A Comparative Study of the Dipole Polarizability of Some Zn Clusters

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We have employed a hierarchy of basis sets and computational techniques in order to approach the polarizability (α) of Zn_m, $m = 2-20$, in a systematic way. This procedure allows the proper approximate results to be selected and validated. More specifically, we have developed in a systematic way a series of basis sets that have been employed for the computation of the polarizability of the Zn atom. Comparison of the computed with the experimental and the best theoretical results allows us to comment on the quality of the basis sets, and to select some of the more successful ones in order to compute the polarizabilities of Zn_m, $m = 2-20$. We have employed a series of methods to take into account the correlation contribution. These include the following techniques: MP2, CC2, CCSD, CCSD(T), and DFT(B3LYP). We have used two effective core potentials, one small ($3s^2 3p^6 3d^{10} 4s^2$) and one large ($4s^2$) core. The relativistic contribution to the properties is found to be significant. Thus we have studied in detail the relativistic effects on the polarizability of some small zinc clusters, by employing the Douglas-Kroll approximation in connection with the polarized basis sets developed by Kellö and Sadlej and the methods HF, CC2, and CCSD. Most of the polarizability values are static, but some frequency-dependent properties have also been computed in order to find out the difference between the dynamic and static ones. It is considered that the sharp changes of $\alpha(Zn_m)/m$ vs m may be correlated with the change of bonding, from van der Waals to covalent and finally to metallic bonding, in Zn_m. The present comprehensive study of the polarizabilities of Zn_m includes a limited number of results for the first and second hyperpolarizability of some of the considered zinc clusters.

I. Introduction

Clusters are of great experimental and theoretical interest, because they may be considered to form the bridge between the microscopic (atoms, molecules) and the macroscopic forms of matter.[1] Problems related to the qualitative differences between clusters of various sizes and bulk,[2] as well as the dependence of the properties of clusters on their size, are of great scientific and technological interest. The possibility of tuning their electro-optical properties by varying their size and shape is one of the current challenges being pursued because of the potential applications of these materials (e.g., light-emitting diodes).[3a] Of particular importance is the correlation between the geometry, the electronic structure, and various physical properties.[3b] Among the properties of the clusters for which there is an increasing interest are the (hyper)polarizabilities.[3b−k] This interest is connected with their role in many (i) significant phenomena and processses (e.g., light scattering and interaction phenomena) and (ii) technological applications (e.g., electronic devices).[3l]

The objective of the current work is to present the (hyper)-polarizabilities of some zinc clusters, by employing state-of-the-art methods. It is known that these properties monitor with great sensitivity the changes in the structure and size of the cluster.[3m] The experimental information on Zn clusters is very limited.[4] However, some studies have been reported on the structure and properties (e.g., spectroscopic constants) of small clusters.[4−6] The bonding in zinc clusters (and other group IIb elements), and in particular the transition from van der Waals to covalent and finally to metallic bonding, has been studied by several teams.[4,7,8] The polarizabilities of Zn and the other group IIb atoms have been discussed by several authors.[9−11] To the best of our knowledge no data are available on the (hyper)polarizabilities of zinc clusters.

The specific questions we address in this work are the following:

(a) How reliable are the computed polarizabilities? To demonstrate the reliability of the reported properties, we have developed a series of basis sets and employed a hierarchy of computational methods.

(b) What is the effect of the correlation contribution and the relativistic correction on the polarizabilities of the considered clusters? The polarized basis sets developed by Kellö and Sadlej in connection with the Douglas-Kroll approximation have been employed in order to discuss this problem.

(c) How does the change of bonding in Zn_m affect its polarizability? The properties of clusters involving up to 20 atoms have been computed in order to trace the effect of van der Waals, covalent, and metallic bonding.

The clusters, the polarizabilities of which are presented, are nanoparticles. The larger clusters (e.g., Zn_{18}) have diameters

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which are approximately 1 nm. It is known that nanoparticles are of great scientific and technological interest.[12]

The property values given in Tables 1−5 and in Figures 2−5 are given in atomic units. Conversion factors to SI and esu are given in ref 13.

II. Computational Methods

When a molecule is set in a uniform electric field F_i, its energy, E, may be expanded in the following way

$$E = E^0 - \mu_i F_i - (1/2)\alpha_{ij}F_iF_j - (1/6)\beta_{ijk}F_iF_jF_k -$$
$$(1/24)\gamma_{ijkl}F_iF_jF_kF_l - ... \quad (1)$$

where E^0 is the field free energy of the atom or molecule, and μ_i, α_{ij}, β_{ijk}, and γ_{ijkl} are components of the dipole moment, linear polarizability, and the first and second hyperpolarizability, respectively. Summation over repeated indices is implied. The average polarizability is given by

$$\alpha = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (2)$$

The properties of Zn_m, $m = 2-20$, have been computed by employing a hierarchy of methods involving the Hartree−Fock (HF), the second-order Møller−Plesset perturbation theory (MP2), the B3LYP DFT technique, and the coupled cluster approximations CC2 (second-order approximate coupled cluster singles and doubles model), CCSD (single and double excitations), and CCSD(T) (perturbative treatment of triples is included), which is known to provide some of the most accurate polarizability values currently available.[14] CC2 and MP2 provide results of similar quality.[15] MP2 and B3LYP have been used in several studies of clusters, and they have provided satisfactory polarizability results.[16−19]

Static and dynamic polarizability values have been computed by employing the time-dependent Hartree−Fock perturbation theory (TDHF). We have calculated the effect of the relativistic contribution to the polarizabilities of Zn_m, $m = 1-4$, by employing the Douglas-Kroll (DK) approximation.[20] For the nonrelativistic and relativistic computations, the polarized basis sets developed by Kellö and Sadlej have been employed.[11] It is known that the DK approximation is sensitive to the basis-set contractions. Thus the contraction coefficients have been reevaluated for the relativistic calculations. The employed basis set involves the following Gaussians: [16s12p6d4f/9s7p3d2f].[11]

We have also used two effective core potentials (ECP) in order to eliminate some atomic core electrons from the calculations and thus reduce the cost of computations. The first is the relativistic ECP, developed by Stevens, Basch, and Krauss [CEP-121G].[21,22] This ECP is denoted as SBK. The original basis associated with SBK involves 4s4p3d, but it has been augmented with diffuse and polarization functions. The valence basis set describes the $3s^23p^63d^{10}4s^2$ electrons of Zn. The extensions of the basis set have been derived by employing a frequently used rule: The Gaussian exponents (ζ) for the sp and d functions were obtained by dividing the most diffuse ζ value of the nonaugmented valence basis set by successive powers of m, where $m = 2-4$. The ζ value (0.8) of the first augmented set of f functions for Zn was taken from the 6-31G-(d) basis.[23] The f orbitals are needed for the polarization of the d shell. The derived basis sets (Z4, Z44, Z444, etc.) are presented in Table 1. An effective core potential developed by the Stuttgart−Dresden group, denoted as ECP28,[24] has also been used. This treats Zn as an atom with 2 valence electrons, and thus the computational cost is similar to that needed for He.

