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# Superatomic states in nickel clusters: Revising the prospects for transition metal based superatoms

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The geometries and electronic structures of small  $Ni_n^z$  clusters ( $n = 8, 9, 10$ ) ( $z = 0, \pm 1, 2$ ) have been elucidated for a range of multiplicities for each cluster size and charge, using density functional theory methods. These clusters have been found to conform in part to the existing superatomic model, with each cluster having a filled superatomic  $S$ -orbital, filled or partially filled superatomic  $P$ -orbitals, and empty or partially filled superatomic  $D$ -orbitals. Despite local states of mixed symmetry being present in the immediate vicinity of the Fermi energy, the addition or removal of a single electron from these systems causes a significant shift in the relative energies of the superatomic orbitals. In addition, this study demonstrates the possibility for  $d$ -electrons to contribute into superatomic orbitals to a greater or lesser extent, depending on the local environment. In summary, these observations lead to the prospect of a predictive model for electronic shell closings in some transition metal cluster systems. Published by AIP Publishing. <https://doi.org/10.1063/1.4990814>

## I. INTRODUCTION

Due to high thermodynamic stability, ionisation potential, and other properties which vary in systematic ways reminiscent of individual atoms, certain metal clusters have attracted considerable scrutiny in recent years.<sup>1–6</sup> These clusters are termed superatoms due to a global electronic structure which is akin to that of an individual atom, with a series of degenerate electron shells being observed which are similar to atomic orbitals. The occupancy of these shells is integral to understanding the physical nature of these clusters.

The primary model which succeeded in explaining this phenomenon is the jellium model. The jellium model treats the nuclei and core electrons of metallic clusters as a typically spherical, uniform smear of charge, forming a potential encompassing the volume of the cluster with the valence electrons of the constituent atoms confined to this potential.<sup>4</sup> This gives rise to a degenerate shell structure that is analogous to that observed in an individual atom. Whilst the ordering of these shells is sensitive to the shape of the potential that is confining them,<sup>4,7</sup> the Aufbau rule is generally

$$1S^2, 1P^6, 1D^{10}, 2S^2, 1F^{14}, 2P^6, 1G^{18}, \dots, \quad (1)$$

where  $S, P, D, F,$  and  $G$  represent the angular momentum character of the orbitals and the superscript denotes the degeneracy. We capitalise the symbols when superatomic orbitals are being referred to, for clarity.

When one of these superatomic shells reaches a closing number of electrons, known as “a magic number,” there is a marked increase in stability for the cluster, as is observed in

atomic orbitals. This has reliably explained why bare clusters of certain metals are discontinuous with respect to size in the gas phase,<sup>1,4</sup> but also why clusters of specific sizes can form macroscopic materials whilst maintaining their nanoscopic identity.<sup>6,8,9</sup>

In addition to the initial studies of simple  $s$ -electron metals, clusters such as  $Al_{13}^-$  have been shown to epitomise this behaviour, with 39 valence electrons from the aluminum atoms allowing the addition of a single electron to close the  $2P$  subshell.<sup>10–13</sup> In the context of  $s$  and  $p$  block metals and metalloids, it is a comparatively simple matter to devise an electron accounting rule for contributions to superatomic orbitals. Transition metals, on the other hand, have much more localised valence electron density in the  $d$ -orbitals, which impedes the formation of electronic shell structure, and they are also known to prefer high spin states in many cases due to the relative degeneracy of the  $d$ -orbitals. Thus the only transition metal for which superatomic clusters have been thoroughly explored is gold, with its single, delocalisable,  $s$ -electron; the other coinage metals are only exceptional in that their lower (chemical) stability makes them less attractive experimental targets.<sup>14–16</sup> Most other transition metals have been used only as dopants, specifically to introduce localised, magnetic, states into a superatomic cluster.

