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## Comment on "A quantitative definition of hypervalency" by M. C. Durrant, *Chem. Sci.*, 2015, 6, 6614

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Consideration is given to (electronically) hypervalent increased-valence structures, which possess 2c–1e bonds, fractional 2c–2e bonds, and usually normal 2c–2e bonds. For singlet-spin electron-rich systems, increased-valence structures, with Heitler–London 2c–2e bond wavefunctions, are equivalent to resonance between non-hypervalent Kekulé and Dewar (or singlet diradical) type Lewis structures. Dewar structures are not considered in the *Chem. Sci.* 2015, 6, 6614 Edge article on hypervalency. Using one-electron delocalizations from lone-pair atomic orbitals into separate bonding molecular orbitals, increased-valence structures for  $\text{PCl}_5$ ,  $\text{O}_3$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{N}_2\text{O}_4$  and  $\text{S}_\text{N}2$  reactions are derived from the Edge-article's Kekulé-type Lewis structures, and compared with the Edge article's hypervalent structures with 2c–2e bonds. It is also shown that Durrant's method to determine the  $\gamma$  parameter for XAY-type systems that possess a symmetrical 3c–4e bonding unit is related to the A-atom charge density.

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### Introduction

Durrant<sup>1</sup> has provided a quantitative definition of hypervalency *via* reference to atomic charges, which were obtained either from experimental or from theoretical electron densities using Bader's quantum theory of atoms in molecules (QTAIM) methodology.<sup>3</sup> Without calculation it was not usually possible to conclude whether a given molecule was hypervalent. For example, the hypercoordinate molecules  $\text{CLi}_6$  and  $\text{SiH}_6^{2-}$  were calculated<sup>1</sup> to be hypervalent and non-hypervalent, respectively.<sup>4</sup>

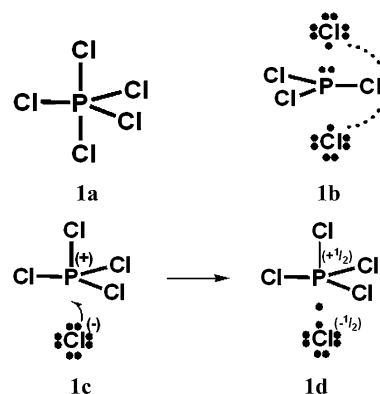
For this comment on hypervalence (primarily for electron-rich molecules), we use and discuss types of hypervalent VB structures that were not considered in ref. 1, and which, since 1968,<sup>8,9</sup> have been designated as "increased-valence" structures without expansion of valence shells. They involve 2-centre, 1-electron (2c–1e) bonds and fractional 2c–2e bonds (with bond-numbers less than unity, and represented by thin bond lines),<sup>6,8,9</sup> and usually non-fractional 2c–2e bonds.

In Schemes 1, 2 and 4–6, increased-valence structures for  $\text{PCl}_5$ ,  $\text{O}_3$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{N}_2\text{O}_4$  are generated from Lewis octet VB structures and compared with the non-octet hypervalent VB structures displayed in ref. 1, namely structures 1a, 2c, 4c, 5c and 6c here. Brief consideration is also given to increased-valence structures for  $\text{S}_\text{N}2$  reactions.

For illustrative purposes, in the Appendix we show that Durrant's method to determine the  $\gamma$  parameter of ref. 1 for XAY-type systems with a symmetrical 3c–4e bonding unit is related to the A-atom charge density obtained from a 3c–4e molecular orbital (MO) configuration. Consideration is also given to the A-atom valence.

