Gaussian basis sets for use in correlated molecular calculations. IV. Calculation of static electrical response properties

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An accurate description of the electrical properties of atoms and molecules is critical for quantitative predictions of the nonlinear properties of molecules and of long-range atomic and molecular interactions between both neutral and charged species. We report a systematic study of the basis sets required to obtain accurate correlated values for the static dipole (α_1), quadrupole (α_2), and octopole (α_3) polarizabilities and the hyperpolarizability (γ) of the rare gas atoms He, Ne, and Ar. Several methods of correlation treatment were examined, including various orders of Moller–Plesset perturbation theory (MP2, MP3, MP4), coupled-cluster theory with and without perturbative treatment of triple excitations [CCSD, CCSD(T)], and singles and doubles configuration interaction (CISD). All of the basis sets considered here were constructed by adding even-tempered sets of diffuse functions to the correlation consistent basis sets of Dunning and co-workers. With multiply-augmented sets we find that the electrical properties of the rare gas atoms converge smoothly to values that are in excellent agreement with the available experimental data and/or previously computed results. As a further test of the basis sets presented here, the dipole polarizabilities of the F^- and Cl^- anions and of the HCl and N_2 molecules are also reported.

I. INTRODUCTION

The success or failure of a specific prescription for the construction of basis sets for the calculation of atomic and molecular wave functions lies in the range of applicability and the degree of accuracy that the sets possess for describing the problems of interest. The methodology of correlation consistent basis sets[1] provides a systematic means of approaching the complete basis set limit and, therefore, provides an internal yardstick for measuring the accuracy of each set in the series. For systems and methods where a sufficiently wide range of sets can be used, the convergence characteristics of the correlation consistent basis sets makes it straightforward to determine the *intrinsic error* of a quantity determined at any given level of *ab initio* theory.[2] The purpose of the present work is to evaluate the ability of these sets to describe the static electrical properties of atoms and molecules and to determine, as necessary, the manner in which to systematically expand the sets to improve their performance for this task. The species that were investigated were limited to the rare gas atoms (Ne, He, and Ar), the fluoride and chloride anions, and the HCl and N_2 molecules, where very large one-electron basis sets could be used. We expect the conclusions drawn here to be generally applicable to other atomic and molecular systems.

An accurate description of atomic and molecular polarizabilties is important in a surprisingly wide range of physical phenomena. The second-order Stark effect arises from the response of a polarizable charge distribution to an external electric field.[3] Rayleigh and Raman scattering represent interactions between photons and bound electrons,[4] mediated by the polarizability (Rayleigh scattering gives rise to macroscopic refraction). An accurate description of polarizabilities, as well as the permanent moments, is also critical to accurately describing intermolecular interactions and weak long-range interactions of molecules with condensed matter substrates.[5] Polarizabilities are also important in determining dielectric constants[6] via the Clausius–Mossotti relation. Dispersion forces even become a relevant issue in the manipulation of surface atoms using a scanning tunneling microscope.[7] The emphasis here will largely focus upon the determination of the static dipole polarizabilty (α_1), although higher polarizabilties and the second dipole hyperpolarizability will also be investigated.

There have been many previous calculations of dipole and higher polarizabilities, especially for the rare gas atoms. It is well known that diffuse polarization functions are critical for calculating accurate polarizabilities. However, in spite of the wealth of previous experience, there is still a need to determine the systematics of the calculations, especially for the new correlation consistent basis sets. It has been demonstrated previously that correlation consistent basis sets lend themselves to making definitive evaluations of methodology and basis set quality for strong chemical bonds and relative energetics in diatomic[2] and triatomic[8] systems as well as hydrogen-bonded systems[9] and even weak van der Waals systems such as Ar_2 and other rare gas dimer interactions.[10] The present work investigates their suitability for describing the static electrical properties of atoms and molecules.

Section II reviews the prescription for constructing correlation consistent basis sets and describes how they have been extended for an improved description of certain

TABLE I. Primitive and contracted standard and augmented correlation consistent basis sets for H, He, N, F, Ne, Cl, and Ar.

Species	Set	Primitive Set	Contracted Set	Set	Augmentation
H, He	cc-pVDZ	$(4s1p)$	$[2s1p]$	aug-cc-pVDZ	$(1s1p)$
	cc-pVTZ	$(6s2p1d)$	$[3s2p1d]$	aug-cc-pVTZ	$(1s1p1d)$
	cc-pVQZ	$(7s3p2d1f)$	$[4s3p2d1f]$	aug-cc-pVQZ	$(1s1p1d1f)$
	cc-pV5Z	$(8s4p3d2f1g)$	$[5s4p3d2f1g]$	aug-cc-pV5Z	$(1s1p1d1f1g)$
N, F, Ne	cc-pVDZ	$(9s4p1d)$	$[3s2p1d]$	aug-cc-pVDZ	$(1s1p1d)$
	cc-pVTZ	$(10s5p2d1f)$	$[4s3p2d1f]$	aug-cc-pVTZ	$(1s1p1d1f)$
	cc-pVQZ	$(12s6p3d2f1g)$	$[5s4p3d2f1g]$	aug-cc-pVQZ	$(1s1p1d1f1g)$
	cc-pV5Z	$(14s8p4d3f2g1h)$	$[6s5p4d3f2g1h]$	aug-cc-pV5Z	$(1s1p1d1f1g1h)$
Cl, Ar	cc-pVDZ	$(12s8p1d)$	$[4s3p1d]$	aug-cc-pVDZ	$(1s1p1d)$
	cc-pVTZ	$(15s9p2d1f)$	$[5s4p2d1f]$	aug-cc-pVTZ	$(1s1p1d1f)$
	cc-pVQZ	$(16s11p3d2f1g)$	$[6s5p3d2f1g]$	aug-cc-pVQZ	$(1s1p1d1f1g)$
	cc-pV5Z	$(20s12p4d3f2g1h)$	$[7s6p4d3f2g1h]$	aug-cc-pV5Z	$(1s1p1d1f1g1h)$

atomic and molecular properties. In Sec. III, we briefly discuss the use of the finite-field approach for calculating the static electric response properties of atoms and molecules. Section IV details the results of the calculations of the static dipole (α_1), quadrupole (α_2), and octopole (α_3) polarizabilities and the (dipole second) hyperpolarizability (γ) of the rare gas atoms, He, Ne, and Ar, while Sec. V presents the calculations of the dipole polarizability of the F$^-$ and Cl$^-$ anions and the HCl and N$_2$ molecules. Section VI then summarizes our conclusions.

II. CORRELATION CONSISTENT BASIS SETS

Although the methodology behind the construction of the correlation consistent basis sets has been discussed previously[1(a)-1(c)] (papers I–III in this series), a brief review will make it easier to introduce the extended sets. The observation[1(a),11] that the differential correlation energy contributions from individual basis functions tend to fall into well defined groups led to the concept of correlation consistent basis sets. Thus, the cc-pV$(X+1)$Z set is derived from the cc-pVXZ set[12] by adding an entire *shell* of functions, all of which make approximately equal contributions to the correlation energy of the atom. The primitive and contracted set sizes for H, He, and first and second row main group elements are listed in Table I.

The cc-pV$(X+1)$Z set extends the cc-pVXZ set by adding functions of the next higher angular symmetry and by including an additional function in each of the remaining angular symmetries. For example, the lowest quality cc-pVDZ set includes functions of *spd* symmetries, so the cc-pVTZ set includes f functions for the first time, as well as an additional set of *spd* functions. The correlation consistent basis sets are the fastest converging, most efficient series of Gaussian sets available for calculating atomic energies. Sets for H and B to Ne were presented in papers I and II in this series, and sets for Al to Ar were released in paper III. Correlation consistent sets for He (double through quintuple zeta quality) are given in Table II of the present work.

It is well known that additional diffuse functions must be added to a standard atomic basis set in order to accu-

rately describe the electronic structure of anions. They can be equally critical for quantitative prediction of properties, such as the dipole moment, which sample the outer regions of the wavefunction. Diffuse functions can also play an important role in providing an accurate description of excited states (i.e., by removing the bias for one state with respect to another) and in describing the long-range interaction of atomic and molecular systems. When paper II developed the augmented correlation consistent sets (aug-cc-pVXZ) for H and B to Ne, the exponents of the diffuse functions were optimized for the anion energies. However, an exhaustive study of one- and two-electron properties of water by Feller[13] suggests that the augmented sets are suitable for modeling atomic and molecular properties as well.