TABLE 1: Exponents of Diffuse and Polarization Functions Used To Augment the Basis Set of Zn[a]

basis set	exponents of the extension[a]		
	sp	d	f
Z2	0.02684	0.1632	0.8
Z22	0.02684	0.1632	0.8
	0.01342	0.0816	0.4
Z222	0.02684	0.1632	0.8
	0.01342	0.0816	0.4
	0.00671	0.0408	0.2
Z3	0.0187	0.1088	0.8
Z33	0.0187	0.1088	0.8
	0.00626	0.0362	0.2667
Z333	0.0187	0.1088	0.8
	0.00626	0.0362	0.2667
	0.00208	0.0121	0.0121
Z4	0.01342	0.0816	0.8
Z44	0.01342	0.0816	0.8
	0.00335	0.0204	0.2
Z444	0.01342	0.0816	0.8
	0.00335	0.0204	0.2
	0.00083	0.00501	0.05
Z42	0.01342	0.0816	0.8
	0.00671	0.0408	0.4
Z422	0.01342	0.0816	0.8
	0.00671	0.0408	0.4
	0.003355	0.024	0.2

[a] The nonaugmented basis set involves 4s4p3d functions.[21] Thus, for example, the Z2 basis set involves the nonaugmented 4s4p3d and the extension sp(0.02684)d(0.1632)f(0.8). All the basis sets of this table have been developed by using the ECP SBK.[21,22]

The employed basis set involves 4s4p2d.[24] The choice of using an ECP and in particular a large core one for polarizability calculations has been discussed in the literature. For example, Jansik et al.[25a] employed a large-core (four valence electrons) ECP for Si in their study of the polarizability and the second hyperpolarizability of silicon clusters. They stated that modern effective core potentials have been shown to provide "excellent approximations to all electron values in all cases; errors for both polarizabilities and hyperpolarizabilities are on the order of 1%". Both employed effective core potentials (SBK and ECP28) include relativistic effects on inner core electrons due to the parametrization procedure used to obtain them.[25b]

At the methodological level, the main problems we will discuss are the following: First, the adequacy of the employed basis sets will be demonstrated, and second, the reliability of the polarizability of the Zn_m, $m = 2-20$, will be discussed. Our analysis of the above problems is presented in the following sections.

The problem of the adequacy of the employed methodology and the basis set in particular is addressed by using the systematically built basis sets already described (Table 1) to compute the polarizability of Zn. For this atom there are theoretical and experimental results of satisfactory accuracy. The polarizability results, which we have calculated by the various basis sets (Table 1), are given in Table 2. The employed methods involve Hartree−Fock, MP2, CCSD, and CCSD(T). These have been used in connection with the SBK ECP. The results of Table 2 allow us to make a systematic study of the effect of the basis set and the employed method on the quality of the polarizability. We observe that the main correlation contribution is recovered at the MP2 level. This contribution significantly reduces the HF value. At the CCSD level, we have a small increase. For example, with the Z422 basis set, the increment is 3.31 au. The contribution of triple excitations, which is taken into account by employing the CCSD(T) approximation, is small (−1.1 au; Z422 basis set). In Table 2, we cite some polarizability values

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TABLE 2: Polarizability of Zn ($^1S_0$) Computed by Various Methods

basis set[a]	α			
	HF	MP2	CCSD	CCSD(T)
Z2	51.10	36.34	39.80	38.65
Z22	51.23	36.64	40.16	39.05
Z222	51.22	36.84	40.24	39.15
Z3	51.24	36.96	40.28	39.17
Z33	51.31	37.07	40.46	39.33
Z333	51.28	37.33	40.47	39.39
Z4	51.24	37.20	40.38	39.28
Z44	51.22	37.09	40.30	39.20
Z444	51.30	37.14	40.32	39.21
Z42	51.21	36.69	40.08	38.98
Z422	51.21	36.89	40.20	39.10

Literature

	HF	MCSCF	CCSD	CCSD(T)	other
Comp. Works					
Goebel et al.					39.2 (8)[b]
Kellö et al.				40.13,[c]	
				37.61(37.74)[d]	
Rosenkrantz et al.	43.2[e]	35.1[e]			
Seth et al.			41.83,[f]	40.55,[f]	
			39.27[g]	38.01[g]	
Experimental					
Goebel et al.					39.03[h]

[a] These basis sets have been used in connection with the SBK ECP.[21] All polarizability values given are in au. [b] Best recommended theoretical value by Goebel et al.[9] [c] Twenty explicitly correlated electrons.[11a] [d] CCSD(T) plus quasi relativistic corrections; 20 explicitly correlated electrons.[11a] The corresponding DK value is given in parentheses.[11b] [e] A relativistic ECP has been employed.[26] [f] Nonrelativistic.[27] [g] Relativistic.[27] [h] Static value obtained from the extrapolation of dynamic values to zero frequency.[9]

from the literature. The theoretical results involve those reported by Goebel et al.,[9] Kellö et al.,[11] Rosenkrantz et al.,[26] and Seth et al.[18] The methods employed by these authors are given in Table 2. There is also an experimentally determined value. This is static, and is obtained from the extrapolation of dynamic values to zero frequency.[9] It is added that the recommended value for the polarizability of Zn by Miller and Bederson is 38.5 au.[28] The main finding resulting from Table 2 is that the computed polarizability values for the Zn($^1S_0$) atom, at the correlated level, are in excellent agreement with the experimental value and the best available theoretical data. The observed agreement verifies the adequacy of the proposed basis sets for the computation of the polarizability of Zn_m. Thus, Z4, which is a small basis set, has been used for the computation of the properties of the relatively large clusters.

Most of the polarizability components have been computed by employing the finite perturbation theory (FPT) approach, although several property values have been computed analytically by using the Dalton software.[29] The field strength we have used is F = 0.003 au. The adequacy of this field has been checked by performing an analytical computation of the polarizability of Zn_8, with the HF/ECP28 method. We found α = 344.56 au (analytical) and α = 344.54 au (numerical).

Structures of Zn_m. We have considered two sets of clusters in this work. The structures of the first set, Zn_m, $m = 2-8$, have been optimized by Erkoç et al.[30,31] The first two structures ($m = 2, 3$) have been optimized by employing density functional theory (B3LYP).[30a] For the other clusters ($m = 4-8$), they employed an empirical many-body potential energy function (PEF), which comprises two- and three-atom interactions, given by the Lennard-Jones[32] and Axilrod−Teller functions,[33] respec-

tively. The explicit form of the total interaction potential energy of the considered clusters is given in ref 30b. A similar PEF has been used in a wide variety of applications.[34−42] The structures were optimized by employing molecular dynamics (MD) simulations based on the Nordsieck−Gear algorithm.[43,44] The detailed procedure that was followed for the MD simulations is described in ref 30b. The structure of the second set of clusters, Zn_m, $m = 2-20$, has been determined by Wang et al.,[4] by employing a DFT approach, in which the density functional has been treated by the generalized gradient approximation. The exchange−correlation potential has been parametrized by Perdew and Wang.[45]

Software. The properties presented in this work have been computed by employing the Gaussian 98[46] and Dalton (1.2.1 and 2.0)[29] programs.

III. Results and Discussion

In this section we shall, first, review the literature that is relevant to our work. Second, we shall discuss the relativistic corrections to the polarizabilities of some zinc clusters. Third, we shall present and analyze the polarizabilities of Zn_m, $m = 2-8$ (structures optimized by Erkoç et al.;[30,31] Figure 1), in connection with a series of methodological problems. Fourth, we shall discuss the polarizabilities of Zn_m, $m = 2-20$; their structures have been optimized by Wang et al.[4] Finally, we shall present some hyperpolarizability results.

