# Physical Limits on Electronic Nonlinear Molecular Susceptibilities

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We apply sum rules to answer the question: What is the largest off-resonance electronic nonlinear susceptibility allowed by quantum mechanics? The sum-rule-restricted three-level model shows that the two-level limit yields the absolute maximum susceptibility, which is found to depend only on the first excited state transition energy and number of electrons—in agreement with a large set of second- and third-order susceptibility data from the literature. As such, the sum rules provide a target for the maximum possible *off-resonant* susceptibilities.

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Many studies have focused on understanding the origin of the nonlinear susceptibilities of molecules with the hope of making better materials for photonics applications. These include two and three state models that consider the competition between transitions [1–4], symmetry models [5], and bond length alternation [6]. This paper, in contrast, asks the question: What is the largest diagonal tensor component of the nonlinear susceptibility that is allowed by quantum mechanics? The answer entails applying sum rules to quantum calculations of the electronic nonlinear susceptibility. Our calculation, when compared with a large collection of experimental data from the literature [7], accurately predicts the upper limit. The sum rules, while general and applicable to any nonlinearity, are applied here to the diagonal tensor component of the off-resonant electronic nonlinear susceptibilities.

We begin with the Thomas-Kuhn sum rules, which are derived for an $N$-particle system by evaluating the matrix elements of the commutators $\langle m|[[H,\sum_{i=1}^{N} x_i], \sum_{j=1}^{N} x_j]|p\rangle$ [8], where $x_i$ is the position of the $i^{\mathrm{TH}}$ particle. This yields

$$\sum_{n=0}^{\infty}\left(E_n - \frac{1}{2}(E_m + E_p)\right)x_{mn}x_{np} = \frac{\hbar^2 N}{2m}\,\delta_{m,p}\,, \quad (1)$$

where $x_{ab}$ is the matrix element of the position between states $a$ and $b$, $E_a$ the energy of state $a$, $m$ the mass of the particle (in our case, the electron), and $N$ the number of particles in the system (here, a molecule). This sum rule applies to any molecule in which the force on the electrons is conservative. The sum, indexed by $n$, is over all states of the system.

Let us consider the case where $m$ and $p$ in Eq. (1) are both the ground state, 0. Solving for $x_{10}$, we get

$$|x_{10}|^2 = \frac{\hbar^2}{2mE_{10}}N - \sum_{n=2}^{\infty}\frac{E_{n0}}{E_{10}}|x_{n0}|^2, \quad (2)$$

where $E_{nm} \equiv E_n - E_m$. Because each of the three terms in Eq. (2) is positive definite, the transition moment to the first excited state is maximum for a two-level model, that is, when $x_{n0} = 0$ for $n \neq 1$. The two-level model does not imply, however, that there are no transitions between excited states, but rather that all transition moments from the ground state to any excited state vanish except for the first excited state. It is interesting to ask whether this sum-rule limit on the oscillator strengths yields a limit on the maximum nonlinear-optical susceptibilities.

Because of the importance of low loss and ultrafast response in many applications, we evaluate the off-resonance susceptibilities [such as the hyperpolarizability, $\beta_{i,j,k}(-\omega_1 - \omega_2; \omega_1, \omega_2)$, with $\hbar\omega_1, \hbar\omega_2 \ll E_{n0}$ for any excited state $n$]. This approximation allows us to ignore the transition width, resulting in real $\beta$. Generalizing these calculations to near resonant conditions is a straightforward procedure that may lead to interesting results, but is not treated here. Secondly, we consider only the diagonal component of the nonlinear susceptibilities. We stress that these results hold for the diagonal components of susceptibilities for three-dimensional molecules.

