

Electric and magnetic properties of fullerenes

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We present fully analytical *ab initio* calculations of the electric polarizability, the second hyperpolarizability, and the magnetizability of the fullerenes C_{70} and C_{84} at the self-consistent field level of theory using large basis sets and—in the case of the magnetizability—London atomic orbitals in order to obtain gauge-origin independent results. These calculations are the first *ab initio* studies of such properties for C_{70} and C_{84} , and all results are expected to be of near Hartree–Fock limit quality. By comparison with similar results reported earlier for C_{60} , valuable insight into the electronic structure of the fullerenes is obtained. © 1998 American Institute of Physics. [S0021-9606(98)30426-2]

I. INTRODUCTION

The fullerenes have been experimentally known for more than 10 years,¹ and a large number of publications, experimental as well as theoretical, have been devoted to this subject.² Many attempts have been made at rationalizing the electronic structure of the fullerenes, in particular to understand how the mixing of five- and six-membered rings in a three-dimensional structure affects the properties of these molecules.

The behavior of the fullerenes in electric fields, and in particular their nonlinear optical properties, attracted early much attention due to the potential use of this class of molecules as efficient nonlinear optical devices. This interest was initiated by the first degenerate four-wave mixing measurements on C_{60} of Blau *et al.*,³ which later was shown to be three orders of magnitude too large.^{4,5} Later studies indicate that the potential of the fullerenes as efficient materials in nonlinear optics can at the best be considered modest.⁶

The presence of five- and six-membered rings in the fullerenes has prompted a number of studies of the magnetic properties of these molecules,² as these molecules could be the prototype for spherical aromaticity, a concept which although discussed in the literature still remains elusive, see the discussion in Ref. 7. A number of *ab initio* calculations of the noble gas shieldings of endohedral fullerenes have been presented,^{8–10} as well as some studies of the magnetizability of C_{60} .^{11,12}

In this work we consider several fullerenes at the *ab initio* level—namely C_{60} , C_{70} , and C_{84} . By investigating several fullerenes at an accurate uniform level of theory, we may hope to gain insight into possible structure-to-property relations for these compounds. To facilitate this goal, we investigate both the electric and the magnetic properties of these molecules at comparable levels of accuracy. By com-

paring the properties of the fullerenes when subject to these different external perturbations, one might indirectly obtain an understanding of the electronic structure of these molecules that would otherwise be difficult to achieve.

We will in Sec. II briefly comment on the method of calculations used in this work. Due to the different nature of the electric and magnetic properties, as well as their different basis set requirements, we discuss the calculations and results in two separate sections, Secs. III and IV. In Sec. V, we use the calculated electric and magnetic properties of the fullerenes to draw some general conclusions about the electronic structure of the fullerenes.

II. METHOD OF CALCULATION

In this work, we calculate the polarizabilities and hyperpolarizabilities from the cubic response function¹³ as recently implemented in the Dalton program¹⁴ at the self-consistent-field (SCF) and multiconfigurational SCF (MCSCF) level of theory.^{15,16} The magnetizabilities are similarly obtained from the linear response function with the use of London atomic orbitals to ensure gauge-origin independence and fast basis set convergence.¹⁷

The calculation of the (hyper)polarizabilities and magnetizabilities of the fullerenes reported here exploits all the recent improvements made to our program. The calculation of the properties is ‘‘double-direct’’: It is integral direct, which means that all two-electron integrals are generated on the fly;^{18,19} and it is matrix direct, which means that the large generalized electronic Hessians needed for solving the response equations are not explicitly constructed, but rather contracted with the response or solution vectors whenever needed.²⁰ The calculation of all two-electron integrals—including the differentiated two-electron integrals needed for the calculation of the magnetizability using London atomic orbitals²¹—have been parallelized and displays a parallel efficiency of more than 97% when up to 64 processors are being used.²² We use integral screening at all stages of the

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calculation that involve undifferentiated two-electron integrals.²³