Small nickel clusters pose interesting questions due to the fact that they are comprised of  $d^{10}$  atoms, ostensibly with a  $d^9s^1$  electronic structure which can become a  $3d^{10}$  structure in the right circumstances.<sup>17</sup> This means that there are a variety of potential competing stabilising effects including Hund’s rule, closure of the  $3d$  subshell, and closure of superatomic orbitals if they are present. It is a common theme for studies of superatomic species involving transition metals, nickel in particular, to assert that  $d$ -orbitals are too localised to contribute to

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superatomic orbitals.<sup>18,19</sup> Thus it has been explicitly stated, for nickel atoms, that only one individual *s* electron per nickel atom can contribute into superatomic orbitals, despite that superatomic *S*, *P*, and *D* orbitals are apparent in the visualisation of molecular orbitals for the Ni<sub>5</sub> cluster. The apparent assumption is that this is exclusively due to contributions from the 4*s* orbitals.<sup>19</sup>

In the work of Medel *et al.* in 2011, atomic *d* orbitals were shown to contribute into the superatomic shell structure for the FeMg<sub>8</sub> cluster, which resulted in partial filling of the 2*D* subshell in accordance with Hund's rule.<sup>18</sup> This study demonstrated that the spatial overlap of the atomic 3*d* orbitals with the superatomic 2*D* orbitals resulted in the stabilisation of the 2*D* orbitals. In this work, the 2*D* orbitals are stabilised to the extent that they occur at lower energies than the 2*P* orbitals.

This work has been furthered by Lebon *et al.* in their work on superatomic Zn<sub>17</sub> clusters which are doped with various transition metal centres.<sup>20–22</sup> This work showed how the superatomic Zn<sub>17</sub> has a sufficient number of electrons to fill up to but not including the 2*P* subshell congruent with the superatomic Aufbau rule. With the addition of a transition metal centre, some localised atomic *d* states were responsible for maintaining a high magnetic moment in these clusters.

In this paper, we not only demonstrate the existence of superatomic structure for small nickel clusters, but we also show that atomic *d* orbitals cannot be neglected upon analysis of the superatomic structure.

## II. METHODS

The software packages employed for this Density Functional Theory (DFT) study were GAUSSIAN '09<sup>23</sup> and the Vienna *ab initio* simulation package (VASP).<sup>24–28</sup> Structural optimisation of the clusters was conducted using GAUSSIAN '09<sup>23</sup> employing the hybrid exchange-correlation functional PBE0<sup>29,30</sup> and the LANL2DZ<sup>31</sup> basis sets. The optimisation methodology employed throughout this study used experimentally elucidated stable structures for Ni atoms as well as structures obtained in previous work, to perform single point energy calculations at every multiplicity possible if the electrons were distributed across the 4*s* and 3*d* subshells.<sup>32</sup> The structure was subsequently optimised at the lowest energy multiplicity found to generate a new structure which was then used to repeat the single point energy step. The lowest energy structure was then taken as the ground state for that symmetry and the lowest energy multiplicity and structure for a given charge state were taken as the ground state for that charge. In conjunction with structure optimisations, frequency calculations were conducted to ensure that local minima had been reached. The coordinates and multiplicity of the ground state structures were subsequently utilised with VASP<sup>24–28</sup> with the projector augmented wave (PAW)<sup>33</sup> method using the generalised gradient approximation (GGA) exchange-correlation functional PBE<sup>29</sup> to perform a spin-polarised single point energy (SPE) calculation. The calculations were performed within a cube of edge length 26 Å, to avoid significant interaction between clusters in neighbouring cells, but minimise

