

# Computational study of the ground state properties of iodine and polyiodide ions

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**Abstract** A computational study on iodine, iodide and polyiodide is carried out using different density functional methods and basis sets. All electron basis sets with hybrid and generalized-gradient approximation (GGA) functionals overestimate the bond distance and underestimate the vibrational frequency and formation energy of the iodine molecule. The local density approximation functionals with an effective core potential (ECP) basis set results in a very good bond distance but overestimates the vibrational frequency and formation energy. Hybrid functionals with ECPs give relatively good values for bond distance and vibrational frequency but hugely underestimate the formation energy. Only GGA functionals with ECP estimate all three parameters very well. The structural and vibrational properties and energetics (electron affinity and formation energy) of I, I<sup>-</sup>, I<sub>2</sub>, I<sub>2</sub><sup>-</sup> and I<sub>3</sub><sup>-</sup> are in good agreement with the corresponding experimental values for PW91 and ECP calculations. However, the basis set with diffuse function (along with polarized function) can describe the iodide and polyiodide better. The spin-orbit contribution needs to be included for a correct description of the energetics.

**Keywords** DFT · Relativistic effect · Spin-orbit · Iodine · Iodide

## 1 Introduction

Starting with the discovery of iodine by the French Chemist Curtius in 1811, the number of reported polyiodide compounds alone are several hundreds [1]. From the early stage of the discovery, these polyiodide compounds have numerous applications in the real world, e.g. the blue-starch iodine complex for iodine detection, tinchar iodine [2], antidote [3], etc. Iodine is used to dope the conjugated polymer where iodine acts as a mediator to transfer an electron, and the conjugated polymers become conductive. This crucial discovery earned the discoverers the Nobel prize in Chemistry in 2000. There is a great variety of other technological areas where iodine and polyiodide compounds are used extensively, such as electronics, fuel cells, batteries, solar cells, optical devices etc.

The iodide ion is the building block of a large number of polyiodide compounds. The great variety of possible polyiodide structure is a consequence of the ability of iodine to catenate through donor-acceptor interactions combined with the influence of counterions. This donor-acceptor capability of iodide and triiodide makes them a unique candidate to use as a redox couple in the dye-sensitized solar cell (DSSC) [4].

In dye-sensitized solar cells, the iodide/triiodide couple is used as a redox couple which is one of the components that determine the open voltage of the cells. After the discovery of the DSSC by Michael Grätzel [5], an intense effort has been made, both experimentally and theoretically, to enhance its conversion efficiency. Most of the research works are devoted to enhance the efficiency by using different dye molecules and/or semiconductor surfaces. In the solar cells operation, there are a few distinct competitive reactions involved. However, the detailed reaction mechanisms of this multi-reactions system have

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received only relatively little attention. To better understand and further develop DSSCs, understanding the detailed mechanism of the individual reactions that are involved in the solar cell operation is needed, along with the continued search for alternate dyes or semiconductor surfaces. Among all the different reactions, the interactions of the redox couple with the dye and semiconductor surface are very important as they are involved in the dye regeneration process and black current. As a matter of fact, although the iodide/triiodide redox couple has a significant effect on the performance of the DSSC, there is hardly any study on the mechanism of the interactions between this redox couple and the semiconductor surface and/or dye molecule. In order to better understand the interactions of the redox couple with either semiconductor surface or dye molecule, one should have prior knowledge about the couple itself. Before starting to study the interactions, we, therefore, here aim to carry out a theoretical study on the few iodide species involved in this redox couple and benchmark our computational protocol for further study.

The synthesis and characterization of iodine and different iodine compounds are widely discussed both theoretically and experimentally [6–10]. Especially those theoretical studies [6, 8] which discussed the structural, electronic and thermodynamic properties have disagreement of one or more properties with experimental studies. Most of the studies did not consider relativistic effects and/or spin–orbit coupling which are very important for iodine. For example, using Glukhovtsev's [11] basis set and the B3LYP [12, 13] level of theory, Kaltsoyannis and Plane [6] reported very good agreement between theory and experiment for the bond distance and frequency but a very poor formation energy of the iodine molecule. One of the reasons for such poor formation energy is that relativistic effects have been neglected for such a heavy atom. However, relativistic effects have an important impact on the structural properties of molecule as described, for instance, P. Pyykkö [14]. Using the appropriate basis set and level of theory for the system of interest also plays a major role in describing the system properly. In this article we perform Density Functional Theory (DFT) calculations on the iodine molecule and a few polyiodides using a wide variety of basis sets, exchange–correlation functionals (local density approximation, LDA; generalized-gradient approximation, GGA and hybrid) and relativistic treatment. The choice of relativistic DFT (as opposed to potentially more accurate high-level wave-function based ab initio methods) is dictated by the need for computational efficiency once we progress to the more complex systems that constitute a typical DSSC. (However, for reference purposes, we have performed calculations using a highly accurate method for a few of the systems of interest.) Non-relativistic, scalar

relativistic and full relativistic treatment with spin–orbit contribution are considered.