For both Ne and Ar, where the anions are not stable, the exponents for the diffuse functions were determined by extrapolating from the two closest atoms (O and F for Ne, S and Cl for Ar). For He (see Table II), the diffuse functions were determined using the corresponding standard and augmented cc-pVXZ sets for H: the ratio between the most diffuse exponents in the standard H sets and the optimized diffuse functions in the corresponding augmented H sets were used to extend the standard He sets. One purpose of the current work is to evaluate the validity of this method of selecting diffuse functions for the rare gas atoms.

In the process of making this evaluation we have explored sets that include more diffuse functions than are present in the augmented correlation consistent sets, where only one diffuse function was added for each angular symmetry present in the standard cc-pVXZ set. Two extended sequences were investigated for all seven species studied here. The *doubly-augmented* polarized valence correlation consistent basis sets (d-aug-cc-pVXZ) include two diffuse functions of each symmetry, and the *triply-augmented* polarized valence correlation consistent basis sets (t-aug-cc-pVXZ) likewise include three diffuse functions. For Ne, F$^-$, and Cl$^-$, we have also employed *quadruply-augmented* polarized valence correlation consistent basis sets (q-aug-cc-pVXZ). The functions become more and more diffuse as the sets are extended and represent an at-

TABLE II. Standard and augmented correlation consistent basis sets for helium. The first function in the set is the atomic $1s$ orbital. The indicated primitive Gaussian functions are then added to this orbital.

| | cc-pVDZ | | cc-pVTZ | | cc-pVQZ | | cc-pV5Z | |
	ζ_i	c_i	ζ_i	c_i	ζ_i	c_i	ζ_i	c_i
s	38.36	0.023 809	234.0	0.002 587	528.5	0.000 940	1145.0	0.000 359
	5.77	0.154 891	35.16	0.019 533	79.31	0.007 214	171.7	0.002 771
	1.24	0.469 987	7.989	0.090 998	18.05	0.035 975	39.07	0.014 251
	0.2976	0.513 027	2.212	0.272 050	5.085	0.127 782	11.04	0.055 566
			0.6669	0.478 065	1.609	0.308 470	3.566	0.162 091
			0.2089	0.307 737	0.5363	0.453 052	1.240	0.332 197
					0.1833	0.238 884	0.4473	0.419 615
							0.1640	0.186 128
s	(0.2976)		(0.6669, 0.2089)		(1.609, 0.5363, 0.1833)		(3.566, 1.240, 0.4473, 0.1640)	
p	(1.275)		(3.044, 0.758)		(5.994, 1.745, 0.560)		(10.153, 3.627, 1.296, 0.463)	
d			(1.965)		(4.299, 1.223)		(7.666, 2.647, 0.914)	
f					(2.680)		(5.411, 1.707)	
g							(3.430)	
Add:	aug-cc-pVDZ		aug-cc-pVTZ		aug-cc-pVQZ		aug-cc-pV5Z	
s	0.07255		0.05138		0.048 19		0.03109	
p	0.2473		0.1993		0.162 6		0.1400	
d			0.4592		0.3510		0.2892	
f					0.6906		0.5345	
g							0.7899	

tempt to saturate the radial component of function space in an outward direction. The even-tempered parameters (α, β) for determining all of the functions used subsequently are given in Table III. The exponents for the additional functions in the d-aug-cc-pVXZ sets are given by $\alpha\beta$, the exponents for the extra functions in the t-aug-cc-pVXZ sets are given by $\alpha\beta^2$, and so on. Here, α is the smallest exponent in the aug-cc-pVXZ set and β (<1) is taken from the ratio of the two most diffuse functions in the set (i.e., in contrast to the usual even-tempered sequence, the present usage proceeds from the diffuse function with the largest exponent to functions with increasing

smaller exponents). In Sec. IV we will often refer to these extended sets as x-aug sets [x=d(oubly), t(riply), and q(uadruply) augmented; in this vein, the aug-cc-pVXZ sets may be denoted as "singly-augmented"].

In the calculations on neon we made an effort to optimize exponents explicitly for specific polarizabilities as well. This tended to be an unsatisfactory exercise beyond a certain point due to strong couplings between the basis set and both polarization and correlation effects,[14] but it is another means of evaluating the augmentation procedure discussed above. We find that the coupling can be reduced if the exponents for the s and d functions are optimized for

TABLE III. Even-tempered parameters α and β for the extended augmented correlation consistent basis sets for He, Ne, Ar, N, F, and Cl.

| | | He | | Ne | | Ar | | N | | F | | Cl | |
Basis Set		α	β	α	β	α	β	α	β	α	β	α	β
cc-pVDZ	s	0.0726	0.2438	0.1230	0.2526	0.0709	0.3034	0.06124	0.2724	0.0986	0.2531	0.0608	0.3137
	p	0.2473	0.1939	0.1064	0.2465	0.0533	0.2878	0.05611	0.2568	0.8502	0.2449	0.0466	0.2877
	d			0.631	0.2866	0.240	0.3252	0.230	0.2815	0.464	0.2829	0.1960	0.3267
cc-pVTZ	s	0.0514	0.2460	0.1133	0.2996	0.0685	0.3506	0.05760	0.3223	0.0916	0.3012	0.0591	0.3637
	p	0.1993	0.2629	0.0918	0.2780	0.0487	0.3152	0.0491	0.2846	0.0736	0.2755	0.0419	0.3221
	d	0.459	0.2237	0.386	0.3522	0.169	0.4122	0.151	0.3220	0.292	0.3415	0.1350	0.3924
	f			1.084	0.4261	0.406	0.4562	0.364	0.3330	0.724	0.3777	0.312	0.4419
cc-pVQZ	s	0.0482	0.2629	0.1054	0.3193	0.0610	0.3559						
	p	0.1626	0.2904	0.0818	0.3072	0.0435	0.3502						
	d	0.351	0.2870	0.273	0.3655	0.1160	0.3730						
	f	0.691	0.2577	0.689	0.4521	0.294	0.5414						
	g			1.224	0.4103	0.459	0.4558						
cc-pV5Z	s	0.0311	0.1896	0.0957	0.3338	0.0538	0.3608						
	p	0.1400	0.3024	0.0654	0.3410	0.0402	0.3665						
	d	0.289	0.3164	0.213	0.3629	0.1210	0.3916						
	f	0.535	0.3131	0.425	0.4021	0.209	0.5123						
	g	0.790	0.2303	0.809	0.4303	0.334	0.5023						
	h			1.628	0.4311	0.742	0.5870						

TABLE IV. Dipole polarizabilty (α_1) of Ne as a function of basis set and level of theory (all values in a.u.).

Level of augmentation	Basis quality	RHF	MP2	MP3	MP4	CCSD	CCSD(T)	CISD
cc-pVXZ	DZ	0.488	0.481	0.483	0.483	0.483	0.483	0.484
	TZ	1.026	1.028	1.030	1.030	1.030	1.030	1.029
	QZ	1.469	1.520	1.510	1.518	1.513	1.517	1.507
	5Z	1.759	1.866	1.840	1.864	1.847	1.858	1.836
aug-cc-pVXZ	DZ	1.832	1.989	1.951	1.993	1.970	1.980	1.957
	TZ	2.194	2.437	2.365	2.444	2.391	2.421	2.368
	QZ	2.329	2.620	2.523	2.626	2.554	2.595	2.525
	5Z	2.363	2.675	2.564	2.681	2.599	2.645	2.567
d-aug-cc-pVXZ	DZ	2.353	2.688	2.591	2.711	2.640	2.671	2.615
	TZ	2.375	2.711	2.599	2.729	2.643	2.689	2.611
	QZ	2.380	2.708	2.592	2.719	2.632	2.679	2.598
	5Z	2.377	2.703	2.584	2.710	2.623	2.671	2.589
t-aug-cc-pVXZ	DZ	2.357	2.695	2.597	2.720	2.647	2.679	2.621
	TZ	2.375	2.712	2.600	2.731	2.645	2.691	2.612
	QZ	2.380	2.709	2.592	2.719	2.632	2.680	2.599
q-aug-cc-pVXZ	DZ	2.357	2.695	2.597	2.720	2.648	2.679	2.622
	TZ	2.375	2.712	2.600	2.731	2.645	2.691	2.612
	QZ	2.380	2.709	2.592	2.719	2.632	2.680	2.599

the dipole polarizability, the p and f exponents for the quadrupole polarizability, and the g exponent for the octopole polarizability. This is consistent with the importance of these functions for the noted properties.