Literature Survey. The information (experimental or theoretical) in the literature on Zn clusters is very limited. We briefly review the articles that are most relevant for our work. Wang et al.[4] used DFT theory to study the lowest-energy structures of Zn_m, $m = 2-20$. Yu and Dolg[5] computed some spectroscopic constants of group IIb (Zn, Cd, and Hg) dimers by employing an energy-consistent small-core pseudopotential. Correlation has been taken into account by employing CCSD(T) and MP4-[SDTQ] (Møller−Plesset perturbation theory with singles, doubles, triples, and quadruples). Zn_m (and Cd_m), $m = 3-125$, have been studied by Doye[6] by employing a Gupta potential.[47] The most stable isomers of Zn (and Cd) clusters ("magic" sizes of 13, 38, 55, 75, and 147) have been studied by Michaelian et al.,[48] who employed an n-body Gupta potential to obtain the lowest-energy configurations. The structures were relaxed with DFT. Difficulties in generating uncharged zinc clusters Zn_m, with $m \geq 3$, have been reported.[49] Thus theoretical studies offer a valuable insight. The bonding in the group IIb clusters has been the subject of various studies.[4,7,8] A question of particular importance is the transition from van der Waals to covalent and finally to metallic bonding. The type of bonding is intimately connected with the polarizability, since this property reflects mainly the behavior of the valence electrons. Thus we review the recent literature on this topic. The bonding in the group IIb dimers has been considered by Yu and Dolg.[5] They employed the occupation number fluctuations, derived from a CASSCF wave function, near the equilibrium distance. They found that the bonding in these dimers may be considered a mixture of van der Waals (3/4) and covalent (1/4) bonding. The bonding for small group IIb clusters has been studied by Flad et al.[50] The covalent contribution to the bonding has been studied by employing the electron localization function (ELF). This parameter has been computed for Zn_m, $m = 2-6$, 13. Flad et al. found that "the covalent contributions are most strongly developed for Zn_4 and Zn_5 clusters". Wang et al.[4] have also studied the bonding in Zn clusters employing various properties, among which are the binding energy per atom and the second difference of binding energies. They suggested that "the
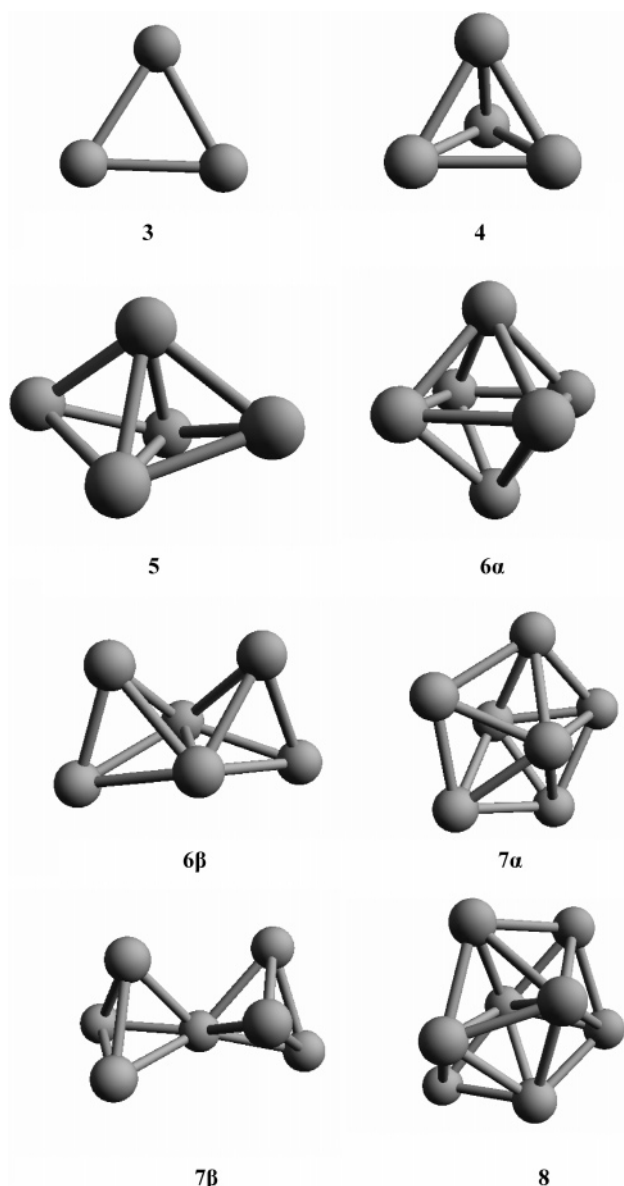
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Figure 1. Structure of Zn_m, $m = 2-8$, optimized by Erkoç et al.[30,31] and Wang et al.[4]

TABLE 3: Polarizability Components of Zn_m, $m = 2-5$, Computed with Relativistic (R) and Nonrelativistic (NR) Methods

method[a]	NR			R		
	α_{xx}	α_{zz}	α^b	α_{xx}	α_{zz}	α^b
			Zn_2			
HF	91.94	154.56	112.81	87.02	142.21	105.42
	105.58[c]	196.72[c]	135.96[c]	99.01[c]	176.79[c]	124.94[c]
CC2[d]	74.65	117.87	89.05	70.63	108.52	83.26
CCSD[d]	73.89	115.34	87.71	69.53	106.32	81.79
			Zn_3			
HF	116.12	205.41	175.65	110.44	191.28	164.33
	130.96[c]	258.76[c]	216.16[c]	123.57[c]	235.72[c]	198.34[c]
CC2[d]	96.53	165.46	142.48	91.81	153.79	133.13
CCSD[d]	95.77	161.52	139.60	91.02	150.18	130.46
			Zn_4			
HF	222.66		222.66	211.01	211.01	211.01
	278.35[c]		278.35[c]	257.35[c]	257.35[c]	257.35[c]
			Zn_5			
HF	229.48	403.44	287.22	219.18	372.34	270.19

[a] All computations have been performed by employing the basis sets developed by Kellö and Sadlej.[11] The structures have been optimized by Erkoç et al.[30,31] All values are in au. [b] The following symmetry relationship is obeyed by the polarizabilty components: Zn_2, $\alpha_{xx} = \alpha_{yy}$; Zn_3, $\alpha_{zz} = \alpha_{yy}$; and Zn_4, $\alpha_{xx} = \alpha_{yy} = \alpha_{zz}$. [c] Frequency-dependent property evaluated at $\omega = 0.072$ au. [d] Twelve electrons for each Zn atom were correlated.

au (-5.75 au). The corresponding value at the CC2 level is given in parentheses. We observe that the CC2 model approximates reasonably well the CCSD values. The relativistic correction leads to the reduction of the polarizability, which is due to the contraction of the 4s shell. Correlation (at the CC2 and CCSD level) reduces, in absolute value, the relativistic contribution. The largest relativistic effect is along the z direction (α_{zz}). For Zn_3, employing HF theory, we found that $\alpha(R) - \alpha(NR) = -11.32$ au; the corresponding values for Zn_4 and Zn_5 are -11.65 and -17.03 au, respectively.

From the results of Table 3, it is deduced that the correlation effect has a larger contribution than the relativistic correction. For example, from the properties of Zn_3, we observe that the relativistic correction at the CCSD level is -9.14 au, whereas the correlation contributions are -36.05 au (NR) and -33.87 au (R). Thus the electron correlation contribution is affected by the relativistic effects. This has also been noted by Kellö and Sadlej,[11] who found that the mixed relativistic−correlation contribution comes from the $3d^{10}4s^2$ shells (Zn).

Figure 2 presents the results for $\{\alpha[Zn_m]/m - \alpha(Zn)\}$ vs m. This difference has been called by Maroulis et al.[16] differential mean polarizability per atom, α_{diff}/m, and provides information for the delocalization of the electron density in the cluster. We have computed α_{diff}/m for $m = 2-5$ (the structures of Erkoç et al.[30,31] have been employed), by using the HF and CCSD methods at the nonrelativistic (NR) and relativistic (R) levels, respectively. It is observed that $\alpha_{diff}/m > 0$. A similar trend has been reported by Millefiori and Alparone.[17] These authors rationalized their polarizability values of some sulfur clusters by invoking the findings of Stout and Dykstra,[52a] who used a point-multipole classical analysis of polarization.

In Table 3 we present, besides the static values, some frequency-dependent polarizability values. For these computations we have selected one frequency ($\omega = 0.072$ au; $\lambda = 6328$ Å, He−Ne laser), which is often employed to avoid proliferation of data. This frequency is far from any resonance; note that the first excitation energies for Zn_2, Zn_3, and Zn_4 are 0.142 (0.149), 0.121 (0.128), and 0.115 (0.122) au, respectively. These values

transition from van der Waals to covalent bond happens around Zn_8, while the transition to metallic bond is around Zn_{17}".

