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New Effective Core Method (Effective Core Potential and Valence Basis Set) for Al Clusters and Nanoparticles and Heteronuclear Al-Containing Molecules

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Abstract: In previous work we have shown that the PBE0 hybrid density functional method with the MG3 all-electron basis set is an accurate method for calculating the atomization energies of small aluminum clusters (Al_2–Al_7). However, the MG3 basis set is very expensive for molecules much larger than Al_{13}; therefore, we have developed a new effective core potential (ECP) method for aluminum to reduce the cost of obtaining accurate results for nanoparticles. Our method involves a hybrid of the Stuttgart semiempirical effective core potential and the compact effective potential (CEP) potential, and it uses a newly optimized polarized valence triple-ζ basis set. The combination of the new ECP and the new polarized valence triple-ζ basis set for Al is called the Minnesota effective core (MEC) method for Al. The method was optimized with a training set of atomization energies and geometries for AlH, AlC, AlO, AlCCH, Al_2H, Al_2C, Al_2O, and Al_3 and atomization energies of three Al_{13} structures, and we tested it on six test sets composed of 20 atomization energies for systems as large as Al_{13}. We also present an improved all-electron polarized triple split basis set for oxygen, called 6-311+G(d*,p). For the test sets, the mean unsigned error (MUE) of the new method with respect to PBE0/MG3 is 0.06 eV for atomization energies and 0.007 Å for bond lengths, which constitutes a very significant improvement over the quality of the results that can be obtained with effective core potentials and valence basis sets in the literature (of the eight methods in the literature, the best previous method had average errors of 0.63 eV and 0.036 Å). We have also tested the MEC method with a variety of hybrid density functional theory, hybrid meta density functional theory, and pure GGA and meta GGA functionals and found that the average MUE, relative to each functional with all-electron basis sets, is 0.04 eV for atomization energies and 0.009 Å for bond lengths for the new effective core method and 0.16–0.20 eV and 0.013–0.033 Å for effective core potential and valence basis sets in the literature.

1. Introduction

Aluminum clusters have been the focus of several studies.[1–18] Clusters are of interest because their energetic and structural properties often differ significantly from the corresponding bulk properties. It is important to study how the properties change as the cluster size is increased into the nanoparticle range and then as the cluster properties eventually converge to the bulk limit. Unfortunately, though, experimental data are limited to small clusters[19–23] and bulk Al. Thus, theory can play an important role in studying clusters and nanoparticles in the intermediate size range.

In previous work,[18] we have begun testing electronic structure methods for Al. We tested several hybrid density functional theory[24–29] (HDFT) methods and found that the PBE0[28] method (also called PBE1PBE) with the MG3[30–36] basis set (which is a polarized triple-ζ basis set with diffuse functions) was accurate to within 0.012 eV per atom (for Al_2–Al_7). Using the PBE0 method with the MG3 basis set

is impractical for systems that have more than about 15 atoms, because the computational effort (measured by CPU time) required for an energy calculation scales as N^4 (where N is the number of basis functions). One could reduce the size of the basis set, but that will reduce the reliability of the calculation. Another alternative would be to use an effective core method (EC method), which uses an effective core potential[37−44] (ECP) with a valence-only basis set (which we will henceforth call a valence basis set); this kind of treatment replaces the chemically inactive core electrons with an analytic potential. This reduces the CPU time required for a calculation because one does not need to expand the core orbitals in basis functions, and thus the overall size of the basis set is reduced. This represents a significant savings for Al, which has 10 core electrons ($1s^2 2s^2 2p^6$) and 3 valence electrons. Thus, for Al, the use of an EC method reduces the 13-electron problem to a 3-electron problem.

2. Effective Core Potentials

A full discussion of ECPs is beyond the scope of this paper. Overviews are available elsewhere,[38,41] but a brief overview of the basic theory is needed here to establish notation and motivate development. As stated in the Introduction, an EC method uses an effective potential to mimic the presence of the core electrons. First the nuclear charge is reduced by the number of missing core electrons. Then, a theoretically justified form of the potential centered at a given nucleus is a sum of angular-momentum-dependent terms

$$V^{eff} = V^{eff}_{L+1}(r) + \sum_{l=0}^{L} [V^{eff}_l(r) - V^{eff}_{L+1}(r)] \sum_{m=-l}^{l} |lm\rangle\langle lm| \quad (1)$$

where l is the angular momentum quantum number, m is the magnetic quantum number, L is the maximum l found in the core, $|lm\rangle\langle lm|$ is the projection operator for quantum numbers l and m, V^{eff}_l is the effective potential for angular momentum l, r is the distance from the nucleus, and V^{eff} is the total effective potential. The projection operators are present in part to represent Coulomb and exchange interactions with the missing core electrons and in part to impose the orthogonality effect of the absent core electrons on the valence electron wave function. Optionally, the effective potential can also include core-valence correlation effects.[43] In principle, the sum in eq 1 should go from $l = 0$ to $l = \infty$, but eq 1 approximates all V^{eff}_l terms for $l \geqslant L + 1$ with V^{eff}_{L+1} since the higher-l orbitals have no orthogonality effect and have similar Coulomb interactions with the core. For Al, the maximum l found in the core is 1, so $L + 1$ is 2. V^{eff}_l is expanded, for ease of integration, as a sum of Gaussian functions

$$V^{eff}_l = \sum_{i=1}^{i_{max}} a_i r^{n_i} e^{-\alpha_i r^2} \quad (2)$$

where a_i is a negative real number if $l = L + 1$ and a positive real number if $l \leq L$, n_i is an integer between 0 and 2, and α_i is a positive real number. The physical interpretation of this potential is that it is repulsive for the angular momenta corresponding to the core orbitals, because of the orthogonal-

ity effect, and it is attractive for the angular momenta that are not present in the core, because of the screened Coulombic interaction with the missing nuclear charge as the valence electrons penetrate into the core region.

Some of the potentials that will be discussed are called ab initio ECPs, because the ECPs are extracted from an ab initio Hartree−Fock (or relativistic Hartree−Fock) atomic wave function. Ab initio ECPs are obtained from an all-electron wave function in two steps: (1) The valence orbitals from the all-electron calculation are transformed into pseudo-orbitals. There are different methods of obtaining the pseudo-orbitals, but all of the methods force the pseudo-orbitals to be smooth and nodeless and have the correct behavior in the valence region. (2) The numerical effective potential for each value of l is determined such that the eigenvalues of the pseudo-orbitals in the field of the effective core potential are equal to the eigenvalues of the all-electron valence orbital. For simulating neutral species, this should be done in a calculation on the neutral atom (as opposed to an ion with a single valence electron).

The ab initio ECPs that we will discuss in this paper are the LP, CEP,[40] LanL2,[42] Stuttgart relativistic ab initio potential,[44] and SHC.[39] In general, ECPs are developed in conjunction with specific basis sets. The LP potential is obtained by the method of Kahn et al.[38] and is available[45,46] with a double-ζ basis set. The CEP acronym stands for compact effective potential and is sometimes referred to as the SBKJC potential, which stands for Stevens, Basch, Krauss, Jasien, and Cundari. The original CEP potential was developed for Li − Ar.[40] Stevens, Basch, Krauss, and Jasien later extended the CEP potential to include elements K − Rn.[47] Cundari and Stevens extended the CEP potential further to include Ce − Lu.[48] The CEP potential is available for Al with optimized single-, double-, and triple-ζ basis sets, and these methods are denoted CEP-4G, CEP-31G, and CEP-121G, respectively. The LanL2 potential is named for Los Alamos National Laboratory, and it also referred to as the Hay and Wadt potential.[42] The LanL2 potential is available for Al with single and double-ζ basis sets; these are denoted as LanL2MB and LanL2DZ, respectively. The SHC ECP stands for shape- and Hamilitonian-consistent ECP; it was developed by Rappe et al. and is available with a double-ζ basis set for A1.[39] The Stuttgart relativistic potential (abbreviated SRP in this paper) is available with a double-ζ basis set and is named as such because it was fit to a relativistic wave function. The LanL2 potential uses a relativistic reference wave function for elements heavier than Kr, and the CEP potential also uses a relativistic wave function for elements heavier than K.