The symmetry of C_{70} is known to be D_{5h} . However, as the Dalton program can use only subgroups of the D_{2h} point group, the calculations on C_{70} were done in the C_s point group. C_{84} can, on the other hand, exist in several different structures of different symmetries. However, it is known experimentally that the dominating ones are the D_2 and D_{2d} symmetries, which exist in a 2:1 ratio according to recent NMR measurements.²⁴ Due to the high cost of the calculations for the C_{84} molecule, we have chosen to investigate only the most abundant of these structures—that is, the D_2 structure. Semiempirical calculations indicate that the difference in the second hyperpolarizabilities of the D_2 and D_{2d} structures is small.^{25,26}

As for C_{60} ,^{6,12} we have used *ab initio* SCF optimized geometries obtained using a contracted $[4s3p]$ set. In the case of C_{70} , the optimized geometry was provided to us by Vahtras,²⁷ whereas for C_{84} we optimized the structure using the first-order geometry optimization routines²⁸ of the Dalton program imposing D_2 symmetry. The geometries for C_{70} and C_{84} are available from the authors on request; the geometry of C_{60} can be found in Ref. 6.

The basis-set requirements for accurate calculations are different for electric and magnetic properties. Although we did attempt to find a basis set suitable for both electric and magnetic properties (*vide infra*), it turned out to be difficult to find a single set of manageable size that gives accurate results for all properties.

III. THE POLARIZABILITIES OF THE FULLERENES

A. Computational details

We have previously calculated the polarizability and second hyperpolarizability of C_{60} .⁶ In that study, we used an extended basis set of 4-31G quality,²⁹ with a diffuse p function and a diffuse polarizing d function added, both with exponent 0.05. Despite being relatively small, this basis set has been shown to give accurate linear and nonlinear electric properties, see for instance Refs. 22 and 30. In the case of C_{60} , this basis set contains 1020 basis functions. For C_{84} this basis set would give a total of 1428 basis functions which, although doable, is a bit larger than is computationally tractable, in particular considering the lower symmetry of C_{70} and C_{84} .

For these reasons, we tested the 6-31++G basis^{31,32} (which does not include the d function but has been shown to perform well in calculations of nonlinear optical properties of large molecules)³³ in calculations of the electric properties of C_6H_6 , C_{24} and C_{60} . The results for this basis compare favorably with the results obtained using the extended 4-31G(p,d) set (see Table I) as well as Sadlej's polarized basis set,^{34,35} designed to give accurate electric properties. On the basis of the results in Table I, the 6-31++G basis was used in the calculations of the electric properties of C_{70} and C_{84} . For C_{84} , the 6-31++G basis set gives a total of 1092 basis functions.

TABLE I. Static polarizability (10^{-24} cm³) and second hyperpolarizability (10^{-36} esu) obtained for some molecules using different basis sets.

Molecule	Basis set	α_{xx}	α_{zz}	α	γ_{xxxx}	γ_{xyxy}	γ_{xxzz}	γ_{zzzz}	γ
C_6H_6	6-31++G	11.2	5.8	9.4	4.01	1.33	2.79	7.65	5.91
	4-31G(p,d)	11.4	5.5	9.4	7.17	2.39	2.80	5.63	7.91
	Sadlej	12.0	6.7	10.3	6.17	2.05	3.19	7.43	7.33
C_{24}	6-31++G	33.4	29.0	32.0	38.5	12.8	9.6	24.0	33.0
	4-31G(p,d)	33.3	28.9	31.8	31.4	10.5	8.3	21.5	27.6
	Sadlej	34.7	30.2	33.2	41.3	13.8	10.1	28.0	35.7
C_{60}	6-31++G	75.1	75.1	75.1	55.0	18.3	18.3	55.0	55.0
	4-31G(p,d)	75.3	75.3	75.3 ^a	57.3	19.1	19.1	57.3	57.3

^aThis number corrects a misprint in our previous paper on C_{60} , Ref. 6.

