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Effect of spin-orbit coupling on small platinum nanoclusters

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We have shown that spin-orbit coupling plays an important role in determining the structures of platinum nanoclusters. We have used spin-orbit coupling self-consistently with density functional theory to study the geometry of platinum clusters and their binding energy. It has been found that the relative energies of the isomers of a cluster of a given size can be changed due to the inclusion of spin-orbit coupling. Planar structures were found for Pt_n clusters with $n \leqslant 5$.

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It is well known that spin-orbit coupling has a significant effect in determining the electronic properties of the heavier transition metals. Computationally, inclusion of spin-orbit coupling not only changes the spectrum of the energy levels of atoms, but also is a key factor in obtaining the right ground-state geometry for molecules and clusters. Clusters are distinctly different from their bulk state mainly because of the large surface-to-volume ratio, and the enhanced quantum mechanical size-effect which makes them interesting to study [1]. Metal clusters are the focus of study, both experimentally and theoretically, for several decades now, mainly because of their use as catalysts. This is due to the fact that metal clusters provide a large surface for the reactions, hence a higher overall reactivity rate. Their potential uses as nanostructured materials with tailored electronic properties are also the driving force to further their study. The advancement of experimental techniques, such as mass spectrometry, enables us to study the clusters and their reactivity.

The simple jellium model of clusters is not capable of predicting transition metal cluster's properties, as the delocalized *s* electrons play only a small role in these clusters, though shell closing and the occurrence of magic numbers are sometimes seen [2]. Platinum clusters are important for various technological reasons. These are widely used as catalytic converters in automobiles for the decomposition of carbon monoxide and nitrous oxide. Apart from this, they play an important role in the development of the hydrogen-based fuel economy, particularly in the proton exchange membrane-type hydrogen fuel cell [3]. Though there is a continuing effort to replace platinum with other materials with similar properties, as platinum is an expensive metal, it is important to understand the properties of these materials at the fundamental level. From a theoretical point of view, the open *sd* shells of platinum are responsible for the varied electronic states and isomers of the clusters, and the inclusion of relativistic effects makes its picture rather challenging. For example, gold clusters, its neighboring element, show pronounced relativistic effects in *sd* hybridization which is manifested by their preference of two-dimensional (2D) structures for as large as 13 atom clusters [4]. There is a possibility that smaller size platinum clusters can also be found in planar geometry. So, the investigation of these types of clusters with a higher level of theory and a better treatment of spin-orbit coupling is always important.

In this paper, our main goal is to study the effect of spin-orbit coupling on the geometric and electronic properties of small platinum clusters $\mathrm{Pt}_n (n=2\text{–}5)$. So far in the literature, as discussed below, when the spin-orbit interaction was taken into account, it was treated either as an effective potential or nonself-consistently. Most of the previous studies predicted a three-dimensional (3D) structure for Pt_4. To predict the proper ground-state geometry for these transition metal clusters, it may be important to treat the spin-orbit coupling self-consistently. In addition to this, it has been shown by some other studies that spin-orbit coupling is the driving force behind the hydrogen activation by small platinum clusters. For example, the ground-state triplet-to-excited-state-singlet transition is necessary for the platinum atom before it can dissociate a hydrogen molecule, and spin-orbit coupling plays an important role in it [5]. Despite the importance of spin-orbit coupling, some of the studies did not consider spin-orbit coupling in their description of small Pt clusters. For example, molecular dynamics was used by Yang *et al.* [6] to study up to 6 atoms and by Sebetci *et al.* [7] up to 21 atom platinum clusters without spin-orbit coupling. Grönbeck *et al.* [8] studied both gold and platinum clusters together, up to 5 atoms, with density functional pseudopotential calculations. The major limitation of this study is that only triplet and singlet states were considered. However, for all of the ground-state clusters, they found planar structures. Among the spin-orbit coupling studies, Balasubramanian *et al.* [9] published a series of extensive studies on platinum clusters, up to Pt_5, by several methods, and discussed the spin-orbit coupling effect on them. Their general conclusion was that the spin-orbit coupling has less of an effect as the clusters get bigger. A similar conclusion was reached by Fortunelli [10] in his study of small Pt clusters with the generalized gradient approximation to density functional theory. Xiao *et al.* [11] used a plane wave basis set to investigate the structural stability of Pt clusters, again in the framework of density functional theory, and commented that the inclusion of spin-orbit coupling merely increases the binding energy of the clusters—but does not change the energy profile of the isomers, which contradicts what we have found in the present study. However, here it should be noted that among these studies, discrepancies exist as to what is the ground-state structure for a given size platinum cluster. Due to the scarcity of experimental study, this question still remains unresolved.

