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The Challenge of *ab Initio* Calculations in Small Neon Clusters

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Dedicated to Professor Pablo Villareal for his mastering on Molecular Physics and long standing friendship

Weakly bound neon dimer, trimer and tetramers are studied at HF and CCSD(T) levels using Dunning, ANO and SIGMA-s basis sets. Their ground-state binding energies are studied along with some structural properties. SIGMA-s basis sets have been developed explicitly for this issue but in a manner that can be readily applied to other atoms for the study of larger weakly bound systems. The difficulties for attaining accurate results on

these systems are assessed by the computation of total, atomization and correlation energies, as well as equilibrium distances, with several basis sets of increasing size, ranging from non-augmented to double-augmented versions. Extrapolations are proposed to predict stabilization energies and the results are compared with previously published data.

Introduction

Clusters of atoms or molecules with a wide variety of sizes have revealed essential in the study of the foundations of intermolecular interactions.^[1,2] In particular, weak dispersion or van der Waals (vdW) forces have deserved much interest that has been maintained along time. In the long-range, vdW interactions are dominated by dispersion, induction and the interaction between permanent multipoles when existing, and at short distances they include other contributions coming from overlap and exchange. Furthermore, the study of weak vdW interactions has always been one of the most challenging applications of *ab initio* computational techniques. To accurately reproduce the experimental data it is necessary to use high-quality basis sets (BS) and high-level electron correlation methods. Among these two sources of error, the BS truncation generally plays a more significant role in determining the accurate binding energies of rare gas complexes than the deficiency in correlation treatment.

Rare gas clusters have deserved much attention as a benchmark for the study of weak vdW interactions with

theoretical and experimental methods.^[3,4] Nevertheless, the calculation of accurate potential energy surfaces for rare gas interactions presents special challenges derived from the structure of these systems. Therefore, the clusters of rare gases are formed by atoms packed into highly symmetric geometries. They have low binding energies and vibrational frequencies, and exhibit extremely floppy behavior. These particular features explain why Ne clusters continue attracting much attention as weakly bound systems.^[5–7]

The natural starting point for studying clusters are dimers. In the particular case of rare gases, due to the fact that the electronic ground states of their atoms have a closed-shell structure and their interactions do not involve permanent multipole moments, numerous theoretical studies have been devoted to their dimers as a model of chemical systems in which binding comes from pure dispersion forces. For this reason too, reliable experimental results are available as well, which facilitate the analysis of the performance of the theoretical models used. The ground state energy curves of rare gas dimers calculated at the Hartree-Fock (HF) level should be repulsive at all distances, although spurious minima may appear when poor BS are employed. The attraction in these dimers is due to the dispersion energy and thus the correlation energy must be considered. To study weak interactions in a systematic way, although the use of bond functions improves the results,^[8] we will focus on atomic BS, in which case it has been claimed that BS augmented with polarization and diffuse functions can adequately reproduce the weak dispersion interactions.

Studies of the binding energy of two neon atoms date back to the 70s when the first experimental and theoretical works were carried out.^[9,10] After several measurements and fittings,^[11,12] a first reference^[13] was established, from the experimentally derived potential surface, with an equilibrium distance $R_e = 5.841$ bohr, and a dissociation energy $D_e = 133.8 \mu\text{E}_h$. Curves of Ne_2 have been previously

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An invited contribution to a Special Collection dedicated to Pablo Villareal Herrán on the occasion of his 70th birthday

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reported^[14,15] using several correlation consistent basis sets and single and double excitation coupled-cluster theory with non-iterative perturbational treatment of triple excitations, CCSD(T). These calculations predict values for the minimum in reasonable agreement with the experimental reference given above. The most accurate results reported so far were obtained with the aug-cc-pV5Z basis set supplemented with an additional (3s3p2d2f1g) set of bond functions^[8] ($R_e = 5.856$ bohr and $D_e = 130.3 \mu E_h$) giving results in good agreement with potentials based on experiments and larger basis sets without bond functions.^[16] The correlation-consistent basis sets doubly augmented with diffuse functions (d-aug-cc-pVnZ) were used to nearly saturate the dispersion energy of Ne dimers and to facilitate extrapolation to the complete basis set (CBS) limit.^[14,16] Accurate values ($D_e = 131.5 \mu E_h$ at $R_e = 5.859$ bohr) were also obtained from a new potential for Ne_2 ^[17] that added corrections for BS incompleteness, for core-core and core-valence correlation, and for relativistic effects.

Multicoefficient correlation method (MCCM)^[18] was used to determine accurate vdW interactions for Ne_2 obtaining $R_e = 5.874$ bohr and $D_e = 128.1 \mu E_h$, with significantly reduced computational effort and without the use of bond functions or counterpoise corrections. The main problem with the supermolecule calculations using conventional Gaussian basis sets for weakly interacting species is the difficulty of saturating the dispersion energy. Other approaches have used non-augmented quadruple-, quintuple- and sextuple-zeta BS without counterpoise corrections, and the CBS limit has been approached by a two-tier extrapolation, using a three-term expression for the correlation energy.^[19] To complete this landscape on the neon dimer studies, we must mention the currently accepted as best references to date. The best experimental reference ($R_e = 5.847$ bohr and $D_e = 134.0 \mu E_h$) comes from the analytical potential fitting of ab initio values by Wuest,^[20] used to derive the rovibrational spectra of the neon dimer, and in good agreement to Aziz and Slaman results.^[12] On the other hand, the best theoretical reference ($R_e = 5.838$ bohr and $D_e = 133.5 \mu E_h$) is due to Helmann,^[21] who computed a very accurate potential energy curve of Ne_2 using high-quality BS up to t-aug-cc-pV6Z, supplemented by binding functions, and ab initio methods up to CCSDT(Q), including extrapolation to the CBS limit. An indication of the continuing interest in neon dimer from a theoretical point of view is the fact that high-level calculations of potential energy curves are still being performed.^[22,23]