B. Results

We have collected the results for the polarizability and second hyperpolarizability in Table II, and focus our attention on the average polarizability and second hyperpolarizability defined according to

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}), \quad (1)$$

$$\gamma = \frac{1}{5} \sum_{i,j} \gamma_{ijij}, \quad i, j \in \{x, y, z\}. \quad (2)$$

Apart from the recent tight-binding Hamiltonian calculations of Fanti *et al.*,³⁶ there does not appear to be any *ab initio* calculations of these properties for C_{70} and C_{84} . Density functional theory (DFT) studies of C_{60} have been presented by Matsuzawa and Dixon.³⁷ At the semiempirical level, three studies of the electric properties of C_{60} , C_{70} , and C_{84} using a sum-over-states valence-electron Hamiltonian (SOS-VEH)^{26,38} and a SOS-complete neglect of differential overlap (CNDO/S) configuration interaction (CI) wave function²⁵ have been presented. In addition, C_{60} and C_{70} have been studied by Matsuzawa and Dixon using finite fields with a modified neglect of differential overlap (MNDO) wave function in the PM3 parameterization,³⁷ and by Li,

TABLE II. Static polarizability (10^{-24} cm³) and second hyperpolarizability (10^{-36} esu) of the fullerenes as obtained using the 6-31++G basis set, and earlier semiempirical results.

Molecule	Ref.	α	γ
C_{60}	This work	75.1	55.0
	37	63.9	25.1
	38	154.0	202.0
	36		154.6
	25		458
	26		24.7
C_{70}	39,40		690
	This work	89.8	75.4
	37	79.0	45.2
	38	214.3	862.3
	36		294.5
	25		857
C_{84}	26		54.5
	39,40		1300
	This work	109.4	82.4
	36		426.9
	25		1812
	26		63.6

Feng, and Sun using SOS intermediate neglect of differential overlap (INDO)-CI methods.^{39,40} The results of these investigations are also collected in Table II.

A direct comparison between the results obtained shows significant differences: All of the SOS approaches give a second hyperpolarizability that is about an order of magnitude larger than that predicted by the *ab initio* calculations. We believe that this discrepancy arises from the truncation of the expansion in excited states in the explicit summation of contributions to the second hyperpolarizability in SOS calculations, which appears to neglect important negative contributions to the second hyperpolarizability. This is further corroborated by the observation that the sum-over-states methods predict larger ratios between the second hyperpolarizabilities for the larger fullerenes than do both the finite-field and our *ab initio* results. The danger of this truncation of the sum over excited states is perhaps most clearly illustrated by Fig. 2 of Ref. 40, where γ_{zzzz} remains almost constant for the first 180 excited states included, and then changes dramatically.

In contrast, the second hyperpolarizability obtained in the finite-field methods^{26,37} are of the same order of magnitude, but somewhat smaller than our results (when corrected for the difference in definition of γ). Matsuzawa and Dixon found that whereas the γ calculated from the energy expansion is stable with respect to the convergence of the wave function, the hyperpolarizability obtained from a dipole expansion is unstable.³⁷ Moreover, their dipole-derived γ differs significantly from the energy-derived, indicating that the calculation of the second hyperpolarizability by finite-field methods might not be numerically stable for these large molecules.

The problems described above are absent in our analytical approach. On the basis of the calculations for the smaller fullerenes described in Sec. III A, we believe our second hyperpolarizabilities to be within 20% of the Hartree-Fock limit—using a rather conservative error bar—with the results being most likely too small. It is difficult to estimate the importance of electron correlation on the calculated properties, but we note that the random phase approximation (RPA) method has been shown to give excellent agreement for optical band gaps and nonlinear properties of larger, conjugated molecules.³³ Correlation effects are therefore expected to be small for these “conjugated” molecules as well.

Comparison with experiment is also difficult. In the case of C_{60} , the experimental results vary by almost 11 orders of magnitude.⁶ Although this may partly be due to differences in the convention for defining γ , medium effects, and differences in dispersion of the various optical processes, it is clear that a significant uncertainty is connected with the experimentally reported hyperpolarizabilities.⁶ For this reason, we concentrate instead on ratios between properties, and consider only experimental numbers from the same laboratories. Dispersion is still a factor that needs to be considered in comparing with our static results, but it will be less crucial for a ratio comparison than for a direct comparison.