III. POLARIZABILITIES VIA FINITE FIELD CALCULATIONS

The static electrical properties of atoms may be determined in a straightforward manner by calculating the change in the energy of the atom in response to a variable electric field, field gradient, or higher derivatives. The response function for ^1S states can be expanded in even powers of a polynomial as

$$\Delta E = -\tfrac{1}{2}\alpha_1 F^2 - \tfrac{1}{24}\gamma F^4 - \tfrac{1}{8}\alpha_2 (F')^2 - \tfrac{1}{72}\alpha_3 (F'')^2 + \cdots ,$$

(1)

where cross terms have been omitted. The electric field, field gradient, and second derivative of the field are F, F', and F'', respectively; α_1, α_2, and α_3 are the dipole, quadrupole, and octopole polarizabilities; and γ is the dipole second hyperpolarizability. This is the commonly used notation for atomic properties, as noted in the recent work of Bishop and Pipin.[15] In practice, one determines the response to F, F', and F'' separately. The coefficients for α_2 and α_3 were chosen to be consistent with atomic usage.[16] Some investigators denote the quadrupole polarizability as C.[17,18] The quadrupole polarizability α_2 is (usually) twice the value of C. The response function for the $^1\Sigma$ molecular states of HCl and N_2 is a modified form of (1) which reflects the nonspherical nature of the charge distribution for these species.

The present calculations have been performed using the MOLPRO92 program suite.[19] MOLPRO92 allows the user to explicitly add electric fields and/or field gradients to the one-electron Hamiltonian. For the determination of the

dipole polarizabilities and the hyperpolarizabilty, fields strengths from 0 to 0.008 a.u. in steps of 0.001 a.u. have been used and a polynomial was fitted to the data. Quadrupole polarizabilities were determined more crudely, by examining only the unperturbed atom and calculations with field gradients of ± 0.001 a.u. Since MOLPRO92 does not possess the capability of adding an octopolar F'' field, appropriate fields were generated using point charges. A value of $F''=0.001$ a.u. can be generated by placing charges of $\pm 90e$ at $Z=\pm 30a_0$ and $\mp 360e$ at $Z=\pm 60a_0$. Although this only approximates an octopolar field, it does eliminate F and F' fields at the origin.

A number of *ab initio* methodologies were used in this work: (restricted) Hartree–Fock (RHF), Møller–Plesset perturbation theory through fourth order (MP2, MP3, and MP4), and singles and doubles coupled-cluster theory without (CCSD) and with the perturbative approximation for inclusion of triple excitations[20] [CCSD(T)].[21] For neon, we have also included singles and doubles configuration interaction (CISD). Only valence electrons were correlated throughout. The convergence criteria for SCF, CCSD, and CISD energies were set to 10^{-12} E_h or tighter in order to ensure accurate differential energy changes.

IV. ELECTRICAL PROPERTIES OF Ne, He, AND Ar

The neon atom was chosen to be the test case for the calculation of the static electrical properties of the rare gas atoms. The methodology established for neon was then applied to the other rare gas atoms.

A. Ne

1. cc-pVXZ and x-aug-cc-pVXZ sets

Values for the dipole properties α_1 and γ for neon were computed using 18 different basis sets (double through quintuple zeta cc-pVXZ, aug-cc-pVXZ, and d-aug-cc-

TABLE V. Dipole second hyperpolarizabilty (γ) of Ne as a function of basis set and level of theory (all values in a.u.).

Level of augmentation	Basis quality	RHF	MP2	MP3	MP4	CCSD	CCSD(T)	CISD
cc-pVXZ	DZ	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	TZ	0.4	0.3	0.3	0.3	0.3	0.3	0.3
	QZ	1.9	1.8	1.8	1.8	1.8	1.9	1.8
	5Z	4.9	5.5	5.4	5.5	5.4	5.5	5.3
aug-cc-pVXZ	DZ	20.3	28.1	25.5	28.9	27.1	27.9	26.3
	TZ	28.2	40.3	35.6	42.2	38.1	40.2	36.5
	QZ	38.6	56.6	48.6	60.0	52.5	56.1	50.1
	5Z	50.1	75.3	63.5	80.0	69.0	74.5	65.6
d-aug-cc-pVXZ	DZ	49.2	77.5	66.0	85.1	74.1	78.6	71.1
	TZ	52.3	90.6	75.3	98.4	84.0	90.8	79.6
	QZ	62.0	98.3	80.8	106.1	89.8	97.6	84.7
	5Z	67.5	107.2	87.6	115.0	97.3	105.8	91.7
t-aug-cc-pVXZ	DZ	53.3	86.8	72.7	96.2	83.1	88.4	79.3
	TZ	66.6	106.5	88.0	115.9	98.6	106.7	93.3
	QZ	67.9	108.4	88.6	116.8	98.8	107.3	93.1
q-aug-cc-pVXZ	DZ	53.3	86.7	72.6	96.3	83.3	88.5	79.4
	TZ	66.9	110.6	91.2	120.4	102.6	111.0	96.9
	QZ	68.1	109.4	89.4	118.0	99.6	108.3	93.9

pVXZ sets, and the double through quadruple zeta t-aug-cc-pVXZ and q-aug-cc-pVXZ sets) and seven levels of theory [RHF, MP2, MP3, MP4, CCSD, CCSD(T), and CISD]. The results are summarized in Tables IV and V.

There are two different basis set dependencies that can be examined for α_1 and γ: (1) the XZ dependence of each series (cc-pVXZ, aug-cc-pVXZ, and so on); and (2) the x-aug dependence of the double through quadruple zeta sets. For the properties of interest here, the XZ dependence is only moderately informative; it does reflect the importance of successive levels of augmentation, but it can be difficult to discern trends from the numbers. On the other hand, the x-aug dependence is a means of ascertaining the appropriate limit through a specific level of angular symmetry. In the case of electrical response properties, where functions of certain symmetries tend to be critical for making accurate predictions, the latter dependence tends to be more informative. Since the abscissa is now the number of diffuse functions, it is very straightforward to determine the convergence as a function of the diffuseness of the basis. Of course, the complete basis set limit can only be ascertained by an extrapolation in both XZ and x-aug. However, as we shall see, convergence is rapid and the best calculations are very near the "complete" basis set limit.

Figures 1(a) and 1(b), and 2(a) and 2(b) depict the trends in α_1 and γ using RHF and MP2 wave functions for the two functional dependencies described earlier. For both XZ and x-aug dependence, the higher quality sets converge most rapidly and smoothly toward the basis set limit for both dipole properties. However, a comparison of the respective plots for XZ and x-aug dependence readily illustrates the greater usefulness of the latter.

Let us first consider α_1 at the MP2 level. The XZ dependence of this property, Fig. 1(a), varies significantly with the number of diffuse functions added to each base
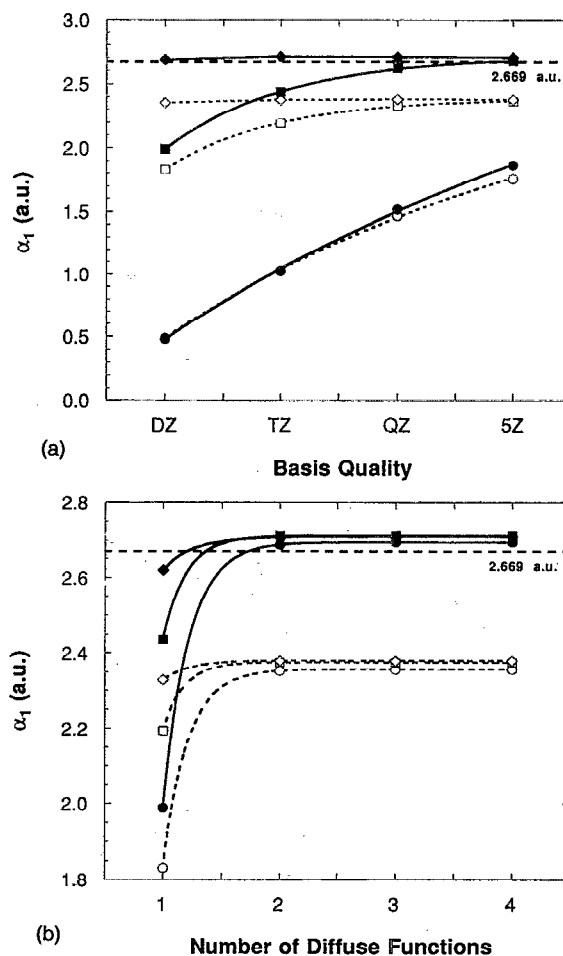