### Increased-valence structures and hypervalence

For  $\text{PCl}_5$ ,  $\text{O}_3$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{N}_2\text{O}_4$ , Durrant<sup>1</sup> has displayed two types of Lewis VB structures that involve non-fractional (2c–2e)

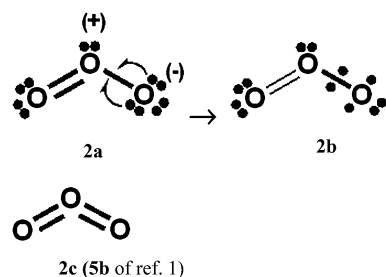


**Scheme 1** Hypercoordinate  $\text{PCl}_5$  valence-bond (VB) structures. Here and in Schemes 2–6, (non-variationally best) atomic formal charges for increased-valence structures are assigned on the assumption that bonding electrons are shared equally by pairs of adjacent atoms,<sup>9</sup> and mirror-image structures are not displayed. Of course the extent of delocalization differs for non-equivalent 3c, 4e bonding units.

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Scheme 2 O<sub>3</sub> VB structures.

bonds between pairs of adjacent atoms, namely familiar, non-hypervalent octet Kekulé type structures **1c**, **2a**, **3a**, **4a**, **5a** and **6a**, and the hypervalent structures **1a**, **2c**, **4c**, **5c**, and **6c** that violate the octet rule. For electron-rich hypercoordinate molecules, such as PCl<sub>5</sub> (*cf.* Scheme 1 of ref. 1 and Scheme 1 here) and for the electron-rich non-hypercoordinate molecules and ions O<sub>3</sub>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and N<sub>2</sub>O<sub>4</sub>, 2c–2e bonds are the only types of bonds that are present in both types of Lewis VB structures.

Dewar/singlet diradical types of Lewis VB structures, such as **1b** and **3b–3d**, were not considered in ref. 1. In ref. 6, it is indicated that hypervalency for electron-rich systems arises when Dewar/type structures participate in resonance with the Kekulé type structures.

When relevant atomic orbitals (AOs) overlap, Lewis-type VB structures for electron-rich species can be stabilized *via* 1-electron delocalizations from separate lone-pair AOs into 2-centre bonding MOs or bond orbitals (BOs), as is shown, for example, in structures **1c** for PCl<sub>5</sub> in Scheme 1, and **2a**, **4a**, **5a** and **6a** for O<sub>3</sub>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and N<sub>2</sub>O<sub>4</sub> in Schemes 2 and 4–6. The resulting VB structures, **1d**, **2b**, **4b**, **5b** and **6b** possess (thin-bond line) fractional 2c–2e bonds and 2c–1e bonds, as well as normal 2c–2e bonds.

By inspection, one can see that more electrons participate in bonding in VB structures **1d**, **2b**, **4b**, **5b** and **6b** than does occur in the Lewis Kekulé structures **1c**, **2a**, **4a**, **5a** and **6a**. Therefore **1d**, **2b**, **4b**, **5b** and **6b** are examples of “increased-valence” structures<sup>6,8,9</sup> without expansion of the valence shell. Because relative to the octet Lewis structures, increased-valence structures involve additional electrons in both nearest-neighbour and non-neighbour bonding, increased-valence structures are hypervalent relative to the Lewis structures.<sup>6,8,9</sup>

### Some properties of increased-valence structures

With Heitler–London AO type wavefunctions for 2c–2e bonds – for example  $a(1)b(2) + b(1)a(2)$  for the 2c–2e A–B bond – increased-valence structures for electron-rich molecules summarize resonance between two types of Lewis structures, namely the familiar, standard/Kekulé type Lewis octet structures, and “long-bond”/formal bond/singlet diradical/Dewar type Lewis (octet) structures. As indicated already, the latter type of Lewis VB structure is not considered in ref. 1. For the O<sub>3</sub> increased-valence structure **2b**, these two types of Lewis octet structures (namely structure **3a** and structures **3b–3d**) are displayed in Scheme 3. None of them is hypervalent, but resonance

