Relativistic Effects for Polarizabilities and Hyperpolarizabilities of Rare Gas Atoms

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(Received May 15, 2001; CL-010446)

The relativistic effects for static polarizabilities α and hyperpolarizabilities γ of rare gas atoms (Ne through Rn) are investigated theoretically with the third-order Douglas–Kroll method. The results yield interesting trends of relativity in going from Ne to Rn: The relativistic effect decreases α values of Ne and Ar and increases the values of Kr, Xe, and Rn, and it decreases γ values of Rn slightly and increases the values of other rare gas atoms, while the electron correlation effect increases α and γ of all rare gas atoms.

The determination of the electric polarizabilities of atoms and molecules is an active field of the recent experimental and theoretical studies. These electrical properties determine various nonlinear optical phenomena in optical materials such as optical devices and optical switches. However, it is difficult to estimate polarizabilities α and hyperpolarizabilities γ both experimentally and theoretically. The reason why the theoretical estimation of these properties is complicated is as follows: An accurate description of dipole polarizabilities α and γ needs adequate representation of the tail of the wave function. Thus, a highly correlated many-electron wave function with an extensive one-particle basis set is required for the reliable estimation of these properties.

The polarizabilities and hyperpolarizabilities of rare gas atoms except the heaviest radon atom have been investigated both experimentally and theoretically. Experimental data of static α and γ of rare gas atoms (Ne through Xe) were obtained by Kumar and Meath[1] and by Shelton,[2,3] respectively. Theoretically, the static α and γ of rare gas atoms (He through Xe) were determined using a high-level electron correlation approach with large one-particle basis sets by Rice et al.[4]

Relativistic effects are important in the study of heavy elements such as xenon and radon. Recent theoretical studies of static α of the alkaline-earth[5] and alkali[6] metals show that the relativistic effect is important for the third-row and heavier atoms. However, there is no theoretical work studied by the method fully including both relativistic and correlation effects for the polarizabilities and hyperpolarizabilities of rare gas atoms. The purpose of the present work is to estimate the relativistic effect for static electrical properties α and γ including the electron correlation effect. The theoretical estimation of α and γ of Rn is interesting and important because there is no experimental data for these values.

The relativistic effect was considered by the spin-free modification of the third-order Douglas–Kroll (DK3) method[7,8] recently developed in our group. The DK3 method is one of quasi-relativistic approaches and gives better agreement with the four-component relativistic Dirac–Hartree–Fock approach. The formalism can easily be applied to any electronic structure theory, as well as the RESC method.[9,10] This method is extended to include the electron correlation by methods analogous to those for the non-relativistic (NR) cases. All basis sets used in this study were derived from the subset of the even-tempered type (32s24p20d14f) universal Gaussian primitive set.[11] These primitive sets were contracted by the corresponding atomic SCF calculations with the DK3 and NR Hamiltonians for the relativistic and NR basis sets, respectively. Two s and p functions were augmented in a universal Gaussian sequence. First- and second-order angular momentum basis functions[12] were used for the diffuse basis functions with higher angular momentum. The resultant basis sets were contracted as [10s9p9d9f], [10s9p9d9f], [11s9p8d8f8g], [11s10p9d9f9g], and [12s11p10d5f5g5h] for Ne, Ar, Kr, Xe, and Rn, respectively. Electron correlation effects were treated at second-order Møller–Plesset perturbation (MP2), coupled-cluster with singles and doubles (CCSD), and CCSD with triples correction (CCSD(T)) levels. Valence *n*s and *n*p electrons for Ne and Ar and *n*s, *n*p, and $(n-1)$d electrons for Kr, Xe, and Rn were correlated in the present study. The polarizabilities and hyperpolarizabilities were obtained by the numerical finite-field approach.[13] All calculations were performed using MOLCAS4.4[14] modified for the inclusion of the DK3 method.

