

Frequency dependent equation-of-motion coupled cluster hyperpolarizabilities: Resolution of the discrepancy between theory and experiment for HF?

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We formulate and apply the EOM-CC method to determine, recursively, any order and any process frequency dependent hyperpolarizability. Combining the theory with systematically chosen n -aug-cc-pVXZ bases, we attempt to converge to the basis set limit. Our best “relaxed” result is -9.8 ± 0.5 a.u. for β_{SHG} compared to an experimental value of -11.0 ± 1 a.u. and 720 ± 40 a.u. for $\gamma_{\text{dc-SHG}}$ compared to 840 ± 120 a.u. If orbital relaxation could be neglected, the results are -10.2 ± 0.5 a.u. and 730 ± 40 a.u., falling within the error bars. © 1997 American Institute of Physics. [S0021-9606(97)03348-5]

A number of papers have studied the hyperpolarizabilities of the FH molecule with correlation since 1979.^{1–8} A critical analysis of all the high-level calculations until 1993⁵ concluded that, contrary to several other molecules whose theoretical frequency-dependent hyperpolarizabilities agreed to within about 10% with gas phase experimental data, the theoretical results for FH showed an error of about 20%. Despite the small difference, and the very small magnitude of the FH hyperpolarizability that can enhance the percent error, high-level, correlated *ab initio* theory should be able to unambiguously provide agreement to within 10% for such a simple molecule, or the experimental value⁹ should be reconsidered.

In prior theoretical work, the frequency dependence had been estimated from time-dependent Hartree–Fock (TDHF) theory,⁵ or from multiconfigurational linear response (MCLR) theory.⁴ However, the former is uncorrelated and the latter includes mostly nondynamic correlation while much of the magnitude of hyperpolarizabilities arises from the large dynamic correlation effects. The latter are, perhaps, most accurately and conveniently included via coupled-cluster (CC) theory, but except for some Kerr effect studies,¹⁰ the prior CC results have not included the correlated frequency dependence that is consistent with CC theory. In this letter we have generalized the equation-of-motion (EOM-CC) method to recursively and analytically compute correlated, frequency dependent hyperpolarizabilities, to *any order*. This provides a correlated measure for the dispersion effect. Furthermore, although many different kinds of basis sets have been considered which appeared to offer consistent results, there has not been a more systematic study based upon a series of n -aug-cc-pVXZ basis¹¹ to attempt to further eliminate this degree of uncertainty in the calculations. Here, we present such EOM-CC frequency-dependent results along with several other bases, to attempt to find basis set limit results.

The EOM-CC approach in its CI-like approximation^{12–14} offers a convenient recursive treatment of second¹² and higher-order properties. We simply consider the usual perturbation expressions that can be used to define such frequency-

dependent properties.¹⁵ Hence, all of the frequency-dependent polarizabilities can be written in the convenient form,

$$\begin{aligned} \chi_{i_1 i_2 \dots i_n i_{n+1}}^{(n)}(\omega_\sigma; \omega_1, \omega_2, \dots, \omega_n) \\ = \mathbf{P}(i_k \omega_k) \langle 0 | (1 + \Lambda) \tilde{q}_{i_1} | \mathbf{h} \rangle \mathbf{R}(-\omega_1 - \omega_2 - \dots - \omega_n) \\ \times \langle \mathbf{h} | \tilde{q}_{i_2} | \mathbf{h} \rangle \mathbf{R}(-\omega_2 - \omega_3 - \dots - \omega_n) * \dots * \langle \mathbf{h} | \tilde{q}_{i_n} | \mathbf{h} \rangle \\ \times \mathbf{R}(-\omega_n) \langle \mathbf{h} | \tilde{q}_{i_{n+1}} | 0 \rangle, \end{aligned} \quad (1)$$

where $\mathbf{P}(i_k, \omega_k)$ denotes all the $(n+1)$ permutations of the pairs $i_1 \omega_\sigma, i_2 \omega_1 \dots$ and

$$\mathbf{R}(\omega_x) = \langle \mathbf{h} | E_0 - H_0 + \omega_x | \mathbf{h} \rangle^{-1} \quad (2)$$

is the resolvent operator for the particular frequency ω_x . Also $\tilde{q}_i = \bar{q}_i - \langle \bar{q}_i \rangle$, where $\langle \bar{q}_i \rangle = \langle 0 | (1 + \Lambda) \bar{q}_i | 0 \rangle$ and $\bar{q}_i = e^{-T} q_i e^T$.