The general expression for $\beta$ is given by an infinite sum over the excited states [9],

$$\beta_{ijk} = KI_{1,2}\left(-\frac{e^3}{\hbar^2}\right)\sum_{n,m}^{\infty}\left(\frac{r_{0n}^{i}\bar{r}_{nm}^{j}r_{m0}^{k}}{(\Omega_{n0}^{*} - \omega_3)(\Omega_{m0}^{*} - \omega_1)} + \frac{r_{0n}^{i}\bar{r}_{nm}^{k}r_{m0}^{j}}{(\Omega_{n0}^{*} + \omega_2)(\Omega_{m0} + \omega_3)} + \frac{r_{0n}^{k}\bar{r}_{nm}^{i}r_{m0}^{j}}{(\Omega_{n0} + \omega_2)(\Omega_{m0} - \omega_1)}\right), \quad (3)$$

where $K$ is a degeneracy factor that depends on the wavelengths of the light beams, $I_{1,2}$ is the permutation operator, and $\bar{r}_{nm} \equiv (r - r_{00})_{nm}$. Most models used to understand the conditions leading to a maximum of Eq. (3) assume that the transition moments, such as $er_{mg}^{j}$, and transition energies, such as $\hbar\Omega_{ng}$, are parameters that can be independently varied. These models calculate the moments and energies as functions of some variable, $\xi$, that is intuitively understood, such as symmetry [5] or bond length alternation [6], and determine which values of these parameters maximize the nonlinear response. Molecules can then be made according to this paradigm, and tested for their response. While this approach provides a method for designing new molecules, it leaves several questions unanswered. For example, if the nonlinearity of a molecule is

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maximum for a given parameter $\xi$, is that the maximum possible? Does this value of the parameter violate quantum mechanics? The purpose of this paper is to investigate the limits imposed by quantum mechanics, independent of the approach.

The maximum possible response can be determined using the sum rules. We begin by evaluating Eq. (3) using the three-level sum rule and evaluating the two-level limit. For a three-level model, the off-resonant hyperpolarizability is

$$\beta_{3L} = \frac{3e^3|x_{10}|^2\Delta x_{10}}{E_{10}^2} + \frac{6e^3\,\mathrm{Re}[x_{01}x_{12}x_{20}]}{E_{10}E_{20}} + \frac{3e^2|x_{20}|^2\Delta x_{20}}{E_{20}^2}, \tag{4}$$

where we have assumed $E_{n0}$ is real for all $n$ and that the operator $x$ is Hermitian so that $x_{ij} = x_{ji}^*$. Note that $\beta$ is real. The first and third terms correspond to a two-level model to the first excited state and the second excited state, respectively. These two terms require a change in the dipole moment, and are therefore referred to as dipolar terms. The middle term, on the other hand, does not require a change in the dipole moment and includes transition moments between all three states. As such, it is called the octupole term [10].

We now evaluate the sum rules that include the first three states. $(m, p) = (0, 0)$ yields

$$|x_{01}|^2E_{10} + |x_{02}|^2E_{20} = \frac{\hbar^2N}{2m}. \tag{5}$$

$(m, p) = (1, 1)$ yields

$$-|x_{01}|^2E_{10} + |x_{12}|^2E_{21} = \frac{\hbar^2N}{2m}. \tag{6}$$

$(m, p) = (0, 1)$ yields

$$x_{01}\Delta x_{10}E_{10} + x_{02}x_{21}(E_{21} + E_{20}) = 0, \tag{7}$$

where $\Delta x_{10} \equiv x_{11} - x_{00}$. $(m, p) = (0, 2)$ yields

$$x_{02}\Delta x_{20}E_{20} + x_{01}x_{12}(E_{10} - E_{21}) = 0, \tag{8}$$

where $\Delta x_{20} \equiv x_{22} - x_{00}$. Note that the sum rules for $(m, p)$ yield the same expression as for $(p, m)$ with $x_{i,j} \rightarrow x_{j,i}$.

We can solve Eqs. (5)–(8) (along with the associated equations with $x_{i,j} \rightarrow x_{j,i}$) for each matrix element in terms of $x_{01}$, which yields

$$|x_{02}| = \sqrt{E(|x_{01}^{2L}|^2 - |x_{01}|^2)}, \tag{9}$$

$$|x_{12}| = \sqrt{\frac{E}{1-E}(|x_{01}^{2L}|^2 + |x_{01}|^2)}, \tag{10}$$

$$|x_{01}|\Delta x_{10} = \frac{2-E}{\sqrt{1-E}}\sqrt{(|x_{01}^{2L}|^4 - |x_{01}|^4)}, \tag{11}$$