computational cost. Due to the inherent challenges that arise from having high electron count molecular species within periodic boundary conditions, several changes needed to be specified in the input files in order to achieve convergence. The AMIX tag was set to 0.2 and the BMIX tag was set to 0.0001 for all clusters, and the AMIX\_MAG was set to 0.8 and the BMIX\_MAG was set to 0.0001 for all clusters. The effect of monopole/dipole/quadrupole corrections (IDIPOL = 4) and dipole-dipole corrections (LDIPOL = .TRUE.) on the density of states was tested and was found to be negligible for the interpretation of the electronic structure. The global electronic structure of the Ni<sub>*n*</sub><sup>*z*</sup> clusters, and consequently the symmetry of the electronic states for each cluster, was studied by projecting the Kohn-Sham functions from both the Gaussian '09 and VASP calculations of the ground state structure onto spherical harmonics providing a projected density of states (PDOS).<sup>34–37</sup> This projection was conducted within a sphere of radius 4 Å for each size of cluster with the centre of the sphere being the centre of mass of the clusters. In conjunction with the PDOS allowing for the study of the symmetry of the states within the global electronic structure, an atom centred projection allowed for some elucidation of the symmetry of the states that contribute into the global states. This atom centred projection will henceforth be referred to a projected local density of states (PLDOS).

## III. RESULTS AND DISCUSSION

In Fig. 1, the optimised structures are given, as a function of charge, for each of the Ni<sub>8</sub><sup>*z*</sup>, Ni<sub>9</sub><sup>*z*</sup>, and Ni<sub>10</sub><sup>*z*</sup> systems. The preferred multiplicity at the PBE0 level of theory is indicated by the number of unpaired electrons (UPE) as is shown in Fig. 1, and from this point forth the lowest energy charge state shall be referred to as the ground state.

The GS structures for the Ni<sub>8</sub><sup>*z*</sup> clusters were from +2 to -2, respectively; capped pentagonal bi-pyramid, capped pentagonal bi-pyramid, bidisphenoid, and bidisphenoid and bi-capped octahedron with the faces that the caps are on sharing no edges or vertices. For the Ni<sub>9</sub><sup>*z*</sup> clusters, the +2 and -2 clusters are both bicapped pentagonal bi-pyramids with the caps in the same half of the bipyramid. The +1, 0, and

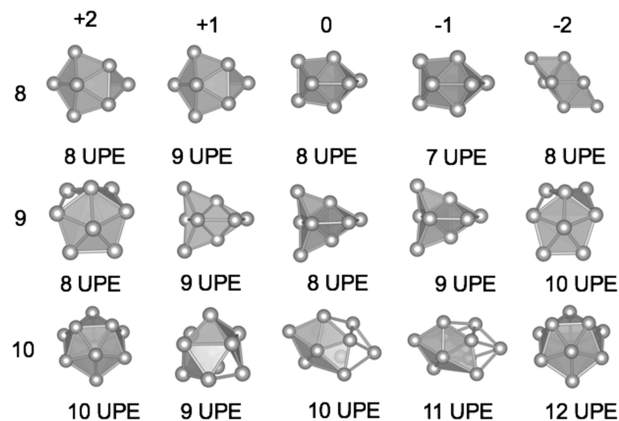


FIG. 1. Presented from top to bottom are the optimised structures for the Ni<sub>8</sub><sup>*z*</sup>, Ni<sub>9</sub><sup>*z*</sup>, and Ni<sub>10</sub><sup>*z*</sup> clusters, respectively, at the most stable multiplicity for each cluster size and charge, along with the number of unpaired electrons (UPE) for each cluster given below.

$-1$  charge states result in bicapped pentagonal bi-pyramids with the capping atoms in the same plane as the peaks of the pyramids and each other. For the  $\text{Ni}_{10}^z$  clusters, the  $+2$  and  $-2$  charge states were tricapped pentagonal bipyramids, which makes up half of an icosahedron, the neutral and  $-1$  charge state clusters were intersecting pentagonal bi-pyramids and the  $+1$  charge state is a capped square antiprism, where the cap is on one of the square faces, with a central atom. This final structure is important because it is the only cluster whose superatomic structure was analysed in which there was an endohedral atom. It is worth pointing out that all clusters have at least one unpaired electron per atom, with three notable exceptions. These three clusters are  $\text{Ni}_8^-$ ,  $\text{Ni}_9$ , and  $\text{Ni}_{10}^+$ , all of which have one fewer unpaired electron than their atom count.