Relativistic Effects. It is known that the relativistic correction has an important contribution to the (hyper)polarizabilities of derivatives involving heavy elements.[51] Thus it was considered useful to perform a detailed study of the relativistic (R) effects on the polarizabilities of Zn_m, $m = 2-5$. The specific topics on which we would like to comment are the following:

(a) The employed ECPs (SBK and ECP28) take into account to some extent the relativistic effects. We would like to find out the magnitude of these effects employing a reasonably accurate approximation, that is, a coupled cluster model (CC2 and/or CCSD) and the polarized basis set of Kellö and Sadlej.[11]

(b) It is of interest to consider *both* the relativistic and correlation effects, and to comment on their contribution and importance. The relativistic ECP results cannot provide information on the interplay of these effects.

For the atom we have at the CCSD level: $\alpha(R) - \alpha(NR) = -2.73$ au (HF:-3.19 au). For Zn_2, we observe (Table 3) at the CCSD level: $\alpha_{xx}(R) - \alpha_{xx}(NR) = -4.38$ au (-4.02 au), $\alpha_{zz}(R) - \alpha_{zz}(NR) = -9.02$ au (-9.35 au), $\alpha(R) - \alpha(NR) = -5.92$
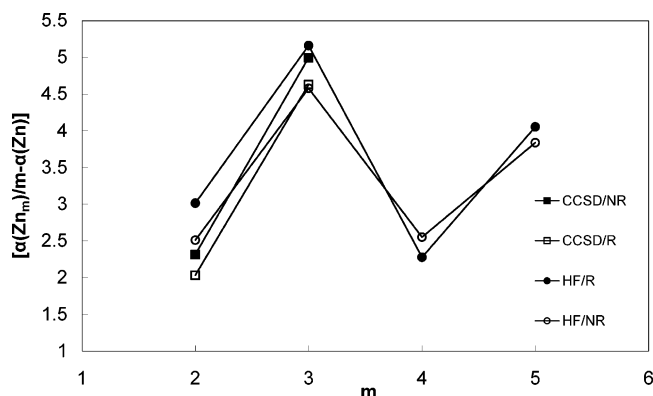
Figure 2. Variation of $[\alpha(Zn_m/m) - \alpha(Zn)]$ as a function of m. Structures optimized by Erkoç et al.[30,31] have been employed. Relativistic (R) and nonrelativistic (NR) results computed by the Pol basis set are used.

have been computed by employing the HF/Pol method at the nonrelativistic level. The corresponding relativistic values are given in parentheses. The effect of frequency on the relativistic contribution is remarkable. For example, the difference $\alpha(R) - \alpha(NR)$ takes the values -11.65 (static) and -21.0 au (dynamic) for Zn_4. The relativistic correction also has a noticeable effect on the dynamic polarizability values. Thus, it has been found that for Zn_4 the difference $\alpha(-\omega; \omega) - \alpha(0)$ takes the values 55.69 and 46.34 au at the nonrelativistic and relativistic levels, respectively. This example also demonstrates the rather large effect of the selected frequency on the polarizability.

Polarizabilities of Zn_m, $m = 2-8$. The structures of these clusters (Figure 1) have been optimized by Erkoç et al.[30,31] The results for Zn_m, $m = 2-4$, show that the basis sets Z4, Z422, and Z444 give very similar polarizability values (Table 4). Thus for the computation of the polarizability of Zn_m, $m = 5-8$, we have used the Z4 basis set. MP2/SBK/Z4 and CCSD(T)/SBK/Z4 give α values for Zn_2 that differ by 4.75 au. We recall that $\alpha[CCSD(T) - \alpha(MP2)] = 2.08$ au for Zn (SBK/Z4; Table 2). Considering the above results, we believe that it is adequate to compute α for Zn_m at the MP2 level, to keep the computational cost at a manageable level. The MP2/ECP28 gives polarizability values, which converge to those of MP2/SBK/Z4 (Figure 3). B3LYP/SBK/Z4, B3LYP/SBK/Z444, and CCSD(T)/SBK/Z4 give similar values for Zn_2. Thus for the bigger clusters we shall use the B3LYP/SBK/Z4 approach. There is a small difference in the results produced by the methods HF/ECP28 and B3LYP/Z4. The only polarizability value for zinc clusters that we could find in the literature was for Zn_2. Schautz et al.[24] reported $\alpha_{zz} = 95.6$ au (z is the molecular axis). This value has been computed at the CCSD(T) level, using a small core pseudopotential. Our α_{zz}, employing the CCSD(T)/SBK/Z4 method, is 106.67 au. The dipole moments are not reported, as they are only fractions of 1 D.

The main findings resulting from the polarizabilities presented in Table 4 are as follows: (i) The basis Z4 gives satisfactory polarizability values that are in very good agreement with those computed by employing larger sets (e.g. Z444, Z422). This finding confirms a similar one deduced from the polarizability of the Zn atom (Table 2). (ii) The method MP2/ECP28 gives satisfactory results and requires a low computational cost, and thus it will be used for the computation of the properties of larger Zn clusters.

For completeness we add that there are several reports in the literature in which DFT approaches have given satisfactory polarizability results.[3f,16,18] However, several failures of DFT

TABLE 4: Average Polarizability of Zn_m, $m = 2-8$, Computed by Employing a Series of Methods[a]

method	α	method	α
Zn₂		MP2/SBK/Z444	166.24
HF/SBK/Z4	107.72	MP2/ECP28	159.23
HF/SBK/Z42	107.81	B3LYP/SBK/Z4	172.35
HF/SBK/Z422	107.87	Zn₅	
HF/SBK/Z222	107.88	HF/SBK/Z4	274.83
HF/SBK/Z444	108.01	HF/ECP28	216.97
HF/ECP28	81.69	MP2/SBK/Z4	206.30
MP2/SBK/Z4	77.55	MP2/ECP28	203.17
MP2/SBK/Z42	76.92	B3LYP/SBK/Z4	217.52
MP2/SBK/Z444	74.84	Zn₆	
MP2/ECP28	73.09	HF/SBK/Z4	312.77
B3LYP/SBK/Z4	83.57	HF/ECP28	249.71
B3LYP/SBK/Z444	83.90	MP2/SBK/Z4	233.94
CCSD(T)/SBK/Z4	82.30	MP2/ECP28	233.43
Zn₃		B3LYP/SBK/Z4	247.97
HF/SBK/Z4	167.58	Zn₇	
HF/SBK/Z42	168.06	HF/SBK/Z4	367.48
HF/ECP28	128.17	HF/ECP28	298.51
MP2/SBK/Z4	123.92	MP2/SBK/Z4	281.67
MP2/SBK/Z42	123.41	MP2/ECP28	282.31
MP2/ECP28	116.77	B3LYP/SBK/Z4	295.39
B3LYP/SBK/Z4	133.88	Zn₈	
Zn₄		HF/SBK/Z4	420.51
HF/SBK/Z4	214.21	HF/ECP28	344.54
HF/SBK/Z444	215.12	MP2/SBK/Z4	326.50
HF/ECP28	170.58	MP2/ECP28	326.46
MP2/SBK/Z4	165.92	B3LYP/SBK/Z4	340.63