Because ab initio ECPs are fitted to SCF wave functions, relativistic effects can only be accounted for if the original SCF wave function is relativistic;[41,44] however, semiempirical ECPs can include relativistic effects if they are fitted to experimental data. The Stuttgart semiempirical potential of Igel-Mann et al.; denoted SECP, is a semiempirical ECP that was fit to the experimental energies of single-valence-electron ions,[43] which is different from the SRP potential, which was fit to a relativistic wave function.[44] Thus, the relativistic effects are implicitly included in the potential, whereas the

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Table 1. Parameters in V_{GFP}

i	n_i	A_i	B_i
1	0	-7.31691×10^{-2}	2.25122
2	0	-1.06549×10^{-1}	0.73006
3	0	-3.91007×10^{-2}	0.01575
4	0	-4.08602×10^{-6}	0.00434
5	1	-2.73705×10^{-3}	0.20601
6	2	-1.95503×10^{-5}	0.06858

SRP potential includes the relativistic effects explicity. The functional form of the semiempirical Stuttgart potential[43] (and the SRP) is

$$V^{eff}(r) = \sum_{l=0}^{L+1} V_l^{eff}(r) \sum_{m=-l}^{l} |lm\rangle\langle lm| + V_{pol} \quad (3)$$

where all notation is defined in eq 1 except for V_{pol}, which is a polarization potential. The form of the polarization potential is

$$V_{pol} = \frac{-\alpha}{2} \frac{(1 - \exp(-\lambda r^2))^2}{r^4} \quad (4)$$

where α is the dipole polarizability of the core, and λ is an adjustable parameter. The Gaussian98[45] and Gaussian03[46] implementations of the Stuttgart semiempirical potential (which we will refer to as SECP for Stuttgart semiempirical effective core potential) do not include the polarization potential. We have fit the polarization potential to a sum of powers times Gaussians

$$V_{GFP} = \sum_{i=1}^{6} A_i r^{n_i} \exp(-B_i r^2) \quad (5)$$

where A_i and B_i are adjustable parameters, n_i is an adjustable integer in the range 0–2, and GFP denotes Gaussian fitted polarization potential. The parameters are given in Table 1. Also, it should be noted that the Stuttgart potentials are not of the physical form specified in eq 1 because they have $V_l^{eff} = 0$ for $l \geq L + 1$. Later in the paper, we will use a modified version of the SECP potential called MSECP (modified Stuttgart effective core potential). In the MSECP, we used the $l = 2$ potential for all values of $l \geq L + 1$, and we rewrote eq 3 so that it is of the same form as eq 1; thus the MSECP is of the same form as the ab initio ECPs.

In this paper, we will present a new EC method based on a training set of dissociation energies and geometries calculated with the PBE0 method and the MG3 all-electron basis set. We parametrized a new combination of ECP and valence basis set for use with the PBE0 method to reproduce the all-electron PBE0/MG3 results. By doing this, we will obtain a physical EC method that accurately reproduces the hybrid density functional theory calculations with the all-electron basis set. If we had instead parametrized against a data set of experimental results or a data set of explicitly correlated results, the EC method would also be canceling the errors that are inherent in the PBE0 density functional method; with such a procedure it would not necessarily be a physical EC method. Thus, the EC method developed here
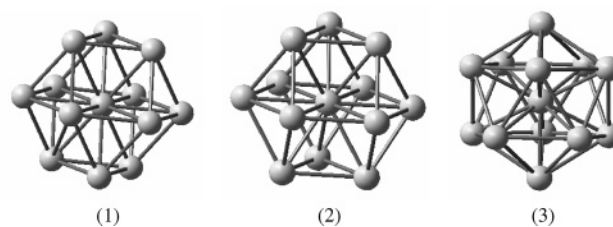
Figure 1. The face centered cubic (1), hexagonally close packed (2), and icosahedron (3).

can also be used with other electronic structure methods; it is not limited to PBE0. This will be explicitly demonstrated in section 6.

3. Test Sets

3.1. Homonuclear Test Set. We will use six test sets in this article. The first test set is called the homonuclear test set. The homonuclear test set includes optimized Al_2 and Al_3 structures and three Al_{13} structures with fixed bond lengths. We use the ground electronic states of Al_2 and Al_3, which are $^3\Pi_u{}^{1,2,5,49}$ and $^2A_1'.^{3,4,6,17}$ The minimum-energy structure of Al_3 is an equilateral triangle; thus, our test set includes two bond lengths (Al_2 and the one degree of freedom in Al_3). The Al_{13} structures have face-centered cubic (FCC), hexagonally close packed (HCP), and icosahedral symmetry (see Figure 1). The bond length that we have used for the FCC, HCP, and icosahedral structures is 2.8635 Å, which is the bond length in the bulk metal. This was obtained by dividing the experimental (298 K) lattice constant, 4.04964 Å,[50] by $\sqrt{2}$.

3.2. Heteronuclear Test Set. The second test set is the called the heteronuclear test set. The molecules in the heteronuclear test set are AlH, AlC, AlO, AlCCH, Al_2H, Al_2C, and Al_2O, and they have all been optimized by the all-electron PBE0/MG3 method. The first and second row diatomics have been thoroughly studied experimentally and computationally.[51] The AlX (X = H − F) diatomics, in particular, have been thoroughly studied by Gustev et al.[52] They concluded that the ground states of AlH, AlC, and AlO are $^1\Sigma^+$, $^4\Sigma^-$, and $^2\Sigma^+$, respectively. Their conclusions agree with previous calculations[51] and our PBE0/MG3 optimizations for AlH, AlC, and AlO.

There has been little theoretical work done on the AlCCH system. Chertihin et al. have studied this system experimentally and theoretically.[53] They found that the structure of AlCCH is linear and that the isomer CCAlH is higher in energy. We have reexamined this system by optimizing different isomers with PBE0/MG3. We found that the linear AlCCH system is the minimum-energy structure, with a ground electronic state of $^1\Sigma^+$. It is interesting to note that the CCAlH systems (both singlet and triplet states) are saddle points. We also examined bent systems and π-bonded system where the Al atom is bonded to the bridge site of the C−C bond in the acetylene fragment. We also located stationary points for nonlinear systems that had C_{2v} and C_s symmetries. The minimum-energy structures are shown in Figure 2, and the results are summarized in Table 2. There is one structure with C_s symmetry that is a minimum, and there is one C_{2v} structure with one imaginary frequency (labeled C_{2v}-$1i$ in
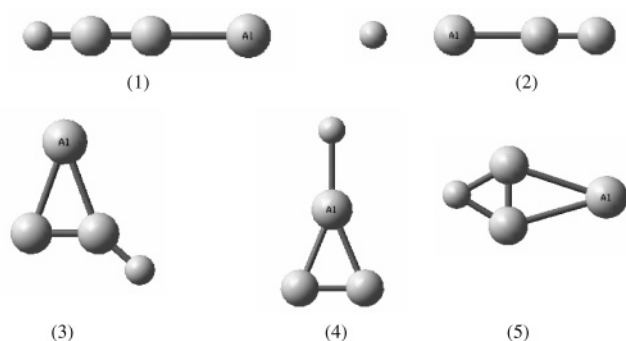
Figure 2. The AlCCH structures. The energetics are reported in Table 2 and are labeled as AlCCH(linear) (1), CCAlH(linear) (2), AlCCH(C$_{2v}$-2i) (3), AlCCH(C$_{2v}$-1i) (4), and AlCCH(C$_s$) (5).

Table 2. D_e Values (in eV) from All-Electron PBE0/MG3 Calculations for the AlCCH Structures Shown in Figure 1

	D_e
AlCCH(linear)[a]	
$^1\Sigma^+$	16.64
$^3\Pi$	15.26
$^3\Sigma^+$	10.92
CCAlH(linear)	
$^1\Sigma^+$	14.24
$^3\Pi$	11.92
$^3\Sigma^+$	6.04
AlCCH(C$_s$)	
$^1A'$	15.94
$^3A'$	14.57
AlCCH(C$_{2v}$-1i)	
$^1A_1$	15.06
$^3B_2$	12.61
AlCCH(C$_{2v}$-2i)	
$^1A_1$	14.14
$^3B_2$	12.41

[a] The $^1\Sigma^+$ state is used in the heteronuclear and small molecule test sets.