FIG. 1. Behavior of the dipole polarizability α_1 of Ne at the RHF (open symbols) and MP2 (solid symbols) levels of theory: (a) XZ dependence for the cc-pVXZ (O,●), aug-cc-pVXZ ($\square$,■), and d-aug-cc-pVXZ ($\Diamond$,♦) sets; (b) x-aug dependence for DZ (O,●), TZ ($\square$,■), and QZ ($\Diamond$,♦) basis sets.
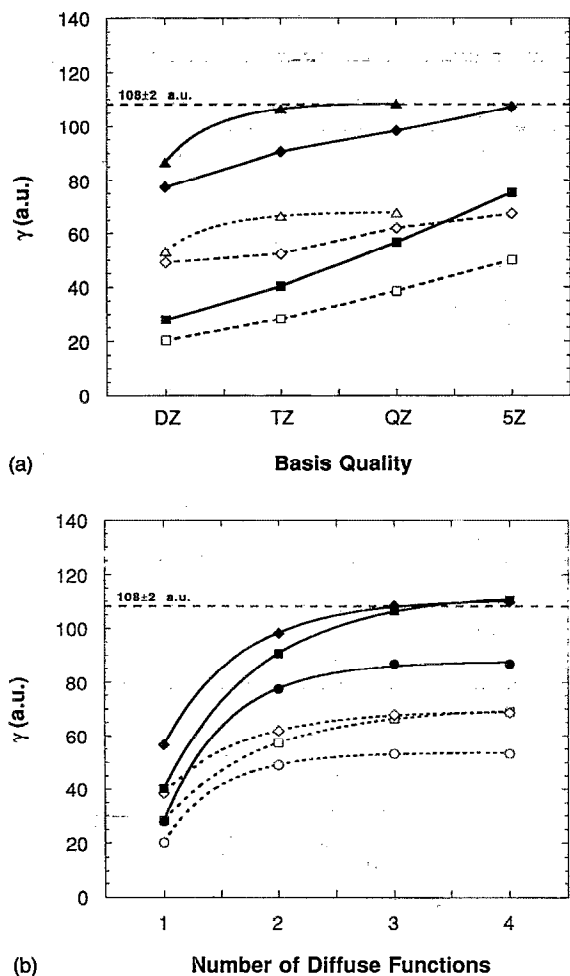
FIG. 2. Behavior of the second hyperpolarizability γ of Ne at the RHF (open symbols) and MP2 (solid symbols) levels of theory: (a) XZ dependence for the aug-cc-pVXZ ($\square$,$\blacksquare$), d-aug-cc-pVXZ ($\Diamond$,$\blacklozenge$) and t-aug-cc-pVXZ ($\triangle$,$\blacktriangle$) sets; (b) x-aug dependence for DZ ($\bigcirc$,$\bullet$), TZ ($\square$,$\blacksquare$), and QZ ($\Diamond$,$\blacklozenge$) basis sets

already near the limit is the key to understanding the basis set behavior of this property—it indicates that functions of greater than d symmetry are not needed for describing the dipole polarizability. The situation is clearly evident in the corresponding x-aug plot, Fig. 1(b). Here we see that the DZ series converges quickly and to nearly the same value as the TZ and QZ series. This indicates that basis sets that contain only d functions can provide accurate predictions of atomic polarizabilities as long as sufficiently diffuse functions are included in the set. f functions increase the calculated polarizability by less than 1%, and g functions have a negligible effect.

The trends observed for α_1 are more pronounced for γ. For the XZ dependence shown in Fig. 2(a), the variation of γ is irregular for both the aug-cc-pVXZ and d-aug-cc-pVXZ series. Only for the triply-augmented sets does a well behaved convergence pattern emerge. Once again, the behavior of the x-aug dependence is straightforward to interpret. The TZ series converges to an MP2 limit that is about 25 a.u., or 28%, above the limit with the DZ series. The QZ series shows no further improvement. Thus, for γ, f functions are quite important, and g functions are significantly less important, a fact noted previously by Taylor et al.[18]

The relative importance of diffuse functions for α_1 and γ can also be very easily seen from the x-aug dependence. The dipole polarizability converges with only two diffuse functions. For the hyperpolarizability, at least three diffuse functions are necessary in order to approach the limiting value. Of course, the need for three functions must be taken as a less-than-optimal scenario since an even-tempered expansion of diffuse functions will not necessarily span the function space with maximal efficiency.

Fits of the x-aug series were attempted using a three-parameter exponential function whose form and rationale has been discussed elsewhere.[2] This is the first time this function has been used for fitting an x-aug expansion, but it performs just as well as it previously has for XZ dependence. Unfortunately, with only three or four data points and a function with three parameters, there is not much meaning to "error of the fit." It is, however, useful to consider the difference between the last data point and the estimated CBS limit—this is a direct measure of the completeness of the basis set.

For the XZ dependence of α_1, only the aug-cc-pVXZ series can extrapolated, while for the x-aug dependence, all

set. The standard cc-pVXZ series is so far from the limit and the variation possesses so little curvature that a meaningful extrapolation is impossible. The aug-cc-pVXZ series converges smoothly to a number slightly larger than the experimental value, while the d-aug-cc-pVXZ series varies little with basis set (as do the triply- and quadruply-augmented series, which are not shown). Actually, the fact that the value of α_1 derived from the d-aug-cc-pVDZ set is

TABLE VI. Extrapolated limits for the x-aug-cc-pVXZ sets of the dipole polarizabilty (α_1) and dipole second hyperpolarizability (γ) of Ne for the cc-pVDZ, cc-pVTZ, and cc-pVQZ sets (all values in a.u.).

Property	Base Set	RHF	MP2	MP3	MP4	CCSD	CCSD(T)	CISD
α_1	cc-pVDZ	2.357	2.695	2.597	2.720	2.648	2.679	2.622
	cc-pVTZ	2.375	2.712	2.600	2.731	2.645	2.691	2.512
	cc-pVQZ	2.380	2.709	2.592	2.719	2.632	2.680	2.599
γ	cc-pVDZ	53.5	87.6	73.2	97.3	84.1	89.4	80.1
	cc-pVTZ	70.2	112.9	93.1	122.9	104.7	113.2	98.9
	cc-pVQZ	69.2	110.6	90.4	119.2	100.7	109.4	94.9

TABLE VII. Quadrupole (α_2) and octopole (α_3) polarizabilties of Ne as a function of basis set and level of theory (all values in a.u.).

Level of augmentation	Basis quality	α_2				α_3		
		RHF	MP2	MP4	CCSD(T)	RHF	MP2	MP4
aug-cc-pVXZ	DZ	2.979	3.551	3.597	3.524	3.286	3.454	3.458
	TZ	3.741	4.279	4.308	4.240	8.671	9.753	9.739
	QZ	4.506	5.093	5.103	5.034	14.288	16.703	16.653
	5Z	5.451	6.207	6.204	6.118			
d-aug-cc-pVXZ	DZ	3.078	3.669	3.724	3.650	15.444	20.053	20.392
	TZ	5.294	6.066	6.092	6.004	18.335	23.765	24.043
	QZ	5.971	6.915	6.922	6.807	25.117	31.601	31.767
	5Z	6.385	7.510	7.513	7.365			
t-aug-cc-pVXZ	DZ	3.081	3.667	3.738	3.663	18.263	24.156	24.574
	TZ	6.220	7.349	7.396	7.249	19.903	26.079	26.456
	QZ	6.351	7.501	7.522	7.367	32.560	41.854	42.101
q-aug-cc-pVXZ	DZ	3.087	3.667	3.806	3.720	18.642	24.221	24.737
	TZ	6.354	7.520	7.583	7.429	20.381	26.511	26.870
	QZ	6.415	7.569	7.591	7.437	35.357	45.421	45.755

three levels of basis sets can be extrapolated. The problems fitting the XZ dependence become even worse for other properties, but the x-aug dependence can be fit reliably for all of the properties considered here. We have chosen to adopt the extrapolated limits of the x-aug dependence as our yardstick for evaluating basis set performance in describing the properties of the rare gas atoms. Table VI lists the x-aug limits (i.e., infinite augmentation) for both the dipole polarizability and the hyperpolarizability using all seven methods noted previously. By comparing these limiting values with the current experimental values of 2.669 a.u. (Ref. 22) for α_1 and 108 ± 2 a.u. (Ref. 23) for γ, we can establish definitive conclusions regarding how well each method performs.

In the case of the dipole polarizability, the DZ, TZ, and QZ x-aug expansions for all seven methods converge to essentially the same number, within the error of the fit. For example, the RHF values only range from 2.36 to 2.38 a.u. For purposes of comparison, the values for the x-aug-cc-pVQZ limits will be used: RHF (2.38), MP2 (2.71), MP3 (2.59), MP4 (2.72), CCSD (2.63), CCSD(T) (2.68), and CISD (2.60). The CCSD(T) value of α_1 is in excellent agreement with experiment, with the MP2 and MP4 values being of comparable accuracy. CCSD, CISD, and MP3 all undershoot, but only by a few percent. The RHF value is nearly 90% of the experimental value, leaving only 10% to be recovered by correlation (a finding previously observed by Rice[24,25] and others).