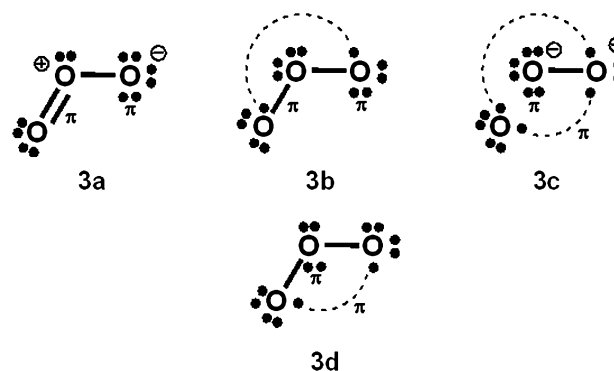
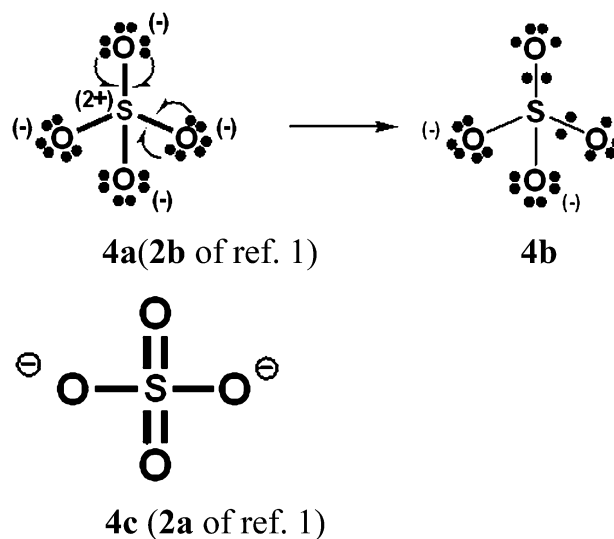
between them generates hypervalence for the resulting increased-valence structure.

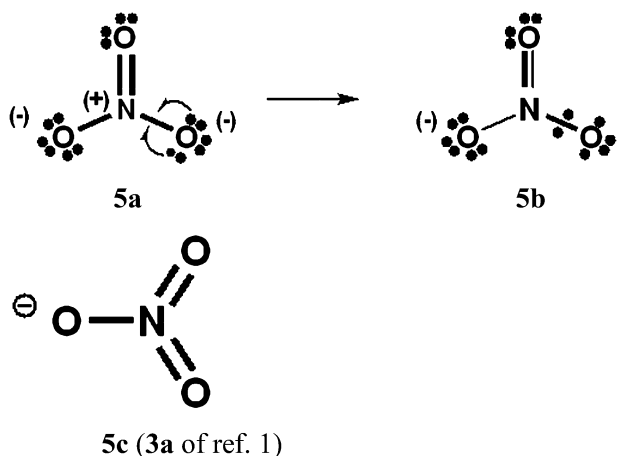
The PCl<sub>5</sub> and O<sub>3</sub> Dewar structures **1b**, **3b** and **3d** do not carry atomic formal charges, and **1b** and **3d** in particular were not considered by Durrant.

For an increased-valence structure that does not involve a valence shell expansion to provide an additional AO for bonding, none of the component Lewis structures violates the octet rule, but resonance between them to generate the increased-valence structure leads to (an apparent) violation of the octet rule.<sup>6,8,9</sup>

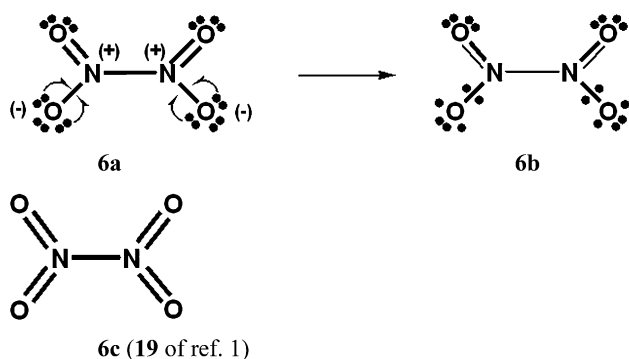
### Increased-valence structures for SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and N<sub>2</sub>O<sub>4</sub>

