Time-dependent Density Functional Results for the Dynamic Hyperpolarizability of C_{60}

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The experimental, as well as theoretical, values for the frequency-dependent hyperpolarizability of C_{60} differ by orders of magnitude. We present the first density functional calculation of a molecular frequency-dependent hyperpolarizability. Our implementation is very economical, enabling the treatment of molecules of this size, in a potentially much more accurate way than can be obtained with alternative methods. Our results strongly support the recent results by Geng and Wright, who report much lower experimental values than previous authors. [S0031-9007(97)03020-2]

At present, there is much interest in the field of nonlinear optics. Possibly interesting technological applications for nonlinear optical materials range from optical signal-processing devices to all-optical computers. Theoretical calculations can be a useful aid in understanding relationships between molecular structure and nonlinear optical properties and in the prescreening of molecules which might exhibit large nonlinear polarizabilities (hyperpolarizabilities). The experimental determination of these properties, on the other hand, is usually much more time consuming and expensive.

Organic molecules with delocalized electron systems are of particular interest because of their potentially large nonlinear optical response. Here, we will treat one of these organic molecules for which huge hyperpolarizabilities have been reported experimentally: the Buckminster fullerene C_{60}. For this system, of great current interest, discrepancies of 10 orders of magnitude [1] exist in the experimental data. An accurate theoretical determination is therefore particularly timely.

For a system of the size of C_{60}, and also for other large organic molecules such as linear polymeric chains, it is important to have a theoretical approach which is both accurate and efficient. For hyperpolarizabilities, accuracy demands that both frequency dispersion and the effects of electron correlation are taken into account. Such an approach could also serve as a benchmark for more approximate calculations. The correlated methods conventionally used in quantum chemistry can be very useful in this respect, but they are too time consuming to be used for large molecules. On the other hand, time-dependent Hartree-Fock (TDHF) and semiempirical calculations may not always be of the desired accuracy.

In the framework of time-dependent density functional theory (TDDFT) (an extensive review is provided by Ref. [2]), the frequency-dependent hyperpolarizability tensors are obtained in a formally exact manner. We have developed a scheme which uses TDDFT for the calculation of the dynamic first hyperpolarizability tensors β. Higher nonlinear polarizabilities can be obtained by finite differentiation. Our scheme applies to molecules as well as atoms

and requires the solution of the first order response equations only, making it both more generally applicable and more efficient than Senatore and Subbaswamy's approach [3]. The N^3 scaling of the computational cost of our hyperpolarizability calculations is the same as for an ordinary DFT calculation, making applications to large molecules possible. Our previous calculations on linear polarizabilities and related properties [4–7] show that an accuracy is obtained which is higher than that obtained at the TDHF level and often comparable to extensive correlated *ab initio* quantum chemical calculations.

Outline of theoretical approach.—In the TDHF case, the starting point for the solution of the higher order response equations is given by [8–10]:

$$FC - i\frac{\partial}{\partial t}SC = SC\varepsilon, \qquad (1)$$

where C is the time-dependent coefficient matrix of the orbitals expanded in a fixed atomic orbital basis set, S is the overlap matrix of the atomic orbitals, F is the Fock matrix, and ε is a Lagrangian multiplier matrix, associated with the constraint that the orbitals remain orthonormal at all times:

$$\frac{\partial}{\partial t}(C^{\dagger}SC) = 0. \qquad (2)$$

In TDHF theory this equation is derived from Frenkel's principle [11]. In TDDFT, one can derive a similar equation, where the Fock matrix F is replaced by the appropriate DFT equivalent. This can be shown by considering orbital variations which minimize the action functional in TDDFT [2,12], under the orthonormality constraint. One could choose the Lagrangian multiplier matrix ε to be identical to zero, in which case the "canonical" time-dependent Kohn-Sham equations [2,12] arise:

$$\left[-\frac{\nabla^2}{2} + v_s[\rho](\mathbf{r}, t)\right]\phi_i(\mathbf{r}, t) = i\frac{\partial}{\partial t}\phi_i(\mathbf{r}, t), \qquad (3)$$

