

Extension of the statistical theory of resonating valence bonds to hyperelectronic metals

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ABSTRACT The statistical treatment of resonating covalent bonds in metals, previously applied to hypoelectronic metals, is extended to hyperelectronic metals and to metals with two kinds of bonds. The theory leads to half-integral values of the valence for hyperelectronic metallic elements.

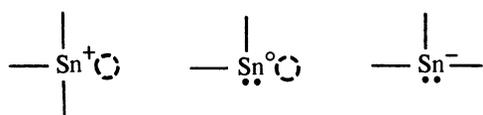
A theory of resonating covalent bonds in metals, developed over the period 1938–1953 (1–3), was recently refined by the formulation of a statistical treatment for hypoelectronic metals (4). We have now extended the statistical treatment to include hyperelectronic metals. This extension has resulted not only in the evaluation of the number of resonance structures for these metals but also in the determination for them of the values of the metallic valence, which have been somewhat uncertain.

In the discussion of hypoelectronic metals in ref. 4, the number of ways of distributing $Nv/2$ bonds among $NL/2$ positions in a crystal containing N atoms with valence v and ligancy L was evaluated. The number per atom is the N th root of this quantity. Structures for which the number of bonds on any atom is other than $v - 1$, v , or $v + 1$ were then eliminated with use of the binomial distribution function [only the charge states M^+ , M^0 , and M^- are allowed by the electroneutrality principle (5)]. In this way the following expression for ν_{hypo} , the number of resonance structures per atom for a hypoelectronic metal, was obtained:

$$\nu_{\text{hypo}} = \frac{v^{v/2}(L-v)^{(L-v)/2}L!}{L^{L/2}v!(L-v)!} \left(\frac{L-v}{L-v+1} + 1 + \frac{v}{v+1} \right). \quad [1]$$

HYPERELECTRONIC METALS

A requirement for metallic character is that unsynchronized resonance of covalent bonds occur, which means that M^+ and M^0 have an unoccupied orbital available to accept an additional bond, changing them to M^0 and M^- , respectively. M^- does not need the extra orbital, because it cannot change to M^{2-} . A hyperelectronic metal is one in which the number of outer electrons is greater than the number of outer orbitals, not including the metallic orbital. An example is metallic tin, with 14 outer electrons and 9 outer orbitals (6s, three 6p, five 5d). Sn^+ and Sn^0 have five unshared electron pairs, and Sn^- has six. Sn^+ and Sn^- form three covalent bonds, and Sn^0 forms two. Sn^+ and Sn^0 have a metallic orbital, and Sn^- does not. They may be represented as



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Here the broken circle represents the metallic orbital.

It is evident that the calculation of the number of resonating structures must be made in a different way from that for hypoelectronic metals, because M^+ and M^- form the same number of bonds and are therefore classed together in the calculation of the number of ways of distributing the bonds. We consider first the valence v of a hyperelectronic metal whose neutral atoms form z bonds and whose ions M^+ and M^- form $z + 1$ bonds. For any atom, with average valence v , the number of structures, b , having n bonds, is, by the assumption used previously (4), proportional to the probability given by the binomial distribution:

$$b(L, v, n) = w' \frac{v^n (L-v)^{(L-n)} L!}{L^n n! (L-n)!}. \quad [2]$$

Here w' , the proportionality constant, is the total number of structures per atom without constraint as to the number of bonds (in the range 0 to L).

To evaluate the valence, we represent the fractions of M^+ , M^0 , and M^- by y , x , and z , respectively. The ratio of the number of neutral atoms (M^0) to ions (M^+ and M^-) is then

$$\frac{x}{2y} = \frac{b(L, v, z)}{b(L, v, z+1)} = \frac{(L-v)(z+1)}{v(L-z)}. \quad [3]$$