In Schemes 4–6, we have generated increased-valence structures for SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and N<sub>2</sub>O<sub>4</sub> from familiar octet Kekulé type Lewis structures *via* 2c–1e delocalizations of oxygen O<sup>-</sup> electrons. In these figures, the hypervalent VB structures with only 2c–2e bonds displayed in ref. 1 are also displayed. We suggest that the

Scheme 3 Component Kekulé and Dewar/singlet diradical Lewis structures for increased-valence structure **2b** of Scheme 2.Scheme 4 SO<sub>4</sub><sup>2-</sup>. As well as structure **4b**, another type of increased-valence structure can be constructed with four fractional 2c–2e bonds + four 2c–1e bonds and oxygen atom formal charges of  $-1/2$ .



Scheme 5  $\text{NO}_3^-$ . As well as 5b, another type of increased-valence structure can be constructed, with two fractional  $2c-2e$  bonds and two oxygen atoms with formal charges of  $-1/2$ .



Scheme 6  $\text{N}_2\text{O}_4$  with  $D_{2h}$  symmetry. The 16 component Kekulé and Dewar Lewis structures are displayed in ref. 9a and b, as well as an increased-valence structure for an ONONO<sub>2</sub> isomer. There are two "cis" type structures for each of 6a and 6b, and two "trans" type structures.

increased-valence structures with 1-electron bonds and fractional  $2c-2e$  bonds provide better insight into the possible origin of some molecular properties than do the hypervalent VB structures of ref. 1. For example:

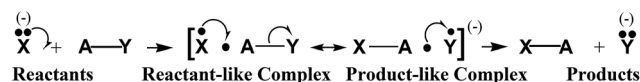
(a) The fractional N–N  $2c-2e$  bond in the increased-valence structure 6b for  $\text{N}_2\text{O}_4$  is in accord with the presence of a long, weak N–N single bond.<sup>9</sup>

(b) The results of VB calculations for  $\text{O}_3$  and related 1,3-dipolar systems from numerous laboratories – see for example ref. 7d and e and 10 and references therein – indicate that their ground-states possess substantial singlet-diradical character. It arises primarily from the contribution of the Lewis structure 3d of Scheme 3 to the ground-state Lewis structure resonance scheme. In contrast to structure 2c (*i.e.* structure 5b of ref. 1), increased-valence structure 2b of Scheme 2 reflects the diradical character.

### $S_N2$ reactions

With Coulson–Fischer<sup>11</sup> type BOs ( $a + k_1b$ ) and ( $b + k_2a$ ) replacing the  $a$  and  $b$  AOs of the Heitler–London wavefunction for

a  $2c-2e$  bond, the course of an  $S_N2$  reaction,  $\text{X}^- + \text{AY} \rightarrow \text{XA} + \text{Y}^-$  has been formulated<sup>12</sup> as



For it, the increased-valence structures for the  $(\text{XAY})^-$  reactant-like and product-like complexes, each with an additional bonding electron relative to the  $\text{AY}$  reactant and  $\text{XA}$  product, are both hypercoordinate and hypervalent relative to the VB structures for the latter species.

### Further comments and conclusion

When 2-centre Coulson–Fischer type BOs, such as the  $a + k_1b$  and  $b + k_2a$  above, are used to accommodate the electrons that form the fractional  $2c, 2e$  bonds in the increased-valence structures, allowance can be made for polarization of these bonds.

In ref. 13, the wavefunctions for 3c–4e VB structures of the types  $\text{X}-\text{A}-\text{Y}$  (as would occur in the Durrant structures 2c, 5c and 6c for  $\text{O}_3$ ,  $\text{NO}_3^-$  and  $\text{N}_2\text{O}_4$  if expansion of the valence shell does not occur) and  $\bullet\text{X} \bullet \text{A} \bullet \text{Y}\bullet$ , and the Rundle-Hach<sup>14</sup>–Pimentel<sup>15</sup> 3c–4e MO configuration have been shown to be special cases of wavefunctions for resonance between the increased-valence structures  $\bullet\text{X} \bullet \text{A}-\text{Y}$  and  $\text{X}-\text{A} \bullet \text{Y}\bullet$ , with 2-centre Coulson–Fischer orbitals, and one variational parameter.<sup>16</sup>