The theoretical studies of the neon trimer ground-state structure have been carried out using different approaches. The first calculations were performed using hyperspherical harmonics and quantum monte carlo methods.^[24,25] Later on, several authors^[26–29] have studied the structural properties and the energy of the ground state of Ne_3 , with a potential using Distributed Gaussian Functions, and have analyzed its rotation-vibration spectrum. These authors suggest a predominant equilateral structure with an expectation value for the atom-atom distance of 6.274 bohr. This value is slightly larger than the value of 5.860 bohr reported by other authors.^[30] Nevertheless, the marked floppiness of this structure is accompanied

by the presence of local minima associated to isosceles and scalene geometries with energies very close to that of the equilateral triangle.^[26] Many other theoretical studies have been carried out on this trimer^[18,31–33] applying different techniques and confirming the equilateral triangle as the equilibrium geometry for the ground state with a distance between atoms $R_e = 5.858$ bohr. A dissociation energy to dimer and atom $D_e(\text{Ne}_2 + \text{Ne}) = 259 \mu E_h$ was reported^[32] using CBS extrapolations at MP2 and CCSD(T) levels, and an atomization energy $D_e(3\text{Ne}) = 390.5 \mu E_h$ was determined,^[18] applying the MCCM approach.

Experimental analysis of the spectrum of kinetic energy release after the Coulomb explosion of Ne_3 ^[34] showed a contribution not only from strictly equilateral configurations but also from a great variety of triangular configurations. The interatomic distance was estimated to be ca 6.236 bohr. Coulomb explosion images were used for the direct mapping of the ground state wave function and were applied for the Ne and Ar dimers, trimers, and tetramers.^[34]

In the case of Ne_4 , theoretical results are lacking, even though the first theoretical works on a cluster of noble gases with four atoms date many years ago^[24,35] where regular tetrahedron and square geometries were compared. In a recent article, the vibrational spectra of Ne_4 were studied using quantum dynamics calculations.^[6] A regular tetrahedron with $R_e = 6.047$ bohr was reported as equilibrium geometry, in good agreement with experiment,^[34] as well as dissociation energies for two channels: $D_e(4\text{Ne}) = 676.4 \mu E_h$ and $D_e(\text{Ne} + \text{Ne}_3) = 338.2 \mu E_h$.

The purpose of this article is to compute equilibrium distances and dissociation energies of small neon clusters ($n = 2, 3$ and 4), as prototypes of vdW bound systems. As previously mentioned, due to the weakness of vdW interactions, meaningful results can be obtained only with high-quality atomic BS and high-level computational methods. In these clusters, given the impossibility of carrying out full-CI calculations as we already did in our study of Helium dimer,^[36] and taking into account the closed-shell character of their ground states, we consider CCSD(T) as the best suited method for this purpose. Moreover, we have developed specific high-quality BS for neon using our recently reported procedure.^[37] The results obtained with these new BS are compared with those obtained using Dunning^[38] and Atomic Natural Orbitals (ANO)^[39] BS. Finally, we discuss the suitability of the different BS for direct extrapolation of the dissociation energies and outline future prospects.

Results and Discussion

SIGMA-s Basis Sets for Ne Atom

We report a new family of SIGMA^[37] BS for Ne atom. The new BS is called SIGMA-s or σsXZ , where the symbol s indicates that each shell is saturated with primitive functions to get the best attainable result with the contractions composition in each set. The best attainable result is defined here in terms of the HF energy for the first two s and the first p contracted functions,

and in terms of CCSD(T) energy for the following ones. The details about the contraction and optimization procedures are the same already reported for Helium,^[36] and the composition of each BS is chosen with the same number of contractions as in the corresponding Dunning BS,^[38] with a number of primitive functions sufficient to achieve the desired goal of saturation. This composition is detailed in Table S1 of the supporting information (SI), where the names of the σ XZ BS have been chosen in parallel to those of Dunning BS of likewise composition. As Table S1 of SI shows, σ XZ BS have been constructed from double-zeta (X=D) to sextuple-zeta (X=6) in standard, augmented and double augmented versions, with a number of contractions ranging from 14 in the smallest BS (standard DZ) to 238 in the highest BS (double augmented 6Z). The σ XZ BS resemble the ANO^[39] BS of similar composition (no double augmented is available in ANO).

To analyze the performance of the σ XZ BS, we start by comparing the results on Ne atom with those obtained with Dunning and ANO BS at HF and CCSD(T) levels, as well as the correlation energy defined as the difference between both energies. The results attained with the three families of BS are collected in Table S2 of SI. As this Table shows, for a given size, the energies obtained with σ XZ lie below those obtained with Dunning and ANO BS both at HF and CCSD(T) levels, and this is accompanied by a higher recovery of correlation energy with the σ XZ BS. It is specially noticeable that HF energy computed

with the σ XZ BS approaches the CBS limit ($-128.547098108 E_h$ ^[40]) even with the smaller BS, with an error below $6\mu E_h$ in all cases. This fact illustrates the meaning of the term *saturation* employed above. The correlation energies obtained with the eighteen Dunning BS and the corresponding σ XZ BS are displayed in Figure 1, which shows the good convergence towards the exact value ($-322.0 mE_h$)^[19] in all cases. To complement this analysis, the correlation energy is compared in Figure 2 for the 5Z members of the three BS families. This figure shows the better performance of σ XZ BS, more noticeable when compared with Dunning BS. In this case even the non-augmented σ XZ BS retrieve more correlation energy than Dunning d-aug-cc-pV5Z. This result is specially remarkable if one considers that the HF energy with all σ XZ BS is very close to the CBS limit.

Ne Dimer

To test the performance of σ XZ BS in polyatomic systems, we have considered first the Ne dimer (Ne_2). Table 1 contains the values of equilibrium distance R_e in bohr, the dissociation energy D_e in μE_h , and the total energy at R_e in E_h , computed for this system at CCSD(T) level. Again, the total energy is lower with σ XZ BS than in the BS of same size of other two families, the lowest value being attained with da σ 6Z BS.