Table 1 shows the static polarizabilities and hyperpolarizabilities of rare gas atoms calculated with the DK3 Hamiltonian in comparison with the NR Hamiltonian. The experimental values are also listed for comparison. The electron correlation effect increases α and γ of all rare gas atoms and is significant for both α and γ. The influence of this effect becomes smaller as the rare gas atoms are heavier. The reason for this finding is that the electron correlation effect in the valence shell is less important for the heavier atoms since the region of space occupied by the valence electrons is greater, as explained by Rice et al.[4] Comparing the relativistic results to the NR ones, the relativity decreases the α values of Ne and Ar slightly and increases the values of Kr, Xe, and Rn as shown in Figure 1. The relativistic contributions to α of Ne, Ar, Kr, Xe, and Rn are +0.15, +0.18, –0.12, –0.84, and –3.0%, respectively. As expected, the relativistic effect for α is largest for the heaviest Rn atom, although the relativistic effect for α of rare gas atoms is relatively small in comparison to the previous study of the alkaline-earth and alkali metals.[5,6] This is due to the small contribution of the relativistic contraction of the s orbital for the rare gas atoms since α is mainly dominated by the s (and d) orbitals as discussed by Woon and Dunning[15] in the case of Ne. Table 1 and Figure 1 also show that the relativistic effect decreases γ values of Rn while it increases the values of other rare gas atoms. The relativity increases the γ values by 10, 30, and 80 au for Ar, Kr, and Xe, respectively, and interestingly reduces γ of Rn by only 10 au.

On the whole, the relativistic DK3-CCSD method gives better agreement with the experimental α and γ of Ne, Ar, and Kr than MP2 and CCSD(T) methods, although MP2 and CCSD(T) give better agreement with an uncertain experimental

Table 1. Static polarizabilities and hyperpolarizabilities of rare gas atoms (in au)

		α		γ	
		NR	DK3	NR	DK3
Ne	HF	2.372	2.374	70.02	70.35
	MP2	2.712	2.717	113.4	114.0
	CCSD	2.647	2.651	105.8	106.3
	CCSD(T)	2.693	2.697	114.5	115.1
	exptl.	2.669[a]		119(±2),[b] 108(±2)[c]	
Ar	HF	10.72	10.73	983.0	990.0
	MP2	11.18	11.20	1248	1257
	CCSD	11.10	11.12	1194	1203
	CCSD(T)	11.20	11.22	1268	1277
	exptl.	11.08[a]		1167(±6)[b]	
Kr	HF	16.47	16.44	2343	2366
	MP2	16.81	16.79	2750	2778
	CCSD	16.69	16.67	2595	2621
	CCSD(T)	16.82	16.80	2728	2756
	exptl.	16.79[a]		2600[b]	
Xe	HF	27.10	26.76	6259	6314
	MP2	27.20	26.98	6996	7085
	CCSD	27.09	26.84	6633	6705
	CCSD(T)	27.29	27.06	6957	7037
	exptl.	27.16[a]		6888[b]	
Rn	HF	34.12	32.81	9309	9331
	MP2	34.19	33.19	10170	10160
	CCSD	33.97	32.90	9607	9598
	CCSD(T)	34.22	33.18	10040	10030

[a] ref 1. [b] ref 2. [c] ref 3.

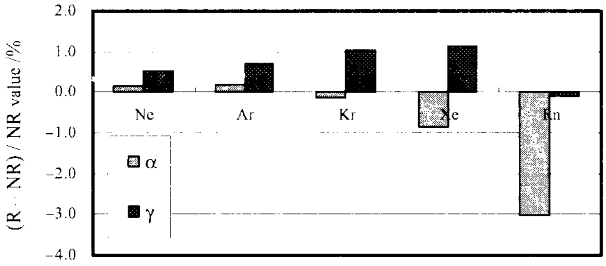

Figure 1. Relativistic correction (R – NR) / non-relativistic values for α and γ.

value for Xe. Both MP2 and CCSD(T) methods give similar results and estimate higher α and γ values than CCSD. These findings seem to imply that the perturbative correction trends to overestimate polarizabilities and hyperpolarizabilities generally. Thus, a further investigation is needed on the influence of the perturbative correction on electrical properties. We are currently studying the influence of (1) basis sets and (2) the spin-orbit effect for α and γ.

The present research is supported in part by the Grant-in-Aid for Scientific Research on Priority Areas "Molecular Physical Chemistry" from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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