Increased-valence structures can also be constructed for: (a) systems that involve 3c–3e bonding units,<sup>17</sup> with non-reactant and non-product ionic structures replacing the singlet-diradical structures of electron-rich systems, and (b) diatomic molecules.<sup>18</sup>

Regardless of the method used to construct the wave-functions for increased-valence structures, because they involve the participation of more electrons in bonding than do the Kekulé-type Lewis structures from which they are derived, increased-valence structures are hypervalent relative to these Lewis structures. As indicated above, for electron-rich systems, this is due to the inclusion of singlet diradical structures in the Lewis structure resonance scheme. Also, increased-valence structures involve at least one Pauling three-electron bond as a diatomic component.<sup>9</sup>

## Appendix: valence electron equivalent parameter $\gamma(\text{A})$ and atomic valencies

In ref. 1, the valence electron equivalent parameter  $\gamma(\text{A})$  for atom  $\text{A}$  is used to determine whether a molecule exhibits hypervalence.<sup>19</sup> Here for the linear, symmetrical, triatomic systems of Table 1, each with one 3c–4e bonding unit, we shall show that the Durrant method<sup>1</sup> to construct  $\gamma(\text{A})$  is equivalent to a method that uses a 3c–4e MO configuration with AO overlap integrals omitted.

### MO wavefunction

As the wavefunction for the 3c–4e electrons, we shall use the Hach–Rundle–Pimentel MO configuration<sup>14,15</sup> of eqn (1).



Table 1  $\gamma(\mathbf{A})$  and A-atom valencies

Molecule	A-atom charge <sup>1</sup>	$k^2$	$\gamma(\mathbf{A})$	A-Atom valence
F <sub>3</sub> <sup>-</sup>	-0.056	2.13 <sub>7</sub>	8.11	1.35
ClF <sub>2</sub> <sup>-</sup>	+0.291	1.09 <sub>8</sub>	7.42	1.11
Cl <sub>3</sub> <sup>-</sup>	-0.019	2.07 <sub>7</sub>	8.04	1.34
BrCl <sub>2</sub> <sup>-</sup>	+0.108	1.16 <sub>0</sub>	7.78	1.27
ICl <sub>2</sub> <sup>-</sup>	+0.263	1.16 <sub>7</sub>	7.47	1.14
XeF <sub>2</sub>	+1.230	1.25 <sub>2</sub>	7.54	1.17
KrF <sub>2</sub>	+1.003	1.98 <sub>8</sub>	7.99	1.06
XeCl <sub>2</sub>	+0.763	3.24 <sub>2</sub>	8.47	1.37

$$|\psi_1^\alpha \psi_1^\beta \psi_2^\alpha \psi_2^\beta| \propto |(2x + ka)^\alpha (2x + ka)^\beta (2y + ka)^\alpha (2y + ka)^\beta| \quad (1)$$

The  $x$ ,  $a$  and  $y$  are the overlapping AOs on the three atomic centres, and  $\psi_1 = x + ka + y$  and  $\psi_2 = x - y$  are the bonding and non-bonding MOs that can be constructed from them.<sup>14,15</sup>

The right-hand side of eqn (1) gives the valence-bond structure<sup>21</sup>  $(\mathbf{X}-\mathbf{A}-\mathbf{Y})^q$ , with fractional 2c-2e bonds that arise from double-occupation of two non-orthogonal BOs, and  $q = -1$  or 0.

To determine the value for  $k$ , we equate the charge  $Q_{\mathbf{A}}$  of ref. 1 for atom  $\mathbf{A}$  to  $X_{\mathbf{A}} - 2k^2/(k^2 + 2)$ . The  $X_{\mathbf{A}}$  is the core charge of atom  $\mathbf{A}$  when the 3c-4e electrons are removed, and  $2k^2/(k^2 + 2) = P_{\text{aa}}$  is the A-atom charge density that arises from the 3c-4e bonding. For the neutral species and anions of Table 1,  $X_{\mathbf{A}} = 2$  and 1, respectively.

