CI+CC
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Hypothetical Energy Curve
of dimer Mg-Ne

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In this work was computed the hypothetical energy curve of Alkaline-Earth $\cdots$ Rare-Gas dimer: MgNe. All the calculations of the curve were carried out using the package GAUSSIAN16 [1]. The levels of theory explored was: *i*) HF-SCF, *ii*) CI-SD and *iii*) CC-SD. All our visualization results was carried out with the help of MATPLOTLIB [2] library.

1. Energy Curve at Sapporo-DZP

For this first part of the work we use the Sapporo-DZP basis set, which was taken from the literature [3, 4]. Just adding the basis set at the last part of the GAUSSIAN16 input. In the input file were also used the `opt=modredundant` GAUSSIAN16 keyword to scan around the dimer bond.

As we can expect by Chemical Intuition the Energy Curve does not have an evident minimum, since the dimer is compounded by Ne which is a Noble Gas and an Alkaline-Earth metal, Mg. Where Ne basically does not make bonds with another atoms. Also we can see how the energy increase in way the distance between the atoms decrease, having accuracy in where the curves starts to go with a higher slope, *i. e.*, the derivatives of the curves would be similar at every method studied.

By the other hand the three methods goes to different values when we look at the energy for long distances. CI-SD and CC-SD goes more similar between itself than HF with them. HF predict more energy, once again as we expected, since HF does not take account the correlation energy.

In Figure 1 are plotted the Energy Curves. To know the minimum for every case was necessary analyze numerically the values, that because the differences are at $10^{-6}\,E_{\mathrm{h}}$ magnitude order, something that with a naked eye is impossible to detect that in the same scale as we plot the whole curve (even if we just look around the minimum is not easy).

The distance values analyzed in this work comes from 0.5 Å to 1.5 Å every 0.02 Å, then until 6.5 Å every 0.1 Å, every 1.0 Å until 56.5 Å, and finally a last calculation at 100.0 Å, all values are presented in Supplementary Information 6..

Analyzing the energy values of the curve we found the dissociation energy (Table 1).The HF level is nearly one magnitude order distanced of CC-SD and CI-SD levels, and these ones are more closer between itself.
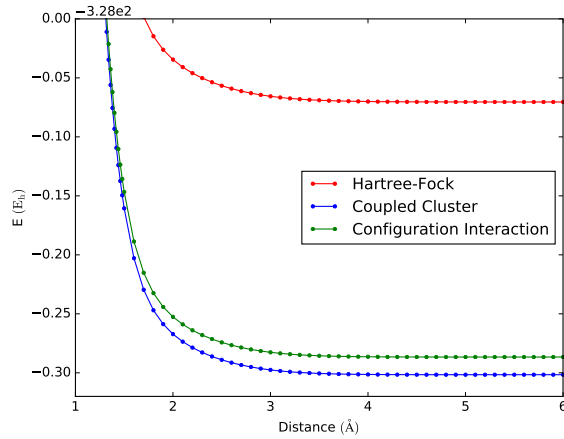

Figure 1: Energy curve at Sapporo-DZP

Table 1: Energy of the system at different theory level, same basis set (Sapporo-DZP)

Distance Table			
Theory Level	Eq. distance (Å)	Eq. energy (kcal/mol)	dissociate energy (kcal/mol)	freq. (cm^{-1})
HF	5.80	-205864.2003	0.000987685	2.84
CC-SD	4.90	-206009.2676	0.016704050	10.20
CI-SD	5.00	-205999.8668	0.014564275	8.82

2. Frequency

Once we know the minimum of the system for the three levels of theory, the harmonic frequency was computed. As we can see in the Table 1, for the three methods the frequency has more or less the same magnitude order, frequency has more accuracy between methods than energy. Whereas we can see again how CC-SD and CI-SD have similar value between each other than with HF.

Knowing that the frequency is quantized, since is modeling by the quantum harmonic oscillator, where for each normal coordinate are given by:

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right) = \hbar \left(n + \frac{1}{2} \right) \sqrt{\frac{k}{\mu}} = hc \left(n + \frac{1}{2} \right) \tilde{\nu}$$

However, we know that the last equation is just in the harmonic case using as approximation the Hooke Law. In some where the molecule would be at the dissociation energy. Then, knowing the dissociation energy, the minimum and how compute the normal coordinate, is just necessary get all together with the $\tilde{\nu}$ already computed.

$$\Delta E = hc\tilde{\nu} \left(n_f + \frac{1}{2} \right) - hc\tilde{\nu} \left(n_i + \frac{1}{2} \right)$$
$$\Delta E = hc\tilde{\nu}(\Delta n)$$

therefore, with an initial n equals to zero: $n = \Delta E(hc\tilde{\nu})^{-1}$.