TABLE I. Binding energy, spin-orbit coupling energy, magnetic moment and HOMO-LUMO gap for the most stable clusters.

Pt_n	Binding energy (eV/atom)		E_{SO} (eV/atom)	HOMO-LUMO gap (eV)
Pt_2	NSO	1.849	0.4795	0.268
	SO	1.694		0.072
Pt_3	NSO	2.443	0.4020	0.479
	SO	2.210		0.128
Pt_4	NSO	2.729	0.4343	0.231
	SO	2.528		0.157
Pt_5	NSO	2.978	0.4544	0.170
	SO	2.797		0.211

Here, we report the results of calculations of small platinum clusters $Pt_n (n=2–5)$ with and without spin-orbit coupling. The Perdew and Wang 1991 (PW91) energy density functional [12] was used for exchange and correlation. The projected augmented wave (PAW) method [13,14] was used within the Vienna *ab initio* simulation package (VASP 4.6.21) [15–17]. All plane waves up to 300 eV were used in the expansion and all atoms were relaxed without any symmetry constraint until the forces on them were less than 10 meV/Å. The spin-orbit coupling was taken into account self-consistently and with spin noncollinearity as described in [18]. To test the reliability of this method, we calculated the ionization potentials (IP) and the electron affinity (EA) of the platinum atom. We found that the ground state of the platinum atom is a triplet, and its IP and EA agree pretty well with the measured values. Its calculated IP and EA are 9.381 eV and 2.219 eV, compared to the experimental values of 8.960 eV and 2.218 eV, respectively. In the following, binding energies of different clusters are calculated along with their geometry to demonstrate the effect of spin-orbit coupling. Because it is quite easy to fall into a local energy minimum, we performed all calculations in two ways: (1) We allowed the computer to search for the energy minimum with spin-orbit included, (2) the calculations were converged for integer spins [19] without spin-orbit, then spin orbit was introduced and the calculations were reconverged. For $n>2$, the second method always found an energy lower than or equal to the first. However, for $n=2$, the first method found the ground state 0.65 meV below that of the second method, with a bond length 0.003 Å shorter. Binding energies are defined here with respect to the separated atom limit, and the spin-orbit energy, E_{SO}, is defined as the difference between the total energies without and with spin-orbit coupling. In Table I, we have listed these quantities along with their highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap. Note that spin-orbit reduces the binding energy in every case because it makes a larger contribution to the atomic energy than to the cluster energy. In Fig. 1, minimum energy structures of Pt_2 to Pt_4 are shown.