## 2 Computational method

All calculations were performed using the Gaussian molecular program (g03) [15] and Amsterdam Density Functional code (ADF) [16–20]. In the g03 calculations, in addition to its implemented basis sets and potentials, a set of pseudopotential and corresponding different basis sets were used from the Stuttgart and Dresden (SDD) basis set library [21]. Different LDA, GGA, and hybrid functionals are employed.

In order to get the energetic contributions due to spin–orbit coupling, fully relativistic calculations are performed with the ADF code. Both geometry optimization and single point calculations at the g03 optimized geometry were performed. Relativistic effects are treated using the Zeroth Order Regular Approximation (ZORA) to the Dirac equation with spin–orbit operator [22, 23]. The non-collinearity is used for systems with odd numbers of electrons in the relativistic calculations. Perdew and Wang (PW91)[24–26] and Perdew, Burke and Ernzerhof (PBE) [27] and a hybrid functional (B3LYP) in conjunction with the TZ2P basis set are employed. Both scalar and spin–orbit relativistic treatments were carried out for all calculations; the energy difference between them was then taken as a spin–orbit contribution.

## 3 Results and discussions

The formation energy of the I<sub>2</sub> molecule is calculated using the following equations [28]:

$$\begin{aligned}\Delta H_f^{298} &= \Delta E^{298} + \Delta(PV) \\ \Delta E^{298} &= \Delta E_e^0 + \Delta(\Delta E_e)^{298} + \Delta E_v^0 + \Delta(\Delta E_v)^{298} \\ &\quad + \Delta E_r^{298} + \Delta E_t^{298}\end{aligned}$$

Here,  $\Delta E_e^0$  is the energy difference between products and reactants at 0K.  $\Delta(\Delta E_e)^{298}$  is the change in the electronic energy difference between 0K and 298K.  $\Delta E_v^0$  is the difference between zero-point energies of the products and reactants.  $\Delta(\Delta E_v)^{298}$  is the change in the vibrational energy difference between 0K and 298K.  $\Delta E_r^{298}$  is the difference in the rotational energies between products and reactants.  $\Delta E_t^{298}$  is the translational energy difference between products and reactants.  $\Delta(PV)$  is the PV work term. It is equal to  $-RT$  since only one mole of gas is involved in the reaction.  $\Delta E_e^0$  is determined from the total energy difference from single point calculations between products and reactants. All other  $\Delta E$  and  $(\Delta PV)$  terms are

combined into the thermal energy correction to the enthalpy predicted by frequency calculation.

The bond length, stretching frequency and formation energies of the iodine molecule are summarized in Table 1. We have employed almost all available (in the g03 package) iodine basis sets for these calculations with one hybrid functional (B3LYP) and two GGA (PW91 and PBE) functionals. If we look at the bond distance and stretching frequency in the Table 1, it is evident that the I–I bond distance and stretching frequency vary in a range of 2.70–2.90 Å and 180–210 cm<sup>-1</sup>, respectively, for different basis sets and functionals whereas the corresponding experimental values are 2.67 Å and 214.50 cm<sup>-1</sup>, respectively [7, 29]. The bond distances obtained in our calculations using all electron SDD, CEP-4G and LanL2DZ basis sets are much longer and consequently correspond to a much smaller stretching frequency than the corresponding experimental values irrespective of functionals. These findings are in agreement with the earlier study of Calabrese and Khan [10]. With the all electron basis sets of DGDZVP and MidiX and any functionals, we obtained bond distance and stretching frequency that agree well with the corresponding experimental values. However, as we discussed in the introduction, relativistic effects need to be treated for iodine to describe its properties properly. In other words, good agreement between theory and experiment for non-relativistic calculations should be due to a fortuitous cancellation of errors. We, therefore, employed

the effective core potential (ECP) and corresponding cc-pVDZ basis sets from the SDD library [30]. In this way, we have obtained the bond distance and stretching frequency with ECP that are in fair agreement with the corresponding experimental values for all functionals. For ECP calculations the small core potential results are better than large core results and, hence, we employed the smallest core ECP available in the SDD [21] library. This finding agrees to earlier results for other heavy elements [31]. Employing CCSD(T) with the smallest core ECP and the cc-pVDZ basis set, we have obtained 2.71 Å for the I–I bond distance.