For the hyperpolarizability, f functions play an important role as can be seen from the gap between the DZ and TZ values, e.g., 87.6 a.u. vs 112.9 a.u. for the MP2 calculations. The TZ and QZ limits, on the other hand, do not vary by more that 5 a.u. (or 5%). Thus, f functions are quite important for the calculation of accurate values for γ, while g functions are only moderately important. As above, the limiting values of the x-aug-cc-pVQZ series can be used to make comparisons between the methods; they are RHF (69.2), MP2 (110.6), MP3 (90.4), MP4 (119.2), CCSD

(100.7), CCSD(T) (109.4), and CISD (94.9). The pattern is nearly the same as for α_1, but with more pronounced differences. Comparison of the RHF and experimental results indicates that electron correlation accounts for approximately 35% of the total value. Again, the CCSD(T) value is closest to the experimental value, but the MP2 result is only marginally larger than the CCSD(T) number. MP3, CISD, and CCSD undershoot by about 17%, 12%, and 6%, respectively, while MP4 overshoots by approximately 10%.

Our x-aug-cc-pVQZ limiting values for α_1 and γ agree very well with previous work where efforts were made to saturate sets for dipole properties (and sometimes for higher effects as well). Cernusak et al.[26] determined values of $\alpha_1=2.712$ a.u. and $\gamma=104.6$ a.u. using MP4 theory and a basis set that included partially optimized d and f functions. Our value of α_1 is essentially the same, but our result for γ is 15 a.u. larger because of the extra diffuse functions included in our sets. Maroulis and Thakkar[27] reported $\gamma=113.9$ a.u. with a partial CCSD wave function using Cernusak's[26] basis set, which they modified in order to improve the quadrupole polarizability. Chong and Langhoff[28] report CCSD(T) values of $\alpha_1=2.684$ a.u. and $\gamma=111.0$ a.u., which are almost identical to ours. Their basis set, like ours, was designed to thoroughly span exponent space (through f-type functions) without being explicitly optimized. A recent value for γ of 106 ± 5 a.u. by Christiansen and Jørgensen[29] was computed using a large restricted active space (RAS) wave function with single through quadruple excitations and is in excellent agreement with Shelton's experimental value.

Several studies by Taylor, Rice, and co-workers[18,24,25] have approached this problem with a thoroughness similar to that applied in the present investigation. They too have considered sets that include $spdfgh$ functions, and they have also utilized an even-tempered expansion of diffuse exponents. Their values for α_1 are essentially the same as
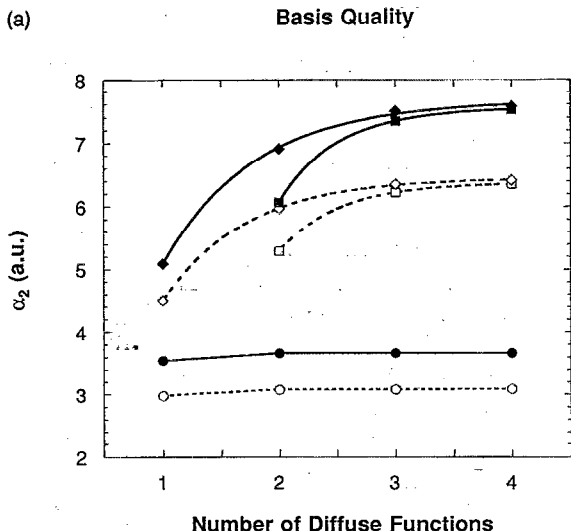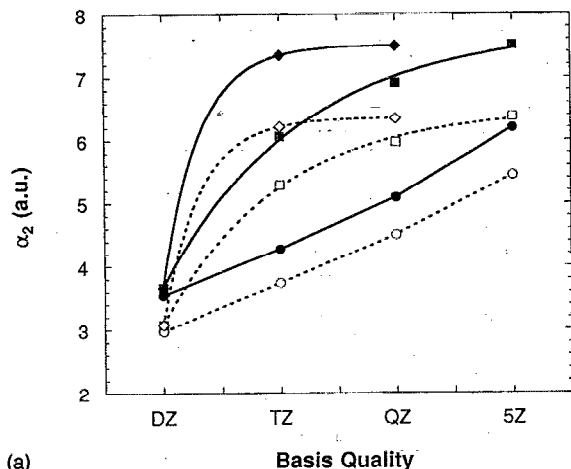
FIG. 3. Behavior of the quadrupole polarizability α_2 of Ne at the RHF (open symbols) and MP2 (solid symbols) levels of theory: (a) XZ dependence for the aug-cc-pVXZ (○,●), d-aug-cc-pVXZ (□,■), and t-aug-cc-pVXZ (◇,◆) sets; (b) x-aug dependence for DZ (○,●), TZ (□,■), and QZ (◇,◆) basis sets.

ours, and their best CCSD(T) numbers for γ are in the range of 110–112 a.u. (Refs. 18 and 25).

Correlation consistent basis sets were also employed to determine the quadrupole (α_2) and octopole (α_3) polarizabilities of Ne for a subset of the methods used for the dipole properties. The numbers (in Table VII) were calculated with a cruder application of the finite field method than used for the dipole properties, the response to one field strength (± 0.001 a.u. for α_2 and 0.001 a.u. for α_3). This approach is usually sufficient to obtain accurate values for polarizabilities, however.

Figures 3(a) and 3(b) depict the XZ and x-aug dependence of α_2 for Ne. Once again, the trends are more visibly evident in the x-aug plot. Functions of f symmetry are clearly more important for α_2 than α_1. The DZ values in Fig. 3(b) show s, p, and d functions make a net contribution that amounts to less than half of the QZ limiting values. There is little improvement in α_2 even when three or four diffuse s, p, and d functions are added to the cc-pVDZ set. Use of the TZ sets essentially eliminates the

TABLE VIII. Extrapolated limits of the x-aug-cc-pVXZ sets of the quadrupole (α_2) and octopole (α_3) polarizabilties of Ne (all values in a.u.).

Property	Base set	RHF	MP2	MP4	CCSD(T)
α_2	cc-pVDZ	3.08	3.67	3.83	3.73
	cc-pVTZ	6.38	7.55	7.61	7.46
	cc-pVQZ	6.45	7.66	7.68	7.52
α_3	cc-pVDZ	18.89	24.71	25.22	
	cc-pVTZ	20.37	26.57	26.95	
	cc-pVQZ	37.04	47.32	47.75	

error. There is little change in the calculated α_2's with the QZ sets; thus, g functions are of minor importance. Sufficient diffuse character is only achieved when three diffuse functions have been added.

Extrapolated limits for α_2 from the x-aug dependence are given in Table VIII. Since there are no experimentally determined values for either α_2 or α_3, the CBS limit of 7.52 a.u. from the QZ sets and the CCSD(T) wave function will be used for evaluating the other levels of theory. The corresponding MP2 and MP4 values of 7.66 and 7.68 a.u., respectively, both slightly overshoot. The value of α_2 from the RHF calculations is 86% of that obtained from the CCSD(T) calculations.

There have been fewer previous calculations of α_2 than for α_1 and γ. Our calculations are again in good agreement with previous work. For example, Cernusak et al.[26] reported a value of $\alpha_2 = 7.7$ a.u. at the MP4 level of theory. The value of Maroulis and Thakkar,[27] determined with a wave function similar to CCSD(T), is 7.525 a.u. Taylor et al.[18] obtained a value of 7.36 au from their CCSD(T) calculations.