Due to the fact that charged nickel clusters have not been studied extensively, to our knowledge, assessment of the accuracy of these structures has been restricted to the neutral species. Both the  $\text{Ni}_8$  and  $\text{Ni}_{10}$  cluster species have the same geometry that was elucidated in the gas phase nitrogen adsorption experiment performed by Parks *et al.* in 1994.<sup>32</sup> The disagreement between our structure for the  $\text{Ni}_9$  cluster and experiment could be attributed to the nitrogen adsorption experiment occurring at finite temperature; however theoretical studies have also observed the tri-capped trigonal prism structure.<sup>38</sup> Our different geometry can be attributed to the sensitivity of the structure to changes in multiplicity and the near degeneracy of the potential structures.

The stability of the negatively charged clusters with respect to ionisation has been evaluated by inspection of the adiabatic ionisation potentials (AIP), and while the singly charged clusters are all stable, the doubly charged anions have negative AIP at the PBE0 level. It is certain that doubly charged anions are a challenge for DFT; it is also clear that these clusters are small enough that they may not be able to support the absorption of a second electron. We do not propose to disentangle these two issues here, but to acknowledge only that the double anions may well not exist in the gas

phase. However the recent extension of the superatomic concept into the study of ligand protected clusters would suggest that this degree of modulation of the electronic structure is not unreasonable to study, and thus it is included here for completeness.

Examining the PDOS of the  $\text{Ni}_8^z$ ,  $\text{Ni}_9^z$ , and  $\text{Ni}_{10}^z$  clusters, presented on the left hand side of Figs. 2–4, respectively, it can be seen that there are states of clearly assignable symmetry alongside states of mixed symmetry at each size and charge. The states of clear symmetry have been assigned as superatomic shells due to the predominant  $S, P, D, F \dots$  ordering of the states, and this assignment is confirmed by visual inspection of the shapes of the orbitals.<sup>39</sup> The states of mixed symmetry according to this projection onto cluster centred spherical harmonics have been assigned as local states, which are predominantly due to atomic  $d$  electrons. This is supported through examination of the PLDOS which is presented on the right hand side of Figs. 2–4. As expected for these clusters, the addition or removal of a single electron has a significant effect on the relative energies of the superatomic states, rationalised as being due to the charge being distributed over the entire cluster.

By first examining the PDOS of the  $\text{Ni}_8^z$  clusters, as is shown in Fig. 2, it can be seen that the frontier superatomic orbitals are the  $1P$  and  $1D$ , indicating that there is approximately one electron per atom contributing into superatomic orbitals. This is further supported through examination of the  $\text{Ni}_8^+$  cluster, which is the first in descending number of electrons in which a  $1P$  orbital crosses the Fermi energy. Direct visualisation of the frontier orbitals verifies that the addition of a single electron to a cluster singly populates a superatom orbital with the notable exception of the previously mentioned  $\text{Ni}_8^-$  cluster. This cluster maintains the closed shell configuration of the  $\text{Ni}_8$  cluster, with the addition of a single electron instead of pairing with one of the localised electrons. From this, it can be inferred that the energetic cost to lowering the degeneracy of the cluster is lower than the cost of losing a closed shell configuration.

