and ω_0 is the resonance frequency. We can estimate the value of the expression by setting $|\mu|$ equal to ea_0, by ignoring ω with respect to ω_0 under the assumed quasi-static conditions, and setting $\hbar\omega_0$ equal to the Rydberg contstant R of equation (4). We thus find that $\gamma = a_0^7/e^2$, in good agreement with the order-of-magnitude estimate given by equation (10 b).

The discussion presented above summarizes the well known results for the electronic contribution to the linear and nonlinear optical properties of a material system under highly off-resonant excitation. In the remainder of this paper, we will see how to derive analogous results for the nuclear and electrostrictive contributions to the nonlinear optical response.

3.   Nuclear response

Let us next consider how the motion of atomic nuclei contributes to the linear and nonlinear optical properties of a material system. We shall find that the nuclear response typically makes a negligible contribution to the linear response at optical frequencies, but that curiously the nuclear response can make a significant contribution to the nonlinear optical properties. Of course, explicit quantum mechanical predictions for the nuclear contribution can be obtained, for instance within the context of the Born–Oppenheimer approximation [14]. Here our goal is to develop simple order-of-magnitude predictions that describe the relative size of the nuclear and electronic responses of a material system to an applied optical field.

As a simple special case, we consider the nuclear contribution to the linear optical response of an isolated atom. In our simplified treatment of section 2, we assumed that the applied electric field induced a displacement of the electron with respect to a fixed atomic nucleus. In reality, the electron and nucleus both move relative to the fixed centre of mass of the system. The displacement of the nucleus will be smaller than that of the electron by the factor m/M, where m is the electron mass and M is the nuclear mass. We thus conclude that the nuclear contribution to the polarization of the medium can be described by a nuclear polarizability given by

$$\alpha(\text{nuclear}) = \frac{m}{M}\alpha(\text{electronic}), \tag{15}$$

where $\alpha(\text{electronic})$ is the polarizability given by equation (6). Since $m/M = 1/1837$ for the hydrogen atom and is much less than unity for any other realistic condition, we see that the nuclear response makes a negligible contribution to the linear optical properties of an atomic system.

The analysis is more complicated for molecules. First, for homonuclear molecules, the conclusion represented by equation (15) should be expected to hold, at least to order of magnitude. The situation can be considerably more complicated for heteronuclear molecules. For simplicity, consider a diatomic heteronuclear molecule of nuclear charges q_A and q_B, masses M_A and M_B, and equilibrium internuclear separation x_0. An applied electric field $E(t)$ will change the internuclear separation to $x_0 + x(t)$, where $x(t)$ obeys the equation of motion

$$M\ddot{x} = -kx - \Delta q E(t). \tag{16}$$

Here $M = M_a M_b/(M_a + M_b)$ is the reduced mass of the vibrational mode, $k = M\omega_v^2$ is the effective spring constant where ω_v is the resonance frequency of the vibrational mode, and $\Delta q = (q_A - q_B)/2$ is the effective charge difference (see figure 3).

One would expect Δq to be of the order of magnitude but somewhat smaller than the electron charge e. Let us assume that the electric field oscillates according to the real part of $E_0 \exp(-i\omega t)$. We can then solve equation (16) to find that the induced dipole moment $p(t) = \Delta q x(t)$ can be described in terms of a nuclear polarizability $\alpha(\text{nuclear})$ as $p(t) = \alpha(\text{nuclear})E(t)$, where

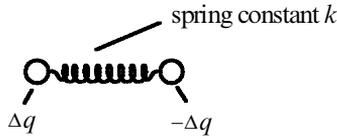$$\alpha(\text{nuclear}) = \frac{\Delta q^2/M}{\omega_v^2 - \omega^2}. \tag{17}$$

Figure 3.   Vibrational mode of a heteronuclear diatomic molecule.

Under typical conditions at optical frequencies, this response is much smaller than the electronic response. For instance, in the typical limit $\omega_v \ll \omega \ll \omega_0$, we find through use of equations (8) and (17) that

$$\frac{\alpha(\text{nuclear})}{\alpha(\text{electronic})} = -\left(\frac{\Delta q^2}{e^2}\right)\left(\frac{m}{M}\right)\left(\frac{\omega^2}{\omega_0^2}\right), \tag{18}$$

which by inspection is seen to be much smaller than unity. We can also consider the nuclear contribution at very low frequencies $\omega \ll \omega_v$. In this case the ratio of the nuclear response to the electronic response is given by

$$\frac{\alpha(\text{nuclear})}{\alpha(\text{electronic})} = \frac{\Delta q^2 / M\omega_v^2}{e^2 / m\omega_0^2} = \left(\frac{\Delta q^2}{e^2}\right)\left(\frac{m}{M}\right)\left(\frac{\omega_0^2}{\omega_v^2}\right). \tag{19}$$

