Z. Phys. D 25, 181–184 (1993)

Atoms, Molecules
Zeitschrift für Physik D and Clusters

Hyperpolarizability of the C_{60} fullerene cluster

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Received: 21 July 1992

Abstract. Motivated by a discrepancy of five orders of magnitude between three different hyperpolarizability measurements on the C_{60} fullerene, we calculated the optical response of this cluster using a tight-binding Hamiltonian and compared the results to those for a benzene molecule. Our Hamiltonian reproduces the linear polarizability and hyperpolarizability of benzene reasonably well. For C_{60}, our calculations of the bare polarizability agree only with two of the optical response measurements and indicate that the corresponding linear and nonlinear response of C_{60} is much larger than that of C_6H_6. We find that screening effects decrease this difference strongly, and also reduce the calculated hyperpolarizability of C_{60} to a value which is two orders of magnitude below the favored measurements.

PACS: 42.65.An; 36.40.+d; 71.45.Gm

In a recent publication [1], a very large absolute value [2] of the third-order optical polarizability $|\gamma| = 1.5 \times 10^{-42}\ \mathrm{m}^5/\mathrm{V}^2 = 1.07 \times 10^{-28}$ esu was reported for C_{60} molecules in benzene solution. This value is enormous compared to that of the benzene solvent [3], $\gamma = 3.85 \times 10^{-36}$ esu, and would make these systems prime candidates for a direct application in nonlinear optical devices. An independent study of the same property, performed on C_{60} in solution using second harmonic generation measurements [4], indicates a substantially smaller value of the hyperpolarizability $|\gamma| = 7.5 \times 10^{-34}$ esu. Similar results to the latter study have been obtained using degenerate four-wave mixing for C_{60} films [5], yielding the third order optical susceptibility for the solid $\chi^{(3)} = 7 \times 10^{-12}$ esu, which corresponds to [6] $|\gamma| \approx 3.13 \times 10^{-34}$ esu.

On top of the discrepancy between the different experimental data, the expression for the nonlinear susceptibility [7] which has been applied to calculate γ in C_{60} is far from its original purpose, and fails by several orders of magnitude to reproduce the data in [1], as also shown in [8]. In an attempt to clarify the situation for these interesting systems [9], we have calculated the optical response of an isolated C_{60} cluster. Since this is not easy even for simple molecules, we first verified the validity of our approach by applying the same computational techniques to the benzene molecule which is well understood.

Let us consider an isolated C_{60} molecule in the electric field $\mathscr{E}$. The induced dipole moment p is given (to the lowest three orders) by

$$p = \alpha \mathscr{E} + \gamma \mathscr{E}^3, \tag{1}$$

where α is the (linear) polarizability and γ is the (third order) hyperpolarizability. Here we also note that the second order hyperpolarizability is zero in centrosymmetric systems such as the C_{60} cluster. These polarizabilities can be determined from the energy change of a molecule due to an external field $\mathscr{E}$ [10]

$$\Delta E = -\tfrac{1}{2} \alpha \mathscr{E}^2 - \tfrac{1}{4} \gamma \mathscr{E}^4. \tag{2}$$

For the corresponding solid, the polarization density P is related to p and $\mathscr{E}$ by the density of constituents N. In cgs units, it is given by [11, 12]

$$P = Np = \chi^{(1)} \mathscr{E} + \chi^{(3)} \mathscr{E}^3. \tag{3}$$

Calculations of higher-order static polarizabilities are very nontrivial due to the high accuracy requirements even in relatively simple systems such as benzene [13]. To evaluate the energy change ΔE in (2) due to an applied electric field, we use a tight-binding Hamiltonian which can be used directly in perturbation theory. Our parametrization has been used successfully to describe the equilibrium structures [14] and electronic excitations [15] of carbon fullerene structures. In presence of the static electric field $\mathscr{E}$ along the z direction, we consider a shift of the on-site energies by $\Delta\varepsilon = -e\mathscr{E}z$.

To obtain the static polarizabilities, we use two approaches. We determine the energy change of the system due to $\mathscr{E}$ using perturbation theory and check the numerical results by directly diagonalizing the Hamiltonian which describes the system in the electric field.