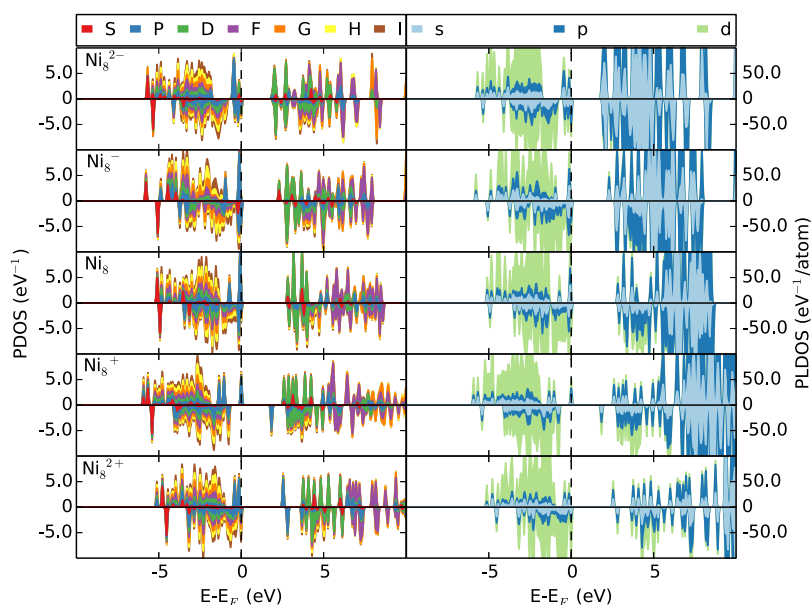


FIG. 2. Left: the PDOS for the  $\text{Ni}_8^z$  clusters presented from top to bottom in decreasing number of electrons. The positive values for density are indicative of the spin up component of the PDOS and the negative values are indicative of the spin down component. The density of each state is stacked on top of each other in order to make the PDOS map onto the density of states and allow for easier elucidation of the symmetry of the states. Right: the atomic orbital contribution to the DOS is given for comparison with the PDOS.

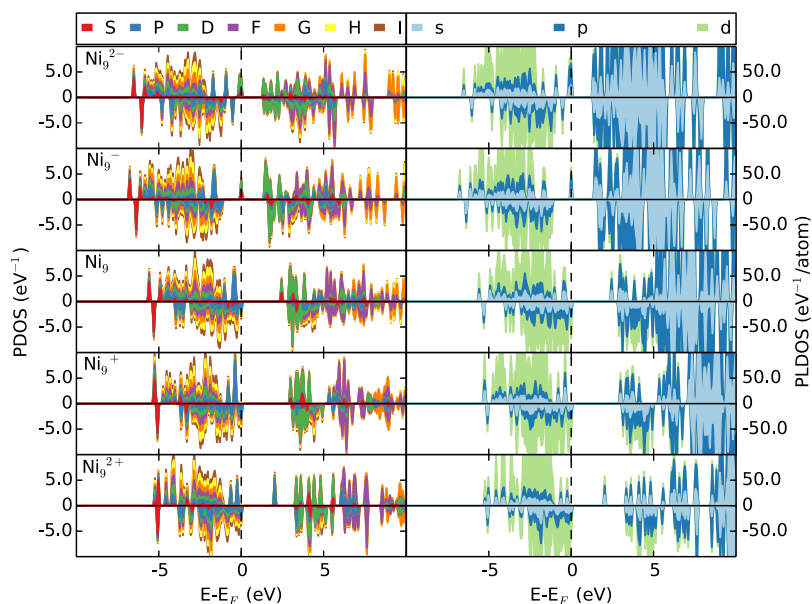


FIG. 3. Left: the PDOS for the  $\text{Ni}_9^z$  clusters presented from top to bottom in decreasing number of electrons. The positive values for density are indicative of the spin up component of the PDOS and the negative values are indicative of the spin down component. The density of each state is stacked on top of each other in order to make the PDOS map onto the density of states and allow for easier elucidation of the symmetry of the states. Right: the atomic orbital contribution to the DOS is given for comparison with the PDOS.

This is reminiscent of the phenomenon observed by Aguado and co-workers, where it was demonstrated that the addition of an adatom to closed shell zinc clusters did not result in population of the LUMO of the closed shell cluster.<sup>21</sup> Instead, a new localised state was observed to appear below the Fermi energy maintaining shell closure for the global electronic structure. While there are differences in the behaviour described here due to the complicating effects of spin multiplicity and charge, the similarity of these two cases does indeed suggest that the coexistence of localised and delocalised states will give rise to similar phenomena across a broad range of transition metal clusters.