Here, Λ is the deexcitation operator introduced previously,¹⁶ and q_i denotes the i th component of the dipole moment vector. It should be clear from the above that, operationally, the repeated evaluation of the vectors

$$\mathbf{T}_{ij}^{(2)}(\omega_x) = \langle \mathbf{h} | \tilde{q}_j | \mathbf{h} \rangle \mathbf{T}_i^{(1)}(\omega_x) \quad (3)$$

and

$$\mathbf{R}(\omega_y) \mathbf{T}_{ij}^{(2)}(\omega_x), \quad (4)$$

where

$$\mathbf{T}_i^{(1)}(\omega_x) = \mathbf{R}(\omega_x) \langle \mathbf{h} | \tilde{q}_i | 0 \rangle \quad (5)$$

are the critical computational steps for *all* hyperpolarizabilities in the perturbation theory definition. This is actually accomplished by solving the corresponding linear equations of which the first is

$$\mathbf{R}^{-1}(\omega_x) \mathbf{T}_i^{(1)} = \langle \mathbf{h} | \tilde{q}_i | 0 \rangle \quad (6)$$

rather than taking the inverse of the resolvent.¹² Hence, there is no truncation of the excited states defined over the configurations $|\mathbf{h}\rangle$ as is often the case in sum over state approximations. Obviously, we can go to any order hyperpolariz-

TABLE I. Static and dynamic ($\omega=0.0656$ a.u./694.3 nm) hyperpolarizabilities of the HF molecule (in a.u.) at $R_{\text{HF}}=1.7328$ a.u., except where indicated.

	POL1++	J	cc-pVTZ	aug-cc-pVTZ	d-aug-cc-pVTZ	t-aug-cc-pVTZ	q-aug-cc-pVTZ	p-aug-cc-pVTZ	t-aug-cc-pVQZ
$\beta_{zzz}(0)$	-10.60	-9.96	-12.87	-11.71	-9.87	-9.84	-9.85	-9.82	-9.83
$\beta_{zzx}(0)$	-1.39	-1.71	-0.38	-0.24	-1.53	-1.68	-1.70	-1.72	-1.74
$\beta_{\parallel}(0)$	-8.03	-8.03	-8.18	-7.31	-7.76	-7.92	-7.95	-7.95	-7.99
SHG ^a	-8.82	-8.85(-9.18) ^c	-9.04	-8.04	-8.52	-8.70(-9.03) ^c	-	-8.8 ^d	-
OR	-8.25	-8.22	-8.41	-7.53	-8.03	-8.22	-	-8.3 ^d	-
$\gamma_{zzzz}(0)$	340	367	306	311	369	378	-	-	-
$\gamma_{zzxx}(0)$	606	671	430	532	604	638	-	-	-
$\gamma_{xxzz}(0)$	150	178	115	140	163	178	-	-	-
$\gamma_{\parallel}(0)$	511	574	382	458	527	558	573 ^d	583 ^d	-
THG	665	741	462	598	669	711	735 ^d	771 ^d	-
dc-SHG ^b	564	650 (653) ^c	429	506	588	629 (632) ^c	650 ^d	670 ^d	-
δ_{zzzz}	-10 860	-13 520							
FHG _{zzzzz}	-20 510	-24 850							

^aExperimental value: -11 ± 1 a.u., Ref. 9.

^bExperimental value: 840 ± 120 a.u., Ref. 9.

^c r_0 values.

^dEstimated from geometric extrapolation of successive differences. Complete basis set limit value under p-aug-cc-pVTZ column.

ability with the same program, just as was accomplished in the open ended TDHF method presented sometime back,¹⁷ making α , β , γ , δ , ϵ , etc., readily accessible for whatever optical process, by virtue of using the correct form of $\mathbf{R}(\omega_x)$.