Table 2 and Figure 2) and one C$_{2v}$ structure with two imaginary frequencies (labeled C$_{2v}$-2i in Table 2 and Figure 2). The lowest energy nonlinear structure is the C$_s$ structure, and the C$_{2v}$-1i structure is lower in energy than C$_{2v}$-2i.

There have also been few theoretical or experimental studies of either Al$_2$H or Al$_2$C. Chertihin et al.[53] indicate that the lowest-energy structure of Al$_2$C is a bent structure with C$_{2v}$ symmetry. We also found that the ground states of Al$_2$H or Al$_2$C had C$_{2v}$ symmetry. Table 3 present the energies of optimized Al$_2$H and Al$_2$C structures. We optimized structures that have D$_{\infty h}$, C$_{\infty v}$, and C$_{2v}$ (see Figure 3) symmetries. For Al$_2$H we find that the lowest energy states for the D$_{\infty h}$, C$_{\infty v}$, and C$_{2v}$ structures are doublets. The ground state for Al$_2$H (C$_{2v}$ symmetry) is the $^2B_1$ state, but the $^2A_1$ state is nearly degenerate with the $^2B_1$ state. The C$_{2v}$ structures for Al$_2$H are all true minima, but the lowest energy C$_{\infty v}$ state is a saddle point and the lowest energy D$_{\infty h}$ structure is a hilltop, i.e., a stationary point with two imaginary frequencies. For Al$_2$C, the lowest energy structures with C$_{2v}$ and C$_{\infty v}$ symmetries are both triplets, but the lowest energy D$_{\infty h}$ structure is a singlet. It is interesting to note that, as for

Table 3. D_e Values (in eV) for the Al$_2$X (X = H, C, O) Molecules that Are Shown in Figure 3[a]

	Al$_2$H[b]		Al$_2$C[c]		Al$_2$O[d]	
	state	D_e	state	D_e	state	D_e
D$_{\infty h}$	$^2\Pi$	3.90	$^1\Sigma_g^+$	6.12	$^1\Sigma_g^+$	10.63
			$^3\Sigma_u^+$	5.87	$^3\Pi_u$	7.42
			$^5\Sigma_g^+$	4.21	$^1\Pi_u$	7.03
C$_{\infty v}$	$^2\Pi$	4.18	$^3\Sigma$	4.57	$^1\Sigma$	7.15
	$^4\Sigma$	3.74	$^5\Pi$	4.29	$^3\Sigma$	6.08
	$^2\Sigma$	3.33	$^1\Pi$	4.10	$^1\Pi$	5.83
			$^1\Sigma$	3.91		
C$_{2v}$	$^2B_1$	4.51	$^3B_2$	6.95	$^3B_2$	8.02
	$^2A_1$	4.46	$^1A_1$	6.40	$^1B_2$	7.67
	$^4B_1$	2.87	$^5A_2$	5.38	$^3A^2$	7.24
	$^4A_2$	2.76	$^3A_1$	5.14		

[a] Calculated by the all-electron PBE0/MG3 method. [b] The C$_{2v}$ ($^2B_1$) state is used in the heteronuclear and small molecule test set. [c] The C$_{2v}$ ($^3B_2$) state is used in the heteronuclear and small molecule test set. [d] The C$_{2v}$ ($^3B_2$) state is used in the heteronuclear and small molecule test set.
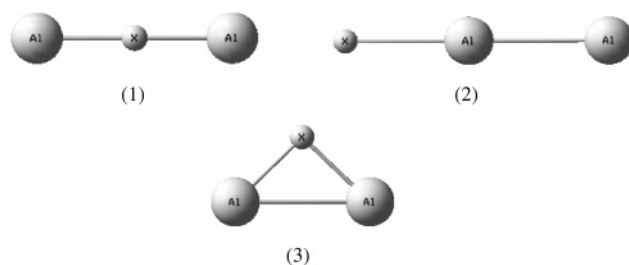

Figure 3. The D$_{\infty h}$ (1), C$_{\infty v}$ (2), and C$_{2v}$ (3) structures of Al$_2$X (X = H, C, and O).

Al$_2$H, the lowest energy D$_{\infty h}$, C$_{\infty v}$, and C$_{2v}$ structures of Al$_2$C are a hilltop, saddle point, and a true minimum, respectively. In fact, all of the C$_{2v}$ structures are minima. However, unlike Al$_2$H, there are no nearly degenerate electronic states. We will use the $^2B_1$ state of Al$_2$H and the $^3B_2$ state of Al$_2$C in our training set.

The Al$_2$O system has been studied more thoroughly.[54-59] In all of the Al$_2$O studies, the lowest energy structure has been a linear (AlOAl) molecule with D$_{\infty h}$ symmetry; the D$_{\infty h}$ structure, because of symmetry, has one independent bond length (the Al−O bond). In fact, this structure is significantly more stable than the other structures. Table 3 presents the optimized Al$_2$O structures. The lowest-energy structure with C$_{2v}$ symmetry is a triplet ($^3B_2$). The Al$_2$O systems also show no nearly degenerate electronic states, unlike the Al$_2$H system that has nearly degenerate electronic states ($^2B_1$ and $^2A_1$). In our training set, however, we have used the Al$_2$O molecule with C$_{2v}$ symmetry instead of the D$_{\infty h}$ structure. This was done because we will ultimately be using this data set to parametrize a new ECP and valence basis set. The C$_{2v}$ structure has an additional Al−Al bond that is not present in the D$_{\infty h}$ structure. All of the data that was used in the heteronuclear set are in the last columns of Tables 4 and 5. The other columns in Tables 4 and 5 will be explained in sections 6, and those in Table 5 will be explained in sections 4, 5, and 6.

3.3. Optimization Test Set. The test set that was used for optimizing our ECP method contains the PBE0/MG3

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Table 4. D_e Values (in eV) for the Homonuclear and Heteronuclear Data Set Calculated with All-Electron PBE0/MG3 and with Valence-Electron PBE0/MSMG3/6-311+G(d,p) and PBE0/MEC/6-311+G(d*,p) Methods[f]

	MSMG3/6-311+G(d,p)[a]	MEC/6-311+G(d*,p)[b]	MG3[c]
Al$_2$	1.49	1.54	1.55
Al$_3$	3.79	3.83	3.86
AlH	2.97	2.98	2.99
AlC	3.48	3.52	3.55
AlO	4.94	5.04	5.08
AlCCH	16.51	16.57	16.64
Al$_2$H	4.41	4.44	4.51
Al$_2$C	6.87	6.89	6.95
Al$_2$O (C$_{2v}$ triplet)	7.80	7.94	8.02
Al$_{13}$(FCC)	31.13	30.82	30.74
Al$_{13}$(HCP)	31.74	31.49	31.43
Al$_{13}$(icosahedron)	32.97	32.42	32.55
MUE[d]	0.18	0.06	
time[e]	747	473	4.3 × 10^6

[a] All-electron with 6-311+G(d,p) for H, C, and O and valence-electron with MSMG3 for Al. [b] All-electron with 6-311+G(d*,p) for H, C, and O and valence-electron with MEC for Al. [c] The all-electron basis set MG3 was used for all atoms. (MG3 is identical to 6-311++G(3d2f,2dp,2p) for element considered in this paper.). [d] Mean unsigned deviation from last column. [e] CPU time in seconds. [f] In the valence-electron calculations, the basis H, C, and O is 6-311G+G(d,p) for MSMG3 and 6-311+G(d*,p) for MEC.