The ratios we obtain for C_{70}/C_{60} , C_{84}/C_{60} , C_{84}/C_{70} are 1.20, 1.45, 1.22 for the polarizability and 1.37, 1.50, 1.09 for the second hyperpolarizability. In most cases, these ratios are

significantly smaller than those obtained in the various semiempirical approaches, which means that the deviations between the semiempirical and the *ab initio* results increase as the molecules grows larger. The only exceptions to this observation are the C_{70}/C_{60} γ ratio of Li *et al.*⁴⁰ (1.30), and the C_{84}/C_{70} γ ratio of Moore *et al.*²⁶ (1.18).

Experimentally, there has been several studies of the second hyperpolarizability of both C_{60} and C_{70} using different optical processes, producing several fairly reliable ratios for these molecules. Rosker *et al.* obtained a C_{70}/C_{60} ratio of 1.5 using degenerate four-wave mixing (DFWM) at 633 nm.⁴¹ A somewhat larger ratio of 1.7 was obtained in an electric-field induced second harmonic generation (EFISH) experiment at 1.91 μm by Wang and Cheng.⁴² Our ratio, although smaller, is consistent with the latter experiment when the error bars are taken into account.

In the case of C_{84} , we are aware of two experiments. In an optical Kerr effect (OKE)⁴³ study, the nonlinear properties of C_{60} , C_{70} , and C_{84} were studied. Although the experiment has been criticized for using an impure sample of C_{84} ,⁴⁴ their ratio of 1.1 for C_{84}/C_{70} is in excellent agreement with our calculated ratio. However, the ratio between C_{70} and C_{60} obtained from these experiments is 2.9, thus significantly larger than that reported in the DFWM⁴¹ and EFISH⁴² experiments, as well as our static second hyperpolarizabilities. It was argued in Ref. 43 that the frequency of the OKE experiment is close to significant absorptions in both C_{70} and C_{84} , thus possibly explaining the large increase observed in the OKE from C_{60} to C_{70} and C_{84} .

In a recent DFWM study of a number of fullerene cages from C_{60} to C_{96} ,⁴⁵ the ratios for the second hyperpolarizability were found to be 3.63, 5.45, and 0.92 for C_{70}/C_{60} , C_{84}/C_{60} , and C_{84}/C_{70} , respectively. Although the ratios are much larger than those obtained in our calculations, these experiments confirm the high nonlinear efficiency of C_{70} . Our calculations do not, however, give a smaller γ for C_{84} than for C_{70} . The DFWM experiment also found C_{78} to possess a large value for γ compared with the other fullerene cages. Clearly, *ab initio* calculations of the DFWM process at the experimental frequency of 532 nm for the fullerenes C_{60} , C_{70} , C_{78} , and C_{84} would be of great interest.

IV. THE MAGNETIZABILITY OF THE FULLERENES

A. Computational details

For the calculation of magnetizabilities from London orbitals, we have in several publications^{46–48} demonstrated the excellent performance of the augmented correlation-consistent basis (aug-cc-pVDZ) set of Dunning and Woon.^{49,50} However, as already discussed in our paper on C_{60} ,¹² there appears to be a favorable basis set saturation for larger molecules, enabling highly accurate results—i.e., results that are less than 1% to 2% off the Hartree-Fock limit—to be obtained even with the smaller cc-pVDZ basis set. In our previous paper, this basis set has been used with good results both relative to basis-set limit extrapolations and relative to experiment.¹²

Attempts were made to find a basis set that is appropriate for the simultaneous study of (hyper)polarizabilities and

TABLE III. The magnetizability of the fullerenes reported in ppm cgs as obtained using the cc-pVDZ basis set and London atomic orbitals.

Molecule	ξ^{dia}	ξ^{para}	ξ
C ₆₀	-13 073	12 714	-359
C ₇₀	-18 222	17 547	-675
C ₈₄	-27 217	26 621	-596