[a] The structures have been optimized by Erkoç et al.[30,31] All values are in au.
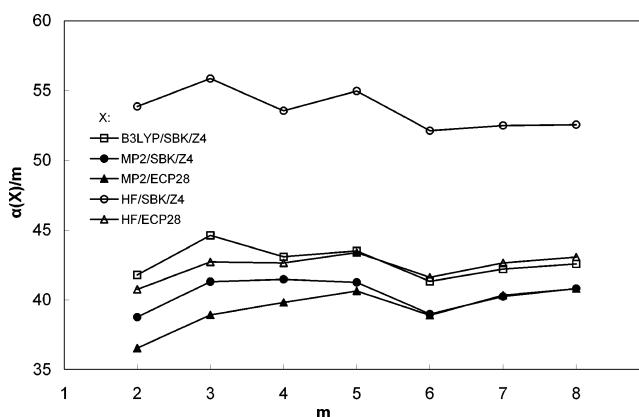

Figure 3. Variation of α as a function of m, for Zn_m, $m = 2-8$. The properties have been computed by using structures given in refs 30 and 31.

on the computation of (hyper)polarizabilities are also known.[52b] For example, Gisbergen et al.[52b] reported that "density functional calculations on the (non)linear optical properties of conjugated molecular chains using currently popular exchange—correlation (xc) potentials give overestimations of several orders of magnitude". This overestimation was found to be especially severe for extended elongated chains, whereas for the smaller molecules the predicted (hyper)polarizabilities were found to be quite reasonable in comparison with those of standard correlated methods. Concerning our results (Table 4), we note that there is a small discrepancy between the B3LYP and MP2 data (employing SBK/Z4), which in general decreases with increasing m. For example, for $m = 2$ and 8, the discrepancy of the MP2 and B3LYP results is 7.8 and 4.3%, respectively. In addition, the MP2 and B3LYP $\alpha(X)/m$ results of Zn_m show the same trend with the variation of m (Figure 3).

One notes the satisfactory agreement between results produced with the HF/Pol/R and HF/SBK/Z4 methods (Tables 3
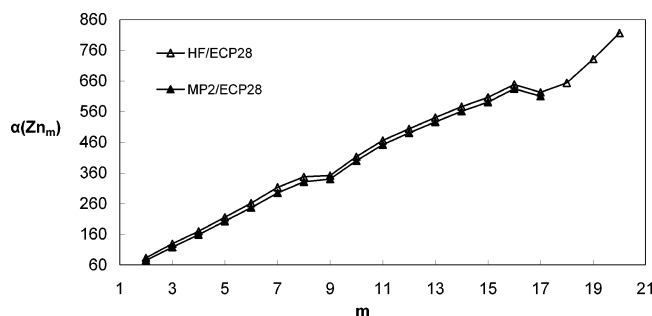
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Figure 4. Variation of α as a function of m, for Zn_m, $m = 2-20$. The properties have been computed by using structures given in ref 4.

Figure 5. Variation of $\alpha(Zn_m)/m$ as a function of m.

and 4). The values produced for Zn_2, Zn_3, and Zn_4 at the R/Pol level are 105.42 (107.72), 164.33 (167.58), and 211.01 (214.21) au, respectively. In parentheses are the corresponding values at the SBK/Z4 level. These computations confirm the adequacy of the ECP approaches used for the calculation of the polarizabilities of Zn_m, $m = 2-20$.

It would be of interest to comment on the effect of the number of correlated shells. We use as an example the polarizability of Zn_3, computed by employing the MP2/SBK/Z4 method. The calculated values are 123.92 au ($3s^2 3p^6 3d^{10} 4s^2$), 126.19 au ($3d^{10}$-$4s^2$), and 161.03 au ($4s^2$). One notes that there is a small difference between the results produced by correlating 12 and 20 electrons. However, we observe a large difference, if we correlate only the electrons of the $4s^2$ shell. For the Zn atom the difference resulting by correlating 12 and 20 electrons is 0.61 au (method MP2/SBK/Z4). It is clear that the effect of the number of electrons that are correlated increases with the cluster size. Thus in the computations presented in Table 2 that employ the SBK, 20 electrons are correlated.

We observe that (Table 2) $\alpha(HF) > \alpha(CCSD(T)) > \alpha(MP2)$. It is understood that the CCSD(T) method does not recover all the correlation contribution. However, it is expected that higher-level approximations will not substantially change the results produced by CCSD(T).[11,52c] Most of the correlation contribution can be taken into account at the MP2 level. This observation is confirmed by both the atomic (Zn) and diatomic results (Zn_2). The MP2 polarizability value is considerably smaller than that of HF. We found that, for the atom, $\alpha(HF/SBK/Z4) - \alpha(MP2/SBK/Z4) = 14.04$ au. The difference $[\alpha(HF/SBK/Z4) - \alpha(MP2/SBK/Z4)]/m$, for $m = 2$ and 3, takes the values 15.09 and 14.55 au, respectively. The average value for $m = 4-8$ is 12.59 au. It seems that as m increases the above difference also decreases, and apparently it approaches its limit for a large enough value of m.

Polarizability of Zn_m, $m = 2-20$. The polarizabilities of Zn_m, $m = 2-20$ (their structures have been optimized by Wang et al.[4]), have been computed by employing the methods HF/ECP28 and MP2/ECP28. We believe that B3LYP would also be a reasonable choice for the computation of $\alpha[Zn_m]$, considering both the literature data on the performance of this approach[16-19] and our computations (Table 4 and Figure 3). It is observed that the methods HF and MP2, with ECP28, give very similar results (Figure 4). In fact, it is noted that the difference $[\alpha(HF) - \alpha(MP2)]/m$ decreases as m increases (using ECP28). This observation holds for both the results of Table 4 (structures optimized by Erkoç et al.[30,31]) and the structures of Wang et al.[4] There are only two exceptions connected with the structures of ref 4, for $m = 7$ and 10.

Figure 5 presents the results for $R_m = \alpha[Zn_m]/m$ vs m. This ratio provides information for the strength of the interaction in the cluster. We have computed this ratio for the structures of
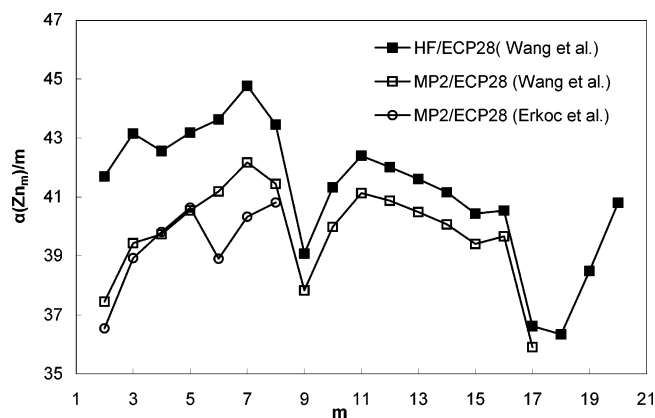
Erkoç et al.[30,31] and Wang et al.[4] It is observed (Figure 5) that there are certain differences in the behavior of R_m vs m for the two sets of structures. In particular the structures of Erkoç et al. present a minimum for $m = 6$, while those of Wang et al. do so for $m = 9$. The structures optimized by Wang et al.[4] are associated with another local minimum for $m = 18$. The rather sharp changes of R_m for Zn_m, $m = 2-20$ (which are connected with the two local minima), may be correlated with the change of bonding from van der Waals to covalent and from covalent to metallic bonding. It should be added that the bonding in Zn_m could be studied by employing the difference $\alpha[Zn_m]/m - \alpha$-(Zn). However, this parameter depends on $\alpha(Zn)$, which is rather poorly approximated by ECP28. On the other hand, it is known that the role of the basis set decreases as the size of the system (e.g., cluster, oligomer) increases.[17,53,54]

The variation of the polarizability of Zn_m with m shows a reasonable regularity (Figure 4). However, for comparison, we add that Deng et al.,[55] who studied the polarizability of Si_m, $m = 9-28$, found a fairly irregular variation with the cluster size.