The equilibrium distance of the dimer presents a similar behavior for ANO and σ XZ BS converging towards the reference value of 5.838 bohr,^[21] as the size of the BS increases from X=2 to 6 and when introducing more polarization functions up to double augmented BS, always starting from higher values for the small bases. In Figure 3, the results obtained with Dunning and σ XZ BS are displayed. As it can be seen, the augmented Dunning BS always give very good values of R_e , even better than most values obtained with double augmented BS. This behavior looks like that previously reported for He dimer.^[36] Nevertheless, it is interesting that, although the R_e values obtained with Dunning BS overcome those obtained with ANO and σ XZ BS, the regular convergence in the latter, which yield higher values (farther from the exact result) the smaller is the BS of each family, contrasts with the more

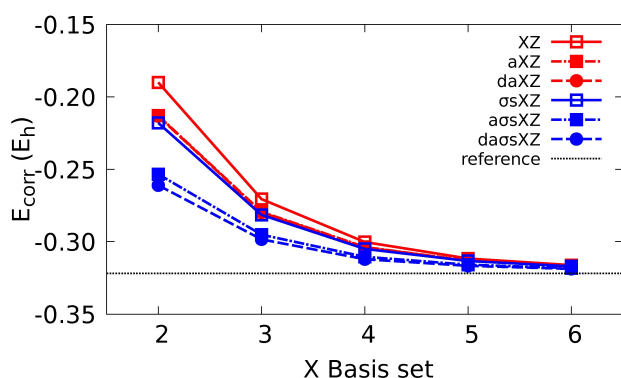


Figure 1. Correlation energy vs BS size for Ne atom.

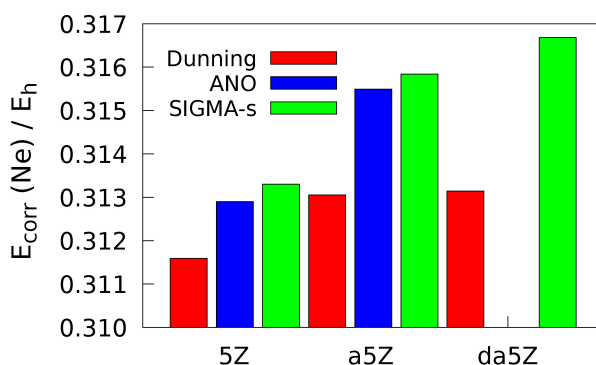


Figure 2. Correlation energy of Ne for Quintuple Zeta BS.

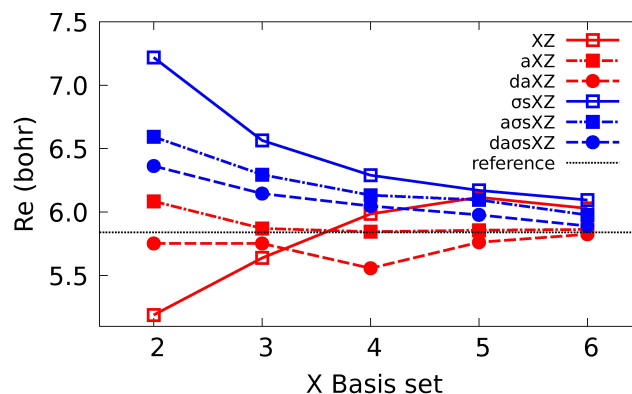


Figure 3. Equilibrium distance vs BS size for Ne dimer.

Table 1. Equilibrium distance (bohr), dissociation energy (μE_h) and minimum energy (E_h) for Ne dimer at CCSD(T) level.

	R_e	D_e	E_{min}
DZ	5.189	161.6	−257.3578341
TZ	5.638	163.3	−257.6050708
QZ	5.985	118.7	−257.6874981
5Z	6.117	75.5	−257.7167925
6Z	6.029	86.3	−257.7266108
anoDZ	6.980	10.2	−257.5265514
anoTZ	6.420	34.9	−257.6552508
anoQZ	6.209	57.1	−257.7030185
ano5Z	6.090	74.5	−257.7198726
σ sDZ	7.219	5.6	−257.5302823
σ sTZ	6.565	25.5	−257.6571964
σ sQZ	6.290	46.9	−257.7042365
σ s5Z	6.137	65.6	−257.7208486
σ s6Z	6.059	77.3	−257.7282163
aDZ	6.085	179.6	−257.4187689
aTZ	5.871	172.1	−257.6254678
aQZ	5.845	151.7	−257.6950708
a5Z	5.857	137.5	−257.7198115
a6Z	5.863	130.4	−257.7282024
aanoDZ	6.468	32.4	−257.6000763
aanoTZ	6.217	56.5	−257.6836312
aanoQZ	6.093	74.4	−257.7142225
aano5Z	6.034	86.3	−257.7251276
a σ sDZ	6.593	24.7	−257.6010227
a σ sTZ	6.295	47.0	−257.6844913
a σ sQZ	6.133	66.0	−257.7150335
a σ s5Z	6.053	78.2	−257.7259499
a σ s6Z	5.968	94.8	−257.7307804
daDZ	5.752	403.3	−257.4197844
daTZ	5.752	308.0	−257.6266686
daQZ	5.557	266.9	−257.6956502
da5Z	5.762	177.4	−257.7200430
da6Z	5.825	148.4	−257.7283651
da σ sDZ	6.363	42.9	−257.6163844
da σ sTZ	6.146	65.8	−257.6910173
da σ sQZ	6.048	79.0	−257.7183740
da σ s5Z	5.959	97.3	−257.7276419
da σ s6Z	5.890	112.9	−257.7311891

irregular convergence in Dunning BS. This fact was already pointed out^[16] and will be discussed later, where it is shown that Dunning's bases clearly need a BSSE correction to be able to extrapolate to the CBS limit.

We have also studied the dissociation energy, whose reference value has been well established, in both theoretical and experimental studies, as $133.5 \mu E_h$.^[21] For σ sXZ and ANO BS, a parallel behavior is observed: a slow convergence starting from very small values for DZ BS, and an improvement when

passing from standard to augmented or double augmented BS. The behavior of Dunning BS is very different. They start with higher values (very high for the daDZ) which decrease as the BS size increases, with the exception of cc-pV6Z. These results are also illustrated in Figure 4, where the dissociation energy has been plotted for the σ sXZ and Dunning BS. The three kinds σ sXZ BS (standard, augmented and double augmented) show a uniform convergence towards the reference value, with double augmented BS yielding the best results. However, for Dunning BS this convergence is irregular, as observed in Figure 4.