Table 5. Equilibrium Internuclear Distance, r_e (in Å), for the Homonuclear and Heteronuclear Test Set Calculated with PBE0 and the MSMG3 and MEC Valence-Only Methods as Compared to Results Obtained with the All-Electron MG3 Basis Set

	MSMG3/6-311+G(d,p)[a]	MEC/6-311+G(d*,p)[b]	MG3[c]
Al$_2$	2.754	2.750	2.730
Al$_3$	2.508	2.513	2.507
AlH	1.662	1.673	1.664
AlC	1.964	1.970	1.964
AlO	1.620	1.621	1.617
Al−CCH	1.968	1.973	1.966
Al−AlH	2.479	2.479	2.479
AlAl−H	1.821	1.827	1.820
Al−AlC	2.798	2.786	2.792
AlAl−C	1.849	1.854	1.853
Al−AlO (C$_{2v}$ triplet)	2.551	2.522	2.527
AlAl−O	1.736	1.737	1.730
MUE[d]	0.006	0.007	

[a] All-electron with 6-311+G(d,p) for H, C, and O and valence-electron with MSMG3 for Al. [b] All-electron with 6-311+G(d*,p) for H, C, and O and valence-electron with MEC for Al. [c] The all-electron basis set MG3 was used for all atoms. (MG3 is identical to 6-311++G(3d2f,2dp,2p).). [d] Mean unsigned deviation from all-electron results.

optimized geometries and D_e values of AlH, AlC, AlO, AlCCH, Al$_2$H, Al$_2$C, Al$_2$O, and Al$_3$, and the D_e values of the three Al$_{13}$s structures with bond lengths fixed at 2.8635 Å. The structural isomers and electronic states of the molecules are the same ones that are used in the heteronuclear and homonuclear test sets.

3.4. Al$_{13}$ Test Set. The Al$_{13}$ test set was constructed to further test the accuracy of the new ECP method. We optimized the geometry and calculated the value of D_e for FCC, HCP, and icosahedral Al$_{13}$ with PBE0/MG3. The Al$_{13}$ test data obtained this way is in the fourth row of Table 6; the other data in this table will be explained in section 6.

The optimum bond lengths of the FCC, HCP, and icosahedral structures are all shorter than the bulk bond length (see Table 6). The minimum energy structure is a Jahn−Teller distorted icosahedron. From one point of view, it would have been preferable to include the Al$_{13}$ data in the optimization procedure, but the optimization procedure

Table 6. D_e (in eV) and r_e (in Å) Values for the Optimized PBE0 Calculations on the Al$_{13}$ Structures[a]

	FCC		HCP		icosahedron		MUE	
	D_e	r_e	D_e	r_e	D_e	r_e	D_e	r_e
CEP-121G(d)	31.14	2.727	31.73	2.727	32.36	2.814	0.44	0.060
LanL2DZ(d)	30.44	2.738	31.05	2.739	31.55	2.817	1.17	0.068
LP-31G(d)	30.55	2.696	31.18	2.698	31.82	2.774	1.00	0.049
MEC	31.63	2.719	32.23	2.723	32.59	2.666	0.05	0.006
MG3	31.60	2.713	32.25	2.715	32.70	2.661		
MSMG3	31.84	2.727	32.43	2.727	33.06	2.814	0.26	0.060
SECP(d)	30.66	2.728	31.25	2.730	31.71	2.811	0.98	0.060
SHC(d)	30.28	2.712	30.90	2.756	31.14	2.838	1.41	0.073

[a] The MG3 row contains all-electron calculations, and the other rows contain valence-only calculations and their mean unsigned deviation from the MG3 row.

(described below) involves repeated evaluation of the test set, and calculating gradients of Al$_{13}$ would have significantly increased the time required to optimize the parameters. From

another point of view though, using these data as a test without including them in the training set provides a useful check on our methodology. The Al_{13} test set is especially important because Al_{13} is the smallest Al cluster in which any atom has the bulk coordination number of 12. In particular, the central atom, which participates in 12 of the 36 bonds of FCC Al_{13}, has this coordination number. It is important to test whether the effective core potential and basis set remain valid not only for binding energies but also for bond lengths for systems with this high coordination number.

3.5. Small Molecule Test Set. We have found PBE0 to be the most accurate HDFT method for pure Al compounds;[18] however, PBE0 is not necessarily the best method for other systems, such as hydrocarbons.[60,61] Since PBE0 might not be the best method for all interesting systems, we will use the small-molecule test set to test the accuracy of the MEC method with other DFT and HDFT methods and compare how well it does with competing EC methods. The small molecule test set includes the atomization energies and bond lengths of Al_2, Al_3, AlH, AlC, AlO, AlCCH, Al_2H, Al_2C, and Al_2O. The DFT methods that will be used are the Becke88-Lee-Yang-Wang model (BLYP),[62,63] modified-Perdew-Wang-Perdew-Wang-1991 model (mPWPW91),[27] PBE;[64] the HDFT methods that will be used are the Becke88 3-parameter-Lee-Yang-Wang model (B3LYP)[65,66] and modified-Perdew-Wang 1-parameter-Perdew-Wang-1991 model (mPW1PW91);[27] and the meta DFT methods that will be used are the 1-parameter Becke88-Becke95 (B1B95)[67] and a recent 1-parameter model for kinetics (BB1K).[68]

3.6. AlX Test Set. We also wanted to test how well the MEC method does with elements that are not present in the training set. The AlX test set contains the dissociation energies for AlX compounds where $X =$ Li, Be, B, N, C, O, and F. We used the electronic states determined by Gustev et al.[52] The dissociation energies were calculated with the PBE0 HDFT method and MG3 basis set.

4. Tests of Literature ECPs and C, H, and O Basis Sets

We first tested how well the currently available EC methods do for the homonuclear test set; the results are given in Table 7. Each EC method consists of an ECP and a valence basis set. Some of the valence basis sets that were developed for the EC methods have d functions. The SHC and CEP methods use the same exponent for the d functions (0.25).[1] The LanL2DZ basis set uses a different exponent for the d functions (0.19).[69] To our knowledge, there are no d functions for the SRP or SECP, so we have also examined all of the EC methods with the standard exponents for d functions (0.325) for Al.[36] The standard d functions were used as both Cartesian d functions (6D) and spherical d functions (5D). This was done because some of the C, H, and O basis sets use the 6D formalism and some used the 5D formalism. The important result is that the choice between using 5D or 6D functions does not have a significant effect on the results. The diffuse functions that we have used are the standard diffuse functions (the s and p exponents are both 0.0318)[47] and were used with the d function that had the smallest error (except for SECP+V_{GFP}, which uses no d functions).

Table 7. Mean Unsigned Error in D_e Values (in eV), r_e Values (in Å), and CPU Times (in s) for the Homonuclear Test Set with the Literature ECPs

	no d[a]	literature	5D[b]	6D[c]	+ diffuse[d]
			CEP-31G		
MUE(D_e)	2.78	0.63	0.79	0.80	0.63
MUE(r_e)	0.106	0.045	0.039	0.040	0.041
time	77	271	1635	261	680
			CEP-121G		
MUE(D_e)	2.30	0.57	0.65	0.64	0.56
MUE(r_e)	0.104	0.038	0.034	0.034	0.038
time	146	464	373	489	1465
			LanL2DZ		
MUE(D_e)	2.95	0.68	0.65	0.66	0.63
MUE(r_e)	0.102	0.028	0.034	0.033	0.043
time	72	160	393	417	1610
			LP-31G		
MUE(D_e)	2.82	1.04	0.78	0.77	0.71
MUE(r_e)	0.071	0.006	0.006	0.005	0.004
time	70	209	209	196	540
			SECP		
MUE(D_e)	2.33		0.32	0.30	0.22
MUE(r_e)	0.082		0.012	0.011	0.012
time	84		328	286	801
			SECP+V_{GFP}		
MUE(D_e)	1.36		3.20	3.11	1.59
MUE(r_e)	0.007		0.077	0.076	0.013
time	87		328	335	260
			SHC		
MUE(D_e)	2.82	0.52	0.74	0.77	0.43
MUE(r_e)	0.169	0.057	0.053	0.046	0.050
time	71	291	258	255	471
			SRP		
MUE(D_e)	2.67		0.58	0.58	0.44
MUE(r_e)	0.101		0.028	0.028	0.023
time	72		719	622	844

[a] No diffuse functions. [b] The d functions are 5D. [c] The d functions are 6D. [d] Best of the previous four columns, augmented by diffuse functions.