It is interesting to note that the dips found in Figure 5, at $m = 9$ and 18, are occurring near the "magic numbers" observed experimentally at $m = 10$, 18, and 20 by mass spectrometry investigations of Zn_m clusters,[56] and have been explained by the shell-closing effect of the s valence electrons in a spherically symmetric potential. Similar dips near the magic numbers predicted by the shell model were found experimentally for the polarizabilities of the alkali-metal clusters of Na and K.[57]

Classically, the polarizability of a conducting sphere α_{sph} with radius r is proportional to r^3; in the jellium model applied to small spherical clusters, an additional "charge spillout" effect is taken into account, which increases the classical polarizability, leading to $\alpha_{sph} \sim (r + \delta)^3$, with δ estimated to be around 1.5 au.[58] This picture applies qualitatively, e.g., to the experimental polarizabilities of Na and K. According to Figure 4, however, the model does not seem to apply to the polarizabilities of the Zn_m clusters in the approximation employed here. This may be due to the changing character of the Zn–Zn bonding predicted in these clusters with increasing m.

We would like to explore in some detail the dependence of the calculated properties on the geometrical structure of the clusters. The structures optimized by Erkoç et al.[30,31] and Wang et al.[4] have certain similarities and differences on which we shall base our discussion. For $m = 2-5$ and 8, the above teams determined structures with no difference in the shape (symmetry). For each of $m = 6$ and 7, there are two different shapes, which are denoted by a and b (Figure 1); 6a and 7a have been optimized by Erkoç et al.,[30,31] and 6b and 7b have been determined by Wang et al.[4] It is observed that the shape of a

cluster affects its polarizability (Figures 1 and 5). The more "open" structure has a larger polarizability than the more "closed" one. In fact, $\langle r \rangle$[59] gets the values 3.485 (3.692) and 3.026 (3.245) au for the structures of Zn_6, determined by Wang et al. and Erkoç et al. In parentheses are the corresponding values for Zn_7. For the total energies (MP2/ECP28), we found the following differences: $E(6a) - E(6b) = +0.0262$ au and $E(7a) - E(7b) = -0.0028$ au. In the framework of this work, we have performed a limited number of optimizations employing some of the methods, which we have used for the calculation of the polarizabilities of Zn_m. We have found that the HF method (connected with ECP28 or SBK/Z4) overestimates the bond lengths. The following comparisons will illustrate this remark. For Zn_3, employing the MP2/SBK/Z4, we have found $R(Zn-Zn) = 3.002$ Å (3.206 Å) and $\alpha = 128.89$ au (123.92 au). In parentheses we present the bond length optimized by Erkoç[30a] as well as the polarizability, which we found by employing this length (Table 4). The bond lengths employing HF/ECP28 and HF/SBK/Z4 are 6.796 Å (153.31 au) and 6.135 Å (154.32 au), respectively. The corresponding polarizability values are given in parentheses.

The connection of the polarizability with the shape of the system under consideration has been observed in systematic studies of molecules as well.[60,61] For completeness it is added that the shape of nanoparticles is a property of considerable significance. Thus several methods have been developed in order to prepare nanoparticles of various shapes (rods, wires, prisms, etc.).[62]

Second Hyperpolarizabilities. Besides the comprehensive study of the polarizabilities of Zn_m, we also present some computations of their hyperpolarizabilities, because we would like to explore the limits of the methodology employed for the computation of the polarizabilities. In addition, there are no hyperpolarizability values for Zn_m in the literature. In Table 5 the values of the nonvanishing average first, β, and second, γ, hyperpolarizabilities are shown, computed with different basis sets given in Table 1. The properties are defined by

$$\beta_{\parallel} = \frac{3}{5}\sum_{i,k=1}^{3} \beta_{ikk}\mu_i/|\mu| \qquad (3)$$

$$\gamma = \frac{1}{5}\sum_{i,j=1}^{3} \gamma_{iijj} \qquad (4)$$

Although only Z42 leads to converged γ values for Zn_2 and Zn_3, considering the difference of 10% as the convergence level, we used the Z4 basis set for the calculation of the properties of the larger clusters, because the Z42 basis set leads to considerable convergence problems at the HF level even for Zn_3. These problems would become worse for the larger clusters. Additionally, the difference of the γ values computed using Z4 or Z42 is decreasing in the series Zn_2 (25% [HF], 19% [MP2]), Zn_3 (14% [HF], 15% [MP2]), and Zn_4 (8% [HF]), with the last number already being lower than the chosen convergence level of 10%. This effect may be due to the basis set "borrowing" of diffuse functions by neighboring atoms.[53]

The polarizabilities are clearly converged with the Z4 basis set (Table 4), but for the first hyperpolarizabilities, convergence does not set in at all in some cases. This holds not only for the composite quantity β shown in Table 5 but also for the single components β_{iij}. Consequently, we will not discuss any further the first hyperpolarizabilities, which are small in many cases, anyway.

TABLE 5: Static First ($\beta_{\parallel}$) and Second ($\gamma/10^3$) Hyperpolarizabilities of Zn_m, $m = 2-6$

	$\beta_{\parallel}$		γ	
cluster[a]	HF	MP2	HF	MP2
	Zn_2			
Z2			90.2	49.7
Z22			123.5	61.8
Z222			142.7	
Z4			114.0	55.3
Z42			142.4	65.6
Z422			145.7	
	Zn_3			
Z4	−6.7	−3.1	195.3	108.7
Z42	−6.8	−2.5	222.4	125.4
Z422	−6.8		226.3	
	Zn_4			
Z4	5.6		223.8	144.2
Z42	4.8		241.4	
	Zn_5			
Z4			483.0	197.3
	Zn_6			
Z4			719.7	220.2

[a] For all the computations presented in this table, the ECP SBK has been used.[21,22] The structures have been optimized by Erkoç et al.[30,31] Property values are given in au.

We tested the effect of the different levels of electronic correlation for Zn_2, employing the Z4 basis set with SBK. We found the following values for γ ($\times 10^3$): 114.0 (HF), 90.8 (B3LYP), 55.3 (MP2), and 71.4 au (CCSD(T)). The employed method is given in parentheses. These results show that the γ values decrease monotonically with the methods HF > B3LYP > MP2, and increase again at the CCSD(T) level, which is the most accurate method employed. The properties computed at the MP2 level are closer to those of the CCSD(T) level than were those of any other methods employed. Considering that CCSD(T) is computationally much too expensive for larger compounds, we chose to compute the properties of the larger clusters at the HF and MP2 levels of theory. For all clusters, the properties decrease dramatically when the electronic correlation is included. The effect is generally more pronounced as m increases; the strongest decrease is found for Zn_6, in which the value of γ decreases by 69% in going from the HF to the MP2 level. From the limited study of the second hyperpolarizabilities, it is clear that an extensive study employing a hierarchy of methods is required in order to demonstrate the convergence of the results, which is essential in the absence of any experimental values.

IV. Conclusions

We have used a hierarchy of methods involving HF, MP2, B3LYP, CC2, CCSD, and CCSD(T) to compute the polarizabilities of Zn_m, $m = 1-20$. Static and some frequency-dependent results have been computed. A systematically built series of basis sets has been developed and used. All the reported basis sets give polarizability values for Zn in very good agreement with the best theoretical and experimental data. This agreement verifies the adequacy of the basis set Z4 for the computation of the polarizabilities of Zn_m, $m = 2-8$. We have also employed two effective core potentials, one small (SBK) and one large (ECP28) core. The satisfactory performance of each has been demonstrated.

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The main findings of the results in which the relativistic correction has been explicitly taken into account are as follows: (i) The correlation effect has a larger contribution than does the relativistic correction. The latter is relatively small but not negligible. (ii) There is a rather large difference between the static and dynamic values (for the selected frequency). (iii) The ab initio values (DK, Pol basis set) confirm the accuracy of the ECP results.