In addition, we have the following constraints:

$$x + 2y = 1 \quad [4]$$

$$v = xz + 2y(z+1). \quad [5]$$

Eqs. 3, 4, and 5 have one solution in the range $z \leq v \leq z + 1$:

$$v = z + \{f(f+1)\}^{1/2} - f, \quad [6]$$

in which

$$f = \frac{z(L-z)}{L-2z-1}. \quad [7]$$

Valence of Hyperelectronic Metals. Cu, Ag, and Au have $z = 5$ and $L = 12$. Eqs. 6 and 7 lead to $v = 5.4965$ for these metals. Each atom of Zn, Cd, and Hg forms six short bonds and six long (presumably weaker) bonds. The effective ligancy is between 6 and 12, which with $z = 4$ gives the range $v = 4.5585$ – 4.4888 . For Sn, with $z = 2$ and four short bonds and two long bonds, L between 4 and 6, the range of values of v is 2.5359–2.4949. For all of the hyperelectronic metals, v equals $z + 1/2$ when the ligancy becomes $2z + 1$, corresponding to half bonds.

Because of the approximation of all of these values to $z + 1/2$, it is, we suggest, justified to assume the half-integral values of the valence of hyperelectronic metals, as was done in 1949 on an empirical basis (2).

The Number of Resonance Structures. In calculating the number of resonance structures per atom, ν , for hyperelectronic metals with $\nu = z + 1/2$, we use the same statistical method as for hypoelectronic metals except that the factor $2^{1/2}$ is introduced to correct for the fact that there are two kinds of atoms forming $z + 1$ bonds, M^+ and M^- , which differ in that M^- has an unshared electron pair and M^+ does not have one. The equation for ν_{hyper} is

$$\nu_{\text{hyper}} = \frac{2^{1/2} L! \nu^{(\nu-1)/2} (L - \nu)^{(L-\nu+1)/2}}{L^{L/2} (\nu - 1/2)! (L - \nu + 1/2)!} \left(1 + \frac{\nu(L - \nu + 1/2)}{(\nu + 1/2)(L - \nu)} \right). \quad [8]$$

This equation is the hyperelectronic analog of Eq. 1.

Values of ν_{hyper} are usually a little larger than those of ν_{hypo} ; for example, they are 33.45 and 33.26, respectively, for $L = 12$, $\nu = 4.5$.

Structures with Two Different Bond Lengths. Eq. 8 and the corresponding equation for hypoelectronic metals apply to crystals in which the bonds all have the same length. For a crystal in which each atom forms two kinds of bonds, L_1 bonds with bond number $n_1 = \nu_1/L_1$ and L_2 bonds with bond number $n_2 = \nu_2/L_2$, the value of ν_{hypo} is

$$\nu = C \sum_{n=\nu-1}^{\nu=1} \sum_{i=\min(0, n-L_2)}^{\max(n, L_1)} \frac{\nu_i^i (L_1 - i)^{L_1 - i}}{i! (L_1 - i)!} \frac{\nu_2^{n-i} (L_2 - \nu_2)^{L_2 - n + i}}{(n - i)! (L_2 - n + i)!} \quad [9a]$$

with

$$C = L_1! L_2! [L_1^{\nu_1} \nu_1^{\nu_1} (L_1 - \nu_1)^{L_1 - \nu_1}]^{-1} L_2^{\nu_2} \nu_2^{\nu_2} (L_2 - \nu_2)^{L_2 - \nu_2}]^{-1/2}. \quad [9b]$$

For a hyperelectronic metal with two different bond lengths the equation is the same as Eq. 9 except that the sum over n is for only $n = \nu - 1/2$ and $n = \nu + 1/2$ and there is an extra factor $2^{1/2}$ in the expression for C .

When $\nu_1/L_1 = \nu_2/L_2 = \nu/L$ Eq. 9a reduces to Eq. 1 and the hyperelectronic counterpart of Eq. 9a reduces to Eq. 8 and there is an extra factor $2^{1/2}$ in the expression for C .

The amount of resonance energy for a metal or intermetallic compound is determined by the number of resonance structures. The resonance energy affects the covalent radius, the stability (as evidenced by the resistance of the noble metals to chemical attack), and other properties, in ways that we hope to discuss later.

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