It has been reported^[8] that weak bonds cannot be well described with atom-centered BS, and the introduction of bond functions has been proposed as a possible solution to this problem. In standard and simply augmented BS, Dunning BS give highly oscillating values of D_e that hinder extrapolation to the CBS limit as noted above, and it is necessary to carry out counterpoise corrections (CP) to overcome this difficulty.^[16]

To complete the analysis on Ne dimer, the HF, CCSD(T) and correlation energies have been collected in Table 2, at the equilibrium distance of 5.858 bohr.^[21] The first thing to notice in Table 2 is that all σ sXZ BS give the same HF energy, namely $-257.094095 E_h$, as a consequence of the saturation of the BS. Furthermore, the HF energy obtained with the small σ sDZ BS is lower than that obtained with the largest available ANO (aANO5Z) and Dunning (d-aug-cc-pV6Z) BS, proving the efficiency of σ sXZ BS for single-determinant calculations. Moreover, as in Ne atom, the lowest energy corresponds to calculations at the CCSD(T) level using the da σ s6Z BS. Regarding correlation energy, the third column of Table 2 shows that, like in Ne atom, the correlation retrieved by σ sXZ BS is always higher than that retrieved by ANO and Dunning BS of the same size. This is also illustrated in Figure 5, where the correlation energy obtained with 5Z BS is displayed. Like in Ne atom, the correlation energy retrieved by non-augmented σ sXZ is higher than that obtained with Dunning BS, both non-augmented and augmented, and despite that the HF energy is lower in σ sXZ also in this case. The poor performance of Dunning 5Z BS, when passing from simply to double augmented BS, is also noticeable both for Ne atom (see Figure 2) and dimer.

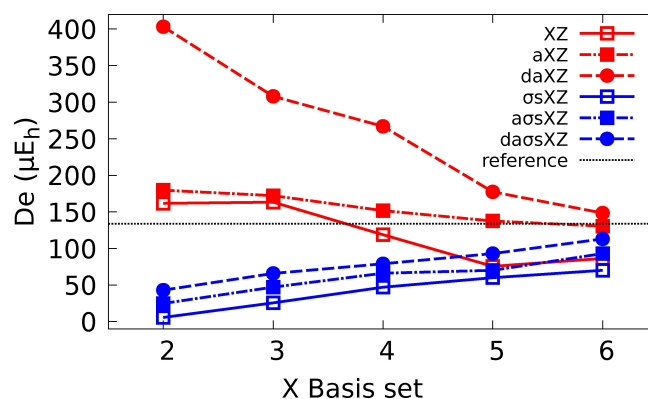
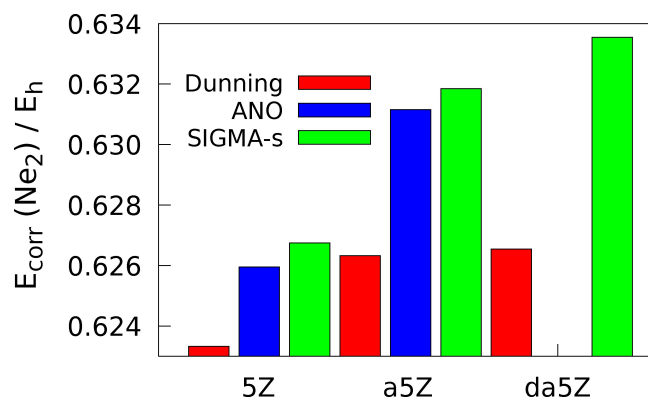
**Figure 4.** Dissociation energy vs BS size for Ne dimer.

Table 2. Ne₂ energies: HF, CCSD(T) and correlation in E_h at R_e = 5.858 bohr (3.1 Å)

	E _{HF}	E _{CCSD(T)}	E _{corr}
DZ	−256.9775861	−257.3577339	−0.38014781
TZ	−257.0637764	−257.6050570	−0.54128057
QZ	−257.0869148	−257.6874952	−0.60058039
5Z	−257.0934562	−257.7167850	−0.62332879
6Z	−257.0940326	−257.7266073	−0.63257476
anoDZ	−257.0917334	−257.5264939	−0.43476046
anoTZ	−257.0934510	−257.6552258	−0.56177485
anoQZ	−257.0937734	−257.7030063	−0.60923291
ano5Z	−257.0939159	−257.7198663	−0.62595035
σsDZ	−257.0940949	−257.5302115	−0.43611666
σsTZ	−257.0940949	−257.6571628	−0.56306796
σsQZ	−257.0940948	−257.7042154	−0.61012067
σs5Z	−257.0940949	−257.7208403	−0.62674538
σs6Z	−257.0940950	−257.7282116	−0.63411662
aDZ	−256.9926403	−257.4187609	−0.42612059
aTZ	−257.0664997	−257.6254678	−0.55896807
aQZ	−257.0874394	−257.6950708	−0.60763143
a5Z	−257.0934858	−257.7198115	−0.62632575
a6Z	−257.0940347	−257.7282025	−0.63416773
aanoDZ	−257.0934509	−257.6000472	−0.50659629
aanoTZ	−257.0937734	−257.6836182	−0.58984480
aanoQZ	−257.0939159	−257.7142161	−0.62030012
aano5Z	−257.0939659	−257.7251238	−0.63115790
aσsDZ	−257.0940949	−257.6009866	−0.50689173
aσsTZ	−257.0940951	−257.6844770	−0.59038192
aσsQZ	−257.0940949	−257.7150401	−0.62094514
aσs5Z	−257.0940950	−257.7259405	−0.63184556
aσs6Z	−257.0940949	−257.7307788	−0.63668391
daDZ	−256.9927901	−257.4197808	−0.42699062
daTZ	−257.0665743	−257.6266663	−0.56009201
daQZ	−257.0874961	−257.6956290	−0.60813298
da5Z	−257.0934954	−257.7200414	−0.62654600
da6Z	−257.0940362	−257.7283649	−0.63432870
daσsDZ	−257.0940951	−257.6163619	−0.52226681
daσsTZ	−257.0940952	−257.6910129	−0.59691771
daσsQZ	−257.0940950	−257.7183942	−0.62429924
daσs5Z	−257.0940951	−257.7276406	−0.63354552
daσs6Z	−257.0940950	−257.7317863	−0.63769133