Let us now look at the formation energy, Table 1. At first glance, it appears from the Table that the best agreement between calculated and experimental formation energy is obtained for the SDD and CEP-4G basis sets with GGA functionals and the DGDZVP basis set with hybrid functional. However, it is already established that spin–orbit effects make an important contribution to the formation energy of the iodine molecule. Therefore, we have calculated the spin–orbit contribution with the ZORA method as implemented in the ADF code. We have calculated the spin–orbit contribution for three geometries of the iodine molecule, i.e., the experimental geometry, the geometry optimized by g03 and the ADF optimized geometry (scalar relativistic calculation). The optimized bond distance with ADF is slightly longer than that obtained with g03. The bond distance obtained with a

**Table 1** Calculated electronic energy difference without ( $\Delta E$ ) and with the inclusion of zero-point correction ( $\Delta E_e^0$ ) (kJ mol<sup>-1</sup>), formation energy,  $\Delta H_f^{298}$  (kJ mol<sup>-1</sup>), bond distance (Å) and vibrational frequency (cm<sup>-1</sup>) for I<sub>2</sub> molecule using hybrid and GGA functionals with different basis sets

Functional	Basis set	$\Delta E$	$\Delta E_e^0$	$\Delta H_f^{298}$	Bond distance	Vibrational frequency
B3LYP	SDD	117.52	116.43	111.34	2.85	184.70
B3LYP	CEP-4G	123.08	121.94	119.25	2.82	190.24
B3LYP	DGDZVP	173.21	171.96	169.26	2.74	208.44
B3LYP	LanL2DZ	115.00	113.89		2.86	–
B3LYP	MidiX	182.54	181.32	178.64	2.72	204.71
B3LYP	ECP-pVDZ	169.01	167.78	165.11	2.73	206.75
PW91	SDD	152.34	151.23	148.54	2.84	184.59
PW91	CEP-4G	157.31	156.17	153.48	2.82	190.18
PW91	DGDZVP	215.92	214.66	212.01	2.73	209.31
PW91	LanL2DZ	149.82	148.73	146.05	2.86	151.93
PW91	MidiX	226.14	224.91	222.32	2.71	205.06
PW91	ECP-pVDZ	209.04	207.80	205.42	2.72	206.54
PBE	SDD	151.71	150.45	147.73	2.85	184.56
PBE	CEP-4G	156.93	155.79	153.02	2.82	190.27
PBE	DGDZVP	215.35	214.09	211.51	2.73	209.68
PBE	LanL2DZ	149.19	148.09	145.54	2.85	181.14
PBE	MidiX	220.0	218.77	216.04	2.71	204.80
PBE	ECP-pVDZ	208.61	207.37	205.11	2.72	206.74
Exp. [29]		–	–	2.67	214.50	–

scalar relativistic calculation is 0.03 Å longer than that with the inclusion of spin–orbit coupling in the ADF calculations. In all three calculations we have found the spin–orbit contribution to be in the range of 53.01–56.90 kJ mol<sup>-1</sup> which is in very good agreement with previous calculations [6, 22, 11]. The spin–orbit contribution of the iodine molecule at the bond distance of 2.72 Å (the bond distance optimized by g03) we have obtained is 55.21 kJ mol<sup>-1</sup>. After including the spin–orbit contribution, the formation energies of the iodine molecule for PBE/ECP, PW91/ECP and B3LYP/ECP calculations are 149.91, 150.23 and 109.91 kJ mol<sup>-1</sup>, respectively. Thus, the formation energies obtained with PBE/ECP and PW91/ECP are in very good agreement with the experimental value.

Considering all three parameters i.e., bond distance, vibrational frequency and formation energy, it is clear that the GGA functionals with (small-core) ECP basis set describe the iodine molecule better than any other DFT model chemistry does.