For all three cases we have a dissociation energy really small, so small to no get an n as Natural Number bigger than zero, *i. e.,* the molecule will never vibrate, since the energy necessary for that is bigger than the dissociation energy.

3. Bigger Basis Set

To get more knowledge in these study was decided study the Sapporo-TZP basis set, recomputing all values with Sapporo-TZP, looking for particularly the minimum value. Specially to know if at the same method with different basis set gives the same minimum, or how the minimum change.

We summarized on the Table 2 how the system accurate with Sapporo-TZP. We can see that the equilibrium distance change: 0.30, 0.40 and 0.30 Å, comparing with Sapporo-DZP. However, since we are at more than 5.00 Å these change are not really significant. Whereas the equilibrium energy does change, around 36, and 75 kcal/mol for HF and CC-SD/CI-SD respectively.

Nevertheless, in chemistry we are more interested on the energy differences, as the dissociate energy. We can see that CC-SD ones again has the higher dissociate energy. However, all changes in dissociate energy are under the 0.1 kcal/mol, not meaning a significant difference with respect the previous calculation.

Also we can see HF is again the higher equilibrium energy and lower dissociate energy. And how CC-SD and CI-SD are more in a agreement between each other than HF for equilibrium distance, equilibrium energy and dissociate energy.

Additionally we compute some curves for Sapporo-QZP, the curves are shown on the Figure 2. For HF theory level the fact that use Sapporo-TZP than Sapporo-DZP has a significant difference, but not too much comparing Sapporo-TZP with -QTP. For CI-SD still has an improvement using Sapporo-TZP than -DZP and also from Sapporo-TZP to -QZP. For CC-SD we have an improvement as in CI-SD.

Knowing that the computing time increase using bigger basis set. We aim that Sapporo-TZP is enough to have a good energies values. Also, because some programs as GAUSSIAN16 has troubles with Sapporo-QTP, being necessary use the next keywords: `integral=NoXCTest integral=grid=ultrafine`.
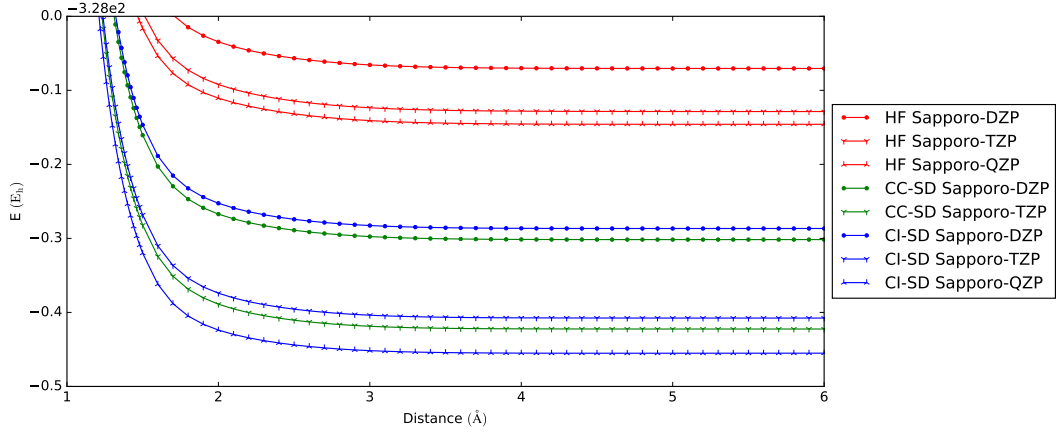
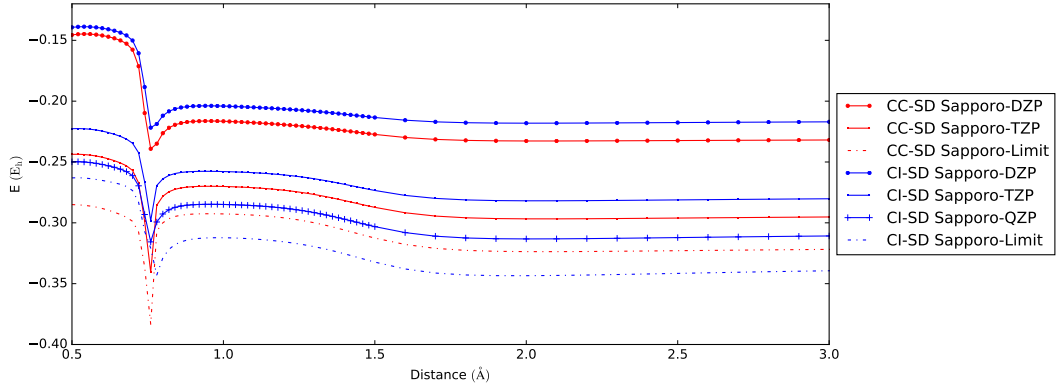Figure 2: Energy curve at different methods with Sapporo D-, T- & Q-ZP basis set.