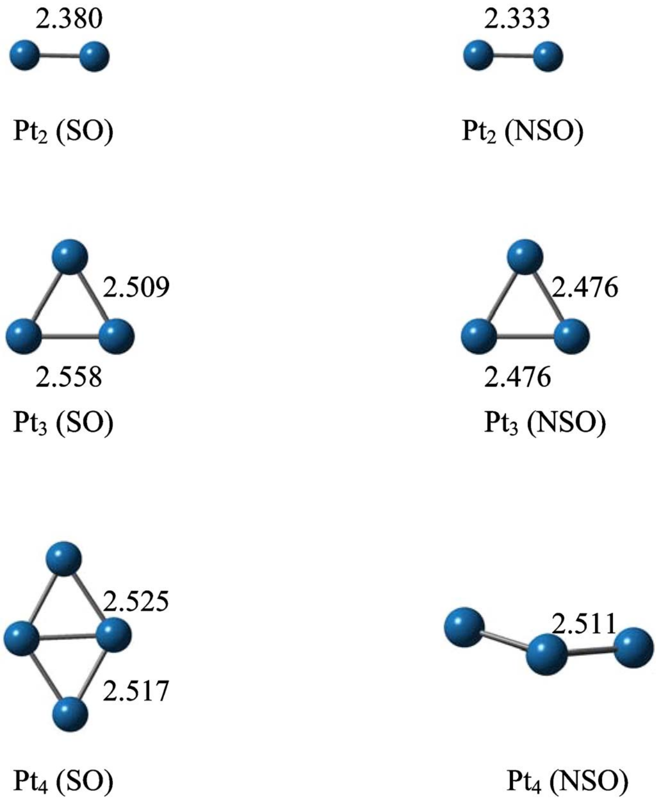

FIG. 1. (Color online) $Pt_n (n=2,3,4)$ clusters. Left side figures are the optimized structures with spin-orbit coupling and the right side are without spin-orbit coupling. The NSO structure of Pt_4, which is almost a rhombus, is shown as a side view to show its 3D nature. Bond lengths are shown in Å.

The binding energy for the Pt dimer was found to be 1.849 eV/atom for the non-spin-orbit (NSO) calculation, while the experimental binding energy is much less, 1.57 eV/atom [20]. Inclusion of the spin-orbit coupling brings down the calculated binding energy to 1.694 eV/atom, which is closer to the experimental value. The dimer bond lengths are 2.333 Å (NSO) and 2.380 Å (SO), while the experimental value is 2.333 Å. Our NSO value agrees with the value calculated in [11], where VASP was also used to study these clusters. However, in contrast to our study, it was commented there that SO does not have a considerable effect on these clusters. However, Balasubramanian—in his 1987 paper [9]—did comment that the SO effect in the Pt dimer is significant. His values for binding energy without and with SO are 1.16 eV/atom and 0.985 eV/atom, respectively. A more recent calculation [10] using the PW91 functional found 0.34 eV more binding energy with SO than its NSO counterpart. The NSO binding energy from this calculation was 1.85 eV/atom, which is similar to our NSO binding energy. However, the author mentioned that their SO calculations might be affected by the numerical problems. Anton *et al.*[21] studied Pt_2 using the four-component Dirac equation with atomic orbitals, the Becke [22] exchange functional, and a Perdew [23] correlation functional. They obtained 1.64 eV/atom for the binding energy and 1.56 eV/atom when the spins were noncollinear [24]. The difference between their results and ours can be attributed to the differences in our exchange functionals and in our noncollinearity schemes.

The ground-state geometry of the Pt_3 cluster was found to be a triangle (Fig. 1), but its spin multiplicity depends on the spin-orbit coupling. Without spin-orbit coupling, it is an equilateral triangle, and its singlet state is 0.05 eV lower in energy than the triplet state. On the other hand, with SO, the singlet structure is 0.02 eV higher than the triplet structure. Also, with SO, it becomes an isosceles triangle. This distortion away from an equilateral triangle lowers the energy by 20 meV. Balasubramanian *et al.* [9] found similar results. In their calculations, the triplet state of Pt_3 is lower in energy by 0.078 eV when spin-orbit coupling was included. While without SO, the singlet state was their ground state which was 0.07 eV lower than the triplet state. These are comparable to our values. We also considered a linear structure which was found to be 0.327 eV higher in total energy with higher spin multiplicity of 5. The NSO and SO binding energies were found to be 2.443 eV/atom and 2.210 eV/atom, respectively. An earlier experimental binding energy estimation [25], 2.18 eV/atom, agrees very well with our SO value. However, a later experimental lower bound of binding energy, 2.37 eV/atom, by collision-induced dissociation [20] lies in between the calculated NSO and SO values. Our bond length is similar to that of another plane wave study [11], but our NSO binding energy is little larger. The bond lengths in the triangle increase by an average of 0.05 Å due to the effect of spin-orbit coupling. The dissociation energy of one Pt atom:

$$Pt_3 \rightarrow Pt_2 + Pt \tag{1}$$

was found to be 3.631 eV and 3.242 eV without and with spin-orbit coupling, respectively. With the experimental binding energy of Pt_2 and Pt_3, this energy is 3.40 eV or 3.92 eV, depending on which of the Pt_3 values is used.

