

Ab-Initio Calculations of the Dissociation Energy and Periodic Properties of the Heavy P-block Dimers

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Abstract. Molecular orbital calculations within the ab-initio framework using SBK-basis set at the RHF level are reported for heavy P-block dimers of the fourth (Ga₂, Ge₂, As₂, Se₂ and Br₂), fifth (In₂, Sn₂, Sb₂, Te₂ and I₂) and sixth (Tl₂, Pb₂ and Bi₂) rows. The results of the molecular orbital interpreted and correlated in terms of equilibrium bond length, bond order, bonded valence, total valence, total energy, nuclear energy, electronic energy, electron-electron energy, electron-nuclear energy, nuclear-nuclear energy and dissociation energy. The effect of d-orbital on the ground state properties is also reported. The results indicate that method used gives fairly satisfactory prediction of the molecular properties.

Introduction

The electronic and spectroscopic properties of small clusters of heavy atoms and metal atoms have been the topics of many experimental^[1-15] and theoretical studies^[16-31]. Experimental progress in this area has been phenomenal in recent years^[32-43] due to the advent of laser vaporization and supersonic jet expansion method. Typically, a sample of a foil or sheet of material containing these elements such as a Ga As crystal, a Si crystal or Pt foil is vaporized with a high energy Nd:YAG laser and passed through a supersonic nozzle. A number of other techniques such as sputtering methods, rare-gas matrix isolation methods, particle bombardment method, ligand-stripping methods and aggregation within zeolites and molecular sieves have been used for cluster generation^[44-53].

Clusters of heavy main group elements comprise a subject themselves, a separate class of unusual compounds whose properties exhibit phenomenal variation as a function of size. Many experimental and theoretical investigation in recent years have demonstrated that the geometries and electronic properties of small clusters containing typically 3-10 atoms have no resemblance at all to the more familiar properties of the bulk. It is this aspect that has made the cluster area perhaps one of the most exciting and challenging areas for both experimental and theoretical activities. Electron affinities and ionization potentials of these species exhibit dramatic alternations as a function of cluster size.

A quick review of the chemical literature, shows that no systematic investigations of the electronic structure and bonding of heavy p-block dimers have been undertaken. Such calculations, together with the experimental of spectroscopic properties could provide a wealth of information on the chemistry of such important class of compounds.

In the present study we reported the calculation of the ground state electronic properties (bond lengths, bond orders, total energies, electronic energies, nuclear energies and dissociation energy) of heavy p-block dimers of the fourth, fifth and sixth rows of the periodic table and correlation of periodic trend.

Method of Calculation

The tremendous cost of ab-initio calculations has motivated many attempts to find computational shortcuts. One such approach is based on the observation that core orbitals are relatively inert to changes in chemical bonding (the so called frozen core approximation)^[54]. Another observation is that the effect of core electrons on valence electrons can be treated through the use of potential energy term expressed as sum of local functions multiplied by the projection operators. Based on these two assumptions effective core potentials (ECP's) or pseudo potentials, as they are sometimes called, reduce the computational problem to dealing with valence electrons only. Early results obtained from ECP's compared favorably well with these obtained from all electron calculations. These calculations trended, however, to yield shorter bond lengths and somewhat deeper potential energy curves. Such problems have been

overcome, and calculations using ECP's or all electrons results are in good agreement.

All calculations were carried out using SBK (Stevens/Basch/Krauss) valence basis set^[55], as implemented in Gaussian 94^[56]. This choice implies an unscaled 3-21G basis.

Results and Discussion

The data obtained using SBK-MO calculations are analysed through three rows, fourth (Ga, Ge, As, Se and Br), fifth (In, Sn, Sb, Te and I) and sixth (Tl, Pb and Bi) and five groups, group III (Ga, In and Tl), group IV (Ge, Sn and Pb), group V (As, Sb and Bi), group VI (Se and Te) and group VII (Br and I).