where $v_s[\rho](\mathbf{r}, t)$ is the time-dependent Kohn-Sham potential, consisting of the external potential, a Hartree

term, and an unknown exchange-correlation term. Equation (2) could alternatively be obtained by replacing the rapidly oscillating orbitals ϕ_i in Eq. (3) by orbitals which differ from these by a time-dependent phase factor $\exp[i \int^t \varepsilon_i(t')dt']$. One may thus proceed similarly in the TDDFT case as in the TDHF case. We have followed Karna and Dupuis [9], who present detailed equations for all first and second order hyperpolarizability tensors associated with external electric perturbations consisting of a static and a monochromatic part:

$$v_{\text{ext}}(\mathbf{r}, t) = \mathbf{E}(1 + e^{i\omega t} + e^{-i\omega t}). \qquad (4)$$

They obtain their results by expanding the matrices F, C, and ε of Eq. (1) into different orders of the external perturbation and in different frequency components (the overlap matrix S is independent of the perturbation). The density matrix D, given by

$$D = CnC^\dagger, \qquad (5)$$

where n is the occupation number matrix, is likewise expanded. The goal is to obtain expressions for the various first hyperpolarizability tensors, such as the tensor $\beta_{ijk}(-2\omega; \omega, \omega)$ governing the second harmonic generation (SHG). This tensor is obtained by taking the trace of the product of the second order density matrix D and the dipole moment matrix H:

$$\beta_{ijk}(-2\omega; \omega, \omega) = -\text{Tr}[H^i D^{jk}(\omega, \omega)]. \qquad (6)$$

This expression contains the second order density matrix D^{jk}. However, the so-called $(2n + 1)$-theorem of perturbation theory states that the energy can be calculated to third order if the wave function is known to first order only. Thus, Eq. (6) can be rewritten such that only first order quantities ($C^{(1)}$, $D^{(1)}$, $F^{(1)}$, and $\varepsilon^{(1)}$) appear on the right-hand side, as explicitly shown by Karna and Dupuis. In the SHG case, the first order equations need to be solved at frequencies 0, ω, and 2ω. The TDHF results [8–10] using the $(2n + 1)$-theorem can directly be used in the DFT case. The only difference worth mentioning is that the exchange-correlation potential in the DFT case depends nonlinearly on the density, which is not true for the HF exchange term. This leads to certain extra terms in the DFT expressions, which do not, however, pose computational problems.

Both for the first and second functional derivatives of the exchange-correlation potential, we apply the so-called adiabatic local density approximation (ALDA) [2], which is by far the most usual approximation and appears to work quite well [4–7]. More details on our implementation will be presented elsewhere. Related DFT work has been done by Colwell *et al.* [13] for static hyperpolarizabilities, Dal Corso *et al.* [14] for the nonlinear optical susceptibility of a solid, and Gonze [15], who reviews density functional perturbation theory for static perturbations.

Frequency-dependent hyperpolarizability of C_{60}.—We have calculated the frequency-dependent hyperpolariza-

bility of C_{60}. Because of the icosahedral symmetry (I_h), the first order hyperpolarizability β of C_{60} vanishes, making the second hyperpolarizability γ the first nonvanishing term after the linear polarizability. Our results for γ are obtained by analytically calculating the β tensors in a small electric field (0.001 a.u.), which leads to a negligible error. This approach enables us to restrict ourselves to the solution of the first order response equations. However, it also implies a limitation to nonlinear optical effects in which no more than two time-varying fields appear. For this reason we can calculate the tensors $\gamma(-2\omega; \omega, \omega, 0)$, $\gamma(-\omega; \omega, 0, 0)$, $\gamma(0; \omega, -\omega, 0)$, and $\gamma(0; 0, 0, 0)$ governing electric field induced SHG (EFISH), the electro-optical Kerr effect (EOKE), the electric field induced optical rectification (EFIOR), and the static second hyperpolarizability, respectively. However, we can only make indirect statements about the tensors governing third harmonic generation (THG), $\gamma(-3\omega; \omega, \omega, \omega)$ and degenerate four wave mixing (DFWM), $\gamma(-\omega; \omega, -\omega, \omega)$. These indirect statements are based upon the following dispersion formula [16,17], which holds for small frequencies:

$$\gamma(-\omega_\sigma; \omega_1, \omega_2, \omega_3) =$$
$$\gamma(0; 0, 0, 0)(1 + A\omega_L^2 + \ldots), \qquad (7)$$

where $\omega_L^2 = \omega_\sigma^2 + \omega_1^2 + \omega_2^2 + \omega_3^2$. We have determined the constant A by a fit to our EOKE and EFISH results, thus obtaining approximate results for THG and DFWM at small frequencies.