Using the above, numerical results in several bases are presented in Table I. The modest J basis used previously consists of $[6s5p5d1f]$ on F and $[5s3p1d]$ on H and appears to be the best converged of our prior calculations.⁵ The POL1 basis, due to Sadlej, is defined for polarizabilities.¹⁸ Here, we augment it with two additional shells of diffuse functions obtained by 0.3 times the most diffuse exponent of each in the POL1 basis to give $[7s5p4d2f]$ on F and $[5s4p1d]$ on H. The series of bases cc-pVTZ, aug-cc-pVTZ, d-aug-cc-pVTZ, t-aug-cc-pVTZ, q-aug-cc-pVTZ, and p-aug-cc-pVTZ, i.e., $[9s8p7d6f/8s7p6d]$ with augmentation as considered elsewhere¹¹ are hoped to provide a converging series. We also consider a t-aug-cc-pVQZ basis $[8s7p6d5f4g/7s6p5d4f]$ to offer a different extension. Of course, as is usually the case for smaller bases, the FH β_{\parallel} [$\beta_{\parallel} = 1/5 \sum_i (\beta_{iiz} + \beta_{zii} + \beta_{izi})$] tends to be too large, while adding further diffuse augmentation reduces the magnitude, which then eventually might grow, gradually, with basis set enhancement.

First, depending upon the n -augmented cc-pVTZ series, we would expect a second harmonic generation (SHG) result of about -8.8 for a pentuply augmented cc-pVTZ basis, a result in line with the others shown. The larger values for $|\beta_{\text{SHG}}|$ correspond to probably excessive values for $|\beta_{zzz}|$, which is smaller in better basis sets. All of these results are at the EOM CCSD level and are still 20% in error compared to the center of the experimental value.⁴ The dispersion correction given by EOM CCSD is 9.9%, in excellent agreement with the 9.6% estimate from TDHF that was previously used, and the 10% MCLR value. Hence, the prior dispersion estimates⁵ were entirely justified for this problem, and did not introduce a significant error. We see a similar behavior for the direct-current induced second harmonic generation

process $\gamma_{\text{dc-SHG}}$. Our extrapolated pentuply augmented result is 670 a.u., also 20% in error.

Besides dispersion and basis, there are several other items previously considered^{5,12} to try to resolve the discrepancy between theory and experiment. These include the role of triple excitations as measured by static CCSD(T) results, vibrational averaging, (i.e., r_e to r_0) in the ground state,² and the pure vibrational correction¹⁹ that arises from vibronic intermediate states in perturbation theory expressions.

The magnitude of the triple excitations in CCSD(T) static values is -0.69 a.u. in the J basis,⁵ giving a CCSD(T) static value of β_{\parallel} equal to -8.72 a.u. In the t-aug-cc-pVTZ basis, CCSD(T) is -8.54 a.u. Using the latter triples effect (-0.62 a.u.), one would estimate a p-aug-cc-pVTZ CCSD(T) $\beta_{\parallel}(0)$ value of -8.57 a.u. (Though the second decimal is certainly not significant in these estimates, we carry it temporarily for ease of analysis.) Applying the same dispersion obtained in the EOM-CCSD calculations to the triples, we would obtain -9.61 a.u. in J and -9.48 a.u. for the estimated CCSD(T) SHG process in the p-aug-cc-pVTZ basis, assuming that there is no effect of the triple excitations on the dispersion. The computed pure vibrational correction is -0.35 a.u.¹⁹ while -0.38 a.u. is the currently determined effect in the J basis for evaluating EOM-CCSD β_{SHG} using formula (24) from Ref. 20 at four different internuclear distances.²¹ Adding these to the EOM-CCSD SHG result gives -10.3 a.u. in J and -10.2 in the p-aug-cc-pVTZ basis, slightly within the error bars of the experiment. Why, then, is this different from all previous calculations^{5,6} which supported a maximum $|\beta_{\text{SHG}}|$ CCSD(T) result of -9.0 , or -9.4 , if the pure vibrational correction is included?