We next demonstrate that the ratio of the nuclear response to the electronic response is of the order of magnitude of unity. We noted above that Δq is of the order of the electron charge e. Note further that the ratio of the nuclear mass to the electron mass is of the order of 10^3, and that ω_v is of the order of $1/30$ of ω_0 for typical molecules. Consequently the product of m/M with ω_0^2/ω_v^2 is of the order of unity. Let us examine more fundamentally why this should be so. The interatomic potential describing the binding of two atoms to form a molecule will be qualitatively of the form shown in figure 4. Note that the depth of the potential well will be of the order of the Rydberg constant R and that the width of the potential well will be of the order of a_0. Thus, the spring constant k that appears in equation (16) will be of the order of R/a_0^2, since $U(x) = \frac{1}{2}k(x - x_0)^2$ near the bottom of the potential well, and hence the resonance frequency $\omega_v = (k/M)^{1/2}$ will be of the order of $\omega_v = (R/a_0^2 M)^{1/2}$ and the product $M\omega_v^2$ will be of the order of R/a_0^2. Note next that the analogous quantity for the electronic response $m\omega_0^2$ will also be of the order of R/a_0^2. We can establish this result by noting that the potential well that binds the electron to the atomic nucleus also has depth R and
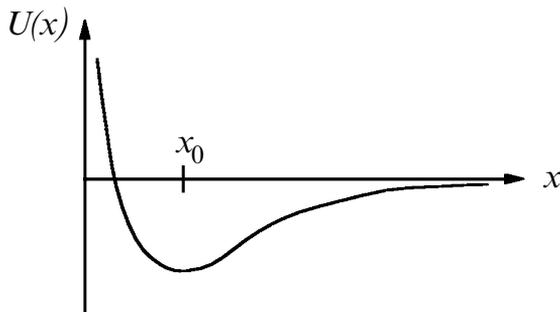

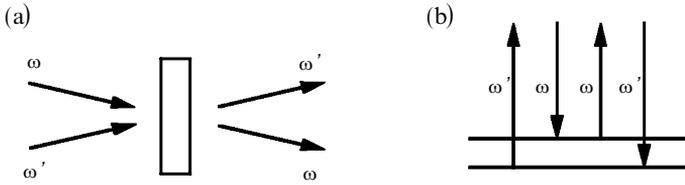Figure 4.   Interaction potential energy of two atoms in a diatomic molecule.

Figure 5.   Third order nonlinear optical response induced by a wave of frequency ω on a wave of frequency ω'.

width a_0, and thus that its spring constant will be of the order of R/a_0^2, its resonance frequency will be of the order of $\omega_0 = (k/m)^{1/2} = (R/a_0^2 m)^{1/2}$, and hence $m\omega_0^2$ will be of the order of R/a_0^2. We thus conclude that to order of magnitude

$$\left(\frac{m}{M}\right)\left(\frac{\omega_0^2}{\omega_v^2}\right) = 1. \tag{20}$$

It thus follows that

$$\frac{\alpha(\text{nuclear})}{\alpha(\text{electronic})} \approx 1 \qquad \text{for} \qquad \omega \to 0. \tag{21}$$

We have thus shown that the nuclear contribution to the linear response is much smaller than the electronic contribution at optical frequencies, but is of the same order of magnitude for frequencies much smaller than the vibrational resonance frequencies. The analysis presented here has assumed that the molecule does not possess a permanent electric dipole moment. For materials that do possess a permanent electric dipole moment, the nuclear contribution can be much larger than the electronic contribution at sufficiently low frequencies. For instance, the zero-frequency dielectric constant of water is 81 and that of one particular tensor component of barium titanate is several thousand.

Let us next consider the nuclear contribution to the nonlinear optical susceptibility. For definiteness, we consider the third-order response with two applied frequencies in the combination described by the susceptibility $\chi^{(3)}(\omega' = \omega' + \omega - \omega)$, as illustrated in figure 5. The nuclear contribution to this process is well known from theoretical treatments of stimulated Raman scattering. The standard result is ([13], equation (9.3.19))

$$\chi^{(3)}(\omega' = \omega' + \omega - \omega) = \frac{(N/12M\omega_v)(d\alpha/dx)_0^2}{\omega' - (\omega - \omega_v) + i\Gamma}, \tag{22}$$

where it has been assumed that the linear polarizability (which is largely electronic in origin) changes with the internuclear separation $x_0 + x$ according to

$$\alpha = \alpha_0 + (d\alpha/dx)_0 x. \tag{23}$$

Clearly, equation (22) predicts a resonance when ω and ω' differ by the vibrational frequency of the material system, but let us here consider only the non-resonant situation in which ω and ω' are equal. We then find that

$$\chi^{(3)}_{\text{NR}}(\text{nuclear}) = \chi^{(3)}(\omega = \omega + \omega - \omega) = (N/12M\omega_v^2)(d\alpha/dx)_0^2. \tag{24}$$