The one EC method that shows unexpected behavior in Table 7 is the SECP+V_{GFP} EC method. This EC method has the smallest MUE for both atomization energies and bond lengths when only an s and p valence-electron basis set was used, but the errors more than double when d functions are used. For the other ECPs, the inclusion of d functions leads to significant improvements in both atomization energies and bond lengths.

The computational times reported in Table 7 are the CPU times required for a single-point calculation of icosahedral Al_{13} on a single-processor of an IBM Power4 supercomputer with a 1.3 GHz Power4 processor. These times should not be interpreted too closely because they depend on the number of SCF iterations required, which can be increased or decreased by using different initial guesses or different SCF routines. Nevertheless they do provide a qualitative indication of the cost that is needed to judge whether increasing the basis set is worth the increased cost and whether including d functions (except for SECP+V_{GFP}) is worth the increased

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Table 8. Mean Unsigned Error for D_e (in eV) and r_e (in Å) for the Heteronuclear Test Set with Literature ECP Methods with d Functions and Various Double-ζ Basis Sets for C, H, and O

	6-31G[a]	6-31G(d)[a]	6-31G(d,p)[a]	6-31+G(d)[a]	6-31+G(d,p)[a]	6-31++G(d,p)[a]
			CEP-121G(d)			
MUE(D_e)	0.34	0.37	0.32	0.26	0.25	0.26
MUE(r_e)	0.039	0.039	0.039	0.032	0.031	0.031
			LanL2DZ(d)			
MUE(D_e)	0.39	0.27	0.19	0.30	0.29	0.31
MUE(r_e)	0.050	0.037	0.038	0.040	0.039	0.039
			LP-31G(d)			
MUE(D_e)	0.21	0.26	0.24	0.28	0.19	0.26
MUE(r_e)	0.025	0.034	0.033	0.032	0.032	0.031
			SECP(d)			
MUE(D_e)	0.28	0.17	0.16	0.18	0.17	0.19
MUE(r_e)	0.017	0.007	0.007	0.010	0.009	0.009
			SHC(d)			
MUE(D_e)	0.36	0.26	0.24	0.27	0.25	0.27
MUE(r_e)	0.053	0.042	0.041	0.045	0.045	0.045
			SRP(d)			
MUE(D_e)	0.30	0.19	0.23	0.20	0.18	0.20
MUE(r_e)	0.024	0.014	0.013	0.016	0.016	0.016

[a] Literature exponents.

computational effort. In general, the addition of diffuse functions did not lead to significant improvements in either atomization energies or bond lengths. The inclusion of diffuse functions, however, did lead to significant increases in the computational time.

The main conclusions drawn from Table 7 is that the SECP method does best for energies, and the LP-31G method does best for bond distances. Note that these are the fifth and second least expensive of the eight methods studied.

We turn next to the heteronuclear test set. For this test set we tested the literature EC methods for Al with all-electron basis sets for H, C, and O. The basis sets that we tested were as follows: (a) double-ζ, polarized valence double-ζ, and polarized augmented double-ζ: 6-31G,[70] 6-31G(d),[70,71] 6-31+G(d),[70-72] 6-31G(d,p),[70,71] 6-31+G(d,p),[70-72] 6-31++G-(d,p);[70-72] and (b) triple-ζ, polarized valence triple-ζ, and polarized augmented triple-ζ: 6-311G,[73] 6-311G(d),[72,73] 6-311+G(d),[72,73] 6-311G(d,p),[73] 6-311+G(d,p),[72,73] and 6-311++G(d,p).[72,73] The double-ζ-type basis sets and the triple-ζ-type basis sets use spherical harmonic sets of five d basis functions. We did not reexamine all of the different permutations of Al valence basis sets, but instead, for each ECP, we used the one with the smallest errors in Table 7. For CEP, we used the triple-ζ basis set with the literature d functions. We used the standard d functions for the LanL2DZ, LP-31G, SECP, SHC, SRP, and SECP potentials. We did not use the SECP+V_{GFP} potential because of its poor performance. With these explanations, then, the methods used for Al are referred to as CEP-121G(d), LanL2DZ(d), LP-31G(d), SECP(d), SHC(d), and SHC(d). The results are in Tables 8 and 9.

None of the H, C, and O basis sets is quite as large as MG3. For H, C, and O the MG3 basis set is the same as 6-311G++G(2df,2p),[35] and for Al it is 6-311+G(3d2f).[35] Atoms heavier than Si, the s and p functions of the MG3 basis set differ from 6-311G.[35]

Tables 8 and 9 show that increasing the size of the basis set on H, C, and O does not systematically improve the results, but in general, the best H, C, and O basis sets have both polarization functions and diffuse functions. The polarization functions lowered the errors for both atomization energies and bond lengths, whereas the diffuse functions mainly lowered the errors for atomization energies. The LP-31G(d) method has the lowest errors when no polarization or diffuse functions are used on H, C, and O. The best method for the heteronuclear test set using polarized or polarized augmented basis sets for H, C, and O is 6-31G-(d,p) and SECP(d) for Al. This is encouraging because the SECP method was also the most accurate for D_e in the homonuclear test set.

5. New ECP Parameters and Basis Set Exponents

5.1. MSMG3 Method. On the basis of the tests in section 4, we chose the SECP method for further improvement, and we began improving it by defining it for all values of l (MSECP) as explained in section 2. Then we developed a valence electron basis set by starting with MG3 basis functions. We were able to obtain very good results for the homonuclear and heteronuclear test sets with a $(3s4p1d)$ valence electron basis set for Al and various basis sets for H, C, and O. We call this method MSMG3 (modified Stuttgart semiempirical ECP with Al basis functions from MG3). The MUE in D_e and r_e (averaged now over both the homonuclear and heteronuclear test sets) decreased from 0.25 to 0.18 eV and from 0.011 to 0.006 Å, respectively.

The main drawback of the MSMG3 method is that it is computationally demanding because there are four p functions on Al. Therefore we tested whether the results can be improved if the Al basis functions are further optimized. We began by testing the sensitivity to the basis set exponents and found that the energies and geometries could be most

Table 9. Mean Unsigned Error for D_e (in eV) and r_e (in Å) for the Heteronuclear Test Set Calculated with the PBE0 Method and Literature ECP Methods with d Functions and Various Triple-ζ Basis Sets for C, H, and O

	6-311G[a]	6-311G(d)[a]	6-311G(d,p)[a]	6-311+G(d)[a]	6-311+G(d,p)[a]	6-311++G(d,p)[a]
			CEP-121G(d)			
MUE(D_e)	0.38	0.30	0.28	0.29	0.32	0.27
MUE(r_e)	0.041	0.034	0.032	0.035	0.033	0.033
			LanL2DZ(d)			
MUE(D_e)	0.42	0.34	0.32	0.33	0.31	0.31
MUE(r_e)	0.051	0.041	0.040	0.042	0.040	0.041
			LP-31G(d)			
MUE(D_e)	0.21	0.24	0.22	0.26	0.32	0.24
MUE(r_e)	0.024	0.031	0.030	0.030	0.030	0.030
			SECP(d)			
MUE(D_e)	0.31	0.22	0.20	0.21	0.18	0.19
MUE(r_e)	0.018	0.011	0.010	0.011	0.010	0.010
			SHC(d)			
MUE(D_e)	0.39	0.30	0.28	0.29	0.27	0.27
MUE(r_e)	0.054	0.046	0.045	0.047	0.046	0.046
			SRP(d)			
MUE(D_e)	0.31	0.23	0.21	0.21	0.20	0.20
MUE(r_e)	0.024	0.017	0.017	0.017	0.017	0.017

[a] Literature exponents.

readily improved by varying the tightest and most diffuse s and p basis functions and/or the d function. The errors for the compounds containing oxygen were much larger than the errors for the C and H compounds, and for this critical case we found that varying the d function on O leads to systematic improvements, whereas varying the diffuse functions on O did not lead improvements for compounds with O. This will be discussed in greater detail in section 6.