Figure 3: Energy curve for E_{corr} with limit of Sapporo Basis Set.

Moreover, with all of these values already computed we can calculate the limit of the basis set, at CC-SD and CI-SD for the E_{corr}. The behavior of the limit is shown in Figure 3. Since we know that we compute the limits as:

$$E_{limit} \approx \frac{E_X - bE_{X-1}}{1 - b}, with: \ b = e^B = \frac{E_X - E_{X-1}}{E_{X-1} - E_{X-2}}$$

but also we can get a good approach with two points, computing:

$$E_{limit} = \frac{E_X X^3 - E_Y Y^3}{X^3 - Y^3},$$

where X and Y are the type of bases that we are in.

Table 2: Energy of the system at different theory level, same basis set (Sapporo-TZP)

Distance Table			
Theory Level	Eq. distance (Å)	Eq. energy (kcal/mol)	dissociate energy (kcal/mol)
HF	6.10	-205900.7260	0.004666090
CC-SD	5.30	-206085.0827	0.021378925
CI-SD	5.30	-206075.7918	0.019345825

As we can see in Figure 3, for both cases CC- & CI-SD the E_{corr} has the same accuracy. The system has a peak around 0.75 Å, where the system has more E_{corr}. That peak has no importance for the final curve, since around 0.75 Å the repulsion energy is larger enough to be the head contribution. Finally the E_{corr} does not have any significant change for distances bigger than 3.00 Å.

4. **Basis Set Superposition Error**

Using the keyword `Massage` on GAUSSIAN16 input, we calculate how the system energy is affected by the others functions in the system. That for two cases, we compute the Ne along with basis set of Mg and vice versa. Also we compute the atoms alone. Therefore, we can compute $E_{cp}(correction)$ by the next formula:

$$E_{cp}(\mathbf{MgNe}) \equiv E(\mathbf{MgNe}_{MgNe}) + E(\mathbf{Mg}_{Mg}) - E(\mathbf{Mg}_{MgNe}) + E(\mathbf{Ne}_{Ne}) - E(\mathbf{Ne}_{MgNe})$$

With the information (plotted in the Figure 4), we can aim that even if we consider or not these correction, the energy is basically the same. However this energy difference is computable and appreciable, in the case where we are, a small system, the correction is not time computing prohibitive, then is also a good over-correction for better results.

Since we already have the alone energy atoms and the values for the system but so far away, we can see the Size Consistence of the methods that we already study. At HF theory level we have the same energy at the whole system at 100 Å and in the addition of the two atoms computed separately. For CC-SD the same and finally for CI-SD we have a difference of 0.01 E_{h}. making sense, since we know CI-SD is not Size Consistent, while the other two methods are.
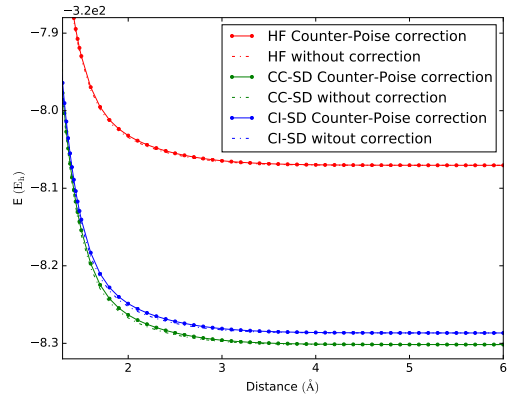

Figure 4: Energy curve with and without the correction of BSSE.

5. **Final Remarks**

In this work we studied the Sapporo-DZP basis set and also -TZP & -QZP, where these family of basis set was studied in some others different ways, as for example the relativistic effects.

Where was developed all-electron relativistic segmented-type basis set for the 15 lanthanide atoms La trough Lu as member of Sapporo-nZP (n = D, T, Q), which efficiently incorporate the correlation among electrons in the valence and core shells as well as the relativistic effect.[5]

Extending the study for all-electron relativistic segmented for the s-, d-, and p-block atoms in the sixth period as a member of the Sapporo-DKH3-nZP (n = D, T, Q). That to use in molecular program packages such as Gaussian, Gamess, Molpro, Molcas, Turbomole, Dirac, Nwche and Alchemy2.[6]

Also was found that the x2c-SV(P)all bases yield much smaller errors than DKH-DZP bases, which are of similar size; x2c-TZVPal and Sapporo-DZP are similar to each other concerning both size errors [7].