magnetizabilities. In particular, as our program calculates integrals in blocks of the same angular momentum of the basis functions, the single *d* orbital in the cc-pVDZ basis set makes the integral calculation significantly more CPU-time consuming than, for example, a pure *sp*-basis like the 6-31++G set. However, test calculations on C₆₀ in the 6-31++G basis set gave an isotropic magnetizability of -389 ppm cgs, which is almost 10% off our estimated Hartree-Fock limit of -359 ± 5 .¹² Thus, although this 6-31++G result is in good agreement with the most recent calculations by Zanasi, Lazzeretti, and Fowler¹¹ of -381/-391 ppm cgs, we consider this to be an overestimation of the Hartree-Fock magnetizability. The overestimation of the magnetizability by the 6-31++G basis is observed also in calculations on benzene and coronene (C₂₄H₁₂). For the isotropic magnetizability of benzene, the results obtained in the cc-pVDZ, aug-cc-pVDZ, and 6-31++G basis sets are -60.7, -60.2, and -63.4 ppm cgs; these results bracket the Hartree-Fock limit of Lazzeretti, Malagoli, and Zanasi of -61.8 ppm cgs.⁵¹ For coronene, the calculated magnetizabilities are -293.3, -292.8, and -300.5 ppm cgs, respectively, showing that whereas the cc-pVDZ and aug-cc-pVDZ results converge, the 6-31++G results continue to overestimate the magnetizability.

Even though the 10% deviation of 6-31++G noted for C₆₀ may be considered small, it is of the order of the effects we are looking for and we have for this reason chosen to use the cc-pVDZ basis set in the following calculations, despite the fact that this means that we use different basis sets for the electric and magnetic properties of the fullerenes. The [3*s*2*p*1*d*] contracted cc-pVDZ basis set gives a total of 1176 basis functions for C₈₄.

B. Results

We have collected the results of our London cc-pVDZ calculations in Table III. Apart from the STO-3G field-independent orbital calculations by Baker *et al.* on C₇₀,⁵² we are unaware of other *ab initio* calculations of the magnetizability of C₇₀ and C₈₄. In contrast, for C₆₀ a number of calculations have been presented by Fowler and co-workers,^{53-55,11} with which we have already compared our London results.¹²

STO-3G calculations on C₇₀ and C₆₀ predicted a fairly modest C₇₀/C₆₀ ratio for the isotropic magnetizability of 1.37 and 1.3 at the no-London⁵² and London¹² levels, respectively, supporting a model where the electrons are fully delocalized. These estimates are significantly smaller than the experimental ratios of 2.1 observed using the Faraday method⁵⁶ and 2.0 obtained using a superconducting quantum interference device (SQUID) magnetometer.⁵⁷ In contrast,

our Hartree-Fock limit magnetizability ratio between C₇₀ and C₆₀ is 1.88, in excellent agreement with the most recent experimental ratio.⁵⁷

The magnetizability of diamagnetic substances is a very small effect. Combined with the difficulties in getting significant quantities of pure C₈₄, these circumstances have probably prevented the experimental determination of the magnetizability of C₈₄. However, considering the excellent agreement for the C₇₀/C₆₀ magnetizability ratio as well as the general reliability of Hartree-Fock London calculations of magnetizabilities, we believe the calculated magnetizability ratio of 1.66 for C₈₄/C₆₀ (0.88 for C₈₄/C₇₀) to be close to what would be observed experimentally.

It is interesting to observe that the magnetizability decreases from C₇₀ to C₈₄. This result confirms previous observations made in both semiempirical London-orbital calculations of the ring current contributions to the magnetizability of the fullerenes⁵⁸ and in Hartree-Fock London-orbital calculations of ³He shieldings in various endohedral fullerenes.⁹ Both studies predict C₇₀ to have significantly larger ring current magnetizability and endohedral chemical shifts than C₆₀ and C₈₄.

Our latest fit of atomic magnetizabilities as obtained from a number of studies of the magnetizability of hydrocarbons⁵⁹ (all calculated at the same level of theory as in this work) gives a carbon magnetizability of -4.53 ppm cgs. This estimate gives an additive magnetizability—following the principles of Pascal's rule^{60,61}—of -272, -317, and -381 ppm cgs for C₆₀, C₇₀ and C₈₄, respectively. Assuming that the differences between our calculated magnetizabilities and those obtained from this additivity scheme are due to ring currents (obtainable from London theory calculations),⁵⁸ these ring currents are estimated to be -87 (C₆₀), -358 (C₇₀), and -216 ppm cgs (C₈₄). Relative to C₆₀, the ring current induced magnetizabilities are 4.1 and 2.5 for C₇₀ and C₈₄, respectively. Although much larger than those predicted by semiempirical London theory⁵⁸ (2.9 and 1.6) the trend is still the same. Our results are also corroborated by the excellent agreement observed with respect to the experimental C₇₀/C₆₀ magnetizability ratio.