Having found that the GGA functionals with ECP-pVDZ is a good choice for the calculation of iodine, one may wonder whether the other functionals will perform in a similar manner. To address this question, we have

carried out a systematic study on the iodine molecule with ECP and various different LDA, GGA and hybrid functionals available in the g03 program. Again, calculated formation energy, bond distance and stretching frequency for the iodine molecule with different functionals are summarized in Table 2. Using LDA functionals we have obtained a bond distance which is in very good agreement with the experimental value, however, the stretching frequency and formation energy are much higher than the corresponding experimental values. On the other hand, using hybrid functionals, we have found a bond distance and stretching frequency that are in good agreement with their corresponding experimental values but much lower formation energy (if the spin–orbit contribution is included). Only when using GGA functionals, we obtain very good agreement with the corresponding experimental values for all three parameters.

After establishing the most suitable basis sets and method for the iodine molecule calculation, we now calculate the structural and spectroscopic properties of a few polyiodides with different levels of basis sets and the PW91 functional.

**Table 2** Calculated electronic energy difference without ( $\Delta E$ ) and with the inclusion of zero-point correction ( $\Delta E_e^0$ ) (kJ mol<sup>-1</sup>), formation energy,  $\Delta H_f^{298}$  (kJ mol<sup>-1</sup>), vibrational frequency (cm<sup>-1</sup>) and bond distance (Å) for I<sub>2</sub> molecule using different functionals with ECP-pVDZ basis set

Functional	Functional type	$\Delta E$	$\Delta E_e^0$	$\Delta H_f^{298}$	Bond distance	Vibrational frequency
PW91PBE	GGA	211.06	209.82	207.90	2.72	207.75
MPW91PW91	Hybrid	178.71	177.38	175.43	2.69	221.94
PBE1PBE	Hybrid	182.50	181.17	179.22	2.69	222.99
SVWN	LDA	265.87	264.54	262.59	2.68	223.10
SVWN5	LDA	259.35	258.03	256.08	2.69	219.44
XAPBE	GGA	307.31	305.84	303.82	2.60	252.18
XAPW91	GGA	305.49	304.02	302.02	2.61	245.91
BPW91	Hybrid	191.35	190.12	188.21	2.74	205.00
B3P86	Hybrid	186.08	184.77	182.83	2.70	218.44
B3PW91	Hybrid	179.0	177.70	175.76	2.70	217.59
B1B95	Hybrid	183.60	182.28	180.33	2.69	220.22
B1LYP	Hybrid	160.53	159.29	157.37	2.73	207.53
O3LYP	Hybrid	190.44	189.13	187.18	2.69	218.79
BHandH	Hybrid	194.04	192.62	190.64	2.67	237.01
BHandHLYP	Hybrid	144.85	143.52	141.57	2.70	222.94
VSXC	GGA	179.10	177.93	176.03	2.74	196.01
PBELYP	Hybrid	194.80	193.66	191.77	2.77	190.20
PW91LYP	Hybrid	202.12	200.98	199.09	2.76	191.25
BPL	Hybrid	170.21	169.11	167.23	2.78	184.41
G96PBE	Hybrid	188.77	187.52	185.60	2.71	209.91
HFS	GGA	213.20	211.54	208.38	2.72	205.01
XAlpha	GGA	221.71	220.43	218.50	2.70	214.17
HFB	GGA	116.54	115.50	113.64	2.84	174.38
B3LYP [6]	Hybrid	–	–	127.00	2.71	214.60
Exp. [7, 29]		–	–	152.30	2.67	214.50

Computational results for I and  $I^-$  are listed in the Table 3. Without including the spin–orbit contributions to the electron affinity of I, the results of calculations with basis sets that do not contain diffuse functions are very close to the experimental values. However, spin–orbit makes a substantial contribution to the electron affinity of iodine. The calculated spin–orbit contribution obtained in our calculations is  $29.38 \text{ kJ mol}^{-1}$ , which is in very good agreement with a previous study [33, 11]. With this contribution, the results for basis sets that include diffuse functions are in very close agreement with experimental value.

The calculated results for the iodine molecule at different basis set levels are summarized in Table 4. The formation energies obtained with all of the basis sets are within 1–2% of the experimental value. The bond distance and stretching frequency with triple zeta basis sets are in better agreement with the corresponding experimental values than the double zeta basis. The calculated electron affinity of  $I_2$  is within 2–3% of the experimental value for all basis sets. We have not found a significant spin-contribution to the electron affinity of  $I_2$ . The calculated spin–orbit contribution for the electron affinity of  $I_2$  is  $0.69 \text{ kJ mol}^{-1}$ . If we correct for this spin–orbit contribution, the electron affinity value for  $I_2$  is in good agreement with experiment.