Ne Trimer and Tetramer

The minimum energy of the three-atom cluster of Ne has been determined both theoretically and experimentally as an equilateral triangle with a reference distance of 5.858 bohr between Ne atoms.^[18,32] In Table 3 the equilibrium Ne–Ne distance for the equilateral triangle structure, obtained with σ sXZ, ANO and Dunning BS, is reported together with the energy at the minimum, the atomization energy and the energy correspond-

**Figure 5.** Correlation energy of Ne₂ for Quintuple Zeta BS.

ing to the dissociation into the dimer plus an atom. Regarding equilibrium distances, the behavior is similar to that found in Ne₂: ANO and σ sXZ BS yield values which are higher than those of the corresponding Dunning BS and decrease as the BS size increases. For Dunning BS, the dependence on BS size is less regular, with very small variations in the augmented BS. Globally, it can be observed that Dunning BS perform better in the calculation of R_e, with a very good performance of the augmented version. In σ sXZ and ANO, although the results tend to the reference value as the BS size increases, the convergence is slow and only the da σ 6Z gives a value comparable in quality to those of Dunning augmented BS.

For atomization energy, a reference value ca. 390 μ E_h has been reported,^[18] corresponding to binding energies computed with the aug-cc-pV6Z BS combined with extrapolated correlation contributions. As shown in the third column of Table 3, the atomization energies calculated with Dunning BS decrease as the BS size increases with some zigzag exceptions. For σ sXZ and ANO BS, the atomization energy values monotonically increase with the BS size.

To facilitate the comparison among BS, the atomization energy computed with QZ BS is plotted in Figure 6 (red bars). As it can be seen, for the three families of BS the atomization energy increases when passing from non-augmented to augmented and double augmented. The values obtained with

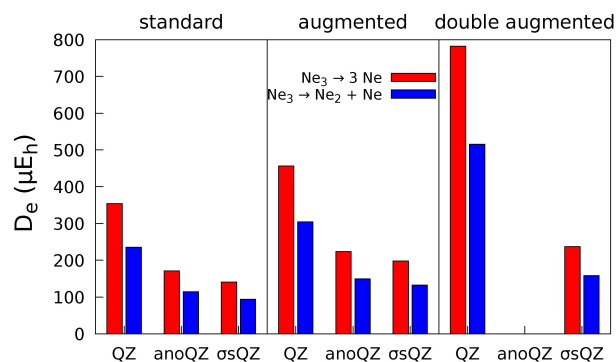
**Figure 6.** Dissociation energies vs Quadruple Zeta BS for different channels of Ne trimer.

Table 3. Equilibrium distance (bohr), dissociation energy (μE_h) and minimum energy (E_h) for Ne trimer at CCSD(T) level.

	R_e	$D_e(3\text{ Ne})$	$D_e(\text{Ne} + \text{Ne}_2)$	E_{\min}
DZ	5.193	481.4	319.7	−386.0369901
TZ	5.643	487.3	323.9	−386.4078485
QZ	5.989	354.3	235.6	−386.5314234
5Z	6.112	226.9	151.3	−386.5753024
6Z	6.022	260.3	174.0	−386.5900471
anoDZ	6.980	30.7	20.5	−386.2898425
anoTZ	6.417	104.7	69.7	−386.4829284
anoQZ	6.204	171.2	114.1	−386.5546133
ano5Z	6.083	224.1	149.6	−386.5799212
σ sDZ	7.275	16.8	11.2	−386.2954318
σ sTZ	6.564	76.4	51.0	−386.4858328
σ sQZ	6.290	140.4	93.9	−386.5564186
σ s5Z	6.135	197.1	131.5	−386.5813717
σ s6Z	6.055	232.4	155.1	−386.5924409
aDZ	6.085	513.2	333.6	−386.1283971
aTZ	5.856	516.0	343.9	−386.4384596
aQZ	5.844	456.3	304.6	−386.5428349
a5Z	5.856	411.6	274.2	−386.5799227
a6Z	5.863	390.5	260.1	−386.5924985
aanoDZ	6.469	97.2	64.7	−386.4001629
aanoTZ	6.216	169.6	113.0	−386.5255315
aanoQZ	6.086	223.8	149.3	−386.5714459
aano5Z	6.026	259.3	173.1	−386.5878214
a σ sDZ	6.595	73.9	49.3	−386.4015710
a σ sTZ	6.293	141.0	94.1	−386.5268075
a σ sQZ	6.130	198.2	132.2	−386.5726495
a σ s5Z	6.049	235.1	156.9	−386.5890352
a σ s6Z	5.964	285.1	190.3	−386.5963135
daDZ	5.744	1209.7	806.4	−386.1302815
daTZ	5.738	936.3	628.3	−386.4404772
daQZ	5.579	782.2	515.3	−386.5438572
da5Z	5.773	516.9	339.5	−386.5803153
da6Z	5.828	438.6	290.2	−386.5927636
da σ sDZ	6.362	128.7	85.8	−386.4246410
da σ sTZ	6.142	197.7	131.9	−386.5366250
da σ sQZ	6.045	237.3	158.4	−386.5776798
da σ s5Z	5.955	292.5	195.2	−386.5916094
da σ s6Z	5.876	336.5	224.7	−386.5978484

SIGMA and ANO BS are significantly lower. The dissociation energy into Ne_2 plus an atom (ca. $259 \mu E_h$ ^[32]) is also analyzed in Table 3 and Figure 6 (blue bars). The behavior of the three families of BS is similar to that observed in the atomization energies, with similar trends with the BS size and type.

In Table 4, several results for the Ne_4 system are given for the regular tetrahedron geometry, which has been reported, both theoretically and experimentally, as having the minimum energy at $R_e = 5.974$ bohr.^[6] In particular, the equilibrium

distance and its energy are displayed with the atomization energy and the dissociation energies in three different channels. Furthermore, these energies have been plotted in Figure 7, for the QZ BS. As it can be observed in both Table 4 and Figure 7, the performance of the three families of BS is similar to that mentioned in Ne_3 and all comments made in that system also apply to Ne_4 . It is remarkable that only the da σ 6Z BS yields values (amazingly) close to the previous reported^[6] for the atomization energy, $D_e(4\text{Ne}) = 674.9 \mu E_h$, and the dissociation into a trimer plus an atom, $D_e(\text{Ne} + \text{Ne}_3) = 338.5 \mu E_h$. The results obtained with the remaining BS are quite far away from these.