Recently, Bishop and Cybulski[30] have reported SCF values of the polarizabilities of He through Xe which were produced using exceptionally large uncontracted basis sets. For Ne, their results with a $(20s\,14p\,10d\,6f)$ set are $\alpha_1 = 2.3766$ a.u., $\gamma = 68.58$ a.u., and $\alpha_2 = 6.4203$ a.u. The
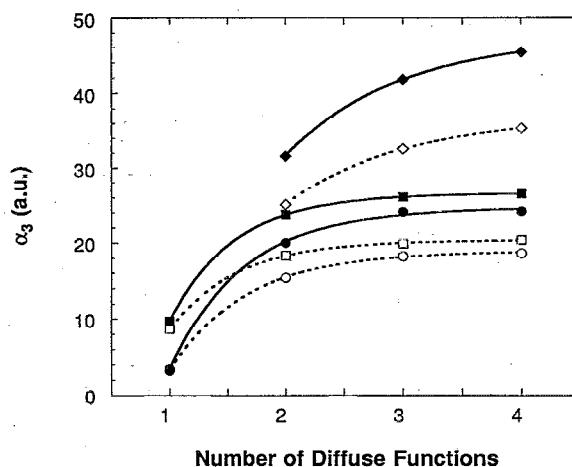

FIG. 4. Behavior of the octopole polarizability α_3 of Ne at the RHF (open symbols) and MP2 (solid symbols) levels of theory showing the x-aug dependence for DZ (○,●), TZ (□,■), and QZ (◇,◆) basis sets.

TABLE IX. Optimization of diffuse functions for Ne at the MP2 level; functions are optimized as follows: s and d for α_1, p and f for α_2, and g for α_3 (all values in a.u.). (a) Optimal exponents; (b) electrical properties.

	(a)		
Symmetry	cc-pVDZ	cc-pVTZ	cc-pVQZ
s	0.1115	0.1111	0.1062
p	0.0346	0.0702	0.0712
d	0.2964	0.2207	0.1917
f		0.2164	0.2088
g			0.1735
	(b)		
Property	cc-pVDZ+opt. spd	cc-pVTZ+opt. $spdf$	cc-pVQZ+opt. $spdfg$
α_1	2.301	2.664	2.689
γ	19.83	82.64	91.69
α_2	4.772	7.252	7.296
α_3	10.080	18.909	37.548

RHF/x-aug-cc-pVQZ limits are very close to these numbers, with a tendency to slightly overestimate.

Finally, we also determined values for the octopole polarizability, α_3. Results with the various basis sets and RHF, MP2, and MP4 methods are shown in Table VII. The x-aug behavior is plotted in Fig. 4. A large jump in the magnitude of α_3 occurs when g functions are present for the first time in the QZ series. Whereas the value α_1 was near the limit with two sets of diffuse functions and α_2 with three, α_3 changes even when the fourth set of diffuse functions are added. The x-aug limits for α_3 are in Table VIII. The MP2 and MP4 limits for the QZ series are very similar, about 47 a.u. The RHF limit of 37.0 a.u. is only 79% of the correlated value.

Literature values for α_3 are scarce. Doran[31] obtained a value of 30.4 a.u. using Brueckner–Goldstone perturbation theory. McEachran et al.[32] used the coupled Hartree–Fock approximation and found a value of 34.271 a.u., which compares well with the RHF limit of the present work (37.0 a.u.). Their values for α_1 and α_2 (2.377 and 6.423 a.u., respectively) are also in good agreement with the present findings (2.37 and 6.45 a.u., respectively).

There are several trends that emerge from studying the basis set dependence for α_1, α_2, and α_3. As expected from perturbation theory arguments, the symmetry type of the most important polarization function for each property progresses from d to f to g. The amount of diffuse character required in the basis set also increases. Finally, the fraction of each property that is due to correlation increases steadily, from 10% to 14% to 21%.

2. Optimized augmenting functions

The even-tempered expansions used to this point have performed in a very consistent manner. They exhibit a decided tendency toward smooth convergence as a function of the number of diffuse functions added to the standard cc-pVXZ sets (x-aug dependence). However, there is no reason to expect that an even-tempered expansion will be the most rapidly convergent one. For that matter, a certain arbitrariness was used in determining the diffuse expo-

nents. It is therefore of some interest to examine explicit optimization of diffuse functions for the static electrical properties.

Unfortunately, various problems developed in the course of the attempted optimizations. Some were questions of stategy, such as which functions should be optimized for which properties. Others were more fundamental difficulties, such as a tendency of properties such as the hyperpolarizability and the quadrupole polarizability to blow up to unphysical values.

In light of the importance of d, f, and g functions for the dipole, quadrupole, and octopole polarizabilities, respectively, exponents for each of these symmetries were optimized for the corresponding property. s and p functions contribute predominantly to α_1 and α_2, respectively. Optimizations were carried out at the MP2 level. Table IX(a) lists the optimal exponents, and Table IX(b) notes the corresponding properties.

The optimized exponents are somewhat more diffuse than the values used in the aug-cc-pVXZ sets (compare to the column of α values for Ne in Table III). It is also clearly evident that a single optimized function performs better than the arbitrary first set of diffuse functions present in the singly augmented sets. For example, the cc-pVDZ set with the optimized spd functions predicts the dipole polarizability (α_1) of Ne to be 2.30 a.u.; this compares to a value of 1.99 a.u. for the aug-cc-pVDZ set, 2.695 a.u. for the extrapolated x-aug-cc-pVDZ limit, and an experimental value of 2.669 a.u. The properties for the cc-pVQZ set plus optimized $spdfg$ functions, $\alpha_1=2.69$, $\gamma=91.7$, $\alpha_2=7.30$, and $\alpha_3=37.5$ a.u., compare fairly well with the MP2/x-aug-cc-pVQZ limits established previously of $\alpha_1=2.71$, $\gamma=112$, $\alpha_2=7.6$, and $\alpha_3=47.3$ a.u. The discrepancies become larger for the higher polarizabilities, and the hyperpolarizability is shy of the limit by 20 a.u.

Unfortunately, all attempts to optimize a second diffuse function of each symmetry failed; problems were encountered with nonphysical, divergent values. There were even problems with the dipole properties. α_1 can be used to optimize a second s and d function (and reoptimize the

TABLE X. Properties of He as a function of basis set and level of theory (all values in a.u.). Estimated x-aug-cc-pVXZ limits are also given.

Basis set	RHF	MP2	CCSD	RHF	MP2	CCSD
	α_1			γ		
aug-cc-pVDZ	1.304	1.338	1.362	6.43	6.89	7.58
d-aug-cc-pVDZ	1.329	1.367	1.394	16.20	18.84	20.61
t-aug-cc-pVDZ	1.330	1.368	1.395	16.40	19.09	20.84
x-aug limit	1.330	1.368	1.395	16.4	19.1	20.8
aug-cc-pVTZ	1.316	1.355	1.379	16.23	18.22	19.79
d-aug-cc-pVTZ	1.324	1.364	1.388	34.56	39.16	41.60
t-aug-cc-pVTZ	1.324	1.364	1.388	34.69	39.37	41.91
x-aug limit	1.324	1.364	1.388	34.7	39.4	41.9
aug-cc-pVQZ	1.322	1.360	1.384	23.79	26.80	28.79
d-aug-cc-pVQZ	1.322	1.361	1.385	35.41	40.06	42.64
t-aug-cc-pVQZ	1.322	1.361	1.385	35.40	40.08	42.36
x-aug limit	1.322	1.361	1.385	35.4	40.1	42.4
	α_2			α_3		
aug-cc-pVTZ	1.314	1.324	1.358			
d-aug-cc-pVTZ	2.236	2.317	2.357			
t-aug-cc-pVTZ	2.236	2.318	2.358			
x-aug limit	2.236	2.318	2.358			
aug-cc-pVQZ	1.721	1.767	1.791	1.657	1.678	1.692
d-aug-cc-pVQZ	2.293	2.376	2.419	9.453	9.791	10.001
t-aug-cc-pVQZ	2.294	2.377	2.420	9.946	10.345	10.578
x-aug limit	2.294	2.377	2.420	9.97	10.39	10.62

first functions of those symmetries), but γ blows up as a consequence. The even-tempered expansion is slower, but the convergence is more consistent and dependable.

B. He

Table X presents data for the properties of He and the estimated x-aug limits. The methods have been restricted to RHF, MP2, and CCSD. With only two electrons to correlate, the latter is equivalent to performing the full CI calculation. The same properties which were examined for Ne (α_1, γ, α_2, and α_3) have also been computed for He. The DZ results for α_2 and the DZ and TZ results for α_3 were identically zero and have been omitted. The trends are much the same as for Ne, though there is a shift in which angular symmetry is most important for each polarizability (p functions are now most important for α_1 and so on). This is a straightforward consequence of the fact that the valence orbital in He is the $1s$ orbital rather than the $(2s,2p)$ orbitals of Ne. The properties of He are easier to describe than those of Ne. Most require only two diffuse functions before saturation is achieved. Even in the worst case, the octopole polarizability, the third set of diffuse functions makes a contribution no larger than about 10%.