Wang et al.[4] observed that there is a change in the type of bonding in the clusters Zn_m; there is a transition from van der Waals to covalent bonding that takes place at m ≈ 8, whereas the transition from the covalent to metallic bond is observed at m ≈ 17. We believe that the change of $\alpha(Zn_m)/m$ vs m near the above values could be correlated with this change of bonding.

References and Notes

(1) De Longh, L. J., Ed. *Physics and Chemistry of Metal Clusters*; Kluwer: London, 1994. Johansson, M. P.; Pyykkö, P. *Phys. Chem. Chem. Phys.* **2004**, *6*, 2907.

(2) Fournier, R.; Cheng, J. B. Y.; Wong, A. *J. Chem. Phys.* **2003**, *119*, 9444.

(3) (a) Sarkar, P.; Spingborg, M. *Phys. Rev. B* **2003**, *68*, 235409. (b) Pouchan, C.; Bégué, D.; Zhang, D. Y. *J. Chem. Phys.* **2004**, *121*, 4628. (c) Chen, W.; Li, Z.-R.; Wu, D.; Li, R.-Y.; Sun, C.-C. *J. Phys. Chem. B* **2005**, *109*, 601. (d) Jackson, K. A.; Yang, M.; Chaudhuri, I.; Frauenheim, T. *Phys. Rev. A* **2005**, *71*, 33205. (e) Lau, K. C.; Deshpande, M.; Pandey, R. *Int. J. Quantum Chem.* **2005**, *102*, 656. (f) Yang, M.; Jackson, K. H. *J. Chem. Phys.* **2005**, *122*, 184317. (g) Wu, K.; Li, J.; Lin, C. *Chem. Phys. Lett.* **2004**, *388*, 353. (h) Baruah, T.; Pederson, M. R.; Zope, R. R.; Beltrán, M. R. *Chem. Phys. Lett.* **2004**, *387*, 476. (i) Calaminici, P. *Chem. Phys. Lett.* **2004**, *387*, 253. (j) Chandrakumar, K. R. S.; Ghanty, T. K.; Ghosh, S. K. *J. Chem. Phys.* **2004**, *120*, 6487. (k) Knickbein, M. *J. Chem. Phys.* **2004**, *120*, 10450. (l) Bonin, K. D.; Kresin, V. V. *Electric Dipole Polarizabilities of Atoms, Molecules and Clusters*; World Scientific: London, 1997. (m) Schwerdtfeger, P.; Wesendrup, R.; Moyano, G. E.; Sadlej, A. J.; Greif, J.; Hensel, F. *J. Chem. Phys.* **2001**, *115*, 7401.

(4) Wang, J.; Wang, G.; Zhao, J. *Phys. Rev. A* **2003**, *68*, 013201.

(5) Yu, M.; Dolg, M. *Chem. Phys. Lett.* **1997**, *273*, 329.

(6) Doye, J. P. K. *Phys. Rev. B* **2003**, *68*, 195418.

(7) Zhao, J. *Phys. Rev. A* **2001**, *64*, 043204.

(8) Busani, R.; Folkers, M.; Cheshnovsky, O. *Phys. Rev. Lett.* **1998**, *81*, 3836.

(9) Goebel, D.; Hohm, U.; Maroulis, G. *Phys. Rev. A* **1996**, *54*, 1973.

(10) Ellingsen, K.; Mérawa, M.; Rérat, M.; Pouchan, C.; Gropen, O. *J. Phys. B: At., Mol. Opt. Phys.* **2001**, *34*, 2313.

(11) Kellö, V.; Sadlej, A. J. *Theor. Chim. Acta* **1995**, *91*, 353. (b) Kellö, V.; Sadlej, A. J. *Theor. Chim. Acta* **1996**, *94*, 93.

(12) Feldheim, D. L.; Foss, C. A., Jr., Eds. *Metal Nanoparticles: Synthesis Characterization and Applications*; Marcel Dekker Inc.: New York, 2002. Ratner, M.; Ratner, D. *Nanotechnology: A Gentle Introduction to the Next Big Idea*; Pearson Education, Inc.: Cranbury, NJ, 2003.

(13) Papadopoulos, M. G.; Waite, J.; Buckingham, A. D. *J. Chem. Phys.* **1995**, *102*, 371.

(14) Jensen, F. *Introduction to Computational Chemistry*; Wiley: New York, 1999. Reis, H.; Papadopoulos, M. G.; Avramopoulos, A. *J. Phys. Chem. A* **2003**, *107*, 3907. Bartlett, R. J. In *Methods in Computational Chemistry*; Yarkony, D. R., Ed.; Advanced Series in Physical Chemistry; World Scientific: Singapore, 1995; Vol. 2.

(15) Christiansen, O.; Koch, H.; Jørgensen, P. *Chem. Phys. Lett.* **1995**, *243*, 409.

(16) Maroulis, G.; Begué, D.; Pouchan, C. *J. Chem. Phys.* **2003**, *119*, 794.

(17) Millefiori, S.; Alparone, A. *J. Phys. Chem. A* **2001**, *105*, 9489.

(18) Chandrakumar, K. R. S.; Ghanty, T. K.; Ghosh, S. K. *J. Chem. Phys.* **2004**, *120*, 6487.

(19) Reis, H.; Papadopoulos, M. G. *J. Comput. Chem.* **1999**, *20*, 679.

(20) Douglas, M.; Kroll, N. M. *Ann. Phys.* **1974**, *82*, 89. Hess, B. A. *Phys. Rev. A* **1986**, *33*, 3742. Barysz, M.; Sadlej, A. J. *J. Mol. Struct. (THEOCHEM)* **2001**, *573*, 181 and references therein.

(21) Stevens, W.; Basch, H.; Kraus, J. J. *J. Chem. Phys.* **1984**, *81*, 6026.

(22) Stevens, W.; Basch, H.; Kraus, J.; Jasien, P. G. *Can. J. Chem.* **1992**, *70*, 612.

(23) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.

(24) Schautz, F.; Flad, H.-J.; Dolg, M. *Theor. Chem. Acc.* **1998**, *99*, 231.

(25) (a) Jansik, B.; Schimmelpfennig, B.; Norman, P.; Mochizuki, Y.; Luo, Y.; Ågren, H. *J. Phys. Chem. A* **2002**, *106*, 395. (b) Dolg, M. In *Effective Core Potentials in Modern Methods and Algorithms of Quantum Chemistry*, 2nd ed.; Grotendorst, J., Ed.; NIC Series; von Neuman Institute for Chemistry: Jülich, Germany, 2002; Vol. 3, p 507.

(26) Rosenkrantz, M. E.; Stevens, W. J.; Krauss, M.; Konowalow, D. D. *J. Chem. Phys.* **1980**, *72*, 2525.

(27) Seth, M.; Schwerdtfeger, P.; Dolg, M. *J. Chem. Phys.* **1997**, *106*, 3623.

(28) Miller, T. M.; Bederson, B. *Adv. At. Mol. Phys.* **1988**, *25*, 37.