As discussed above, the linear polarizability is related to the energy change of the system. In second-order perturbation theory, this energy change is given by

$$\Delta E^{(2)} = 2 \sum_h \sum_p \frac{V_{hp} V_{ph}}{E_h - E_p}. \qquad (4)$$

Here, p and h label single particle and hole states, respectively, and E_p (E_h) denote the corresponding energies. For the electric field along the z direction, the transition matrix elements are given by $V_{ij} = \langle i | -e\mathscr{E} z | j \rangle$. The prefactor 2 takes care of the spin degeneracy. The third-order nonlinear polarizability is related to the energy change in fourth-order perturbation theory which is given by [16]

$$\begin{aligned}\Delta E^{(4)} = 2 \Bigg[& \sum_h \sum_p \sum_{p'} \sum_{p''} \\ & \times \frac{V_{hp} V_{pp'} V_{p'p''} V_{p''h}}{(E_h - E_p)(E_h - E_{p'})(E_h - E_{p''})} \\ & -2 \sum_h \sum_p \sum_{p'} \sum_{h''} \\ & \times \frac{V_{hp} V_{pp'} V_{p'h'} V_{h'h}}{(E_h - E_p)(E_h - E_{p'})(E_{h'} - E_{p'})} \\ & + \sum_h \sum_p \sum_{h'} \sum_{h''} \\ & \times \frac{V_{hp} V_{ph''} V_{h''h'} V_{h'h}}{(E_h - E_p)(E_{h'} - E_p)(E_{h''} - E_p)} \\ & - \sum_h \sum_p \sum_{p'} \sum_{h'} \\ & \times \frac{V_{hp} V_{ph'} V_{h'p'} V_{p'h}}{(E_h - E_p)(E_h - E_{p'})(E_{h'} - E_p)} \Bigg]. \end{aligned} \qquad (5)$$

$\Delta E^{(4)}$ can also be calculated in perturbation theory using a basis of many-particle states [17]. However, that formula is more difficult to use numerically since its energy denominators can be small, unlike the particle-hole energies in (5). The expressions in (4) and (5), together with (2), yield directly the optical polarizabilities α and γ. We find that the values for α and γ obtained using perturbation theory agree with values which we calculate directly by diagonalizing the tight-binding Hamiltonian.

In order to determine the reliability of our approach, we first calculate the linear and third-order polarizabilities of the benzene molecule, a system which has been studied extensively both experimentally [3, 18] and theoretically [13]. For this purpose, we have to augment our tight-binding Hamiltonian for carbon by parameters suitable for hydrogen. We adjust the difference between the H1s and C2p energies to the difference of the atomic ionization potentials, which gives $\varepsilon(\mathrm{H}1s) = -2.3$ eV. For the hydrogen-carbon hopping integrals, we use $ss\sigma = -3.15$ eV and $sp\sigma = 1.7$ eV at the H—C distance of 1.07 Å found in C_6H_6, obtained by fitting the level spectrum of a CH radical which we calculated using the local density approximation [19]. Our results for C_6H_6 are presented in Table 1. The calculated polarizability in the plane of the benzene molecule is $\alpha_{\parallel} = 31.1$ Å^3. Assuming the same value of the polarizability along the two principal axes in the molecular plane and zero perpendicular to it, we would predict $\langle \alpha \rangle = (2/3)\alpha_{\parallel} = 20.7$ Å^3. This value is consistent with the experimental result $\langle \alpha \rangle = 10.0$ Å^3 obtained for the solution [3] in view of the fact that we have neglected internal screening in the benzene molecule. The third order polarizability turns out to be $\gamma_{\parallel} = 13.5 \times 10^{-36}$ esu, giving $\langle \gamma \rangle = 9.0 \times 10^{-36}$ esu. This is again comparable to the ab initio results [13] in the range of $\langle \gamma \rangle = 1.3 - 1.7 \times 10^{-36}$ esu and experimental data of [3] giving $\langle \gamma \rangle = 3.85 \times 10^{-36}$ esu. Our hyperpolarizability is somewhat larger than the ab initio results which again is to be expected due to our neglect of intramolecular screening.

Table 1. Calculated and observed optical susceptibilities of C_{60} and C_6H_6 molecules

	$\langle \alpha_{\text{bare}} \rangle$ (Å^3)	$\langle \alpha_{\text{screened}} \rangle$ (Å^3)	$\chi^{(1)}$ (esu)	$\langle \gamma_{\text{bare}} \rangle$ (10^{-36} esu)	$\langle \gamma_{\text{screened}} \rangle$ (10^{-36} esu)	$\chi^{(3)}$ (10^{-12} esu)
C_6H_6 [a]	20.7			9.0		
C_6H_6 [b]		10.02			3.85	0.101
C_{60} [a]	215.0	35.7	0.063	346.2	2.3 [c]	0.05 [d]
C_{60} [e]	195	56	0.116			
C_{60} [f]					1.07×10^8	
C_{60} [g]					750	
C_{60} [h]			0.239 [d]		313	7

[a] Present calculation
[b] Experimental values of [3]
[c] This value is obtained using $\langle \alpha_{\text{bare}} \rangle$ and $\langle \alpha_{\text{screened}} \rangle$ of [21]
[d] This value is obtained using the experimental value $n = 2$ of [5] in the expression $n^2 = 1 + 4\pi\chi^{(1)}$
[e] Theoretical values of [21]
[f] Experimental values of [1]
[g] Experimental values of [4]
[h] Experimental values of [5]