As in Ne, there is little variation in the x-aug limits for each basis set. For example, the DZ, TZ, and QZ limits for α_1 at the CCSD level of theory decrease, respectively, from 1.395 to 1.388 to 1.385 a.u. Correlation is much less important for He than it is for Ne, but it does become more significant for the higher polarizabilities. Using the QZ lim-

its for RHF and CCSD, the correlation effects are α_1, 4.6%; γ, 16.5%; α_2, 5.2%; and α_3, 6.1%.

Helium has been treated very accurately by previous workers. The recommended values of the present work (CCSD/x-aug-cc-pVQZ limits) are $\alpha_1 = 1.385$ a.u., $\gamma = 42.4$ a.u., $\alpha_2 = 2.42$ a.u., and $\alpha_3 = 10.62$ a.u. The values of Rice et al.[24] for α_1 and γ are 1.384 and 43.6 a.u., respectively (CCSD with $spdf$ functions). Visser et al.[33] computed values of $\alpha_1 = 1.385$ a.u., $\alpha_2 = 2.445$ a.u., and $\alpha_3 = 10.60$ a.u., while Bishop and Pipin[15] find values of $\alpha_1 = 1.383$ a.u., $\alpha_2 = 2.445$ a.u., and $\alpha_3 = 10.62$ a.u. using explicitly correlated wave functions. The value of Bishop and Rérat[34] for γ is 43.1 a.u. There is excellent agreement between all of these results and the present numbers. The SCF results of Bishop and Cybulski[30] computed with a $(18s14p10d6f)$ uncontracted set are $\alpha_1 = 1.3222$ a.u., $\gamma = 36.03$ a.u., and $\alpha_2 = 2.3263$ a.u. The RHF/x-aug-cc-pVQZ limits are slightly below these numbers.

C. Ar

Table XI presents data for the properties of argon along with the estimated x-aug limits. The methods include RHF, MP2, MP4, and CCSD(T). Except for γ, the MP4 and CCSD(T) values are in nearly exact agreement and differ little from the MP2 results. The dipole hyperpolarizability is the one area where the correlated methods substantially disagree, and this is due to the instability of the total energies computed using MP theory (the MP2 results are too unstable to even include in Table XI).

TABLE XI. Properties of Ar as a function of basis set and level of theory (all values in a.u.). Estimated x-cc-pVXZ limits are also given.

Basis set	RHF	MP2	MP4	CCSD(T)	RHF	MP2	MP4	CCSD(T)
			α_1				γ	
aug-cc-pVDZ	9.565	9.762	9.829	9.837	296		355	364
d-aug-cc-pVDZ	10.573	10.959	11.041	11.050	720		955	968
t-aug-cc-pVDZ	10.575	10.959	11.043	11.052	707		982	954
x-aug limit	10.58	10.96	11.04	11.05				
aug-cc-pVTZ	10.438	10.814	10.840	10.841	457		559	560
d-aug-cc-pVTZ	10.701	11.169	11.191	11.190	844		1099	1079
t-aug-cc-pVTZ	10.702	11.170	11.193	11.192	945		1231	1210
x-aug limit	11.70	11.17	11.19	11.19	981		1274	1254
aug-cc-pVQZ	10.705	11.110	11.084	11.076	687		797	817
d-aug-cc-pVQZ	10.726	11.156	11.127	11.117	893		1055	1078
t-aug-cc-pVQZ	10.726	11.156	11.126	11.117	951		1125	1148
x-aug limit	10.73	11.16	11.13	11.12	974		1151	1174
			α_2				α_3	
aug-cc-pVDZ	20.20	21.68	22.06	22.11	137.9	135.0	137.1	137.3
d-aug-cc-pVDZ	20.54	22.10	22.51	22.57	277.9	298.2	301.8	302.1
t-aug-cc-pVDZ	20.66	22.22	22.62	22.69	288.2	311.4	314.3	314.4
x-aug limit	20.7	22.3	22.7	22.7	289	313	315	315
aug-cc-pVTZ	33.26	34.47	34.65	34.68	231.3	232.9	234.1	234.2
d-aug-cc-pVTZ	46.77	48.96	49.06	49.07	312.2	328.4	328.2	328.1
t-aug-cc-pVTZ	49.68	52.39	52.41	52.41	318.4	336.6	336.3	336.6
x-aug limit	50.5	53.5	53.4	53.4	319	337	337	337
aug-cc-pVQZ	40.33	41.91	41.88	41.87	331.7	337.2	335.4	335.2
d-aug-cc-pVQZ	48.50	50.91	50.71	50.67	465.1	481.8	476.7	476.0
t-aug-cc-pVQZ	50.04	52.72	52.44	52.39	524.0	548.5	540.8	539.9
x-aug limit	50.4	53.2	52.9	52.8	571	606	594	593

The trends for Ar are very similar to those of Ne and He. Using the x-aug-cc-pVQZ limits for RHF and CCSD(T), the correlation effects are α_1, 3.5%; γ, 17.2%; α_2, 4.6%; and α_3, 3.7%. Correlation actually makes a smaller contribution for Ar than for Ne and He.

The recommended values for the properties of Ar from the present work [CCSD(T)/x-aug-cc-pVQZ limits] are $\alpha_1=11.12$, $\gamma=1174$, $\alpha_2=52.8$, and $\alpha_3=593$ a.u. The measured value for α_1 is 11.08 a.u.[22] The two experimental numbers for the hyperpolarizability are 1167 ± 6 a.u. (Ref. 35) and 1101 ± 8 a.u. (Ref. 36). The best theoretical values from the literature compare very well with the current results, although there is more variation for Ar than for Ne and He. Rice et al.[24] found $\alpha_1=11.2$ au and $\gamma=1220$ a.u. Cernusak et al.[37] report values of $\alpha_1=11.23$ a.u., $\gamma=1329$ a.u., and $\alpha_2=53.58$ a.u. using MP4 and a contracted set of $[9s7p5d3f]$. The values of Maroulis and Bishop[38] near the HF limit are $\alpha_1=10.73$ a.u., $\gamma=1190$ a.u., and $\alpha_2=49.26$ a.u. Finally, Bulski et al.[39] used MP4 and a $[9s7p3d2\ f2g]$ contracted basis set and found $\alpha_1=10.77$ a.u., $\alpha_2=50.51$ a.u., and $\alpha_3=525$ a.u. Our values for α_1 and α_2 are comparable to previous work, and our result for α_3 is probably the most-converged value to date. The variation in γ is very large, however. Although our recommended CCSD(T)/x-aug-cc-pVQZ limit of 1174 a.u. is close to the most recent experimental result of 1167 a.u., the CCSD(T)/x-aug-cc-pVTZ limit is much larger, 1254 a.u. In light of the problems that have been encountered with optimizing functions

in Ne, it may not be possible to predict a correlated value for γ with much certainty. The SCF results of Bishop and Cybulski[30] using a $(23s17p13d7f)$ set are $\alpha_1=10.757$ a.u.; $\gamma=958.9$ a.u.; and $\alpha_2=50.193$ a.u. Agreement with the RHF/x-aug-cc-pVQZ limits is very good for α_1 and α_2, but our RHF value for γ is apparently overestimating by about 15 a.u.

V. DIPOLE POLARIZABILITIES OF SELECTED ANIONS AND MOLECULES

To further test the multiply augmented basis sets discussed here, calculations were carried out on the fluoride and chloride anions and on the HCl and N_2 molecules.

A. F⁻ and Cl⁻

Although the fluoride and chloride ions are isoelectronic with Ne and Ar, they are more difficult to describe due to the diffuse character of the anionic charge distributions. However, understanding the properties of these species is of interest to workers who model the solvation of negative ions.[40] Table XII presents data for the dipole polarizabilities of F⁻ and Cl⁻ and the estimated x-aug limits. RHF, MP2, MP4, and CCSD(T) results are shown for the DZ and TZ series of basis sets with up to four sets of diffuse functions added. While it is clear that for the neutral rare gas atoms α_1 is not strongly dependent on f functions, it is not obvious a priori that this will also hold for

TABLE XII. Dipole polarizabilities (α_1) of F^- and Cl^- as a function of basis set and level of theory (all values in a.u.). Estimated x-aug limits are also given (fits used last three points only).

