THEORETICAL CHEMISTRY

# Magnetic superatoms

Clusters of atoms are generally only stable enough to form superatoms when they have filled electron shells, so how can they have magnetic properties?

R. Bruce King

An area at the interface of physics and chemistry that has developed extensively in recent years is the study of clusters of atoms. In some cases, such an assembly of atoms can mimic the chemical behaviour of individual [**Au: OK?**] atoms and, thus, are sometimes called 'superatoms'. For example, a centred icosahedral aluminium cluster $Al_{13}^-$ has many of the properties of the chloride ion, including a particularly stable electronic configuration[1]. Thus, for the familiar chloride ion, this stable electronic configuration consists of eight valence electrons corresponding to the next noble gas, namely argon. For the cluster superatoms, a stable electronic configuration comprises the 40 valence electrons of the $Al_{13}^-$ cluster arising from the three valence electrons of each of the 13 aluminium atoms plus the negative charge.

The study of cluster superatoms has until now been concerned with species with stable electronic configurations, such as the 40 valence electrons of $Al_{13}^-$. In such stable electronic configurations, all of the electrons are paired and the resulting species are therefore non-magnetic. To produce materials with interesting magnetic properties, structures need to be designed with the maximum number of unpaired electrons. On page XXX of this issue[2], Khanna and collaborators report their development of a theoretical approach for the design of novel magnetic materials, referring to them as 'designer magnetic superatoms'. The materials discussed in their paper contain vanadium atoms embedded in alkali-metal hosts, with $VCs_8$ being the prototypical material. Their theoretical work relates to experimental studies on the Hall effect of thin films of sodium, potassium and caesium atoms containing vanadium impurities, which exhibit relatively large magnetic moments[3].

To understand the design of magnetic superatoms, the placing of electrons in the orbitals of spherical structures such as atoms or superatom clusters needs to be considered. Such orbitals can contain one or two electrons. The two electrons in a filled orbital are paired, thereby
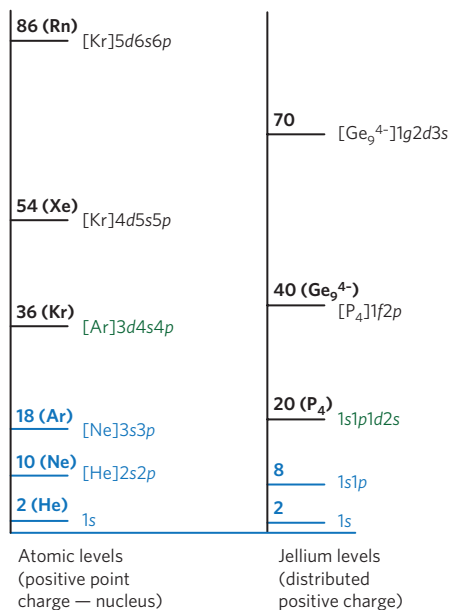


**Figure 1 |** A comparison of the energy levels (shells) for an atom and for a jellium sphere. The filled orbitals in $Mn^{2+}$ (for the atom) and $VCs_8$ (for the jellium sphere) are indicated in blue. The energy levels containing a half-filled $d$ shell for $Mn^{2+}$ and $VCs_8$ are indicated in green.

cancelling out their magnetic moments and removing the possibility of interesting magnetic properties. However, half-filled orbitals containing only single electrons can lead to such properties. [**Au: OK, to avoid repetition of 'interesting magnetic properties'?**] Thus, the design of interesting magnetic materials involves a search for accessible materials with a maximum number of half-filled molecular orbitals.

The orbitals containing single electrons or electron pairs in individual atoms or spherical clusters of atoms are grouped according to their energies into 'shells' consisting of orbitals of essentially the same energies. The numbers of orbitals in these shells are governed mathematically by patterns of spherical harmonics, thus implying the approximation of an atom or an atomic cluster by a sphere. Such shells

always contain odd numbers of molecular orbitals and are conventionally designated by the series of letters $s, p, d, f, g, h, \ldots$ corresponding to shells containing 1, 3, 5, 7, 9, 11, $\ldots$ orbitals, respectively. The relative energies of the shells of different types in a spherical structure depend on the distribution of the positive charge counterbalancing the negative charge of the electrons. For atoms, with the positive charge concentrated in a small nucleus in the centre, the distribution of the shells follows the familiar pattern of atomic orbitals. The very unreactive noble gases helium, neon, argon, krypton, xenon and radon correspond to the 'magic-number' closed-shell configurations of 2, 10, 18, 36, 54 and 84 electrons, respectively.