Screening is even more important in the large C_{60} cluster than in benzene, and we shall include it in our calculations of this system. For a spherical molecule such as the C_{60} fullerene, the screened linear and third order nonlinear polarizabilities are given by $\alpha_{\text{screened}} = \alpha_{\text{bare}}/(1+(\alpha_{\text{bare}}/R^3))$ and $\gamma_{\text{screened}} = \gamma_{\text{bare}}/(1+(\alpha_{\text{bare}}/R^3))^4$, where R is the radius of the fullerene. The matrix surrounding the cluster in a bulk sample also modifies the external field and hence the screening. We determine the bulk linear susceptibility using $\chi^{(1)} = N\alpha_{\text{screened}}/(1-(4\pi/3)N\alpha_{\text{screened}})$, which is equivalent to the Clausius-Mossotti relation. In the same way, we calculate the third-order nonlinear susceptibility using $\chi^{(3)} = N\gamma_{\text{screened}}/(1-(4\pi/3)N\alpha_{\text{screened}})^4$. In these equations, $N \approx 1/720$ Å^3 is the density of clusters and α_{screened} and γ_{screened} are the screened linear and nonlinear polarizabilities of an isolated cluster, respectively.

Our results for the C_{60} clusters and the solid are given in Table 1. As mentioned above, our perturbation theory calculations are consistent with results obtained by a direct diagonalization of the Hamiltonian in a weak external field. We fit the energy to (2) using $\mathscr{E} = 0 - 0.01$ V/Å which is much weaker than the field $\mathscr{E} \approx 0.7$ V/Å when the first level crossing occurs. We find a large bare polarizability $\alpha_{\text{bare}} = 215$ Å^3, which is reduced considerably due to the internal depolarization field to $\alpha_{\text{screened}} = 35.7$ Å^3, in agreement with our previous calculation [15]. The latter value is very close to that for a classical metallic sphere with a radius $R = 3.5$ Å, $\alpha_{\text{screened}} = R^3 = 42.9$ Å^3. Of course, such large screening cannot be expected in the planar benzene molecule.

The polarizability of an isolated cluster can be inferred from the linear susceptibility or index of refraction of the bulk material using the Clausius-Mossotti equation. Our predicted susceptibility is $\chi^{(1)} = 0.06$, in relatively poor agreement with the experimental value $\chi^{(1)} = 0.24$ [5]. Part of the reason for this discrepancy is that Coulomb interaction is overestimated by the approximation of [15]; a better treatment of the Coulomb interaction with the tight-binding Hamiltonian yields a susceptibility of $\chi^{(1)} = 0.116$ [21]. Also, the crystal field in the bulk breaks the symmetry of the C_{60} molecule, so that direct HOMO→LUMO transitions can occur. The susceptibility of the solid would also be increased by the possibility of a virtual electron transfer between C_{60} molecules.

We find a very large *positive* value of $\langle\gamma_{\text{bare}}\rangle = 3.5 \times 10^{-34}$ esu for the bare third order hyperpolarizability, more than one order of magnitude larger than in benzene. Our value is in fact within the range of two of the experiments, [4] and [5]. However, this value gets screened by the induced dipole field in the C_{60} which will be much stronger than in the planar C_6H_6 structure [20]. Using the screening factor $\alpha_{\text{screened}}/\alpha_{\text{bare}} = 3.5$ from [21], we find $\langle\gamma_{\text{screened}}\rangle = 2.3 \times 10^{-36}$ esu, about the same as in benzene. For the solid, we obtain $\chi^{(3)} = 5 \times 10^{-14}$ esu using the empirical susceptibility, which is almost two orders of magnitude smaller than the experimental value of [5].

We do not understand the origin of this large discrepancy. One possible reason is the high laser frequency $\hbar\omega \approx 1.2$ eV used in the experiments. We have considered the effect of the frequency dependence in the perturbation calculation, (5). We find that a substantial change in the hyperpolarizability only occurs due to virtual two-photon transitions within a very narrow energy range of the HOMO − LUMO transition. Since the transition is spread out by crystal field effects, we ignore this enhancement in the present paper. Another possibility is that one must go beyond the tight-binding approximation to calculate this quantity, as seems to be the case for the linear susceptibility. It would be advisable to perform a more detailed study of the optical response of the C_{60} cluster using ab initio techniques such as the LDA. In any case, our result is more than seven orders of magnitude below the data quoted in [1], and we conclude that these data are probably in error.

We thank Aurel Bulgac, Neng-Jiu Ju, Gregor Overney and Weiqing Zhong for useful discussions. We acknowledge financial support by the National Science Foundation under Grant No. PHY-8920927.

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11. For the solids, the conversion factors from SI to esu are $\chi^{(1)}[\text{SI}] = 4\pi\chi^{(1)}[\text{esu}]$ and $\chi^{(3)}[\text{SI}] = 4\pi/(9\times10^8)\chi^{(3)}[\text{esu}]$
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