To take advantage of the possible improvements noted in the previous paragraph, we optimized a new basis set for Al and a new ECP. We did not want to develop a new ECP from scratch, so instead we took a linear combination of two of the already defined ECPs

$$V_{H-X-MSECP} = cV_X + (1-c)V_{MSECP} \qquad (6)$$

where X stands for either CEP, LanL2DZ, LP, and SHC and H-X-MSECP stands for hybrid X-MSECP. After some initial trials we found that a combination of the CEP and MSECP potentials led to the most improvement in D_e and r_e for both the homonuclear and heteronuclear test sets. We also tried using different linear combinations that used different values of c for the various l-components but found that the improvement obtainable in that way was marginal.

5.2. Optimization Procedure. We optimized the Al valence-electron basis set, the d function for O, and c in eq 6 with a microgenetic algorithm (μGA), which has been described elsewhere.[74-76] Briefly stated, the μGA optimizes a set of parameters by maximizing a fitness function. For this paper, the fitness function is

$$f = -\left(\frac{1}{a}MUE(D_e) + \frac{1}{b}G\right) \qquad (7)$$

where MUE(D_e) is the mean unsigned error in the D_e, G is the root-mean-square of the gradients calculated with the EC method at the geometries of the PBE0/MG3 optimized molecules, $a = 1$ eV, and $b = 2$ eV/Å, and f is the unitless

Table 10. Parameters for the MEC Method

	s exponent	p exponent	d exponent	c
Al	0.75752	1.94530	0.45580	0.461
	0.20680	0.20064		
	0.08507	0.07073		

fitness function. The evaluation of f involves computing the dissociation energies for all of the molecules in the optimization test set and the gradients of the PBE0/MG3 optimized geometries in the optimization test set. This strategy allows us to parametrize against geometries without having to do an expensive geometry optimization at each step. The final parameters define what we call the MEC method, and they are given in Table 10. The parametrization was done with the 6-311++G(d,p) basis set for C, H, and O, except that the d function was also optimized on O. The optimized d function on O is 0.63924 and may be compared to the standard one (in 6-311++G(d,p)) of 1.292. Any basis set that uses the new value of the oxygen d exponent instead of the standard value will be denoted d^*; the d exponent for C is not changed. The heteroatom basis set will often be explicitly stated after the EC method. For example, PBE0/MEC/6-311+G(d*,p) means that the PBE0 HDFT method was used with the MEC method for Al atoms, and the 6-311+G(d*,p) basis set was used for non-Al atoms.

6. Results and Discussion

All of the calculations in this paper were done with either GAUSSIAN98[45] or GAUSSIAN03,[46] except for the Al$_{13}$ geometry optimizations which were done with NWCHEM version 4.5.[77] As mentioned in section 5, the method that we have developed (as specified in Table 10) is called the MEC (Minnesota effective core) method. The results obtained with the MEC method are given in Tables 4−6 and 11.

The MUE in D_e and r_e for both the homonuclear and heteronuclear test set with the PBE0/MEC method are given

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Table 11. Mean Unsigned Error for D_e (in eV) and r_e (in Å) for the Heteronuclear Test Set Calculated with PBE0 and the MEC Valence-Electron Method for Al and Various All-Electron Basis Sets for C, H, and O

	MUE(D_e)	MUE(r_e)
6-31G[a]	0.20	0.009
6-31G(d*)[a]	0.09	0.006
6-31G(d*,p)[a]	0.08	0.006
6-31+G(d*)[a]	0.08	0.006
6-31+G(d*,p)[a]	0.06	0.006
6-31++G(d*,p)[a]	0.07	0.006
6-311G[a]	0.22	0.009
6-311G(d*)[a]	0.10	0.007
6-311G(d*,p)[a]	0.08	0.007
6-311+G(d*)[a]	0.08	0.006
6-311+G(d*,p)[a]	0.05	0.005
6-311++G(d*,p)[a]	0.05	0.005

[a] The d-function used for O is 0.63924 (see Table 14), and the remaining functions are unchanged from their standard values.

in Tables 4 and 5, respectfully. It can be seen that the MUE for D_e for both the heteronuclear test sets and homonuclear test sets is 0.06, which is 0.12 eV lower than PBE0/MSMG3, and it is 0.19 eV lower than the most accurate literature potential. The MUE in r_e (for the heteronuclear and homonuclear test sets) is 0.001 Å larger with PBE0/MEC than with PBE0/MSMG3, but the MUE in r_e for PBE0/MEC is 0.005 Å lower than the most accurate literature potential. In another test of the PBE0/MEC method, given in Table 6, the MUE in D_e for the Al_{13} test set is 0.04 eV, and the error in bond lengths for the Al_{13} test set is 0.006 Å.

As described above, Table 5 involves tests of the MEC model with the recommended 6-311+G(d*,p) basis for H, C, and O. We also tested the MEC model with other basis sets for H, C, and O, and the results are given in Table 11. We found that the 6-311+G(d*,p) and 6-311++G(d*,p) basis sets give the best results for D_e and r_e, and the mean unsigned errors for both of these basis sets are 0.05 eV and 0.005 Å, respectively. Removing the diffuse functions on C, H, and O altogether does not lead to a significant increase in errors for the heteronuclear test set. For example, the MUE in D_e and r_e with the 6-311G(d,p) basis set is 0.08 eV and 0.007 Å, respectively.

An issue that requires special discussion is that the d-function for O was reoptimized for use in conjunction with the MEC basis set. The standard value of the oxygen d exponent in the 6-311G(d) or 6-311+G(d) basis set is 1.292, and the standard value in the 6-31G(d) or 6-31+G(d) basis set is 0.800, whereas the recommended value of the d exponent for use with the MEC is 0.63924; this is denoted d*. This does not mean that the MEC is inappropriate for general use, but instead it indicates a deficiency in the 6-311+G(d) basis set for O. The MUEs in dissociation energies and bond lengths for AlO and Al_2O calculated with PBE0/MEC/MG3 (the MG3 basis set for O is 6-311+G-(2df)) are 0.06 eV and 0.003 Å, respectively, but these MUEs are 0.18 eV and 0.006 Å, respectively, if the dissociation energies and bond lengths are calculated with PBE0/MEC/6-311+G(d). In contrast, the errors for the dissociation energies and bond lengths are 0.06 eV and 0.003 Å,

Table 12. Calculated Dissociation Energies for the AlX Training Set and MUEs for Various Basis Sets

non-Al basis	AlLi	AlBe	AlB	AlN	AlC	AlO	AlF	MUE
6-31G(d)[a]	0.88	0.80	2.17	2.45	3.48	4.93	6.72	0.07
6-31+G(d)[a]	0.89	0.81	2.14	2.54	3.50	5.02	6.79	0.03
6-311G(d)[a]	0.90	0.81	2.14	2.46	3.49	4.87	6.59	0.10
6-311+G(d)[a]	0.91	0.83	2.16	2.52	3.52	4.94	6.64	0.07
6-31G(2d)[b]	0.89	0.83	2.19	2.50	3.53	4.96	6.70	0.07
6-31+G(2d)[b]	0.89	0.84	2.18	2.59	3.56	5.08	6.76	0.03
6-311G(2d)[b]	0.90	0.83	2.17	2.52	3.53	4.97	6.69	0.06
6-311+G(2d)[b]	0.91	0.85	2.19	2.59	3.56	5.07	6.74	0.04
6-31G(1d)[c]	0.89	0.82	2.19	2.49	3.54	4.90	6.71	0.07
6-31+G(1d)[c]	0.89	0.83	2.18	2.58	3.57	5.03	6.77	0.03
6-311G(1d)[c]	0.90	0.82	2.17	2.51	3.54	4.91	6.70	0.07
6-311+G(1d)[c]	0.91	0.84	2.19	2.58	3.57	5.02	6.75	0.04
6-311+G(d*)[d]	0.91	0.83	2.16	2.52	3.52	5.04	6.64	0.06

[a] The exponents are all unchanged from those defined in the literature (see Table 14). [b] The exponents used in the d-functions for this basis set are the same ones used in the MG3 basis set (see Table 14). [c] The exponent used in the d-functions for this basis set are the same as the most diffuse d-exponent used in the MG3 basis set (see Table 14). [d] The exponent used in the d-functions used for O is 0.63924, and the remaining exponents are unchanged from their standard values.