Much of the discussion of the magnetic properties of fullerenes has focused on the presence of dia- and paramagnetic ring currents in the fullerenes and the implications that such currents would have for the possible aromatic nature of these molecules.^{1,62,53} We note that, whereas the ratio of the isotropic magnetizability between C₇₀ and C₆₀ and between C₈₄ and C₇₀ are 1.9 and 0.88, respectively, the corresponding ratios of the separate dia- and paramagnetic contributions (which are almost identical but oppositely directed) are 1.4 and 1.5, respectively. In violation of Pascal's rule, both ratios are larger than the corresponding ratios of the number of atoms. However, the ratios do suggest the presence of strong dia- and paramagnetic ring currents giving a nonadditive increase in the dia- and paramagnetic contributions to the magnetizability. The magnitude of the dia- and paramagnetic contributions relative to the total residual magnetizability (which constitute only about 3%) indicate that the balance between dia- and paramagnetic ring currents is a delicate one and that it should be difficult to estimate *a priori* the

strengths of either of these from simple models only based on geometrical parameters.

V. DISCUSSION

The previous two sections have presented high-level theoretical results for the electric and magnetic properties of the fullerenes. Although the effects of correlation are difficult to estimate, we believe that we have arrived at quite reliable descriptions of the behavior of C_{60} , C_{70} and C_{84} in electric and magnetic fields.

For the polarizability, the increase from C_{60} to C_{70} and then to C_{84} shows an almost linear dependence on the number of atoms in the molecules, with the increase in the polarizability slightly larger than the ratio of the atoms. This behavior should be contrasted to that of the second hyperpolarizability and of the magnetizability, which both show a significantly enhanced increase relative to the increase in the number of atoms when going from C_{60} to C_{70} . In contrast, for the second hyperpolarizabilities the C_{84}/C_{70} ratio is less than the ratio of the number of the atoms, and for the magnetizability it is less than one.

The fullerenes studied here are similar in that they all have 12 isolated (not adjacent) pentagons, differing only in the number of hexagons. In C_{60} , the smallest fullerene with all pentagons isolated, the hexagons are associated with diamagnetic ring currents, whereas the pentagons give rise to opposing paramagnetic ring currents.⁵⁵ Therefore, one would naively expect a steady increase in the diamagnetic ring current contribution to the magnetizability with the number of carbon atoms. Nevertheless, this prediction contrasts with the results obtained here as well as in other studies of the magnetic properties of the fullerenes.^{58,9} The construction of C_{70} from C_{60} may be envisaged as arising by inserting an equatorial belt of five hexagonal rings between the two eclipsed hemispherical parts of the C_{60} molecule. This insertion of a hexagonal band does not appear to break but rather to enforce the electronic delocalization when going from C_{60} to C_{70} . By adding more hexagons, beyond C_{70} , the efficiency in the electron delocalization breaks down, giving less efficient diamagnetic ring currents—although they are enhanced compared to the paramagnetic currents (as seen from the general increase in the dia- and paramagnetic contributions).

Hyperpolarizabilities are known to be tangible measures of electron delocalization, as they increase significantly with increased oligomeric length and reduced bond length alternation, both indicative of electron delocalization. The above rationalization for changes in the electronic structure of the fullerenes is thus corroborated by our results for the second hyperpolarizability. The enhanced electron delocalization from C_{60} to C_{70} displays itself in significantly increased values of γ . As this delocalization becomes less efficient when passing to C_{84} , a smaller increase in the (hyper)polarizability is observed.

On the basis of these results, it is difficult to say whether C_{70} has exceptional electron delocalization, or whether this pronounced delocalization applies to both C_{60} and C_{70} . However, the fact that these allotropes are the most abundant ones experimentally may indicate that both these molecules

have increased electronic delocalization, and thus stability, relative to other fullerenes.

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