Table 1 presents molecular orbitals, molecular states, total energies and dissociation energies of the studied dimers. Among the values given in Table 1 one can reveal the followings:

1. Within fourth row, the most stable dimer formed is Ga₂ as indicated from the drop of the total energy. The order of stability of the fourth row are Ga > Br₂ > Se₂ > As₂ > Ge₂. Hence the Ge₂ dimer is the lowest stable dimer in fourth row.

2. With the fifth row, again In₂ is the most stable dimer whereas, Sn₂ dimer is the lowest stable one. The order of stability are In > I₂ > Te₂ > Sb₂ > Sn₂.

3. Due to the lack of experimental data in sixth row, three dimers are considered Tl₂, Pb₂ and Bi₂. The stability of Bi₂ is greater than Pb₂ by about 3.9au.

4. Within the group III, Ga₂ dimer still the most stable dimer of all heavy p-block elements.

5. Within group IV, Ge₂ is more stable than Sn₂ and Pb₂ whereas, Sn₂ and Pb₂ have the same stability.

6. Within group V, As₂ is the more stable than Sb₂ and Bi₂. The order of stability are As₂ > Bi₂ > Sb₂.

7. Within group VI, Se₂ dimer is more stable than Te₂ dimer by about 2.55 au.

8. Within group VII, Br₂ dimer is more stable than I₂ dimer by about 3.83 au.

9. Thermodynamic studies^[57] of Ga₂ revealed that the dissociation energy of Ga₂ is about 1.4eV, whereas, the theoretical dissociation

energy calculated at complete active space self consistent field (CASSCF) is 1.2eV. The difference may be attributed to the using the incorrect partition function of Ga₂.

Table 1. Molecular orbitals, molecular states, total energies and dissociation energies of the studied dimers using SBK-basis set.

Dimer	MO – configuration	Molec. state	E _T , au		D,eV	
			SBK	SBK+d	Exp.	Calc.
Ga ₂	$^2 2\sigma_u^2 1\sigma_g 1^2\sigma_g$	\sum_g^{1+}	-514.24	-514.21	1.20	1.40
Ge ₂	$^2 \pi_u^2 1\sigma_g^2 2\sigma_u^2 1\sigma_g 1$	\sum_g^{3-}	7.28	-7.30	2.29	2.65
As ₂	$^4 \pi_u^2 1\sigma_g^2 2\sigma_u^2 1\sigma_g 1$	\sum_g^{+1}	-12.06	-12.11	2.71	3.96
Se ₂	$^2 \pi_g^4 1\pi_u^2 1\sigma_g^2 2\sigma_u^2 1\sigma_g 1$	\sum_g^3	-18.22	-18.27	2.91	3.19
Br ₂	$^4 \pi_g^4 1\pi_u^2 1\sigma_g^2 2\sigma_u^2 1\sigma_g 1$	\sum_g^{1+}	-26.25	-26.28	1.88	1.97
In ₂	$^1 \pi_u^1 1\sigma_g^2 2\sigma_u^2 1\sigma_g 1$	$^3\pi_4$	-376.45	-376.4	0.83	0.87
Sn ₂	$^2 \pi_u^2 1\sigma_g^2 2\sigma_u^2 1\sigma_g 1$	\sum_g^{3+}	-6.66	-6.49	1.86	1.94
Sb ₂	$^4 \pi_u^2 1\sigma_g^2 2\sigma_u^2 1\sigma_g 1$	\sum_g^{1+}	-10.55	-10.59	2.17	3.09
Te ₂	$^2 \pi_g^4 1\pi_u^2 1\sigma_g^2 2\sigma_u^2 1\sigma_g 1$	\sum_g^{3+}	-15.69	-15.72	1.69	2.68
I ₂	$^4 \pi_g^4 1\pi_u^2 1\sigma_g^2 2\sigma_u^2 1\sigma_g 1$	\sum_g^{1+}	-22.42	-22.45	2.06	2.68
Tl ₂	$^1 \pi_u^1 1\sigma_g^2 2\sigma_u^2 1\sigma_g 1$	$^3\pi_4$	-343.40	-343.41	0.58	0.63
Pb ₂	$^2 \pi_u^2 1\sigma_g^2 2\sigma_u^2 1\sigma_g 1$	\sum_g^3	-6.66	-6.67	0.88	0.86
Bi ₂	$^4 \pi_u^2 1\sigma_g^2 2\sigma_u^2 1\sigma_g 1$	\sum_g^{1+}	-10.61	-10.63	2.30	2.04

