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Connected Triple Excitations in Coupled-Cluster
Calculations of Hyperpolarizabilities: Neon

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Abstract

We have calculated the second hyperpolarizability γ of neon using the CCSD(T) method. The accuracy of the CCSD(T) approach has been established by explicit comparison with the single, double and triple excitation coupled-cluster (CCSDT) method using extended basis sets that are known to be adequate for the description of γ . Our best estimate for γ_0 of 110 ± 3 a.u. is in good agreement with other recent theoretical values and with Shelton's recent experimental estimate of 108 ± 2 a.u. Comparison of the MP2 and CCSD(T) hyperpolarizability values indicates that MP2 gives a very good description of the electron correlation contribution to γ_0 . We have combined MP2 frequency-dependent corrections with the CCSD(T) γ_0 to yield values of $\gamma(-2\omega; \omega, \omega, 0)$ and $\gamma^K(-\omega; \omega, 0, 0)$.

1. Introduction

Theoretical determination of hyperpolarizabilities has been a topic of much interest recently, since knowledge of atomic and molecular hyperpolarizabilities is central to the understanding of the non-linear response of matter to light. In particular, organic materials with large hyperpolarizabilities are candidates for applications such as optical switching and second harmonic generation, and there is great potential for interaction between theory and experiment in the study of these systems.

From a theoretical point of view, it is important to understand the requirements for determining accurate hyperpolarizabilities for small systems, because it is possible to use large one-particle basis sets and sophisticated electron correlation treatments for these species, and thereby to evaluate the effects of approximations that will be necessary for the study of the hyperpolarizabilities of larger systems. Hence for small systems it is desirable to estimate the accuracy of the calculated hyperpolarizability. This may be accomplished in two ways. First, the quality of the one and n -particle approximations used in the calculation can be systematically improved and the convergence of the result can be monitored. This is perhaps the preferred approach from a theoretical standpoint. Alternatively, the theoretical value can be compared directly with experiment, although the possibility of error cancellation between the one and n -particle approximations must always be borne in mind.

Study of the hyperpolarizabilities of the rare gas atoms has a number of advantages. In particular, for neon sophisticated levels of theory and large one-particle basis sets can be employed. Experimental gas-phase electric-field-induced second harmonic generation data for the rare gases is available over a range of frequencies¹, which makes extrapolation to the static limit possible for the purposes of comparison with a theoretical static value. In addition, vibrational effects (which have been shown to be non-negligible for some molecular values, see, for example, Refs. 2 and 3) vanish for atoms.

It must be noted, however, that it is a non-trivial task to demonstrate convergence of calculated values for hyperpolarizabilities. Previous work has shown that there can be a much larger electron correlation contribution to hyperpolarizabilities than for linear polarizabilities, and that the contribution of higher excitations is not insignificant (see, for example, Refs. 4–6). For example, in the case of γ of neon, where the effect of electron correlation is about 40 a.u., or 40% of γ , the perturbational estimate of triple excitations contributes 8 a.u. or 20% of the total electron correlation contribution.⁴ Since the contribution of higher excitations is so large, the applicability of approximate methods for estimating the effects of higher excitations in hyperpolarizability calculations might be questioned. For example, the single and double excitation coupled-cluster method including an estimate of triple excitations through the fourth and partially the fifth order of perturbation theory, (CCSD(T))⁷ has had great success in describing the structure and frequencies of a number of ‘difficult’ chemical systems — that is, systems whose wave functions are not dominated by a single reference.^{8,9} This success notwithstanding, it is essential to investigate the utility of this approach specifically for determining accurate hyperpolarizabilities.

The reliability of a correlation treatment is best evaluated by comparison with a full configuration-interaction (CI) calculation in the same one-particle basis set. However, since even at the self-consistent field (SCF) level of theory diffuse f type functions contribute 10 a.u. to the hyperpolarizability of Ne^4 , a full CI calibration in a realistic basis set is not feasible. Here, in order to establish the accuracy of the CCSD(T) method for γ of neon, we compare instead to results obtained with the full single, double and triple excitation coupled-cluster method (CCSDT),^{10,11} in a basis set which is known to be adequate for the description of hyperpolarizabilities. We can thus assess the accuracy of the computed CCSD(T) value, as well as compare it with experimental and other theoretical values. We note that a previous study has demonstrated that for correlation energies, CCSD(T) is an

excellent approximation to CCSDT.¹²

2. Computational Methods

The one-particle basis sets used in this work are similar to those employed previously.⁴ They were derived from van Duijneveldt's (13s8p) primitive set¹³ augmented with a (6d4f) polarization set, with exponents chosen as an even-tempered sequence $\alpha = 2.5^n \alpha_0$; $n = 0, \dots, k$ with $\alpha_0 = 0.20, 0.61$ for the d and f functions, respectively. This was contracted to [4s 3p 2d 1f] using atomic natural orbitals.¹⁴ The two outermost sets of spd functions and the outermost f function were uncontracted to give basis C, denoted [4+1+1s 3+1+1p 2+1+1d 1+1f]. We use the notation C in order to be consistent with our previous study.⁴ Additional diffuse functions were then added by extrapolating from the outermost function in an even-tempered sequence, $\alpha = 2.5^{-n} \alpha_0$. For example, the addition of one set of diffuse functions is denoted + (1s1p1d1f). In some calculations the basis was further augmented with two diffuse g functions with exponents of 0.29 and 0.11. Basis set C was completely uncontracted, and two tight d functions were included ($\alpha_d = 123.53, 49.41$) for calculations in which core correlation was included. Only the true spherical harmonic components of the basis functions were used throughout.