The trends observed for the  $\text{Ni}_8^z$  clusters are also present in the  $\text{Ni}_9^z$  clusters, as is illustrated in Fig. 3 where successive addition of electrons causes shell closure of the  $\text{Ni}_9^+$  cluster  $1P$  subshell. As was observed for the  $\text{Ni}_8^z$  clusters, the addition of a single electron to the closed shell system does not cause population of the  $1D$  subshell but instead causes lowering of

the multiplicity of the system with  $\text{Ni}_9^z$  having fewer than one unpaired electron per atom. Subsequent addition of electrons to the nine atom system causes population of the  $1D$  orbitals as expected.

In line with the observed phenomena for the  $\text{Ni}_8^z$  and  $\text{Ni}_9^z$  clusters, Fig. 4 shows clear evidence of shell closure for both the  $\text{Ni}_{10}^+$  and  $\text{Ni}_{10}^{2+}$  clusters, with the  $\text{Ni}_{10}^+$  cluster having a reduction in the multiplicity of the cluster to fewer than one unpaired electrons per atom. As is expected, the  $\text{Ni}_{10}$  cluster starts to populate the  $1D$  subshell, which continues to fill with increasing numbers of electrons added to the system. A feature worth noting for the  $\text{Ni}_{10}^+$  cluster is that there are several low energy states which appear to be  $d$ -like. As opposed to this being indicative of some erroneous Aufbau rule, it is predicted that this is an artefact that arises as a result of there being a central atom. Any molecular orbital which has strong contributions from the  $d$  orbitals of the central atom will appear as  $D$  states in a projection which is centred on that atom.

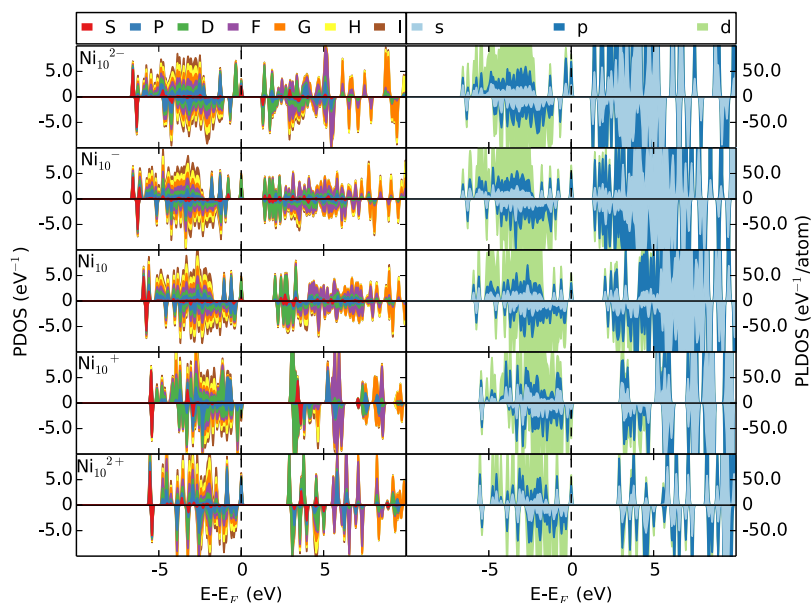


FIG. 4. Left: the PDOS for the  $\text{Ni}_{10}^z$  clusters presented from top to bottom in decreasing number of electrons. The positive values for density are indicative of the spin up component of the PDOS and the negative values are indicative of the spin down component. The density of each state is stacked on top of each other in order to make the PDOS map onto the density of states and allow for easier elucidation of the symmetry of the states. Right: the atomic orbital contribution to the DOS is given for comparison with the PDOS.