For the Pt_4 cluster, the two lowest-energy structures are planar. A rhombus is found to be the ground-state geometry, while the square cluster is 0.09 eV higher in energy with SO. However, the rhombus without the spin-orbit coupling is not an exact 2D structure, rather the angle between the two triangular planes is 157.21°. Inclusion of spin-orbit coupling makes this a planar structure. Tetrahedral geometry is an additional 0.06 eV (SO) higher. This is in contrast with some other published results. However, Yang *et al.* [6] also reported a rhombic structure with binding energy of 2.56 eV/atom, but did not report any spin multiplicity. In the present study, the calculated binding energy for the rhombus is 2.729 eV/atom (NSO) and 2.528 eV/atom (SO) with a spin multiplicity of 5. It is interesting to note that the NSO binding energy of tetrahedral Pt_4 in the triplet state is 2.707 eV/atom, which is fairly close to that of the ground-state rhombic structure. However, inclusion of spin-orbit coupling lowers the binding energy of the tetrahedral clusters to 2.493 eV/atom. This implies that the spin-orbit coupling favors the planar geometry. Ref. [9] predicted a triplet tetrahedral geometry as a ground-state structure. Their quintet rhombus is 0.47 eV higher in energy than the triplet tetrahedral one. We did not find the linear structure to be stable. The fragmentation energies for the following channel,

$$Pt_4 \rightarrow Pt_3 + Pt, \tag{2}$$

are 3.587 eV (NSO) and 3.482 ev (SO). And the dissociation energy into dimers is

$$Pt_4 \rightarrow Pt_2 + Pt_2, \tag{3}$$

3.520 eV (NSO) and 3.336 eV (SO). At NSO, the difference in fragmentation energies between channels (2) and (3) is 0.067 eV, whereas with SO the difference is higher, 0.146 eV. It suggests that with SO, dissociation of Pt_4 into dimers is more probable.

Finally, we will discuss the Pt_5 clusters. In Fig. 2, the five most energetically favorable isomers are shown with their bond lengths. For this cluster too, we got a planar structure as ground state, though most of the other studies predicted

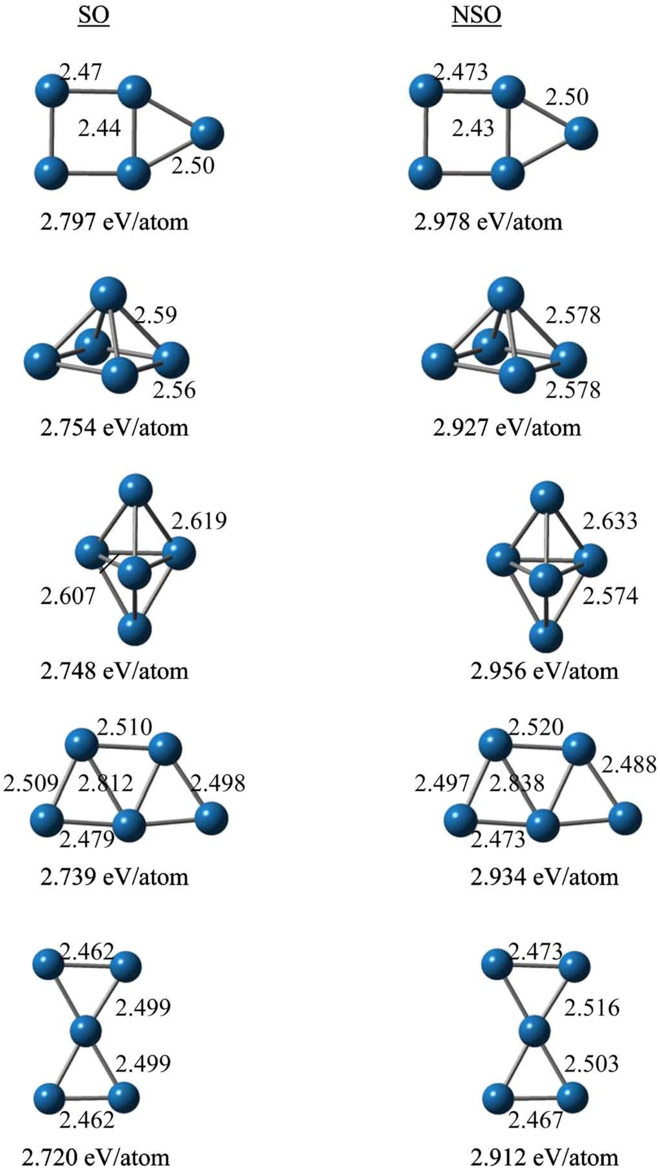

FIG. 2. (Color online) The five most low-energy isomers of the Pt_5 cluster. Left side and right side figures are optimized structures with and without spin-orbit coupling, respectively. Bond lengths in Å and binding energies in eV per atom are shown.