We can make an order-of-magnitude estimate of the size of this response by assuming that $(d\alpha/dx)_0$ is of the order of magnitude of the square of the Bohr

radius a_0 [15]. By comparing equations $(13\,c)$ and (24), we find that to order of magnitude the relative nuclear response is given by

$$\frac{\chi^{(3)}_{NR}(\text{nuclear})}{\chi^{(3)}(\text{electronic})} = \frac{Na_0^4/M\omega_v^2}{Na_0^6/\hbar\omega_0} = \left(\frac{m}{M}\right)\left(\frac{\omega_0^2}{\omega_v^2}\right) = 1, \tag{25}$$

where the second-to-last form is obtained by introducing $R = e/2a_0^2$ for $\hbar\omega_0$ and where the last step follows from equation (20). We thus see that the non-resonant nuclear contribution to the optical frequency nonlinear optical response is expected to be of the same size as the electronic contribution. We can also see from equation (23) that the Raman resonant response will be ω_v/Γ times larger than the non-resonant response.

4. Electrostrictive response

Another contribution to the nonlinear susceptibility results from the tendency of materials to become more dense in the presence of an electric field, a phenomenon known as electrostriction. This process is illustrated schematically in figure 6. The process of electrostriction can be understood theoretically in the following manner ([13], section 8.2). The presence of an electric field within a material produces a pressure given by

$$P_{str} = \gamma_{str}E^2/8\pi, \tag{26}$$

where

$$\gamma_{str} = \rho(\partial\epsilon/\partial\rho) \tag{27}$$

is known as the electrostrictive constant. This pressure tends to compress the material, which leads to a change in the dielectric constant of the material given by

$$\Delta\epsilon = \left(\frac{\partial\epsilon}{\partial\rho}\right)\left(\frac{\partial\rho}{\partial p}\right)P_{str} = \left(\rho\frac{\partial\epsilon}{\partial\rho}\right)\left(\frac{1}{\rho}\frac{\partial\rho}{\partial p}\right)P_{str} = \gamma_{str}CP_{str}, \tag{28}$$
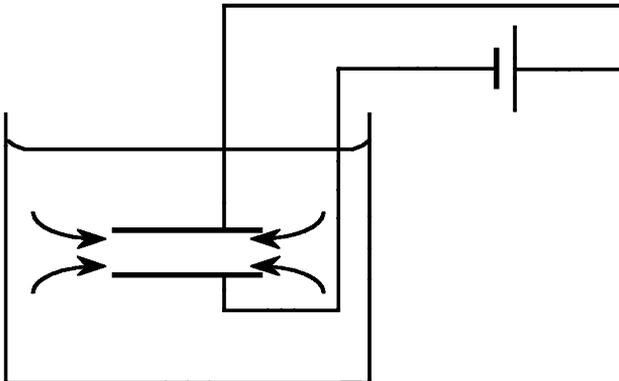
where

Figure 6.   Physical origin of the electrostriction process. Materials become more dense in the presence of an electric field.
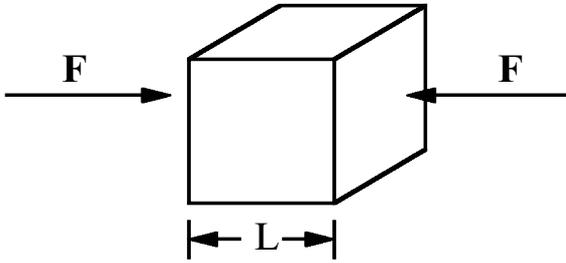
Figure 7.   Calculation of the compressibility.

$$C = \frac{1}{\rho}\frac{\partial \rho}{\partial P} \tag{29}$$

is known as the compressibility. Since $\epsilon = 1 + 4\pi\chi$, it follows that $\Delta\chi = (1/4\pi)\Delta\epsilon$ and consequently with the usual field conventions of nonlinear optics that

$$\chi^{(3)}(\mathrm{str}) = \gamma_{\mathrm{str}}^2 C/48\pi^2. \tag{30}$$

We now estimate the value of $\chi^{(3)}(\mathrm{str})$. We expect γ_{str} to be of the order of unity, because of the relation (valid ignoring local field effects) $\epsilon = 1 + 4\pi N\alpha$ which (since the mass density ρ is proportional to the number density N) implies that $\gamma_{\mathrm{str}} = \epsilon - 1$. To estimate the value of the compressibility, we begin by expressing the compressibility as