The other feature of interest amongst the  $\text{Ni}_{10}^z$  clusters is the narrow band which comprises the  $1D$  orbitals for the  $\text{Ni}_{10}^+$  clusters as well as the blue shifting of the  $2S$  orbitals for this cluster. The minimal splitting of the  $1P$  and  $1D$  orbitals is attributed to the roughly spherical symmetry of the cluster, meaning that the electronic environment of each orbital is approximately equivalent. The shifting of the  $2S$  orbitals to higher energies is attributed to the presence of a central atom which localises central electron density.<sup>40</sup> This causes destabilisation of the  $2S$  orbital causing it to shift relative to the  $1D$  orbital.

The PLDOS, as is shown on the right hand side of Figs. 2–4, reveals features which are consistent across all clusters. The  $1S$  orbitals have strong  $s$  and  $d$  contributions, the bands of mixed symmetry are predominantly comprised of  $d$  electrons, and states above the Fermi energy are predominantly comprised of  $s$  and  $p$  electrons. The frontier  $P$  orbitals appear to have strong  $s$ ,  $p$ , and  $d$  character; however, their proximity to the states of mixed symmetry makes this at times challenging to confirm.

To give further visual clarification of the difference between the superatomic states and the localised  $d$  states, Fig. 5 presents an orbital diagram for  $\text{Ni}_{10}^+$  with the PDOS presented below, for comparison. This was conducted by visual inspection of the spin up and spin down orbitals for this cluster.<sup>39</sup> This image illustrates that not only have the bands been correctly assigned as superatom orbitals but also that the system is indeed closed shell, with the  $1P$  orbital completely occupied. This also confirms that the low energy  $D$ -like states for this cluster are largely comprised of the  $d$  orbitals of the central Ni atom.

The  $\text{Ni}_{10}^+$  cluster illustrating shell closure is complex due to the fact that there is evidence to suggest that endohedral Ni atoms preferentially adopt a  $d^{10}$  local electronic structure<sup>20</sup> and as such may not necessarily be following the same trend as the other closed shell structures, where the additional electron

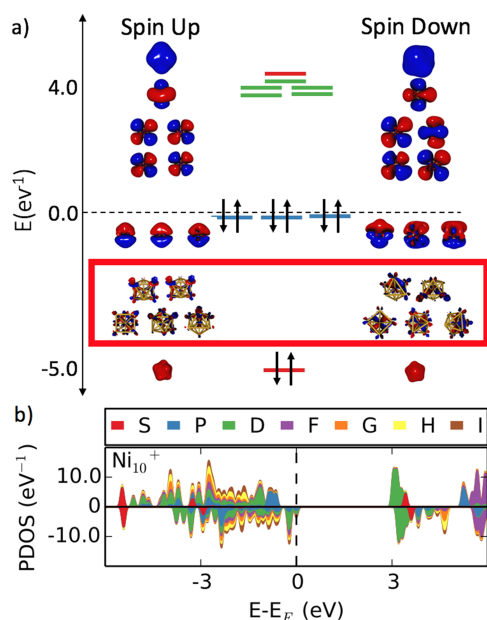


FIG. 5. The MOs for  $\text{Ni}_{10}^+$  are presented in part (a). These correspond to the states shown below in (b) in the PDOS for this cluster.

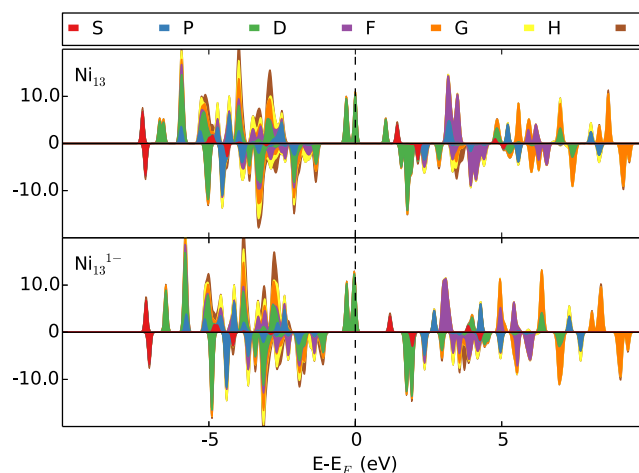


FIG. 6. The PDOS for the  $\text{Ni}_{13}$  and  $\text{Ni}_{13}^-$  clusters.