Table 13. Calculated Dissociation Energies for the AlX Training Set and MUEs for Various Basis Sets and EC Methods

non-Al basis	AlLi	AlBe	AlB	AlN	AlC	AlO	AlF	MUE
CEP-121G(d)								
6-311G(d)[a]	0.87	0.72	1.92	2.05	3.20	4.27	6.08	0.39
6-311+G(d)[a]	0.88	0.72	1.92	2.10	3.20	4.34	6.15	0.36
6-311G(2d)[b]	0.88	0.73	1.95	2.23	3.30	4.56	6.32	0.27
6-311+G(2d)[b]	0.88	0.73	1.96	2.28	3.31	4.61	6.36	0.25
6-311G(1d)[c]	0.88	0.72	1.95	2.23	3.31	4.57	6.33	0.27
6-311+G(1d)[c]	0.88	0.72	1.96	2.27	3.32	4.61	6.37	0.24
LanL2DZ(d)								
6-311G(d)[a]	0.88	0.73	1.94	2.08	3.23	4.32	6.10	0.37
6-311+G(d)[a]	0.88	0.73	1.94	2.14	3.24	4.40	6.18	0.34
6-311G(2d)[b]	0.88	0.75	1.99	2.24	3.33	4.57	6.33	0.25
6-311+G(2d)[b]	0.89	0.74	1.99	2.30	3.34	4.64	6.39	0.23
6-311G(1d)[c]	0.88	0.73	1.99	2.23	3.34	4.58	6.34	0.25
6-311+G(1d)[c]	0.88	0.74	1.99	2.29	3.35	4.65	6.41	0.22
SECP(d)								
6-311G(d)[a]	0.88	0.70	1.92	2.05	3.20	4.27	6.08	0.39
6-311+G(d)[a]	0.88	0.72	1.92	2.10	3.21	4.34	6.15	0.36
6-311G(2d)[b]	0.88	0.73	1.97	2.23	3.31	4.54	6.32	0.27
6-311+G(2d)[b]	0.88	0.73	1.96	2.28	3.32	4.60	6.37	0.24
6-311G(1d)[c]	0.88	0.72	1.97	2.23	3.32	4.55	6.33	0.26
6-311+G(1d)[c]	0.88	0.73	1.96	2.27	3.33	4.61	6.38	0.24

[a] The exponents are all unchanged from those defined in the literature (see Table 14). [b] The exponents used in the d-functions for this basis set are the same ones used in the MG3 basis set (see Table 14). [c] The exponent used in the d-functions for this basis set are the same as the most diffuse d-exponent used in the MG3 basis set (see Table 14).

respectively, using PBE0/MEC/6-311+G(d*). Thus, the reoptimizatin of the d-function does not cancel errors in the Al potential, but rather it corrects deficiencies in the O basis set when it is reduced from a 2*df* polarization level (for which the d exponents are 2.584 and 0.646) to a single d function. Interestingly, the standard d exponents for the 6-311+G-

Table 14. Exponents for the *d*-Polarization Functions Used in the Non-Al Basis Sets

		d_1	d_2
Li	6-31G(d)[a]	0.20000	
	6-311G(d)[a]	0.20000	
	MG3[a]	0.10000	0.400
Be	6-31G(d)[a]	0.40000	
	6-311G(d)[a]	0.25500	
	MG3[a]	0.12800	0.510
B	6-31G(d)[a]	0.60000	
	6-311G(d)[a]	0.40100	
	MG3[a]	0.20100	0.802
N	6-31G(d)[a]	0.80000	
	6-311G(d)[a]	0.91300	
	MG3[a]	0.45700	1.826
C	6-31G(d)[a]	0.80000	
	6-311G(d)[a]	0.62600	
	MG3[a]	0.31300	1.252
O	6-31G(d)[a]	0.80000	
	6-311G(d)[a]	1.29200	
	6-311G(d*)[b]	0.63924	
	6-311+G(d*)[b]	0.63924	
	MG3[a]	0.64600	2.584
F	6-31G(d)[a]	0.80000	
	6-311G(d)[a]	1.75000	
	MG3[a]	0.87500	3.500

[a] Literature exponents. [b] Optimized in this work.

(2*df*) basis set for O, namely 2.584 and 0.646, are similar to the standard exponents for the cc-pVTZ[78] basis set for O, namely 2.314 and 0.645. Since the d* function has an exponent of 0.63924, we conclude that when one combines a polarized triple-ζ valence all-electron basis set on O with a core potential on Al, it is more important to polarize the diffuse part of the valence triple-ζ space than the tighter part.

We have used the AlX test set to test the MEC method with elements that were not included in the parametrization (specifically Li, Be, B, N, and F). Table 12 gives the dissociation energies and MUEs calculated with the PBE0 HDFT method and the MEC method for Al and 13 different basis sets for B, Be, C, F, Li, N, and O atoms. The errors are calculated by comparing to all-electron PBE0/MG3 dissociation energies. The 13 different basis sets used are 6-31G(d), 6-31+G(d), 6-311G(d), 6-311+G(d), 6-31G(2d), 6-31+G(2d), 6-311G(2d), 6-311+G(2d), 6-31G(1d), 6-31+G-(1d), 6-311G(1d), 6-311+G(1d), and 6-311+G(d*,p), where (d*) is the same as (d) except for O where the exponent is changed to 0.63924. The *s* and *p* functions used in the 6-31G-(2d) and 6-31G(1d), 6-31+G(2d) and 6-31+G(1d), 6-311G-(2d) and 6-311G(1d), and 6-311+G(2d) and 6-311+G(1d), are the same as those used in the 6-31G(d), 6-31+G(d), 6-311G(d), and 6-311+G(d) basis sets, respectively. The *d*-functions used in the 6-31G(2d), 6-31+G(2d), 6-311G-(2d), and 6-311+G(2d) are the same as the ones used in the MG3 basis set. The *d*-functions used in the 6-31G(1d), 6-31+G(1d), 6-311G(1d), and 6-311+G(1d) basis sets are the same as the most diffuse *d*-function used in the MG3 basis set basis set. The *d*-functions are presented in Table 14. Comparison of rows 11 and 12 to rows 3 and 4 in Table 12 shows that errors are significantly lower if one polarizes

the diffuse part of the valence triple-ζ space than the tighter part. The MUE if the 6-311+G(1d) basis set is used is 0.04 eV. Thus, we conclude that the MEC method can be used with all of the first-row elements if the 6-311+G(1d) basis set is used.

We did some further tests to see if the need for diffuse *d* functions is specific to the MEC method or is a more general feature of Al EC methods. We have calculated atomization energies for the molecules in the AlX training set using the PBE0 HDFT method and 6 different heteronuclear basis sets (6-311G(d), 6-311+G(d), 6-311G(2d), 6-311+G(2d), 6-311G-(1d), and 6-311+G(1d)) and 3 different EC methods for Al (CEP-121G(d), LanL2DZ(d), SECP(d)) and calculated the MUEs relative to PBE0/MG3 results. The results are in Table 13. It can be seen that the good performance of (1d) basis sets relative to (d) sets is not specific to the MEC method but is a much more general trend. For atoms bonding to Al, the errors are much lower if the diffuse part of valence space is polarized rather than using the usual (d) exponent.

Another test was to see how well the 6-311++G(d*,p) basis does for compounds that contain no Al atoms. We optimized the geometries and calculated the dissociation energies of BeO, CH_3OCH_3, CH_3OH, H_2CO, H_2O, and LiO within all-electron calculations with the PBE0/6-311+G(d,p), PBE0/6-311+G(d*,p), and PBE0/MG3. The MUEs, relative to PBE0/MG3, for the Be–O, C–O, Li–O, and O–H bond lengths with PBE0/6-311+G(d*,p) and PBE0/6-311+G(d,p) are 0.006 Å and 0.003 Å, respectively, and the MUEs for the atomization energies for PBE0/6-311+G(d*,p) and PBE0/6-311+G(d,p) are both 0.11 eV. The bond lengths for Be, C, H, Li, and O compounds are marginally less accurate if PBE0/6-311+G(d*,p) is used in place of the PBE0/6-311+G(d,p) basis set, whereas the errors for atomization energies are equal. However, Table 15 shows that the bond lengths and atomization energies are significantly more accurate if PBE0/6-311+G(d*,p) is used instead of PBE0/6-311+G(d,p) for Al containing compounds.