and

$$|x_{02}|\Delta x_{20} = (2E - 1)|x_{01}|\sqrt{\frac{E}{1-E}(|x_{01}^{2L}|^2 + |x_{01}|^2)}, \tag{12}$$

where $|x_{01}^{2L}|^2 = \hbar^2N/2mE_{10}$ is the maximum possible value of the position matrix element given by Eq. (2) and $E \equiv E_{10}/E_{20}$. Multiplying Eq. (8) by $x_{20}$ yields

$$x_{01}x_{12}x_{20} = |x_{02}|^2\Delta x_{20}/(1 - 2E). \tag{13}$$

Equations (9)–(13) can be substituted into Eq. (4) to evaluate the second-order susceptibility.

We begin by considering the two-level model, which is calculated from Eq. (4) with $E_{20} \rightarrow \infty$, or, equivalently, $E \rightarrow 0$. Using Eq. (11), this yields

$$|\beta_{2L}^{\mathrm{SR}}| = \frac{3e^3(2|x_{10}|\sqrt{(|x_{01}^{2L}|^4 - |x_{01}|^4)})}{E_{10}^2}, \tag{14}$$

where $\beta_{2L}^{\mathrm{SR}}$ is the sum-rule-restricted two-level $\beta$. Equation (14) vanishes when $x_{01} = 0$ and at $|x_{01}| = |x_{01}^{2L}|$, and is maximum when $|x_{01}|^4 = \frac{1}{3}|x_{01}^{2L}|^4$. Using the Lorentz local field model, the maximum two-level dressed susceptibility given by Eq. (14) is

$$\beta_{2L}^{*\mathrm{SR}} \le \sqrt[4]{3}\left(\frac{n^2+2}{3}\right)^3\left(\frac{e\hbar}{\sqrt{m}}\right)^3\frac{N^{3/2}}{E_{10}^{7/2}}. \tag{15}$$

Figure 1 shows $\beta_0/N^{3/2}$ as a function of wavelength of maximum absorbance of the first excited state for experimentally measured values of a large number of molecules as tabulated in the literature (points) [7], and the theory, given by Eq. (15). The number of electrons participating, $N$, is determined by twice the number of double (or triple) bonds in the molecule, an estimate that has been shown to be good for conjugated systems [11]. Because of the large number of molecules represented, it is not possible to provide figures for the molecular structures associated with

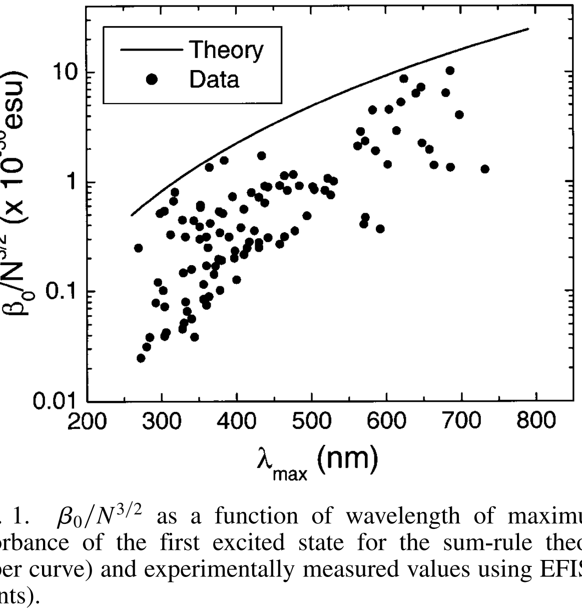

FIG. 1. $\beta_0/N^{3/2}$ as a function of wavelength of maximum absorbance of the first excited state for the sum-rule theory (upper curve) and experimentally measured values using EFISH (points).

the data points. Readers are referred to the tabulations for more information [7]. It is intriguing that the sum-rule-restricted two-level model gives an upper bound.