In the static case, the γ tensor has only one independent component, γ_{zzzz}, which is equal to the average γ. Because this is still approximately true in the frequency-dependent case (Kleinman symmetry) in the off-resonant region, we have restricted our calculations to γ_{zzzz}. We performed our calculations at the Becke-Perdew optimized geometry, where the two different C—C bond lengths are 1.397 Å (C=C) and 1.452 Å (C—C), respectively, in very good agreement with experimental NMR data [18] of 1.40 and 1.45 Å.

We have tested that the accuracy for certain technical parameters [concerning numerical integration, convergence of the ordinary self-consistent field (SCF), and the iterative solution of the first order response equations] in the calculation is more than sufficient for our present purposes.

The basis set for our calculation consists of a valence triple zeta Slater type orbital basis set with one polarization function. In order to improve the flexibility of the basis in an economic and numerically stable way, we added several diffuse functions in the center of the molecule, describing both the regions inside and far outside the C_{60} cage. Further improvements in the basis set will slightly increase our results, but probably not by more than 5% to 10%.

We use both the local density approximation (LDA) and LB94 [19] exchange-correlation potentials in our calculations, using the ALDA for its derivatives. The LB94 potential substantially improves the LDA results

in linear response calculations [5,7], due to its correct Coulombic asymptotic behavior. The LDA potential decays exponentially, resulting in overestimations for polarizabilities ($\sim$5%) and hyperpolarizabilities (a factor of 2 for the rare gases [3]). For this reason, we focus on the LB94 results, and expect them to be lower and more reliable than our LDA results.

We fitted our linear polarizability results to the expression $\alpha(\omega) = \alpha(0) + C\omega^2$, obtaining $543.7 + 6890\,\omega^2$ for LB94 and $556.7 + 7020\,\omega^2$ for LDA (α and ω in a.u.). The static polarizabilities are in good agreement with previous theoretical results as gathered in Ref. [20]. Our results show a higher frequency dispersion than the TDHF values of Ref. [20], which is the usual picture, as the TDHF values tend to be too low.

The polarizability curves show the first strong pole near 3.33 eV (LB94) or 3.42 eV (LDA), close to an approximate LDA value of 3.36 eV [21] and in much better agreement with the experimental value of 3.78 eV [22] than the TDHF value [20] of 5.5 eV. This supports our confidence in the TDDFT results.

The hyperpolarizability results with the LB94 potential are shown in Fig. 1, where the EFIOR results are identical to the EOKE results. The EOKE and EFISH results at 11 frequencies from $\omega = 0$ to 0.01 a.u. (0.27 eV) have been fitted to Eq. (7). Using only frequencies up to 0.005 a.u. hardly influences the fitted value (about 1% deviation). The resulting constant A has been used to draw an estimate for the THG curve, which is reliable for small frequencies only. Both the fitted and real curves are shown for EOKE and EFISH. They start to diverge at the point where higher order terms in ω^2 become important (in the vicinity of a pole). The EFISH curve exhibits a pole near 0.90 eV. The INDO-TDHF value of Ref. [23] is still small there, indicating a different position of the pole.