$$C = -\frac{\Delta V/V}{F/A}, \tag{31}$$

where $\Delta V/V$ is the fractional change in volume induced in the material by an applied stress F/A. We note that in order to appreciably decrease the separation between two atoms in a solid, we would have to push them together with a force comparable to the atomic Coulomb force $F_{at} = eE_{at} = R/a_0$. Consider now a cubic region of volume $V = L^3$ with forces F applied to two opposing faces (see figure 7). Any cross-section of this cube will have an area $A = L^2$ and will contain approximately $A/(2a_0)^2$ atoms. The force F required to compress the cube appreciably (i.e. to produce $\Delta V/V \approx \frac{1}{2}$) is of the order of the number of atoms in each cross-sectional plane $A/(2a_0)^2$ times the force $F_{at} = eE_{at} = R/a_0$ per atom, that is, $F = [A/(2a_0)^2] \times F_{at}$. Thus the applied strain F/A required to produce such a compression is of the order of $F_{at}/4a_0^2 = R/4a_0^3$. We therefore predict that, to order of magnitude,

$$C = \frac{\frac{1}{2}}{R/4a_0^3} = \frac{2a_0^3}{R} = 1.2 \times 10^{-14}\ \mathrm{cm}^3\ \mathrm{erg}^{-1} = 1.2 \times 10^{-13}\ \mathrm{m}^3\ \mathrm{J}^{-1}. \tag{32}$$

We can combine this result with equation (30) to find that, to order of magnitude,

$$\chi^{(3)}(\mathrm{str}) = \frac{a_0^3}{24\pi^2 R} = \frac{a_0^4}{12\pi^2 e^2}, \tag{33}$$

where the last form comes by introducing expression (4) for the Rydberg constant. Next, by comparison with equation (13 c), we can rewrite this result as

$$\chi^{(3)}(\text{str}) = \frac{2}{3\pi^2}\chi^{(3)}(\text{electronic}). \qquad (34)$$

We see that the electrostrictive contribution to the third-order susceptibility is predicted to be approximately of the same order of magnitude as the electronic contribution.

The largest uncertainty in this result is due to the accuracy of the prediction for the compressibility of bulk matter. In fact, inspection of tables [16] of compressibilities of bulk matter (or of its inverse, the bulk modulus) shows that compressibilities are typically in the range of 10^{-12} to 10^{-11} $\text{cm}^3\,\text{erg}^{-1}$, at least 100 times larger than the simple estimate given by equation (32). Of the various numerical estimates presented in the present work, the estimate of the compressibility is probably the least accurate. Reasons for this discrepancy include the simplicity of the model presented and especially the fact that the forces that confine individual atoms to their equilibrium positions in bulk matter are considerably smaller than the force that binds electrons to the atomic nucleus, which was the assumption made in the present calculation.

5. Conclusions

We have developed simple order-of-magnitude estimates of the values of a number of physical constants that are conventionally used to describe the nonlinear optical properties of a material system. These estimates show how these quantities depend on fundamental physical constants. We obtain the new and somewhat surprising result that the resulting expressions for the three dominant contributions to the third-order susceptibility show the same functional dependences and predict that these contributions (electronic, nuclear, and electrostrictive) should be equal, at least to order of magnitude. Finally, we note that these three processes possess different response times and different tensor properties, which allow these processes to be distinguished in laboratory measurements.

Acknowledgments

Appendix: systems of units

The present paper is written in the gaussian system of units. Conversion to the SI system can be performed using well known procedures. See for example the appendix to Jackson [17] for a discussion of this topic in general or to appendix A of Boyd [13] for a discussion of conversion between systems of units within the context of nonlinear optics.

As an example of the results of such a conversion, we display one of the key results of the present paper (equations 13) in the SI system of units. We define the material polarization within the SI system by

$$P(t) = \epsilon_0[\chi^{(1)}E(t) + \chi^{(2)}E^2(t) + \chi^{(3)}E^3(t) + \cdots]. \tag{A 1}$$

Through use of the standard procedures for converting to the SI system we then find that equations (13) become

$$\chi^{(1)} = \frac{\pi}{2}, \tag{A 2a}$$

$$\chi^{(2)} = N(4\pi)^2 \epsilon_0 a_0^5 / e = 2\pi^2 \epsilon_0 a_0^2 / e = 3.05 \times 10^{-12}\,\mathrm{m\,V^{-1}}, \tag{A 2b}$$

$$\chi^{(3)} = N(4\pi)^3 \epsilon_0^2 a_0^7 / e^2 = 8\pi^3 \epsilon_0^2 a_0^4 / e^2 = 5.95 \times 10^{-24}\,\mathrm{m^2\,V^{-2}}, \tag{A 2c}$$

where we have set N equal to $(2a_0)^{-3}$.

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