10. The theoretical CASSCF De value for the ground state $^3\Sigma_g^-$ of Ge_2 is 2.29 eV. This is a reasonable agreement with the experimental value of 2.65 eV. The small discrepancy between the calculated and observed values could be attributed to the high order correlation correction as well as the effective core potentials.

11. The theoretical CASSCF dissociation energy of the ground state of Se_2 was found to be 2.91 eV. A number of experimental De values were obtained (3.41, 3.16 and 3.110 eV)^[58]. Photoionization and thermochemical studies^[59] seem to favor the higher value. Balasubramanian^[60] thus obtained an upper value for De, eliminating the highest value of the three possible De values. Thus the De value should be about 3.19 eV.

12. The main effect of higher order correlations was found to be on the dissociation energies of Sb_2 dimer. The calculated De increased by 17% due to the higher order correlations. The refined theoretical De (2.17 eV) was still about 30% smaller than an experiment (thermodynamic) value of 3.09 eV obtained by Knudsen effusion mass spectrometric method.

13. The theoretical dissociation energy De obtained with the CASSCF method for Te_2 dimer was found to be 1.69 eV. The spin-orbit interaction decreased the De value, since the separated atoms are more stabilized by the spin-orbit interaction compared to the molecule. The experimental value reported for Te_2 is 2.68 eV based on a weighted mean of a number of values obtained from spectroscopic and thermochemical methods. The difference between theoretical and experimental may be attributed to limitation of the calculations.

14. The theoretical De for Pb_2 dimer is 0.88 eV was almost in exact agreement with an experimental value of 0.86 eV. The agreement of such magnitude on a very heavy dimer such as Pb_2 , for which both spin-orbit effects and relativistic effects are large, must be considered impressive.

Periodic Properties

Bond length, bond order, total valence, bonded valence, nuclear energy, electronic energy, electron-electron repulsion energy, electron-nuclear attraction energy and nuclear-nuclear repulsion energy are presented and plotted in Tables 2-5 and Fig. 1-6. The periodicity of the studied dimers explained within a row on going from left to right (increasing of molecular weight) and in the group on going from up to

down (increasing of outer orbital shells). Among the values given in Tables 2-5 and Fig. 1-6 one can reveal the following:

Table 2. Bond length and bond order of the studied dimers.

Dimer	Bond length (Å ^o)		Bond order	
	SBK	SBK+d	SBK	SBK+d
Ga ₂	2.5771	2.5780	1.307	1.330
Ge ₂	2.2322	2.2004	2.020	2.225
As ₂	2.1163	2.0723	2.653	2.815
Se ₂	2.2337	2.1527	1.715	1.814
Br ₂	2.3920	2.2838	0.871	0.917
In ₂	2.8881	2.9001	1.380	1.339
Sn ₂	2.5571	2.5382	2.108	2.219
Sb ₂	2.4722	2.4349	2.761	2.869
Te ₂	2.6351	2.5654	1.801	1.892
I ₂	2.7700	2.6750	0.883	0.950
Tl ₂	3.0277	3.0344	1.173	1.158
Pb ₂	2.6424	2.6342	1.925	2.013
Bi ₂	2.5871	2.5645	2.763	2.849

Table 3. Total valence and bonded valence of the studied dimers.