Species	Basis set	α_1			
		RHF	MP2	MP4	CCSD(T)
F^-	aug-cc-pVDZ	5.618	6.766	6.997	6.699
	d-aug-cc-pVDZ	9.832	14.524	17.195	14.835
	t-aug-cc-pVDZ	10.594	16.627	20.649	17.245
	q-aug-cc-pVDZ	10.596	16.624	20.645	17.272
	x-aug limit	10.60	16.62	20.65	17.27
	aug-cc-pVTZ	7.091	8.888	9.348	8.774
	d-aug-cc-pVTZ	10.314	15.566	18.501	15.731
	t-aug-cc-pVTZ	10.670	16.718	20.528	17.124
	q-aug-cc-pVTZ	10.672	16.727	20.550	17.151
	x-aug limit	10.67	16.73	20.55	17.15
Cl^-	aug-cc-pVDZ	21.434	22.731	23.046	23.108
	d-aug-cc-pVDZ	30.704	35.732	36.752	36.626
	t-aug-cc-pVDZ	31.282	36.853	37.962	37.795
	q-aug-cc-pVDZ	31.288	36.866	37.980	37.870
	x-aug limit	31.29	36.87	37.98	37.88
	aug-cc-pVTZ	25.498	27.810	28.128	28.109
	d-aug-cc-pVTZ	31.206	36.493	37.104	36.823
	t-aug-cc-pVTZ	31.475	37.080	37.733	37.415
	q-aug-cc-pVTZ	31.476	37.084	37.738	37.424
	x-aug limit	31.48	37.09	37.74	37.43

anions. The results, however, do indicate that f functions do not make a significant contribution to the dipole polarizability of F^- and Cl^-. The x-aug-cc-pVTZ series limits are, in fact, slightly smaller than the corresponding DZ limits. The value of α_1 for the rare gas atoms also dropped slightly, but only on expanding from the TZ to the QZ series.

For F^-, there is significant variation in the limiting values of α_1 at different levels of theory, with the ordering MP4 > CCSD(T) > MP2 > RHF. The same ordering occurs for Cl^-, but the numbers exhibit less variation. In particular, the CCSD(T) and MP4 numbers for Cl^- are nearly the same, while the corresponding values for F^- differ by more than 3 a.u.

Correlation is important to both species, although much more so for F^- than for Cl^-. Using the CCSD(T) and RHF limiting values for comparison, almost 40% of

the dipole polarizability of the fluoride ion is due to correlation. This decreases to 17% for Cl^-.

The recommended values of α_1 from the present work are 17.27 a.u. (F^-) and 37.89 a.u. (Cl^-). Very few values for these properties have appeared in the literature. Nelin et al.[41] report a value for F^- of 15.1 a.u., which is slightly below our CCSD(T)/x-aug-cc-pVDZ limit. The MP4 result of Diercksen and Sadlej[42] for Cl^- is 37.5 a.u. A more recent number by Kellö et al.,[43] 38.1 a.u., is in nearly exact agreement with the present work.

B. N_2 and HCl

To test the use of the proposed basis sets in molecular calculations, the dipole polarizability components of N_2 and HCl have been calculated. The results may be found in Tables XIII and XIV, respectively. For both molecules, the

TABLE XIII. Dipole polarizability components (α_{xx} and α_{zz}) of N_2 as a function of basis set and level of theory (all values in a.u.).

Basis set	α_{xx}				α_{zz}			
	RHF	MP2	MP4	CCSD(T)	RHF	MP2	MP4	CCSD(T)
aug-cc-pVDZ	9.667	10.031	10.159	10.189	15.373	14.661	15.414	15.312
d-aug-cc-pVDZ	9.956	10.254	10.395	10.423	15.507	14.788	15.543	15.442
t-aug-cc-pVDZ	9.967	10.265	10.407	10.435	15.511	14.794	15.549	15.448
x-aug limit	9.97	10.27	10.41	10.44	15.51	14.79	15.55	15.45
aug-cc-pVTZ	9.842	10.155	10.252	10.258	15.176	14.412	15.023	14.964
d-aug-cc-pVTZ	9.887	10.190	10.288	10.293	15.192	14.444	15.053	14.993
t-aug-cc-pVTZ	9.888	10.192	10.289	10.294	15.192	14.445	15.054	14.994
x-aug limit	9.89	10.19	10.29	10.29	15.19	14.45	15.05	14.99

TABLE XIV. Dipole polarizability components (α_{xx} and α_{zz}) of HCl as a function of basis set and level of theory (all values in a.u.).

Basis set	α_{xx}				α_{zz}			
	RHF	MP2	MP4	CCSD(T)	RHF	MP2	MP4	CCSD(T)
aug-cc-pVDZ	14.753	15.191	15.276	15.292	17.352	17.714	17.814	17.814
d-aug-cc-pVDZ	16.054	16.702	16.847	16.860	18.069	18.558	18.696	18.694
t-aug-cc-pVDZ	16.055	16.704	16.850	16.862	18.071	18.561	18.700	18.698
x-aug limit	16.06	16.70	16.85	16.86	18.08	18.56	18.70	18.70
aug-cc-pVTZ	15.816	16.297	16.460	16.448	17.805	18.152	18.293	18.276
d-aug-cc-pVTZ	16.134	16.672	16.876	16.857	17.995	18.372	18.534	18.513
t-aug-cc-pVTZ	16.129	16.668	16.873	16.853	18.009	18.388	18.549	18.528
x-aug limit	16.13	16.67	16.87	16.86	18.01	18.39	18.55	18.53

equilibrium geometries determined at the CCSD(T) level with the appropriate cc-pVXZ sets were used for all methods. For HCl, the extra diffuse functions were added only to the Cl atom; only singly-augmented sets were used for H.

It is evident that additional diffuse functions play a very reduced role for N_2. The doubly-augmented values are generally only 0.03 to 0.25 a.u. lower than the singly augmented results. The third diffuse function contributes very little. The x-aug-cc-pVDZ series has limiting values of 10.44 a.u. for the perpendicular α_{xx} component and 15.45 a.u. for the parallel α_{zz} component at the CCSD(T) level of theory. The average polarizability [$\bar{\alpha} = (2\alpha_{xx} + \alpha_{zz})/3$] is 12.11 a.u., which overshoots the experimental value of 11.8 a.u. (Ref. 44) by less than 3%. The average polarizability using the TZ series, 11.86 a.u., is closer to the experimental result. Maroulis and Thakkar[45] found RHF values of $\alpha_{xx} = 9.788$ a.u., $\alpha_{zz} = 14.960$ a.u., and $\bar{\alpha} = 11.51$ a.u. with a [$6s4p3d1f$] contracted set. Sekino and Bartlett[46] reported CCSD(T) values of $\alpha_{xx} = 10.1290$ a.u., $\alpha_{zz} = 14.9975$ a.u., and $\bar{\alpha} = 11.75$ a.u. Correlation makes only a minor contribution to describing the polarizability of N_2, and there is little difference between the MP4 and CCSD(T) numbers.

In HCl the additional diffuse functions in the doubly-augmented sets make somewhat larger contributions than in N_2, but the third function again contributes very little. There is also much better agreement between the x-aug-cc-pVDZ and x-aug-cc-pVTZ estimated limits. The x-aug-cc-pVTZ limits of $\bar{\alpha}$ at the RHF and CCSD(T) level are 16.76 and 17.42 a.u., respectively. Correlation therefore accounts for less than 4% of α_1 in HCl, which is much smaller than the 17% contribution noted above for Cl$^-$. The recent work by Hammond and Rice[47] reports CCSD(T) results of $\alpha_{xx} = 16.649$ a.u., $\alpha_{zz} = 18.420$ a.u., and $\bar{\alpha} = 17.24$ a.u., which are very similar to the present values.

VI. CONCLUSIONS

This work focused upon the use of correlation consistent basis sets for calculating the electrical response properties (dipole, quadrupole, and octopole polarizabilities and hyperpolarizability) of the rare gas atoms. Several correlated methods were studied, including MP2, MP3, MP4, CCSD, CCSD(T), and CISD. To converge the polarizabil-

ities, even-tempered sets of diffuse functions were added to the aug-cc-pVXZ basis sets to form doubly-, triply-, and quadruply-augmented sets. With the multiply augmented sets, converged results were obtained for all of the electrical properties of the rare gas atoms. These calculations show that CCSD(T) wave functions provide an accurate description of the electrical response properties of the rare gas atoms; both MP2 and MP4 wave functions provide results of nearly comparable accuracy.

Calculations of the dipole polarizability were also performed on a selected group of anions and molecules. Regular convergence was again observed. Correlation makes substantial contributions to the polarizabilities of the F$^-$ and Cl$^-$ anions but is much less important for N_2 and HCl.

Besides their obvious use in calculating the electrical response properties of other atoms and molecules, the extended basis sets can be used to investigate the convergence of the dispersion forces that bind the weakly interacting rare gas dimers He$_2$, Ne$_2$ and Ar$_2$. Studies paralleling the present work[10] indicate that calculations performed with these sets do very well at describing the van der Waals binding force of these very weakly bound species.

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