The static LB94 result is 5.50×10^{-36} esu (in the definition of γ used by experimentalists), about 34% lower than the LDA result of 7.34×10^{-36} esu. This is
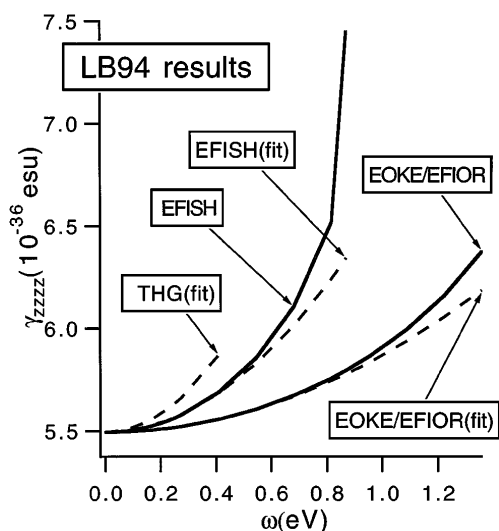
in good agreement with Quong and Pederson's static LDA result [24] of 7.0×10^{-36} esu. The difference between the LDA and LB94 result shows the large influence of the asymptotic behavior of the potential on properties which depend strongly upon the density in the outer region of the molecule.

The fitted lines in Fig. 1 correspond to a value of the constant A of (25.1 ± 0.2) a.u. [LDA yields $A = (23.0 \pm 0.2)$ a.u.]. As in the linear polarizability case, the two potentials yield similar results for the frequency dependence.

Comparison with experimental and theoretical results.—Some theoretical and experimental results for the hyperpolarizability of C_{60} have been collected in Table I. Large values are obtained in the older experiments and in the semiempirical calculations. The newer experimental data give upper bounds, which are more than an order of magnitude lower. Those results are supported by static LDA values such as the one of Ref. [24]. However, very large enhancements due to frequency dispersion were found in terms of a simple three-level model [25], questioning the relevance of static calculations. Our results, on the contrary, show that there is only a moderate frequency dispersion effect in the off-resonant region.

Geng and Wright [1] list several difficulties, circumvented in their approach, in the experimental determination of γ, such as the need to perform absolute intensity measurements. In the semiempirical sum-over-

TABLE I. Experimental and theoretical results for γ of C_{60}.

Method	ω (eV)	Property	γ (10^{-36} esu)
LB94[a]	0	static	5.50
LB94[a]	1.50	EOKE	6.69
LB94[a]	0.65	EFISH	6.04
LDA[a]	0	static	7.34
LDA[b]	0	static	7.0
INDO-TDHF[c]	0	static	4.95
INDO-TDHF[c]	0.905	EFISH	5.49
INDO/SDCI-SOS[d]	0.65	EFISH	690
CNDO/S[e]	0.94	THG	654.8
CNDO/SCI-SOS[f]	0	static	-458
Expt., in film[g]	0.68	THG	430
Expt., in toluene[h]	0.65	EFISH	750
Expt., in benzene[i]	1.17	DFWM	$< 60 \times \gamma$ (benzene)
Expt.,[j]	various	nondeg. FWM	<37

[a]This work.
[b]Quong and Pederson [24].
[c]Talapatra *et al.* [23].
[d]Li *et al.* [27].
[e]Hara *et al.* [26].
[f]Fanti *et al.* [28].
[g]Meth *et al.* [29].
[h]Wang and Cheng [30].
[i]Tang *et al.* [31], γ^{LDA}(benzene) $\approx 1.85 \times 10^{-36}$ esu [24].
[j]Geng and Wright [1], nondegenerate four wave mixing experiment in 1,2-dichlorobenzene.

FIG. 1. LB94 results for γ of C_{60}.

states (SOS) calculations, the results may be artificially large due to the limited number of states taken into account. A further uncertainty is the level of configuration interaction (CI) which is needed for a converged result. The single CI approximation seems to be insufficient [26].

In our calculations, we have neglected vibrational and solvent effects, which may be important. The vibrational effects are usually small when optical fields are involved, leaving solvent effects as probably the largest source of error when comparing to experimental values. The solvent can increase both the static hyperpolarizability and its frequency dependence considerably. It will have to be considered when excellent agreement between theory and experiment is required.

On the basis of our gas phase results for γ of C_{60}, in which frequency dispersion, screening, and electron correlation effects are (approximately) taken into account, we confirm the experimental upper bounds for γ which were recently presented in the literature.

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