Energies were calculated using self-consistent field (SCF), single and double excitation coupled-cluster (CCSD) and second-order Møller-Plesset perturbation theory (MP2). The effect of triple excitations was investigated using (a) the CCSD(T) method, which includes an estimate of the triples through fourth and partially fifth order of perturbation theory, based on the CCSD amplitudes in the perturbation energy expressions; (b) the CCSDT method, which explicitly includes all single, double and triple excitations; and (c) the CCSD + T(CCSD) method¹⁵ which includes only the fourth-order perturbation theory contribution based on CCSD amplitudes.

The dipole polarizabilities are defined¹⁶ by the energy response to an applied electric

field of strength F :

$$E(F) = E_0 - \frac{1}{2}\alpha F^2 - \frac{1}{4!}\gamma F^4 - \frac{1}{6!}\epsilon F^6$$

Electric fields of 0, 0.002, 0.004, 0.008, 0.012, 0.016 and 0.020 a.u. were applied and the energy responses were fitted to the sixth-order polynomial in the field strength. The SCF value of γ obtained from the fit agrees with the SCF value obtained from finite displacements of analytic β values to within 0.1 a.u. Tests of the fit for the correlated values indicate the error in γ due to the fit is less than 0.2 a.u.

The SCF, MP2 and most of the coupled-cluster calculations were performed using the MOLECULE-SWEDEN,¹⁷ CADPAC,¹⁸ and TITAN¹⁹ programs. The CCSDT calculations were performed with a program written by one of us (GES).¹¹ The SCF energies were converged to $10^{-13} E_h$ or better and the CCSD and CCSDT energies to 10^{-12} .

3. Results and Discussion

The values for the linear polarizability, α and the hyperpolarizability, γ determined in this work are summarized in Table 1. We note first that the SCF, MP2, CCSD and CCSD(T) results for both α and γ are essentially identical in basis sets C+(3s3p2d3f) and C+(2s2p1d2f). This establishes that these values are converged with respect to further addition of diffuse s , p , d , and f functions in the one-particle basis set. It also verifies that basis C+(2s2p1d2f) is a good choice for comparison of the CCSDT and CCSD(T) results. The CCSDT γ value of 110.9 a.u. in this basis is in very good agreement with that from the CCSD(T) method (111.2 a.u.). This establishes that the (T) correction is a reliable estimate of the contribution from connected triple excitations to the hyperpolarizability of Ne, even though the contribution is large. Comparison of the CCSD(T) and CCSD + T(CCSD) results with the C+(3s3p2d3f) basis shows that the fourth-order correction alone is a substantial overestimate.

The effects of diffuse higher-order angular momentum functions and of core correlation have also been investigated at the CCSD(T) level of theory, in order to improve upon

our previous best computed value of 111 a.u.⁴ and to assess further our error estimate of ± 4 a.u. Uncontraction of the one-particle basis set reduces γ from 111.0 a.u. to 110.3 a.u., and core correlation gives a further reduction of 0.5 a.u. Conversely, diffuse g functions increase γ by 0.2 a.u. These changes are very similar to the values of -0.7 , -0.5 , and 0.2 a.u., respectively, obtained at the CCSD level of theory, whereas the MP2 values indicate that second-order perturbation theory may underestimate the effects of uncontraction (-0.4 a.u.) and core correlation (-0.3 a.u.). This is consistent with the results for argon,²⁰ where the CCSD estimate of the reduction in γ due to core correlation is larger than the MP2 value. The CCSD(T) results thus support our earlier conclusions⁴ that the combination of further augmentation of the one-particle basis set and further improvement in the treatment of core correlation is likely to have little effect on γ .

The importance of higher than triple excitations also requires discussion. Single and double excitations increase γ by 34 a.u. and triple excitations by a further 9 a.u. However, the coupled-cluster expansion should be rapidly convergent, since all the corresponding disconnected terms are included to infinite order at each level of CC theory. The next most important contribution comes from connected quadruple excitations: these can be expected to contribute substantially less than connected triple excitations. It is highly unlikely that these terms contribute as much as 3 a.u. We have previously established⁴ that the CCSD(T) energy, at least, agrees almost perfectly with full CI benchmark results for Ne. We thus arrive at a best estimate of 110 a.u., with an uncertainty of 3 a.u. The latter is almost entirely due to uncertainty in the estimated contribution of connected quadruple (and higher) excitations. We can compare our result with Shelton's most recent estimate of 108 ± 2 a.u.²¹ based on extrapolation of electric-field-induced second harmonic generation values. This differs from his earlier static value of 119 ± 2 due to his discovery of a systematic error in some of the measurements.²¹ Our value is also in good agreement with other recent theoretical values. These include Maroulis and Thakkar's estimate of