bipyramidlike structures. The spin multiplicity of these bipyramid structures varies in different studies. For example, Balasubramanian *et al.* [9] predicted a triplet distorted trigonal bipyramid, whereas Ref. [11] predicted a quintet state. For the trigonal bipyramid structure, we also found a quintet state without spin-orbit coupling, while inclusion of SO makes triplet and quintet states almost degenerate. In particular, the ground-state structure of [9] can be seen as a pyramid structure on an irregular rectangle. We tried this structure and it optimized to our rectangular pyramid structure. It is to be noted that Yang *et al.* [6] predicted a rectangular pyramid to be the ground-state structure. Spin-orbit coupling plays an important role in the isomer structures of Pt_5. For example, without spin-orbit coupling, the trigonal bipyramid is 0.142 eV more stable than the rectangular pyramid. When the spin-orbit coupling is applied, the rectangular pyramid becomes more stable only by 0.026 eV. A trapezoidal-type planar structure with NSO gives binding energy in between the previous two structures, though with SO its total energy is 0.047 eV higher than the trigonal bipyramid structure. For the ground state, we got another triplet planar structure, which is an almost square rectangle and with one side and the fifth atom forming an isosceles triangle. This has a binding energy of 2.978 eV/atom (NSO) and 2.797 eV/atom (SO), and its E_{SO} is 2.272 eV. Grönbeck *et al.* [8] also found a planar structure as a minimum energy state, but in our study this structure (the last one in Fig. 2) was found to be 0.327 eV (NSO) and 0.383 eV (SO) higher in energy. The E_{SO} for this structure is 2.215 eV. The E_{SO} for the other planar structure is 2.200 eV. The difference in energy between the two lowest-energy structures with NSO is 0.109 eV, whereas with SO it is almost two times higher, 0.215 eV. This is another indicator that spin-orbit coupling favors a planar structure. Also, the average bond length in the planar structures is almost the same, whereas in the 3D structures the average atomic separation is slightly larger. However, it can be said that spin-orbit coupling does not have a significant effect on the bond length of the isomers of Pt_5. For the most stable structures, the geometry remains almost the same before and after the inclusion of spin-orbit coupling.

For Pt_5, we consider the following dissociation channels:

$$Pt_5 \rightarrow Pt_4 + Pt, \tag{4}$$

$$Pt_5 \rightarrow Pt_3 + Pt_2, \tag{5}$$

$$Pt_5 \rightarrow Pt_2 + Pt_2 + Pt. \tag{6}$$

With NSO, the fragmentation energies are 3.974 eV, 3.863 eV, and 7.494 eV, respectively. With SO, these values are 3.873 eV, 3.967 eV, and 7.209 eV respectively. These energies show that with SO dissociation along the first reaction channel [Eq. (4)] is more favorable, where the end product Pt_4 has a planar structure. However, at NSO, Pt_4 is not a planar structure (Fig. 1). Interestingly, with NSO, the second channel [Eq. (5)] becomes the more favorable. The reason for the higher fragmentation energy in the third channel [Eq. (6)] is that it is the sum of the fragmentation energies for channels (4) and (3). It should be mentioned here that all fragmentation energies discussed so far are positive, indicating that the clusters are stable against any spontaneous dissociation to smaller fragments.

TABLE II. *l*-projected charge distribution per atom for the most stable Pt_n structures.