Effect of the Basis Set Superposition Error and Extrapolations to Complete Basis Set

The effect of the overlap between the atomic BS functions in molecular calculations is known as the Basis Set Superposition Error (BSSE).^[41] This error is caused by the unbalanced performance of the BS in molecular calculations where each atom borrows functions from the other nearby atoms and generally causes an overestimation of the interaction energy. The most used approach to correct BSSE is the CP correction.^[42] The accuracy of the simple CP correction as a measure of BSSE has been the subject of some debate, and several authors^[43–45] have proposed an alternative consisting of extrapolations to the CBS limit from results attained with increasing BS size. In this work, we have applied the generalized Boys and Bernardi equation for several bodies,^[42] dealing with clusters atomization and excluding other fragmentation processes.

In particular, the effect of CP correction in the energy, geometry and atomization energy of Ne aggregates (dimer, trimer and tetramer) is discussed in this section for the three non-augmented BS. The results attained using the CP correction are collected in Table 5 and can be compared with the uncorrected results reported in Tables 1 to 3 for Ne_2 , Ne_3 and Ne_4 respectively. As it can be seen, the changes in the electronic energy at the equilibrium geometry are very small in ANO and SIGMA-s and bigger in the smaller members of Dunning BS. Nevertheless, the most significant differences occur in the equilibrium geometry. In this regard, it is noticeable that the CP

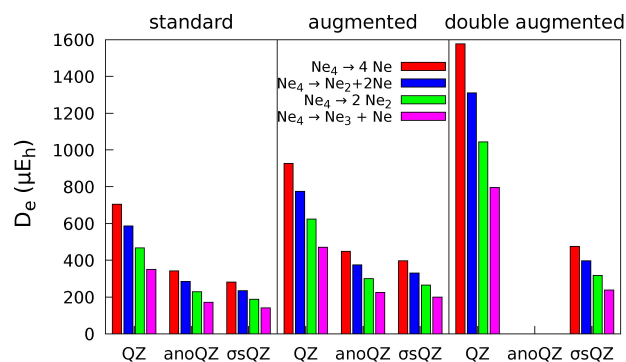
**Figure 7.** Dissociation energies vs Quadruple Zeta BS for different channels of Ne tetramer.

Table 4. Equilibrium distance (bohr), dissociation energy (μE_h) and minimum energy (E_h) for Ne tetramer at CCSD(T) level.

	R_e	$D_e(4 \text{ Ne})$	$D_e(2 \text{ Ne} + \text{Ne}_2)$	$D_e(2 \text{ Ne}_2)$	$D_e(\text{Ne} + \text{Ne}_3)$	E_{\min}
DZ	5.198	955.9	794.2	632.6	474.5	−514.7163009
TZ	5.649	969.2	805.9	642.5	481.9	−515.2107842
QZ	5.993	705.2	586.5	467.8	350.9	−515.3754640
5Z	6.107	454.4	378.9	303.4	227.6	−515.4338885
6Z	6.016	523.4	437.1	350.8	263.0	−515.4535724
anoDZ	6.981	61.4	51.2	40.9	30.6	−515.0531438
anoTZ	6.418	209.1	174.1	139.2	104.4	−515.3106408
anoQZ	6.202	342.3	285.3	228.2	171.2	−515.4062652
ano5Z	6.078	449.5	375.0	300.5	225.3	−515.4400456
osDZ	7.280	33.7	28.0	22.4	16.8	−515.0605870
osTZ	6.565	153.0	127.4	101.8	76.4	−515.3144946
osQZ	6.288	280.8	234.2	187.3	140.4	−515.4086517
os5Z	6.131	394.8	329.2	263.5	197.7	−515.4419608
os6Z	6.051	465.9	388.6	311.3	233.5	−515.4567439
aDZ	6.073	994.8	815.2	635.6	481.5	−514.8381734
aTZ	5.833	1047.0	874.9	702.7	530.9	−515.2516384
aQZ	5.838	927.0	775.3	623.6	470.7	−515.3907652
a5Z	5.851	826.0	688.6	551.1	414.4	−515.4401742
a6Z	5.861	782.4	652.0	521.6	291.9	−515.4569264
aanoDZ	6.470	194.1	161.6	129.1	96.9	−515.2002817
aanoTZ	6.213	339.2	282.6	226.0	169.6	−515.3674885
aanoQZ	6.081	448.7	374.3	299.8	224.9	−515.4287449
aano5Z	6.021	519.9	433.7	347.5	260.6	−515.4506027
aosDZ	6.594	147.7	123.1	98.5	73.9	−515.2021439
aosTZ	6.292	282.1	235.1	188.1	141.1	−515.3691707
aosQZ	6.126	396.8	330.8	264.8	198.6	−515.4303319
aos5Z	6.044	471.2	393.0	314.8	236.1	−515.4522047
aos6Z	5.957	571.6	476.8	382.0	286.5	−515.4619428
daDZ	5.725	2504.6	2101.3	1698.0	1294.7	−514.8412669
daTZ	5.698	1983.5	1675.4	1367.4	1047.1	−515.2547047
daQZ	5.600	1577.6	1310.8	1044.0	795.5	−515.3923444
da5Z	5.781	1016.4	839.1	661.7	499.6	−515.4407477
da6Z	5.831	869.4	721.0	572.5	430.8	−515.4573028
daosDZ	6.361	257.4	214.5	171.6	128.6	−515.2329404
daosTZ	6.139	395.9	330.1	264.3	198.2	−515.3822989
daosQZ	6.041	475.5	396.5	317.6	238.1	−515.4370655
daos5Z	5.953	586.1	488.8	391.5	293.6	−515.4556753
daos6Z	5.873	674.9	563.2	451.4	338.5	−515.4640241

correction to R_e in ANO and SIGMA is very moderate, ranging from the 2–3% in the smaller BS to less than 1% in the larger ones, whereas the effect in Dunning BS is much higher in the smaller members, ranging from ca. 30% in the DZ to 8% in the QZ. For the dissociation energy, the difference in the effect of the CP correction in the three families of BS is even more remarkable. Thus, the change in the value of D_e in the ANO BS ranges from ca. 20% for the smaller member to ca. 10% for the larger one, whereas for SIGMA-s BS these differences range from 10% to 7% and, finally, in Dunning BS the differences

range from 96% to 10% (always the percentages are referred to the values without BSSE correction). It is noticeable also that in all cases, CP correction increases the value of R_e and decreases that of D_e , with respect to the uncorrected results, and the corrected values are far from the reference value of ca. $133 \mu E_h$.^[21]