Dimer	Total valence		Bonded valence	
	SBK	SBK+d	SBK	SBK+d
Ga ₂	1.307	1.330	1.307	1.330
Ge ₂	2.020	2.225	2.020	2.225
As ₂	2.653	2.815	2.653	2.815
Se ₂	1.715	1.814	1.715	1.814
Br ₂	0.871	0.917	0.871	0.917
In ₂	1.380	1.339	1.380	1.339
Sn ₂	2.108	2.219	2.108	2.219
Sb ₂	2.761	2.869	2.761	2.869
Te ₂	1.801	1.892	1.801	1.892
I ₂	0.883	0.950	0.883	0.950
Tl ₂	1.173	1.158	1.173	1.158
Pb ₂	1.925	1.925	1.925	1.925
Bi ₂	2.763	2.849	2.763	2.849

Table 4. Nuclear energy, electronic energy and total energy of the studied dimers.

Dimer	Nuclear energy		Electronic energy		Total energy	
	SBK	SBK+d	SBK	SBK+d	SBK	SBK+d
Ga ₂	90.55	90.49	-604.79	-604.70	-514.24	-514.24
Ge ₂	3.79	3.84	-11.07	-11.14	-7.28	-7.30
As ₂	6.25	6.38	-18.31	-18.49	-12.06	-12.10
Se ₂	8.52	8.84	-26.75	-27.11	-18.22	-18.26
Br ₂	10.83	11.35	-37.08	-37.63	-26.24	-26.27
In ₂	80.80	80.46	-457.25	-456.92	-376.45	-376.46
Sn ₂	3.31	3.33	-9.79	-9.82	-6.47	-6.49
Sb ₂	5.35	5.43	-15.90	-16.02	-10.55	-10.58
Te ₂	7.22	7.42	-22.91	-23.14	-15.68	-15.71
I ₂	9.36	9.69	-31.78	-32.14	-22.42	-22.44
Tl ₂	77.07	76.90	-420.49	-420.32	-343.41	-343.41
Pb ₂	3.20	3.21	-9.86	-9.88	-6.66	-6.67
Bi ₂	5.11	5.15	-15.72	-15.78	-10.60	-10.62

Table 5. Electron-electron energy, electron- nuclear energy and nuclear-nuclear energy of the studied dimers.

Dimer	E _{e-e}		E _{e-N}		E _{N-N}	
	SBK	SBK+d	SBK	SBK+d	SBK	SBK+d
Ga ₂	498.40	498.35	-1452.67	-1452.38	90.55	90.46
Ge ₂	7.55	7.67	-21.20	-21.20	3.79	3.84
As ₂	13.11	13.37	-35.62	-36.08	6.25	6.38
Se ₂	19.83	20.25	-52.83	-53.64	8.52	8.84
Br ₂	28.14	28.72	-74.00	-75.16	10.83	11.35
In ₂	371.07	370.70	-970.27	-969.52	80.80	80.46
Sn ₂	6.64	6.72	-18.47	-18.59	3.31	3.33
Sb ₂	11.31	11.50	-30.33	-30.64	5.35	5.43
Te ₂	16.89	17.19	-44.44	-44.97	7.22	7.42
I ₂	23.96	24.37	-62.14	-62.92	9.36	9.69
Tl ₂	337.48	337.32	-867.16	-866.81	77.07	76.90
Pb ₂	6.55	6.60	-18.50	-18.57	3.20	3.21
Bi ₂	11.05	11.18	-29.90	-30.08	5.11	5.15

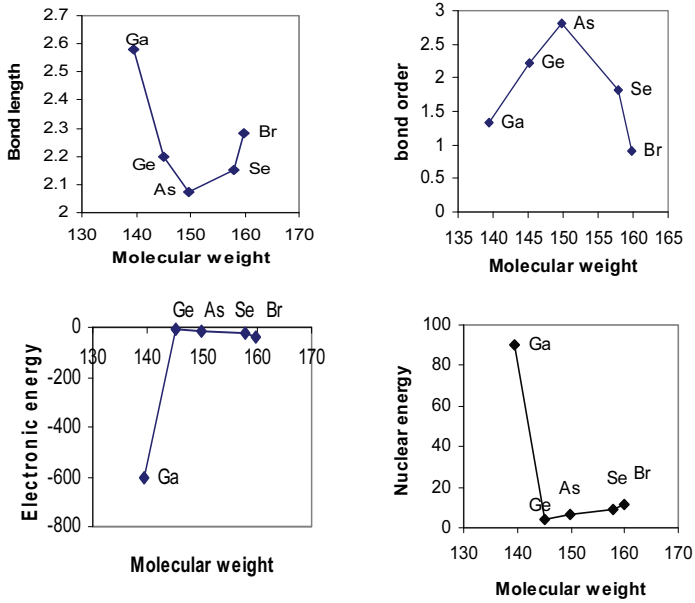


Fig. 1. The variations of bond length, bond order, nuclear energy and electronic energy of the fourth row with molecular weight.