We can prove that *adding another state to the system leads to a decrease in* $\beta$. To do so, we consider the three-level model. Substituting Eqs. (9)–(13) into Eq. (3) yields

$$\beta_{3L}^{\mathrm{SR}} = \pm \frac{3e^3 f(E)\,(|x_{10}|\sqrt{(|x_{01}^{2L}|^4 - |x_{01}|^4)})}{E_{10}^2} = \pm \frac{1}{2} f(E) \beta_{2L}^{2R}, \tag{16}$$

with

$$f(E) = \left[ \frac{2 - E}{\sqrt{1 - E}} - \frac{2E^2}{\sqrt{1 - E}} + \frac{2E - 1}{\sqrt{1 - E}} E^3 \right], \tag{17}$$

where the plus (minus) sign in Eq. (16) is used when $\Delta x_{10}$ is positive (negative). For a fixed value of $E$, the three-level model is maximized when $x_{01}^4 = \frac{1}{3}(x_{01}^{2L})^4$, as we found for the two-level model. Interestingly, $\beta$ vanishes when the two excited states become degenerate. Figure 2 shows a plot of each term in $f(E)$ (i.e., two-level term, octupole term and two-level term for the second state) as a function of $E$. $f(0) = 2$ is the two-level model result. $f(E)$ monotonically decreases with $E$ and $\lim_{E \to 1} (f(E)) = 0$, so the two-level model yields the maximum value. It is clear that adding a third state decreases $\beta$, so molecules with closely spaced excited states will never result in the largest response.

While the two-level model yields maximum $\beta_0$, larger diagonal components of $\beta$ are possible only nearer to resonances. Another fruitful approach may be to study off-diagonal components of $\beta$, such as those that are important in octupolar molecules. Indeed, there is experimental evidence that the octupolar molecules, as measured with harmonic light scattering [12] [electric field induced second harmonic generation (EFISH) cannot measure only the octupolar part [10] ], may have larger second-order susceptibilities through "octupoling" alignment [13]. This more general case will be presented later [14].

The same analysis leading to Eq. (15) can be used to calculate the absolute maximum diagonal component of the second hyperpolarizability, $\gamma$, and yields [15]

$$-\frac{e^4 \hbar^4}{m^2} \left( \frac{N^2}{E_{10}^5} \right) \leq \gamma \leq 4 \frac{e^4 \hbar^4}{m^2} \left( \frac{N^2}{E_{10}^5} \right), \tag{18}$$

where the negative limit is for a centrosymmetric molecule and the positive limit for an asymmetric molecule. Figure 3 shows experimental values of $\gamma_0$ [16] of several series of molecules as shown in Fig. 4. The theory, again, correctly predicts the upper bound. A larger set of data comparisons will be presented elsewhere [14].

Given these results, we can speculate on the largest achievable susceptibilities. Considering a 50 $\pi$-electron molecule such as a donor-acceptor version of sexithienyl, with $\lambda_{\max} = 800$ nm and one dominant state, it would yield a dressed hyperpolarizability of $\beta_0^* = 8400 \times 10^{-30}$ esu. These same parameters give $\gamma_0^* = 350\,000 \times 10^{-36}$ esu. These are larger than molecules that are typically measured to have a "large" response, such as $\gamma_0^* = 7500 \times 10^{-36}$ esu [17] to $\gamma_0^* = 10\,000 \times 10^{-36}$ esu [16]. There are clearly more complex issues that determine how $\beta$ and $\gamma$ scale with the length and number of electrons. Nevertheless, the sum rules provide an upper bound as a target.

The sum rules can be applied to many other cases, such as $\beta$ and $\gamma$ near resonance, problems that go beyond the dipole approximation (as is used to calculate the sum-over-state expressions), device figure of merits, and other nonlinear mechanisms such as photorefraction and molecular reorientation. For example, consider the third-order susceptibility that describes all-optical molecular reorientation, which is of the form $a\alpha^2/kT$ where $a \leq 1$ is a Kirkwood factor with $a = 1$ for a noninteracting gas and