Extrapolation to the CBS limit of the dissociation energies is a technique used by many authors^[46] in an attempt to improve the results attained with the currently available BS. Several procedures have been proposed and a two-tier scheme^[47–50] is

Table 5. CP corrected equilibrium distances (bohr), atomization energies (μE_h) and minimum energies (E_{\min}) for Ne_2 , Ne_3 and Ne_4 at CCSD(T).

Ne_2			
	R_e	D_e	E_{\min}
DZ	6.682	6.6	−257.3576834
TZ	6.754	18.1	−257.6049529
QZ	6.453	34.7	−257.6874755
5Z	6.207	58.3	−257.7167919
6Z	6.066	78.5	−257.7266107
anoDZ	7.171	8.4	−257.5265511
anoTZ	6.596	28.0	−257.6552498
anoQZ	6.305	49.2	−257.7030179
ano5Z	6.141	67.6	−257.7198723
σ sDZ	7.409	5.0	−257.5302822
σ sTZ	6.714	21.8	−257.6571958
σ sQZ	6.389	41.3	−257.7042290
σ s5Z	6.199	59.5	−257.7084710
σ s6Z	6.097	71.7	−257.7282161
Ne_3			
	R_e	D_e	E_{\min}
DZ	6.683	19.7	−386.0365415
TZ	6.757	54.1	−386.4074967
QZ	6.455	103.6	−386.5313563
5Z	6.199	176.0	−386.5753007
6Z	6.058	237.7	−386.5900467
anoDZ	7.171	25.3	−386.2898416
anoTZ	6.594	84.2	−386.4829255
anoQZ	6.300	148.2	−386.5546117
ano5Z	6.133	203.8	−386.5799206
σ sDZ	7.409	15.0	−386.2954316
σ sTZ	6.713	65.4	−386.4858313
σ sQZ	6.387	124.0	−386.5564127
σ s5Z	6.192	180.0	−386.5813709
σ s6Z	6.091	216.1	−386.5924405
Ne_4			
	R_e	D_e	E_{\min}
DZ	6.683	39.4	−514.7154104
TZ	6.760	108.0	−515.2100845
QZ	6.459	206.2	−515.3753307
5Z	6.191	354.3	−515.4338853
6Z	6.051	479.3	−515.4535717
anoDZ	7.170	50.6	−515.0531419
anoTZ	6.591	168.5	−515.3106350
anoQZ	6.294	297.2	−515.4062623
ano5Z	6.126	409.5	−515.4400445
σ sDZ	7.409	30.1	−515.0605865
σ sTZ	6.712	130.9	−515.3144916
σ sQZ	6.383	248.3	−515.4086426
σ s5Z	6.187	360.9	−515.4419595
σ s6Z	6.085	433.9	−515.4567432

well suited^[19] for the Ne_2 system. In this procedure, the HF energy, for a given geometry, is fitted to:

$$E_{\text{RHF}}(X) = a + b e^{-cX} \quad (1)$$

where X stands for the higher angular quantum number in the BS, and the fitting parameter a yields the corresponding CBS limit. The correlation energy for the same geometry is fitted to:

$$E_{\text{corr}}(X) = A + B X^{-3} + C X^{-5} \quad (2)$$

Here we have carried out three different types of extrapolation to illustrate the performance of Dunning, ANO and SIGMA-s BS in this respect: a two-tier extrapolation scheme as mentioned above (CBS1), an extrapolation (CBS2) of the full energies (HF + correlation) to an expression like that of Eq (2), and a direct extrapolation (CBS3) of the dissociation energies to the functional form:

$$D_e(X) = A + B X^{-1} + C X^{-5} \quad (3)$$

The results attained with non-augmented BS for Ne_2 , Ne_3 and Ne_4 are summarized in Table 6, and the corresponding standard errors are reported in Table S3 of the SI.

The first point to notice is that direct extrapolation (CBS3) is not possible for Dunning BS, because of the dispersion of the D_e values that prevents any meaningful fit to a suitable functional form with the correct behavior in the CBS limit. On the other hand, this extrapolation is possible with both ANO and with SIGMA-s results and the values attained in Ne_2 are in good agreement with those reported by other authors. Furthermore, their standard deviations are sufficiently small when compared with the values of the corresponding D_e to assert the validity of the CBS estimations to one or two significant figures, despite the fact that the number of freedom degrees is very reduced (one for ANO and two for SIGMA-s BS).

Regarding CBS1 and CBS2, it can be noticed that their results are very different in Dunning BS, where CBS1 tends to yield values closer to the reference in Ne_2 , and to the CBS3 values of ANO and SIGMA-s in all cases. On the other hand, in ANO and SIGMA-s both extrapolations yield very similar results, which lie rather far from the CBS3. Here it is interesting to notice too that, although the fitting of the energies performs very well for the two-tier procedure, the standard error of the extrapolated energies (see Table S3 in the SI) is one order of magnitude greater than the value of the D_e itself (ca. $10^3 \mu E_h$ for the total CCSD(T) and correlation energies). Therefore, the good results obtained with the CBS1 in Dunning BS (also attained by Bytautas and Ruedenberg for Ne_2 with the same method^[19]) may be attributed more to a fortunate cancellation of errors than to the accuracy of the process. In direct extrapolation, an error cancellation also occurs, now in the subtraction of total energies within each BS, which is more likely than the cancellation between total energies extrapolated from several BS. Therefore, in our opinion, direct extrapolation, when feasible, seems to be the appropriate procedure to estimate dissociation energies, and ANO and SIGMA-s BS are suitable for

Table 6. Extrapolated HF/total/correlation energies (E_h) and extrapolated dissociation energies (μE_h) at CCSD(T).