causes lowering of the degeneracy. As can be seen in Fig. 6, we have presented evidence that endohedral Ni atoms do indeed adopt  $d^{10}$  with the neutral 13 atom cluster having 12 assigned superatom electrons. With the addition of a single electron this cluster exhibits half filling of the  $1D$  subshell illustrating the presence of 13 superatom electrons.

Finally, we comment on the level of theory used to determine the preferred multiplicities of these clusters, as a function of size and charge state. The results presented have been obtained with the PBE0 functional, which through the inclusion of exact exchange partially corrects for the band gap error which is of significance for states close to the Fermi level.

However, the electronic structure has subsequently been obtained for the exact same structure with the PBE functional and in the VASP code based on PAW potentials, and we find a consistent analysis overall (see the [supplementary material](#)). While the quantitative prediction of HOMO-LUMO gaps is challenging for DFT, the assessment of the character of the states given here, and the magnetic states that these are based on, seems to be robustly described.

The effect of the inclusion of exact exchange in the PBE0 functional is apparent from inspection of the PDOS, even allowing for additional differences due to the use of periodic boundary conditions in VASP. The occupancy of the superatomic orbitals is consistent between PBE and PBE0 calculations; however, the hybrid functional results in a larger HOMO-LUMO gap, as expected. In addition, we see the differing effect of exact exchange on the localised and delocalised electronic states: the localised states of mixed symmetry are systematically shifted to lower energies, relative to the delocalised (superatomic) states. This can even lead to the promotion of the superatomic  $1P$  orbital above the localised, mixed states, in some cases even changing the qualitative character of the HOMO.

#### IV. CONCLUSION

In the framework of this study, DFT methods have been used to elucidate the geometric and electronic structure of  $\text{Ni}_n^z$  ( $n = 8, 9, 10$ ) ( $z = 0, \pm 1, 2$ ) clusters. In conjunction with states of mixed symmetry close to the Fermi energy,

these clusters exhibit clear superatomic structure, with the *P* and *D* subshells being the frontier superatomic orbitals. Although these clusters exhibit superatomic structure coexisting with states of local symmetry, we have shown that the addition or removal of an electron to our system causes an electronic rearrangement with a shift in energy for the superatomic orbitals. This means that the superatomic model should not be ignored as a driver of stability in these transition metal clusters.

In conjunction, we have shown that small nickel clusters contribute one electron per atom in the general case. Superatomic shell closing, however, can provide sufficient cause for this rule to be broken. This has consequences for the expected multiplicities of these clusters. In addition, this implies that the assumption that *d* electrons are too localized to contribute to superatomic orbitals should be reassessed.

## SUPPLEMENTARY MATERIAL

See [supplementary material](#) for the PDOS and the PLDOS for the  $\text{Ni}_n^z$  ( $n = 5, 6, 7$ ) ( $z = 0, \pm 1, 2$ ) clusters obtained using the same methods outlined in this manuscript. In conjunction with this, it contains the PDOS and PLDOS for the VASP calculations performed on the  $\text{Ni}_n^z$  ( $n = 8, 9, 10$ ) ( $z = 0, \pm 1, 2$ ) clusters. Finally it also contains all of the cluster symmetry and energy data for the most stable clusters at each size, charge, and multiplicity for the  $\text{Ni}_n^z$  ( $n = 5, 6, 7, 8, 9, 10$ ) ( $z = 0, \pm 1, 2$ ) clusters.

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