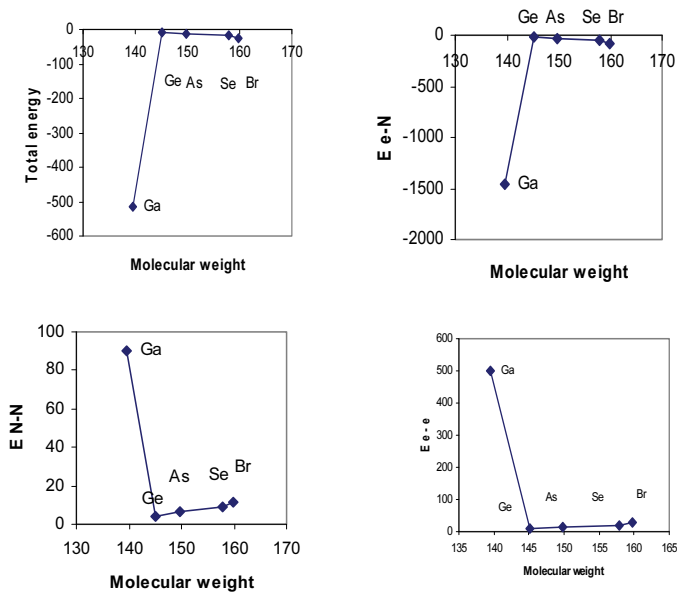


Fig. 2. The variations of total energy, E_{e-N} , E_{N-N} and E_{e-e} of the fourth row with molecular weight.

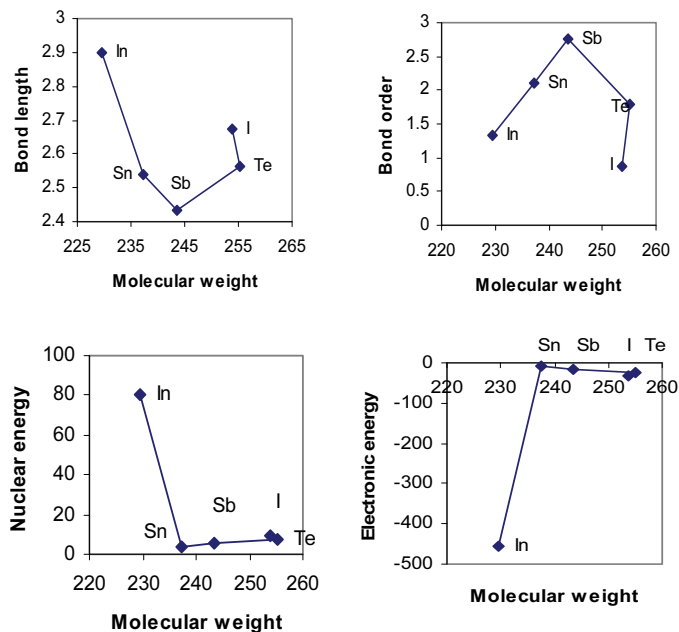


Fig. 3. The variations of bond length, bond order, nuclear energy and electronic energy of the fifth row with molecular weight.