114±9 a.u. based on the double-excitation coupled-cluster method augmented with a perturbational estimate of single and triple excitations, denoted CCD+ST(CCD),²² as well as Chong and Langhoff's CCSD(T) value of 111.0 a.u.²³, and 108±5 a.u. from the restricted active space self-consistent field calculations of Jensen and co-workers.²⁴

It is clearly much easier to demonstrate convergence for α than for γ . The electron correlation contribution is smaller (around 11%) for α and the CCSD(T) and CCSDT values agree to 3 decimal places. The diffuse function requirement is also less stringent than for γ . The largest remaining corrections are for core correlation and uncontraction of the one-particle basis set which decrease α by 0.013 a.u., or 0.5%. Our best computed value for α is 2.677 a.u. to which we conservatively assign an uncertainty of 0.015 a.u. This is in excellent agreement with the value of 2.669 a.u. derived from dipole oscillator strength distributions by Kumar and Meath.²⁵

Finally, the rather good agreement between the MP2 and CC polarizability and hyperpolarizability suggests that the former method may be useful even where, as is the case for neon, the correlation contributions are large. Because it is much simpler to evaluate dynamic polarizabilities with MP2 than with CC methods, this suggests that an efficient route to reliable frequency-dependent results may be to correct CC static values with MP2 differences between static and dynamic values. It is certainly the case that the MP2 values in themselves would be much more reliable than values obtained using SCF methods to describe the frequency dependence. We may also note that the experimental frequencies are far from resonance, so an error in the frequency-dependent hyperpolarizability arising from the error in the prediction of the poles at the MP2 level of theory is not a matter for concern.

In this work we have combined the MP2 frequency-dependent corrections²⁶ for $\gamma(-2\omega; \omega, \omega, 0)$ of neon with our best estimate for the static value and arrive at 112±3 a.u. ($\lambda=1319$ nm), 113±3 a.u. ($\lambda=1064$ nm), 124±4 a.u. ($\lambda=514.5$ nm), to

be compared with experimental second harmonic generation values of 111.1 ± 0.8 a.u.¹, 109.9 ± 0.5 a.u.¹ and 122.2 ± 0.5 a.u.²¹, respectively. The theoretical results show no negative dispersion (note that the uncertainties in the theoretical numbers are not independent and are likely to be strongly correlated with one another), and are also in good agreement with the revised experimental values. We may also combine the MP2 frequency-dependent correction²⁶ for $\gamma^K(-\omega;\omega,0,0)$ of neon with our best estimate of the static value and obtain 113 ± 3 a.u. for $\lambda = 632.8$ nm. This value is somewhat higher than the Kerr effect measurement of 101 ± 8 a.u.²⁷

4. Conclusions

We have demonstrated by comparison with full CCSDT results that the CCSD(T) method provides an accurate description of the hyperpolarizability of neon. Since the CCSD(T) method has the advantage of being rather inexpensive, it allows extensive investigation of the one-particle basis set requirements and the core correlation treatment for α and γ of neon. Our best computed CCSD(T) value for γ of neon, including the effects of multiple sets of diffuse *s*, *p*, *d* and *f* functions and of core correlation, is 109.8 a.u. After incorporating corrections for diffuse *g* functions and a more complete treatment of triple excitations our best estimate is 110 a.u. with an error estimate of 3 a.u. This result is in agreement with all of the most recent theoretical values^{22–24} and in line with the static value extrapolated from experimental frequency-dependent measurements.^{1,21} Together with our assignment of uncertainty, this fulfils our criteria for establishing the accuracy of the computed value.

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Table 1
Neon dipole polarizabilities (a.u.)

Basis set	Method	α	γ
$C^a + (2s2p1d2f)$	SCF	2.377	68.66
	MP2	2.713	110.6
	CCSD	2.643	102.2
	CCSD(T)	2.690	110.9
	CCSDT	2.690	111.2
$C^a + (3s3p2d3f)$	SCF	2.377	68.68
	MP2	2.713	110.7
	CCSD	2.643	102.2
	CCSD + T(CCSD)	2.703	115.3
	CCSD(T)	2.690	111.0
$C^a + (3s3p2d3f2g)$	SCF	2.377	68.67
	MP2	2.716	110.9
	CCSD	2.645	102.4
	CCSD(T)	2.692	111.2
$(13s8p8d4f)+(3s3p2d3f)^b$	SCF	2.377	68.67
	MP2	2.708	110.3
	CCSD	2.636	101.5
	CCSD(T)	2.684	110.3
$(13s8p8d4f)+(3s3p2d3f)^c$	MP2	2.703	110.0
	CCSD	2.628	100.8
	CCSD(T)	2.677	109.8

^a See text for the definition of C.

^b Uncontracted basis with 8 electrons correlated

^c Uncontracted basis with 10 electrons correlated