(29) Helgaker, T.; Jensen, H. J. A.; Joergensen, P.; Olsen, J.; Ruud, K.; Aagren, H.; Auer, A. A.; Bak, K. L.; Bakken, V.; Christiansen, O.; Coriani, S.; Dahle, P.; Dalskov, E. K.; Enevoldsen, T.; Fernandez, B.; Haettig, C.; Hald, K.; Halkier, A.; Heiberg, H.; Hettema, H.; Jonsson, D.; Kirpekar, S.; Kobayashi, R.; Koch, H.; Mikkelsen, K. V.; Norman, P.; Packer, M. J.; Pedersen, T. B.; Ruden, T. A.; Sanchez, A.; Saue, T.; Sauer, S. P. A.; Schimmelpfennig, B.; Sylvester-Hvid, K. O.; Taylor, P. R.; Vahtras, O. *DALTON*, a molecular electronic structure program, release 1.2; 2001. Helgaker, T.; Jensen, H. J. A.; Joergensen, P.; Olsen, J.; Ruud, K.; Aagren, H.; Auer, A. A.; Bak, K. L.; Bakken, V.; Christiansen, O.; Coriani, S.; Dahle, P.; Dalskov, E. K.; Enevoldsen, T.; Fernandez, B.; Haettig, C.; Hald, K.; Halkier, A.; Heiberg, H.; Hettema, H.; Jonsson, D.; Kirpekar, S.; Kobayashi, R.; Koch, H.; Mikkelsen, K. V.; Norman, P.; Packer, M. J.; Pedersen, T. B.; Ruden, T. A.; Salek, P.; Sanchez, A.; Saue, T.; Sauer, S. P. A.; Schimmelpfennig, B.; Sylvester-Hvid, K. O.; Taylor, P. R.; Vahtras, O., *DALTON*, a molecular electronic structure program, release 2.0; 2005.

(30) (a) Erkoç, Ş. *Chem. Phys. Lett.* **2003**, *369*, 605. (b) Amirouche, L.; Erkoç, Ş. *Phys. Rev. A* **2003**, *68*, 043203.

(31) Amirouche, L.; Erkoç, Ş. *Int. J. Mod. Phys. C* **2003**, *14*, 905.

(32) Lennard-Jones, J. E. *Proc. R. Soc. London, Ser. A* **1930**, *129*, 604.

(33) Axilrod, B. M.; Teller, E. *J. Chem. Phys.* **1943**, *11*, 299.

(34) Pearson, E.; Takai, T.; Halicioglu, T.; Tiller, W. A. *J. Cryst. Growth* **1984**, *70*, 33.

(35) Amirouche, L.; Erkoç, Ş. *Phys. Status Solidi B* **2004**, *241*, 292.

(36) Choi, D. K.; Takai, T.; Erkoç, Ş.; Halicioglu, T.; Tiller, W. A. *J. Cryst. Growth* **1987**, *85*, 9.

(37) Choi, D. K.; Koch, M. S.; Takai, T.; Halicioglu, T.; Tiller, W. A. *J. Vac. Sci. Technol., B* **1988**, *6*, 1140.

(38) Erkoç, Ş.; Halicioglu, T.; Tiller, W. A. *Phys. Status Solidi B* **1989**, *155*, K105.

(39) Takai, T. Ph.D. Thesis, Stanford University, Stanford, CA, 1984.

(40) Lee, C. *Phys. Status Solidi B* **1987**, *139*, K93.

(41) Oymak H.; Erkoç, Ş. *Phys. Rev. A* **2002**, *66*, 33202.

(42) Erkoç, Ş.; Oymak, H. *J. Phys. Chem. B* **2003**, *107*, 12118.

(43) Nordsieck, A. *Math. Comput.* **1962**, *16*, 22.

(44) Gear, C. W. *Numerical Initial Value Problems in Ordinary Differential Equations*; Prentice Hall: Englewood Cliffs, NJ, 1971.

(45) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.

(46) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E., Jr.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9.; Gaussian Inc.: Pittsburgh, PA, 1998.

(47) Gupta, R. P. *Phys. Rev. B* **1981**, *23*, 6265.

(48) Michaelian, K; Beltrán, M. R.; Garzón, I. L. *Phys. Rev. B* **2002**, *65*, 041403.

(49) Ruppel, M.; Rademann, K. *Chem. Phys. Lett.* **1992**, *197*, 280.

(50) Flad, H.-J.; Schautz, F.; Wang, Y.; Dolg D. M.; Savin, A. *Eur. Phys. J. D* **1999**, *6*, 243.

(51) Benkova, Z.; Sadlej, A. J. *Mol. Phys.* **2004**, *102*, 687. Roos, B. O.; Lindh, R.; Malmqvist, P. A.; Veryazov, V.; Windmark, P. O. *J. Phys. Chem. A* **2004**, *108*, 2851. Jansik, B.; Schimmelpfennig, B.; Norman, P.; Macak, P.; Ågren H.; Ohta, K. *J. Mol. Struct. (THEOCHEM)* **2003**, *633*, 237. Pecul, M.; Rizzo, A. *Chem. Phys. Lett.* **2003**, *370*, 578. Saue T.; Jensen, H. J. A. *J. Chem. Phys.* **2003**, *118*, 522. Norman, P.; Schimmelpfennig, B.; Ruud,

K.; Jensen, H. J. A.; Ågren, H. *J. Chem. Phys.* **2002**, *116*, 6914. Avramopoulos, A.; Ingamelles, V. E.; Papadopoulos, M. G.; Sadlej, A. J. *J. Chem. Phys.* **2001**, *114*, 198. Raptis, S. G.; Papadopoulos, M. G.; Sadlej, A. J. *J. Chem. Phys.* **1999**, *111*, 7904.

(52) (a) Stout, J. M.; Dykstra, C. E. *J. Chem. Phys.* **1995**, *117*, 5127. (b) van Gisbergen, S. J. A.; Schipper, P. R. T.; Gritsenko, O. V.; Baerends, E. J.; Snijders, J. G.; Champagne, B.; Kirtman, B. *Phys. Rev. Lett.* **1999**, *83*, 694. Champagne, B.; Perpéte, E. A.; van Gisbergen, S. J. A.; Baerends, E.-J.; Snijders, J. G.; Soubra-Ghaoui, C.; Robins, K. A.; Kirtman, B. *J. Chem. Phys.* **1998**, *109*, 10489. Champagne, B.; Perpéte, E. A.; Jacquemin, D.; van Gisbergen, S. J. A.; Baerends, E.-J.; Soubra-Ghaoui, C.; Robins, K. A.; Kirtman, B. *J. Phys. Chem. A* **2000**, *104*, 4755. (c) Urban, M.; Černušác, I.; Kellö, V.; Noga, J. In *Methods in Computational Chemistry*; Wilson, S., Ed.; Plenum Press: New York, 1987; Vol. 1, p 117.

(53) Christiansen, P. A.; McCullough, E. A., Jr. *Chem. Phys. Lett.* **1979**, *63*, 570.

(54) Hurst, G. J. B.; Dupuis, M.; Clementi, E. *J. Chem. Phys.* **1988**, *89*, 385.

(55) Deng, K.; Yang J.; Chan, C. T. *Phys. Rev. A* **2000**, *61*, 025201.

(56) Fujita, Y.; Matsuo, T.; Sakurai, T.; Matsuda, H. *Int. J. Mass Spectrom. Ion Processes* **1986**, *69*, 109.

(57) Knight, W. D.; Clemenger, K.; de Heer, W. A.; Saunders, W. A. *Phys. Rev. B* **1985**, *31*, 2539. Knight, W. D.; de Heer, W. A.; Clemenger, K.; Saunders, W. A. *Solid State Commun.* **1985**, *53*, 445.

(58) de Heer, W. A. *Rev. Mod. Phys.* **1993**, *65*, 612.

(59) $\langle r \rangle = \dfrac{2}{N(N-1)} \sum\limits_{i}^{N} \sum\limits_{i<j}^{N} r_{ij}$, where r_{ij} is the interatomic distance of atoms i and j and N is the number of atoms in the cluster.

(60) Raptis, S. G.; Nasiou, S. M; Demetropoulos, I. N.; Papadopoulos, M. G. *J. Comput. Chem.* **1998**, *15*, 1698.

(61) Papadopoulos, M. G.; Raptis, S. G.; Demetropoulos, I. N.; Nasiou, S. M. *Theor. Chem. Acc.* **1998**, *99*, 124.

(62) Kim, F.; Connor, S.; Song, H.; Kuykendall, T.; Yang, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 3673 and references given therein.