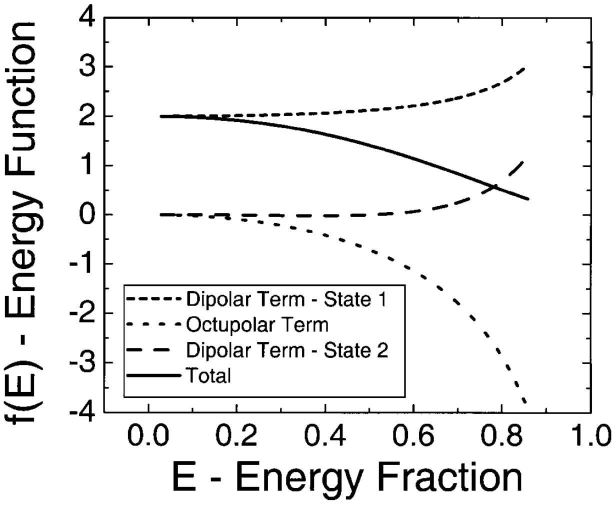

FIG. 2. $f(E)$ as a function of $E$ and its associated two-level terms and octupolar terms.

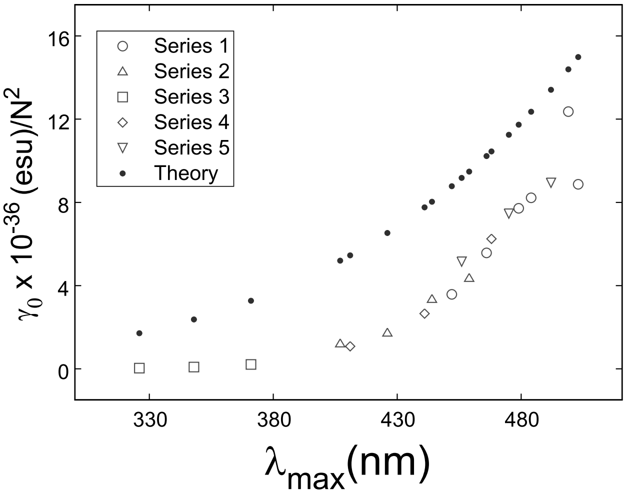

FIG. 3. Measured $\gamma_0/N^2$ as a function of $\lambda_{\max}$ for several molecules, and, the sum-rule theoretical upper limit.

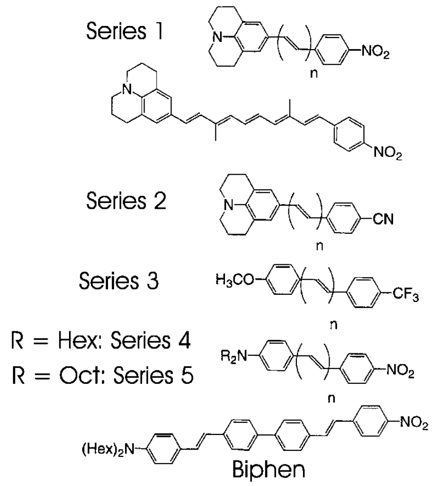

FIG. 4. Chromophores measured in Fig. 3.

$\alpha$ the linear susceptibility. The maximum value of $\alpha$ can be determined using the sum rules, yielding a ratio between electronic and reorientational $\gamma$ of $\gamma^{\mathrm{el}}/\gamma^{\mathrm{reo}} \sim kT/E_{10}$. Given that, at room temperature, $kT < E_{10}$, the reorientational effect can be larger than electronic, but much slower in response. Clearly, the sum rules provide a powerful approach for the study of the limits on nonlinear optical mechanisms.

In summary, we have applied quantum sum rules to calculate the absolute maximum values of off-resonant electronic $\beta$ and $\gamma$ allowed by nature. We find that the three-level model yields the absolute maximum response in the two-level limit and is consistent with observations for all molecules measured with EFISH for $\beta$ and several sets of measurements for $\gamma$. The present paradigms used to design new molecules have resulted in structures whose $\beta_0$ and $\gamma_0$ approach the theoretical limit for a given value of $N$ and $\lambda_{\max}$. The only avenue available to increase the off-resonant hyperpolarizability is to make molecules with one dominant state, redshifted $\lambda_{\max}$, and as many electrons as possible. Perhaps more importantly, the sum rules provide a broader framework that goes beyond the cases that we treat here, in which basic issues can be addressed by considering the relationships between fundamental properties.

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