		Charge/atom		
Pt_n		*s*	*p*	*d*
Pt_2	NSO	0.605	0.069	7.825
	SO	0.626	0.067	7.753
Pt_3	NSO	0.527	0.106	7.950
	SO	0.531	0.110	7.906
Pt_4	NSO	0.585	0.149	7.795
	SO	0.590	0.159	7.782
Pt_5	NSO	0.607	0.160	7.817
	SO	0.615	0.171	7.785

In Table I, binding energies, spin-orbit coupling energies and HOMO-LUMO gaps are listed. We can see that binding energies per atom are increasing with the cluster size, and also, as discussed earlier, SO binding energies are always lower than the NSO binding energies. It is also to be noted that stability of Pt_3 over Pt_2 increases by 0.52 eV per atom, whereas from Pt_3 to Pt_4 or Pt_4 to Pt_5 the binding energy per atom increases by almost 0.3 eV per atom. The spin-orbit energies, E_{SO}, are also listed in Table I. Here, after Pt_3 these energies are increasing with the cluster size. Except for Pt_5, HOMO-LUMO gaps are decreased due to the spin-orbit coupling. These gaps, as listed in Table I, do not follow any specific pattern at the NSO level. On the other hand, at the SO level, these gaps increase with the cluster size, which might change if larger clusters were considered. It should be mentioned that one-particle energy eigenvalues of DFT do not represent actual excitation energies. In this view the HOMO-LUMO gap in the context of density functional theory can be considered only for qualitative discussion purposes.

In Table II, *l*-projected total charges for the *s*, *p*, and *d* orbitals are listed for the ground-state structures for each of the clusters. It should be noted that the sum of the total charge is not equal to the total valence charge due to the fact that the VASP code only projects the plane-wave part of the valence function and that only into an inscribed sphere. As one would expect for an equilateral triangle for Pt_3 with NSO, we find charge distribution on all the atoms to be equal to each other. The first point to be noted is that there are *p* contributions, albeit small, for all sizes of clusters, and the average *p* contribution per atom increases as the clusters get bigger. For example, in Pt_2 the *p*-orbital contribution is 0.067*e* per atom, whereas for Pt_5 it is 0.171*e* per atom, a total 155% increase in *p* contribution from that of Pt_2. On the other hand, the *d*-orbital contribution remained almost the same as the clusters got bigger, 7.753*e* per atom and 7.785*e* per atom for Pt_2 and Pt_5, respectively, which is only a 4.25% increase. This suggests that, in addition to *sd* hybridization, *sp* hybridization is an important feature of these clusters. This may be one of the major factors responsible for the planar structures of the platinum clusters studied here. One point to note that, except for the Pt dimer, inclusion of SO slightly increases the *s* and *p* contributions, while decreasing the *d* contribution. For both 3D structures of Pt_5, the *p*-orbital charge is higher and *s*-orbital charge is lower than that of the corresponding planar structures noted in the Table II. For the *d* orbital, it is a mixed picture. The p/s ratio of the charge contribution from Table II for Pt_3, Pt_4, and Pt_5 clusters are 0.208, 0.270, and 0.278, respectively, with spin-orbit coupling. With NSO, these numbers are 0.202, 0.255, and 0.263, respectively. This shows an increased contribution from the *p* orbital with respect to the *s* orbital as the clusters get bigger. For the two 3D structures of Pt_5, the p/s ratios are 0.343 (0.325) and 0.334 (0.311) with SO (NSO) for tetrahedral and rectangular pyramid, respectively, which clearly shows a higher *p* contribution. Hence, from these we can infer that clusters bigger than those studied here would be three dimensional. However, the issue of when this 2D to 3D transition takes place is a subject of further study.

In conclusion, we have studied the effect of spin-orbit coupling on platinum clusters, $Pt_n (n=2–5)$. Different structures, and their isomers of these clusters, were studied with and without spin-orbit coupling. Almost degenerate isomers and spin states pose the hardest problem in recognizing the ground-state structures for platinum clusters. Similar to the gold clusters, planar structures were found for these set of clusters when spin-orbit coupling was considered. We found that spin-orbit coupling has a significant effect on the stability of platinum clusters. Other than Pt_4, the ground-state structures do not change due to spin-orbit coupling. However, for Pt_5, we found that the relative stability of its isomers is affected by the spin-orbit coupling. So, to understand the physical behavior of Pt clusters theoretically, spin-orbit coupling is necessary.

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