The principal difference between the present calculations and the prior ones is that in EOM-CC (or the related CCQR treatment of second- and higher-order properties^{22,28}), the orbitals are not allowed to relax to accommodate the perturbation, as they would be in a full derivative calculation. The important role of orbital relaxation for hyperpolarizabilities

TABLE II. CCSD and (CCSD(T)) orbital relaxation and basis set effects in the β and γ static hyperpolarizabilities of HF.

Basis	Relaxed orbitals		Unrelaxed orbitals	
	Spherical	Cartesian	Spherical	Cartesian
J				
$\beta_{ }$	-7.50	-6.89 (-7.60)	-8.06	-8.03 (-8.72)
$\gamma_{ }$	-	478 (526)	-	574 (631)
d-aug-cc-pVTZ				
$\beta_{ }$	-7.24	-7.07	-7.76	-7.63
$\gamma_{ }$	(538)		527 (591)	-
t-aug-cc-pVTZ				
$\beta_{ }$	-7.51	-7.37	-7.92	-7.84
$\gamma_{ }$	530 (582)	539	558 (613)	571
q-aug-cc-pVTZ				
$\beta_{ }$	-7.60 (-7.87)	-	-7.95 (8.19)	-

has been demonstrated previously.²³ This relaxation effect can be estimated by a finite field static calculation. This effect can be quite large as shown in Table II. In the J Cartesian basis, the reduction in $\beta_{||}(0)$ is from -8.03 to -6.89 (!). With the triples (whose relaxed value is -0.54 a.u.), we see how the best previous CCSD(T) $\beta_{||}(0)$ value of -7.4 a.u. arises. If we assume the same relaxation for the SHG process, our J basis result would be -7.71 which is close to the estimated CCSD J basis result before,⁵ and is more than 20% in error. Adding the above triples with estimated dispersion and vibrational corrections (i.e., -1.27 a.u.), our J basis SHG result would be -9.0 a.u., consistent with the best previous estimate. Doing the same exercise for the d-aug-cc-pVTZ, we obtain a relaxation effect of $+0.52$ in the spherical basis, giving a result of -9.3 a.u. If we also add the change due to the extra Cartesian components, assuming that in the absence of linear dependencies (none are found) the more functions, the better, we get a final extrapolated result of -9.1 a.u., quite close to that in the J basis. In the t-aug-cc-pVTZ case the Cartesian and relaxation effect is $+0.55$ a.u. (two linearly dependent functions are removed in the calculation). That makes the result become -9.4 a.u., still outside the error bars, but identical to the previous $|\beta_{\text{SHG}}|$ maximum of -9.4 a.u. The extrapolation to p-aug-cc-pVTZ gives $-8.8 + (-1.3) = -10.1$ a.u., while geometric extrapolation of the relaxation/Cartesian effect in the p-aug-cc-pVTZ basis suggests $+0.3$ a.u. to return to -9.8 a.u. still slightly outside the error bars, but better than the previous -9.4 a.u. estimate. Since we certainly believe that barring pathological situations, “relaxed” orbitals, are better than unrelaxed ones, and particularly for a property like hyperpolarizabilities that the more functions the better, which favors Cartesian bases over spherical ones; the best J , d-aug-cc-pVTZ and t-aug-cc-pVTZ results are consistent with all prior calculations, while the more extensive extrapolated p-aug-cc-pVTZ result suggests some improvement to -9.8 a.u. Even the use of the very large t-aug-cc-pVQZ basis does not change this result.

We can make the same type of estimate for the experimentally known dc-SHG process for γ . The previous theoretical results (with exclusion of the pure vibrational correc-

tion) were estimated to show a value of 660 ± 60 a.u.⁵ compared to 840 ± 120 , experimentally.