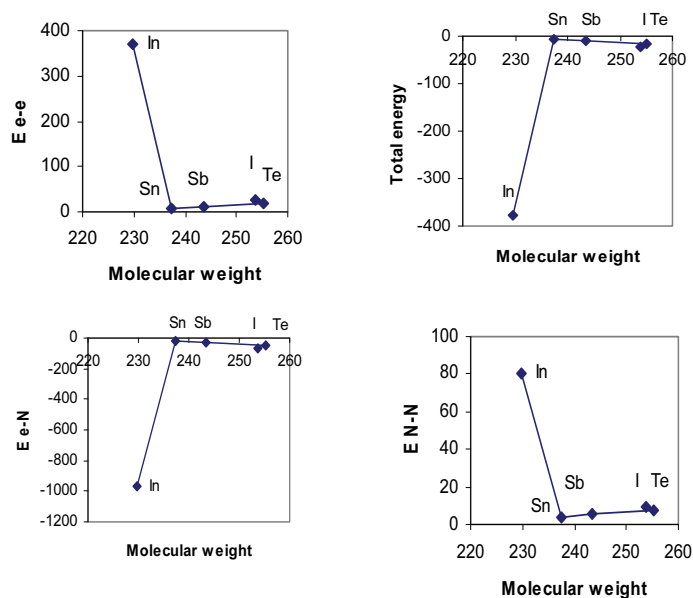


Fig. 4. The variations of total energy, E_{e-N} , E_{N-N} and E_{e-e} of the fifth row with molecular weight.

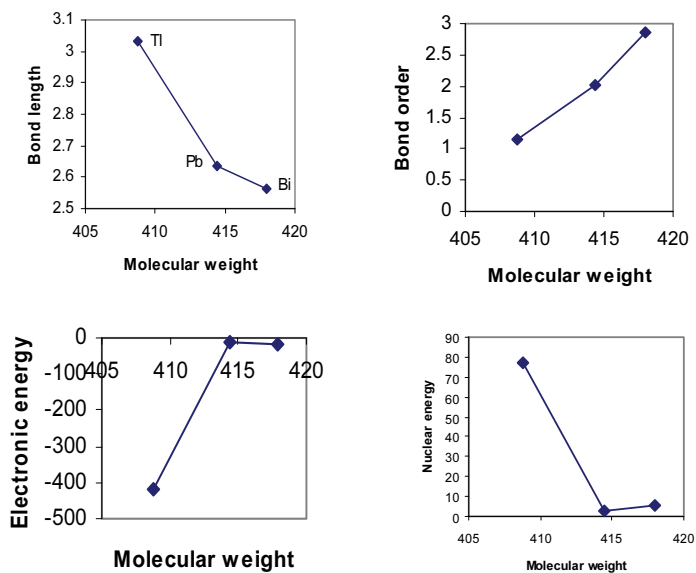


Fig. 5. The variations of bond length, bond order, nuclear energy and electronic energy of the sixth row with molecular weight.

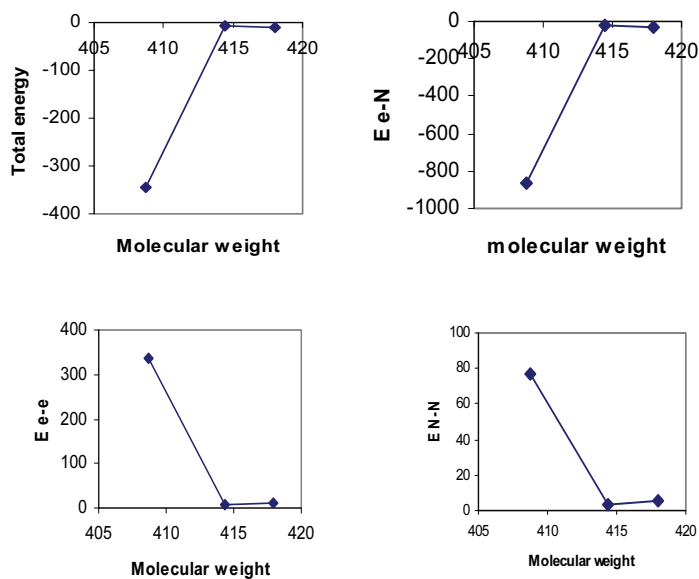


Fig. 6. The variations of total energy, E_{e-N} , E_{N-N} and E_{e-e} of the sixth row with molecular weight.