The situation is quite different for a superatom cluster such as $Al_{13}^-$, which consists of a collection of atoms in a compact spherical arrangement, generally called a jellium sphere[4,5]. In this case, the counterbalancing positive charge is divided between the nuclei of the atoms forming the cluster rather than being concentrated at a single point in the centre. Such a jellium sphere, with the positive charge distributed throughout the sphere rather than concentrated at the centre, has an orbital shell distribution different from that of a single atom (Fig. 1). The magic numbers of 2, 8, 20 and 40 electrons for clusters modelled by a jellium sphere are thus seen to differ from those of an individual atom[6]. The cluster $Al_{13}^-$ is an example of a jellium sphere with the magic number of 40 electrons[1]. White phosphorus, which is a tetrahedral $P_4$ molecule, is an example of a jellium sphere with the magic number of 20 electrons.

To maximize the magnetic moment of an individual atom or atomic ion, a species is needed with a half-filled shell. A familiar atomic species with a half-filled $3d$ shell is the manganese(II) ion, $Mn^{2+}$, which is found in typical manganese salts, such as the chloride or sulphate. The $Mn^{2+}$ ion has five electrons in excess of the closed-shell 18-electron argon configuration, which consists of the nine orbitals in the $1s, 2s, 2p, 3s$ and $3p$ [**Au: OK?**] shells, each containing

an electron pair. The 'extra' five electrons of $Mn^{2+}$ are placed singly into each of the five orbitals of the $3d$ shell so that they are all unpaired. These five unpaired electrons correspond to the maximum number of unpaired electrons for a single atom until the $f$ block of elements is reached much farther down the periodic table.

The $VCs_8$ superatom of Khanna and collaborators[2] is the superatom analogue of $Mn^{2+}$. The neutral vanadium atom with five valence electrons is isoelectronic with the $Mn^{2+}$ ion. For practical reasons, the neutral species $V^0$ is chosen rather than the ion $Mn^{2+}$, because the outer $Cs_8$ unit is strongly reducing owing to the thermodynamically favourable oxidation to $8Cs^+$. The electronic configuration of $VCs_8$, considered as a jellium sphere (Fig. 1), consists of the five vanadium electrons in excess of the closed-shell eight-electron configuration, which contains the four orbitals in the $1s$ and $1p$ [**Au: OK?**] shells, each with an electron pair. The extra five electrons from the vanadium atom are then placed singly into each of the five orbitals of the $1d$ shell so that they are all unpaired.

This theoretical discovery of Khanna and collaborators[2] suggests a completely new class of materials for which some experimental evidence has been obtained in the unusual medium of alkali-metal films. Such exotic media are not likely to be useful for many practical applications, because of their air sensitivity. However, the ideas from this paper may eventually be useful in designing stable magnetic molecules consisting of central units magnetically equivalent to $VCs_8$ protected by suitable combinations of external ligands[3].

*R. Bruce King is in the Department of Chemistry and Center for Computational Chemistry, University of Georgia, Athens, Georgia 30602, USA.*
*e-mail: rbking@chem.uga.edu*

### References
1. Bergeron, D. E., Castleman, A. W. Jr, Morisato, T. & Khanna, S. N. *Science* **304,** 84–87 (2004).
2. Reveles, J. U. *et al. Nature Chem.* **1,** XXX–XXX (2009).
3. Song, F. & Bergmann, G. *Phys. Rev. Lett.* **88,** 167202 (2002).
4. De Heer, W. A. *Rev. Mod. Phys.* **65,** 611–676 (1993).
5. Castleman, A. W. Jr & Khanna, S. N. *J. Phys. Chem. C* **113,** 2664–2675 (2009).
6. King, R. B. & Silaghi-Dumitrescu, I. *Dalton Trans.* 6083–6088 (2008).