The best of the new EOM-CCSD results, the extrapolated p-aug-cc-pVTZ used J basis is 670 a.u. The EOM-CCSD dispersion effect for dc-SHG is 12.7% in the t-aug-cc-pVTZ basis compared to TDHF value of 12.5% and much higher MCLR value of 19%.⁴ For $\gamma_{\text{dc-SHG}}$, we can estimate the contributions from triples corrections, vibrational averaging and the pure vibrational part from our current work and from Ref. 19. In the J basis triples corrections amount to 57 a.u. plus 8 a.u. for dispersion (65 a.u.). Adding the pure vibrational correction of -5.5 a.u. from Ref. 19, and 3 a.u. computed by changing r_e to r_0 , without orbital relaxation, we get 62 a.u. added to the $\gamma_{\text{dc-SHG}}$ EOM-CCSD result, to give 712 a.u. as the estimated CCSD(T) $\gamma_{\text{dc-SHG}}$ in the J basis, just outside the experimental error bars. If we include the very large static CCSD(T) relaxation (-105 a.u.) in the J basis, we get 607 a.u., well outside the error bars. In the d-aug-cc-pVTZ basis the relaxation is reduced to -53 a.u. In the t-aug-cc-pVTZ basis, the effect of triples is 55 a.u. plus dispersion (62 a.u.), but the relaxation effect is only -31 a.u., giving 663 a.u. The Cartesian components would appear to add 9 a.u. plus -5.5 a.u. for the pure vibrations to give 667 a.u. Finally, the estimated p-aug-cc-pVTZ CCSD(T) dc-SHG (extrapolation of relaxation effects suggests ~ -10 a.u.) gives about 720 a.u.

Despite the best efforts from 18 years of quantum chemistry, it would appear that there is still some disagreement between theory and experiment for β_{SHG} and $\gamma_{\text{dc-SHG}}$ for the FH molecule. The best current theoretical results for $\gamma_{\text{dc-SHG}}$ and β_{SHG} do not quite fall within the rather generous error bars. If orbital relaxation could be neglected, agreement would be achieved even in modest basis sets. In a complete basis, of course, there is no relaxation effect, but other than that, there are two arguments for dismissing orbital relaxation, one practical and one formal. Practically, when using an RHF reference in a correlated calculation, at large bond lengths, relaxed RHF orbitals have the wrong behavior, since RHF goes to an ionic separated atom limit, which the correlated method is attempting to undo. However, at equilibrium, even for a fairly ionic molecule like HF, one would not be-

lieve that unrelaxed orbitals are closer to the truth than relaxed orbitals. The formal objection is that inclusion of Hartree–Fock orbital relaxation introduces artificial excitation energy poles in the dynamic polarizability, in addition to the correct ones.²⁴

However, it is absolutely necessary to use relaxed orbitals in gradient and Hessian calculations, as the critical point would not be well defined otherwise. Why should it be different for other kinds of properties? The orbital relaxation terms introduced by adjusting the orbitals in the presence of the perturbation would correspond to an infinite sum of diagrams if they were introduced via evaluation in terms of the unrelaxed orbitals.^{25,23} CCSD easily sums many of these diagrams,²³ (CCSDT sums more) but not all. For many properties, the infinite sums inherent in CC makes orbital choice largely irrelevant,²⁶ but apparently not for the hyperpolarizabilities of FH, at least at the CCSD(T) level, as this subtle effect accounts for the current and previously observed differences between theory and experiment.

In a complete basis, relaxation is irrelevant, but we do not seem to approach that in the current calculations, even in the p-aug-cc-pVTZ basis. For the more common applications to polyatomic molecules, it is even less likely, and it would appear orbital relaxation should not be neglected in rigorously computed answers. Here, our best final, “relaxed” results are -9.8 a.u. for β_{SHG} and 720 a.u. for $\gamma_{\text{dc-SHG}}$. Considering the estimates made, a $\pm 5\%$ error would probably be justified in each (-9.8 ± 0.5 a.u. and 720 ± 40 a.u.), causing the experimental and theoretical error bars to overlap. However, the center of the experiment and theoretical calculation remains about 11% apart for β_{SHG} and 15% for $\gamma_{\text{dc-SHG}}$. If orbital relaxation could be neglected, our best results would be -10.2 ± 0.5 a.u. and 730 ± 40 a.u. compared to -11 ± 1 and 840 ± 120 , experimentally.

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