Not only relativistic studies was developed. Moreover, was studied already all electrons non-relativistic until Xe atom [8]. Even was already studied the BSSE for alkali and alkali-earth metal atoms [9], and atoms from K to Xe [10]. These last two papers has an accuracy with our work, since they aim that the correction around BSSE change their calculations is around 0.01 eV for D_0, 0.01 Å for equilibrium distances at r_e and values near to 1 and 3 cm^{-1} for ω_e.

6. Supplementary Information

The unit for distance is Å, and for the energy in all cases is E_{h}.

distance	HF	CC-SD	CI-SD
0.50	-315.78295858	-315.92849684	-315.92227849
0.52	-317.02298268	-317.16794513	-317.16187962
0.54	-318.08661556	-318.23137257	-318.22539742
0.56	-319.00128270	-319.14616707	-319.14022651
0.58	-319.78990025	-319.93521469	-319.92925985
0.60	-320.47167797	-320.61770586	-320.61169402
0.62	-321.06277663	-321.20980063	-321.20369276
0.64	-321.57686402	-321.72520375	-321.71895893
0.66	-322.02561922	-322.17572368	-322.16928382
0.68	-322.41927766	-322.57200544	-322.56524031
0.70	-322.76749366	-322.92518902	-322.91762782
0.72	-323.08151923	-323.25279858	-323.24213343
0.74	-323.37960200	-323.58940256	-323.56799210
0.76	-323.68614876	-323.92531226	-323.90793459
0.78	-324.22198341	-324.45692459	-324.44070893
0.80	-324.58588494	-324.81221061	-324.79782671
0.82	-324.92062133	-325.14251035	-325.12898319
0.84	-325.22538684	-325.44483497	-325.43175055
0.86	-325.50145430	-325.71948183	-325.70665155
0.88	-325.75083410	-325.96801648	-325.95534210
0.90	-325.97574587	-326.19243508	-326.17985890
0.92	-326.17839818	-326.39482287	-326.38230766
0.94	-326.36089316	-326.57720853	-326.56472854
0.96	-326.52518652	-326.74150142	-326.72903796
0.98	-326.67307414	-326.88946692	-326.87700586
1.00	-326.80619202	-327.02272027	-327.01025063
1.02	-326.92602283	-327.14272972	-327.13024279
1.04	-327.03390583	-327.25082442	-327.23831313
1.06	-327.13104806	-327.34820431	-327.33566286
1.08	-327.21853590	-327.43595094	-327.42337442
1.10	-327.29734627	-327.51503806	-327.50242232
1.12	-327.36835718	-327.58634192	-327.57368332
1.14	-327.43235753	-327.65065074	-327.63794601
1.16	-327.49005601	-327.70867340	-327.69591959
1.18	-327.54208913	-327.76104740	-327.74824170
1.20	-327.58902853	-327.80834590	-327.79548563
1.22	-327.63138747	-327.85108411	-327.83816663
1.24	-327.66962673	-327.88972494	-327.87674766
1.26	-327.70415986	-327.92468413	-327.91164444
1.28	-327.73535800	-327.95633472	-327.94323006
1.30	-327.76355417	-327.98501115	-327.97183901
1.32	-327.78904720	-328.01101291	-327.99777089
1.34	-327.81210529	-328.03460779	-328.02129371
1.36	-327.83296922	-328.05603492	-328.04264688
1.38	-327.85185525	-328.07550751	-328.06204403
1.40	-327.86895778	-328.09321544	-328.07967554
1.42	-327.88445169	-328.10932773	-328.09571105
1.44	-327.89849442	-328.12399484	-328.11030171
1.46	-327.91122787	-328.13735097	-328.12358244
1.48	-327.92278005	-328.14951617	-328.13567403
1.50	-327.93326651	-328.16059829	-328.14668501
1.60	-327.97303608	-328.20288375	-328.18866916
1.70	-327.99820634	-328.22962492	-328.21521242
1.80	-328.01474232	-328.24697731	-328.23244932
1.90	-328.02615944	-328.25876051	-328.24416714
2.00	-328.03448666	-328.26721194	-328.25257895
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2.40	-328.05368712	-328.28615674	-328.27141102
2.50	-328.05663521	-328.28900293	-328.27422616
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2.70	-328.06121460	-328.29338786	-328.27854984
2.80	-328.06296845	-328.29505036	-328.28018439
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3.40	-328.06857321	-328.30020041	-328.28522888
3.50	-328.06898216	-328.30055225	-328.28557286
3.60	-328.06930591	-328.30082446	-328.28583936
3.70	-328.06956123	-328.30103358	-328.28604461
3.80	-328.06976190	-328.30119305	-328.28620175
3.90	-328.06991915	-328.30131372	-328.28632132
4.00	-328.07004199	-328.30140422	-328.28641166
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