		Dunning			ANO			SIGMA-s		
		CBS1 ^a	CBS2 ^b	CBS3 ^c	CBS1 ^a	CBS2 ^b	CBS3 ^c	CBS1 ^a	CBS2 ^b	CBS3 ^c
Ne ₂	$E_{\text{HF}}/E_{\text{tot}}$	−257.100578	−257.749136	–	−257.094088	−257.741576	–	−257.094095	−257.741032	–
	E_{corr}	−0.649014	–	–	−0.647560	–	–	−0.646937	–	–
	D_e	125	59	–	87	87	139	84	85	135
Ne ₃	$E_{\text{HF}}/E_{\text{tot}}$	−385.650782	−386.623793	–	−385.641004	−386.612496	–	−385.641007	−386.611673	–
	E_{corr}	−0.973795	–	–	−0.971601	–	–	−0.970667	–	–
	$D_e(3\text{Ne})$	376	177	–	264	263	419	252	252	405
	$D_e(\text{Ne} + \text{Ne}_2)$	251	119	–	177	175	280	169	167	270
Ne ₄	$E_{\text{HF}}/E_{\text{tot}}$	−514.200929	−515.498513	–	−514.187835	−515.483504	–	−514.187831	−515.482400	–
	E_{corr}	−1.298758	–	–	−1.295818	–	–	−1.294571	–	–
	$D_e(4\text{Ne})$	753	358	–	532	527	841	507	505	811
	$D_e(2\text{Ne} + \text{Ne}_2)$	628	300	–	445	440	703	423	420	677
	$D_e(2\text{Ne}_2)$	503	241	–	358	352	564	340	336	543
	$D_e(\text{Ne} + \text{Ne}_3)$	377	181	–	268	264	422	255	253	407

^a Computed from the extrapolated HF and CCSD(T) correlation energies of the atom and clusters. ^b Computed from the extrapolated total CCSD(T) energies of the atom and clusters. ^c Direct extrapolation of the dissociation energies.

this purpose. Finally, it can be mentioned that direct extrapolation is also possible with Dunning BS if the CP is applied, as shown in Table S4 of the SI, which also shows that CP scarcely affects the direct extrapolation in ANO and SIGMA-s BS.

Conclusions

Theoretical studies of neon clusters require a high computational level combined with high-quality BS. In this work it has been proved that the reported SIGMA-s BS perform as the best available BS of similar size, yielding absolute energies lower than those attained with Dunning correlation consistent and ANO BS of similar size, both at HF and CCSD(T) levels. Furthermore, the CCSD(T) has proven to be appropriate to achieve meaningful results in these weakly bounded systems.

It is noticeable that the dissociation energies computed with the best available BS are quite far from the more reliable estimations reported so far. To overcome this difficulty, dissociation energies of the Ne dimer and trimer have been computed by several authors using extrapolations from absolute energies, with a satisfactory concordance in the results. It is worth mentioning that this occurs despite the fact that the standard error in the best electron energy fittings ($\sim 10^3 \mu E_h$) is one order of magnitude larger than the value of the dissociation energy itself ($\sim 10^2 \mu E_h$). Therefore, this consistency in the results seems to be caused by a lucky cancellation of errors when subtracting extrapolated absolute energies.

Unlike Dunning BS, the SIGMA-s and ANO BS are suitable for direct extrapolation of dissociation energies. These extrapolations with SIGMA-s and ANO BS, whose standard errors are at least one order of magnitude lower than the values of the

dissociation energies themselves, yield results in good agreement with those reported using the extrapolation from absolute energies, thus reinforcing their mutual reliability.

CP corrections permit direct extrapolations from Dunning BS with results comparable to those reported with SIGMA-s and ANO BS, although with a higher standard error. On the other hand, CP correction scarcely affects the results attained with SIGMA-s and ANO BS.

Experimental Section

Computational methods. Calculations were carried out using Molpro^[51] suite on a system with an Intel(R) Xeon(R) Gold 6252 CPU @ 2.10GHz processor. Dunning cc-pVZX and ANO BS were taken from Molpro internal BS. SIGMA-s BS were supplied as external BS. Extrapolations were carried out using Mathematica 9.1.^[52]

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Neon clusters • SIGMA-s basis set • Extrapolation to complete basis set • Dissociation energies

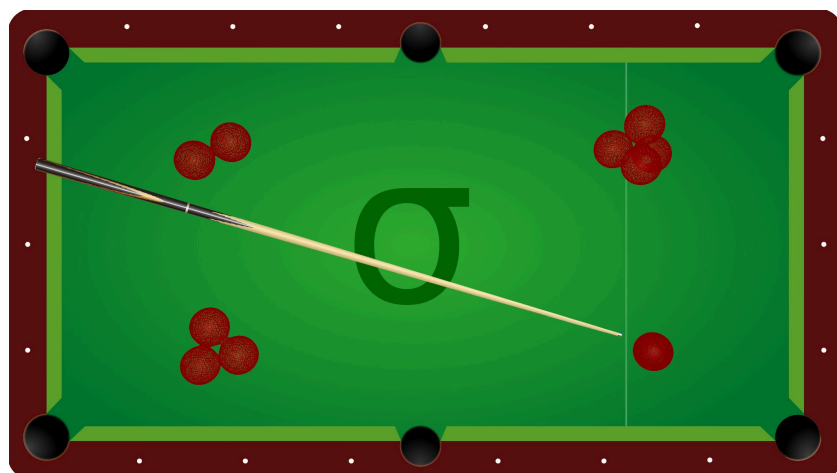
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Neon clusters ($n=2$ to 4) ground states are computed at CCSD(T) level with new developed σXZ basis sets. They resemble grouped billiard balls,

easily separable with a slight perturbation (a delicate touch with a cue stick).

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The Challenge of *ab Initio* Calculations in Small Neon Clusters