**Table 3** Calculated electron affinity ( $EA_f^{298}$  = without spin–orbit correction and  $EA_f^{298,SO}$  = with spin–orbit correction) for I atom with PW91 functional and different basis sets

Basis set	$EA_f^{298}$	$EA_f^{298,SO}$
cc-pVDZ	298.56	249.18
Aug-cc-pVDZ	326.83	297.45
cc-pVTZ	293.10	263.72
AUG-cc-pVTZ	317.72	288.34
Exp. [32]	–	294.31
Ref. [11]	319.36	289.45

The units are in  $\text{kJ mol}^{-1}$

**Table 4** Calculated bond distance,  $r_e$  (Å), vibrational frequency,  $\nu_e$  ( $\text{cm}^{-1}$ ), formation energy ( $\Delta H_f^{298}$  = without spin–orbit correction,  $\Delta H_f^{298,SO}$  = with spin–orbit correction) and electron affinity, EA for  $I_2$  with PW91 functional

Basis set	$r_e$	$\nu_e$	$\Delta H_f^{298}$	$\Delta H_f^{298,SO}$	EA
cc-pVDZ	2.72	206.54	205.40	150.23	244.87
AUG-cc-pVDZ	2.72	206.7	205.11	150.28	256.06
cc-pVTZ	2.695	213.86	210.64	155.50	243.38
AUG-cc-pVTZ	2.693	215.35	210.71	155.57	257.80
Exp. [29]	2.67	214.50	–	152.30	246.03
Ref. [11]	–	–	–	–	232.53

Energy units are in  $\text{kJ mol}^{-1}$

Computational results for  $I_2^-$  are listed in Table 5. The diffused function basis sets are better in describing the structural and vibrational properties than non-diffuse function basis sets. From our four calculations with different basis sets, a trend is evident that the structural and vibrational properties are getting better with larger basis set. Our findings are in agreement with previous theoretical calculations [8]. Our calculated formation energies of  $I_2^-$  ( $I + I^- \rightarrow I_2^-$ ) are in very good agreement with experimental data. The calculated spin–orbit coupling is  $39.29 \text{ kJ mol}^{-1}$  which is a little higher than previously reported [34]. Diffuse function basis set calculations results are in better agreement with experimental value than those that lack the diffuse functions.

Finally, calculated results for  $I_3^-$  are listed in Table 6. To the best of our knowledge, there is no experimental structural data available for  $I_3^-$ . Our results are in agreement with previous theoretical calculations [8]. The bond distance for heavier basis set calculation are shorter than what we have seen for  $I_2^-$  before. The formation energy for  $I_3^-$  ( $I_2 + I^- \rightarrow I_3^-$ ) is lower with heavier basis set calculations. We have found very little spin–orbit contribution in

**Table 5** Calculated bond distance,  $r_e$  (Å), vibrational frequency,  $\nu_e$  ( $\text{cm}^{-1}$ ) and formation energy ( $\Delta H_f^{298}$  = without spin–orbit correction,  $\Delta H_f^{298,SO}$  = with spin–orbit correction) for  $I_2^-$  with PW91 functional

Basis set	$r_e$	$\nu_e$	$\Delta H_f^{298}$	$\Delta H_f^{298,SO}$
cc-pVDZ	3.34	88.06	171.25	127.66
AUG-cc-pVDZ	3.32	90.17	154.24	114.41
cc-pVTZ	3.30	91.54	160.63	120.80
AUG-cc-pVTZ	3.28	94.60	150.50	110.67
Exp. [9, 34]	3.23	115.01	–	113.85

Energy units are in  $\text{kJ mol}^{-1}$

**Table 6** Calculated bond distance,  $r_e$  (Å), vibrational frequency,  $\nu_e$  ( $\text{cm}^{-1}$ ) and formation energy ( $\Delta H_f^{298}$  = without spin–orbit correction,  $\Delta H_f^{298,SO}$  = with spin–orbit correction) for  $I_3^-$  using PW91 functional