1. The total energy of row IV dimers increases on going from left to right, *i.e.* from Ga₂ to Br₂. The increase in energy are systematic in case of Ge₂, As₂, Se₂ and Br₂ in which a single double and triple bonds are formed. The order of stability follow Br₂ > Se₂ > As₂ > Ge₂.

2. In case of Ga₂-dimer a dramatic change in the total energy reaches up to ≈ 480 au *i.e.* the most stable dimer in row IV is Ga₂.

3. The addition of d-orbitals as polarized function does not affect the total energies of all dimers, this may be attributed to the filling of d-orbitals.

4. The same trend were observed in case of electronic energy and electron-nuclear attraction energy but it reverse in case of nuclear energy, nuclear-nuclear repulsion and electron-electron repulsion energies. (*c.f.* Fig. 1 and 2).

5. The bond length of fourth row heavy dimers varies in a systematic way on going from left to right (*i.e.* increasing of molecular weight). It is found that the smallest value is As₂ (triple bond) and the largest value is Ga₂ (single bond).

6. The variation of bond lengths are supported by the variation of the bond order values, As₂ dimer have the largest bond order and Br₂ dimer (single bond) have the smallest bond order. The same trend can be observed in case of total valence and bonded valence.

7. The bond order, total and bonded valence are affected by the addition of d-orbitals to the SBK-basis set (*c.f.* Tables 2-5).

8. The same trend observed in the fifth row dimers at which In₂ is the most stable dimer. The rest of the fifth row dimers follows the order In₂ > Te₂ > Sb₂ > Sn₂.

9. The largest bond order dimer of fifth row is Sb₂-dimer (smallest bond length), this may be attributed to the formation of triple bond. On the other hand, the smallest bond order is I₂.

10. The variation of energy components of the fifth row follow the same trend as that of the fourth row.

11. In case of the sixth row Tl₂-dimer is the most stable one, whereas, Bi₂-dimer is more stable than Pb₂-dimer by about 4au. Due to the lack of experimental data and parametrization in SBK-basis set, the rest of sixth row (Po and At) cannot be studied.

12. Tl₂-dimer (single bond) is the largest bond length (smallest bond order) whereas, Bi₂-dimer (triple bond) is the smallest bond length (largest bond order).

13. Within the groups (III \rightarrow VII) the stability as measured by the total energy decreases on going from up to down. This may be attributed to the increase of the total valence and bonded valence. Ga₂-dimer is more stable than In₂ and Tl₂-dimer by ≈ 138 and ≈ 171 au respectively.

14. In case of group IV and V Ge₂ and As₂ are more stable than (Sn₂ and Pb₂) and (Sb₂ and Bi₂). Both (Sn₂ and Pb₂) and (Sb₂ and Bi₂) dimers have the same stability.

15. In group VI and VII, Se₂-dimer is more stable than Te₂ and Br₂ than I₂ by about 3 au and 4 au respectively.

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طاقة التفكك والخواص الدورية لثنائي العناصر الثقيلة باستخدام حسابات Ab-Initio

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المستخلص. تمت دراسة الخواص الدورية وطاقة التفكك لثنائي العناصر الثقيلة، وذلك باستخدام قاعدة المجموعة SBK عند مستوى RHF والثنائيات المستخدمة هي ثنائيات الدورة الرابعة (Br_2, Se_2)، وثنائيات الدورة الخامسة ($As_2, Ge_2, Ga_2, In_2, Sn_2, Sb_2, Te_2, I_2$)، وثنائيات الدورة السادسة (Tl_2, Pb_2, Bi_2). وقد نوقشت نتائج الحسابات المدارية في ضوء كل من: طول الرابطة، ورتبة الرابطة، والتكافؤ الكلي، والتكافؤ الرابط، والطاقة النووية، والطاقة الإلكترونية، والطاقة الكلية. كما تمت دراسة تأثير المدار (d) على خواص الثنائيات. وقد أظهرت نتائج الطريقة المستخدمة قدرتها على تحليل الخواص الدورية لهذه الثنائيات.