We also used the small molecule test set to test the accuracy of the MEC method and literature EC methods with functionals other than PBE0. The tests include not only hybrid functionals such as PBE0 (in particular, B3LYP[65,66] and mPW1PW91[27]) but also pure GGA functionals (BL-YP,[62,63] mPWPW91,[27] and PBE[64]) and hybrid meta functionals (B1B95[67] and BB1K[68]). The MUEs for atomization energies and bond lengths are given in Table 15. The errors are the unsigned differences between the values computed with the all-electron MG3 basis set and those computed with the EC method. For the MEC method, the average MUEs for atomization energies and bond lengths for all of the functionals in Table 15 are 0.04 eV and 0.009 Å, respectively. The most accurate literature EC method for all of the functionals is SECP(d), which has an average MUE of 0.16 eV for atomization energies and 0.013 Å for bond lengths. The results show that the MEC method is useful not only for the PBE0 density functional but also that it can be used advantageously with more general electronic structure methods.

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Table 15. Mean Unsigned Errors for a Variety of Density Functionals, Relative to the Results Obtained with the Same Functional with the MG3 Basis Set, in D_e (in eV) and r_e (in Å) for the Small-Molecule Test Set

	B1B95[a]	B3LYP	BB1K	BLYP	mPW1PW91[b]	mPWPW91[c]	PBE	PBE0[d]	av
				D_e					
CEP-121G(d)/6-311+G(d,p)[e]	0.22	0.18	0.24	0.15	0.23	0.20	0.20	0.21	0.20
LanL2DZ(d)/6-311+G(d,p)[e]	0.18	0.13	0.20	0.09	0.17	0.14	0.15	0.28	0.17
MEC/6-311+G(d,p)[e]	0.06	0.04	0.09	0.05	0.06	0.02	0.04	0.07	0.06
MEC/6-311+G(d*,p)[f]	0.03	0.05	0.06	0.07	0.04	0.01	0.02	0.04	0.04
SECP(d)/6-311+G(d,p)[e]	0.16	0.11	0.18	0.09	0.15	0.13	0.14	0.19	0.16
				r_e					
bond lengths									
CEP-121G(d)/6-311+G(d,p)[e]	0.042	0.026	0.043	0.022	0.034	0.031	0.033	0.034	0.033
LanL2DZ(d)/6-311+G(d,p)[e]	0.029	0.014	0.031	0.012	0.022	0.020	0.021	0.038	0.023
MEC/6-311+G(d,p)[e]	0.013	0.008	0.013	0.010	0.007	0.007	0.007	0.007	0.009
MEC/6-311+G(d*,p)[f]	0.011	0.010	0.012	0.011	0.006	0.007	0.007	0.007	0.009
SECP(d)/6-311+G(d,p)[e]	0.017	0.009	0.018	0.009	0.010	0.009	0.010	0.019	0.013

[a] Note that we used the correct B1B95 functional with 28% Hartree−Fock exchange, not the incorrect functional present in ref 46. [b] Also-called mPW1PW91 and mPW0. [c] Also-called mPWPW. [d] Also-called PBE1PBE. [e] The all-electron 6-311+G(d,p) basis set was used for H, C, and O. [f] The all-electron 6-311+G(d*,p) basis set was used for H, C, and O. The 6-311+G(d*,p) basis set is identical to the 6-311+G(d,p) basis set except for the exponent used in the O polarization functions, which was optimized in this work (see text).

Table 16. Mean Unsigned Errors in PBE0 Values of D_e (in eV) and r_e (in Å)

	quantity					
	D_e			r_e		
test set	homo	hetero	Al$_{13}$	homo	hetero	Al$_{13}$
average literature	0.62[a]	0.26[b]	1.00[c]	0.024[a]	0.030[b]	0.053[c]
best literature	0.22[d]	0.16[d]	0.44[e]	0.012[d]	0.007[d]	0.060[e]
MEC/6-31G(d,p)[f]	0.07	0.10	0.05	0.013	0.001	0.006
MEC/6-31+G(d,p)[f]	0.07	0.07	0.05	0.013	0.008	0.006
MEC/6-311+G(d,p)[f]	0.07	0.09	0.05	0.013	0.006	0.006
MEC/6-31G(2d$_O$,d$_C$,p)[g]	0.07	0.08	0.05	0.013	0.006	0.006
MEC/6-31+G(2d$_O$,d$_C$,p)[h]	0.07	0.06	0.05	0.013	0.006	0.006
MEC/6-311+G(2d$_O$,d$_C$,p)[i]	0.07	0.05	0.05	0.013	0.005	0.006
MEC/6-31G(d*,p)[g]	0.07	0.08	0.05	0.013	0.006	0.006
MEC/6-31+G(d*,p)[g]	0.07	0.06	0.05	0.013	0.006	0.006
MEC/6-311+G(d*,p)[g]	0.07	0.05	0.05	0.013	0.005	0.006

[a] Average of eight methods in Table 7. [b] Average of 72 methods in Tables 8 and 9. [c] Average of 5 methods in Table 6. [d] SECP(d) for Al with 6-31G(d,p) for H, C, O. [e] CEP-121G(d) for Al. [f] The basis after the / is used for H, C, and O; the basis used for Al is the polarized triple-ζ basis set of the MEC method. The H, C, and O basis set is unchanged. [g] The basis after the / is used for H, C, and O; the basis used for Al is the polarized triple-ζ basis set of the MEC method. Two sets of d-polarization functions are used for O, one set of d-polarization functions are used for C, and one set of p-polarization functions are used for H. The exponents for the O d-polarization functions are taken from the MG3 basis set, and the polarization functions for the C and H polarization functions are taken from the 6-31G(d,p) basis sets. [h] The basis after the / is used for H, C, and O; the basis used for Al is the polarized triple-ζ basis set of the MEC method. Two sets of d-polarization functions are used for O, one set of d-polarization functions are used for C, and one set of p-polarization functions are used for H. The exponents for the O d-polarization functions are taken from the MG3 basis set and the polarization functions for the C and H polarization functions are taken from the 6-31+G(d,p) basis sets. [i] The basis after the / is used for H, C, and O; the basis used for Al is the polarized triple-ζ basis set of the MEC method. Two sets of d-polarization functions are used for O, one set of d-polarization functions are used for C, and one set of p-polarization functions are used for H. The exponents for the O d-polarization functions are taken from the MG3 basis set and the polarization functions for the C and H polarization functions are taken from the 6-311+G(d,p) basis sets. [g] The basis after the / is used for H, C, and O; the basis used for Al is the polarized triple-ζ basis set of the MEC method. The 6-311+G(d*,p) basis set is identical to the 6-311+G(d,p) basis set except the for exponent used in the O polarization functions, which was optimized in this work (see text).

7. Concluding Remarks

A summary of the improvements obtained in this paper is given in Table 16. Table 16 shows that the best literature EC method is considerably better than the average literature method (factor 1.5−3 for bond energies and factor of 2−4 for bond lengths). However, our new effective core method for Al gives another factor of about 3 improvement in bond energies and a slight (on average) improvement in bond lengths.

8. Summary

We have developed a new effective core method for Al for use with electronic structure methods. The quality of a calculation with this EC method is comparable to a calculation with the high-quality, all-electron MG3 basis set. (Note: for elements in this paper, MG3[30−36] is identical to 6-311++G(3d2f,2df,2p)). With the new MEC method, the mean unsigned errors, where the error is defined as the difference between values computed with the MG3 basis set

and the EC method, for dissociation energies and bond lengths are 0.06 eV and 0.007 Å, respectively. This is a significant improvement over previous EC methods, where the best literature method has an MUE of 0.27 eV for dissociation energies and 0.026 Å for bond lengths.

The basis set and EC can be obtained online at comp.chem.umn.edu/basissets/basis.cgi.

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