Basis set	$r_e$	$\nu_e$	$\Delta H_f^{298}$	$\Delta H_f^{298,SO}$
cc-pVDZ	3.00	53.48, 101.66, 142.37	188.62	187.37
AUG-cc-pVDZ	3.00	52.23, 101.97, 139.49	162.81	161.56
cc-pVTZ	2.98	54.06, 106.49, 145.12	172.78	171.28
AUG-cc-pVTZ	2.98	53.16, 106.53, 143.54	157.65	156.40
cc-pVQZ	2.97	53.42, 106.76, 143.80	160.16	158.66
AUG-cc-pVQZ	2.97	53.19, 106.82, 143.54	155.98	154.48
cc-pV5Z	2.97	53.41, 107.04, 143.95	157.67	156.17
AUG-cc-pV5Z	2.97	53.34, 107.02, 143.65	153.01	151.51
Exp. [35]	–	–	–	126.40

Energy units are in  $\text{kJ mol}^{-1}$



this case. This would have been expected, given that both reactants and products are formally closed-shell species in this case. Unlike I, I<sup>-</sup>, I<sub>2</sub> and I<sub>2</sub><sup>-</sup>, the energetic value of I<sub>3</sub><sup>-</sup> (the formation energy) is estimated higher compared to the experimental value. Therefore, we have used larger basis sets for the I<sub>3</sub><sup>-</sup> calculations. From the calculations with progressively heavier basis sets (Table 6), it is clear that the formation energy is getting closer to the experimental value as we use these heavier basis set. Results for the basis sets with diffuse functions are closer to the experimental value than those with basis sets without diffuse functions. But even for the heaviest basis set calculation, the formation energy is around 25 kJ mol<sup>-1</sup> higher than the experimental value. We have then employed B3LYP with the whole set of basis sets that we used with the PW91 functional. The estimated formation energies for B3LYP calculations with the cc-pVDZ, AUG-cc-pVDZ, cc-pVTZ, AUG-cc-pVTZ, cc-pVQZ, AUG-cc-pVQZ, cc-pV5Z and AGU-cc-pV5Z basis sets are 163.47, 137.98, 146.77, 131.46, 132.20, 131.98, 130.12 and 128.80 kJ mol<sup>-1</sup>, respectively. Similar to the PW91 calculations, the formation energy is decreasing with heavier basis set calculations and basis sets with diffuse functions provides results that agree better with experiment. The formation energies for heavier (better than cc-pVTZ) basis set calculations are in very good agreement with experiment. In general, we have observed that iodide and polyiodide can be described best using basis sets that have diffuse (along with polarization) functions.

#### 4 Conclusion

We have carried out a systematic study on iodine and a few polyiodides using different theoretical methods and basis sets. The bond distances obtained with hybrid and GGA functionals in conjunction with all electron basis sets are much longer than the experimental value. Vibrational frequency and formation energy, on the other hand, are much lower than the corresponding experimental values for the iodine molecule. Thus, the non-relativistic all-electron basis sets should not be used. On the other hand, GGA functionals with an ECP basis results are in good agreement with experiment and previous theoretical results.

The LDA calculations with an ECP basis sets are in agreement with experiment as long as structural properties are concerned. However, such calculations hugely overestimate the formation energy and vibrational frequency. Hybrid functionals, on the other hand, nicely estimate the bond distance and vibrational frequency but underestimate the formation energy. Only GGA functionals estimate all three parameters (bond distance, vibrational frequency and formation energy) for I<sub>2</sub> very nicely. The spin-orbit has a

large contribution to the energetics of the I<sub>2</sub> molecule. The calculated formation energy is in nice agreement with experimental values only after it has been corrected for the spin-orbit contribution.

The bond distances, vibrational frequencies, electron affinities and formation energies of I, I<sup>-</sup>, I<sub>2</sub>, I<sub>2</sub><sup>-</sup> and I<sub>3</sub><sup>-</sup> are in good agreement with the corresponding experimental values for calculations employing a GGA functional (PW91) with ECP basis sets. However, the results obtained for iodide and polyiodide with basis sets containing diffuse functions are better than those without diffuse functions. It is very important that for describing any iodide and polyiodide with GGA functionals, the diffuse (and polarization) functions of the basis sets need to be included. The spin-orbit has a significant contributions to the energetics data. The energetics data are in nice agreement with the corresponding experimental values only after the correction of spin-orbit contribution. Therefore, it is essential to include the spin-orbit correction to the energetics data to describe any iodine and polyiodide compounds.

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