### Durrant's method<sup>1</sup> to construct $\gamma(\mathbf{A})$

To construct the  $\gamma(\mathbf{A})$  parameter for the systems considered in Table 1, initially we follow Durrant's methodology,<sup>1</sup> as described in ref. 1 for CO, and for SCl<sub>4</sub> in the ESI for ref. 1. We use the expanded valence-shell (hypervalent) covalent structure  $\mathbf{X}-\mathbf{A}^{(q)}-\mathbf{Y}$  (with two non-fractional 2c-2e bonds) and the ionic structure  $\mathbf{X}^{(-)}\mathbf{A}^{(q+2)}\mathbf{Y}^{(-)}$  (with  $q = X_{\mathbf{A}} - 2$ ).

These structures are weighted according to the value of  $q = X_{\mathbf{A}} - 2$  so that the QTAIM charge  $Q_{\mathbf{A}}$  of ref. 1 is reproduced *via* eqn (2)

$$xq + (1 - x)(q + 2) = Q_{\mathbf{A}} \quad (2)$$

to give  $x = (X_{\mathbf{A}} - Q_{\mathbf{A}})/2$ .

The  $\gamma(\mathbf{A})$  is then calculated from eqn (4) *via* eqn (3),

$$\gamma(\mathbf{A}) = 10x + 6(1 - x) \quad (3)$$

$$= 6 + 2(X_{\mathbf{A}} - Q_{\mathbf{A}}) \quad (4)$$

in which 10 and 6 are the number of A-atom electrons associated with the covalent and ionic structures.

### MO method to construct $\gamma(\mathbf{A})$

Alternatively we can use the 3c-4e MO configuration of eqn (1), and a  $k$ -dependent probability density function ( $P(k)$ ) for the 3c-4e bonding unit. If we choose  $P(k) = 4k^2/(k^2 + 2) \equiv 2P_{\text{aa}}$ , with  $Q_{\mathbf{A}} = X_{\mathbf{A}} - 2k^2/(k^2 + 2)$ , the resulting  $\gamma(\mathbf{A})$  parameter is given by eqn (6) *via* eqn (5).

$$\gamma(\mathbf{A}) = 6 + 4k^2/(k^2 + 2) \quad (5)$$

$$= 6 + 2(X_{\mathbf{A}} - Q_{\mathbf{A}}) \quad (6)$$

Therefore eqn (3) is identical to eqn (5), thereby showing that the Durrant methodology to determine  $\gamma(\mathbf{A})$  for a symmetric 3c-4e bonding unit corresponds to using a contribution by the A-atom's charge density to a MO formulation of 3c-4e bonding.

Three of the calculated values for  $\gamma(\mathbf{A})$  reported in Table 1 are greater than 8, which indicates hypervalency<sup>1</sup> for the associated species. However of course different numerical values and conclusions would be obtained with different types of 3c-4e wavefunctions and  $P(k)$  functions.

### A-Atom valence

In ref. 22, with AO overlap integrals omitted, it is deduced that the A-atom valence ( $V_{\mathbf{A}}$ ) for the MO configuration of eqn (1) is given by eqn (7),

$$V_{\mathbf{A}} = V_{ax} + V_{ay} = 16k^2/\{(k^2 + 4)(k^2 + 2)\} \quad (7)$$

with a maximum value of 1.3726 when  $k^2 = 2\sqrt{2}$ .

In Table 1, the MO estimates of the A atom valence for each species exceeds unity, and therefore its A atom is hypervalent. However, regardless of the values of the A-atom valence and the  $\gamma(\mathbf{A})$ , because of the presence of 2c-1e bonds in addition to the 2c-2e bonds, more electrons participate in nearest-neighbour and non-neighbour bonding<sup>6,8,9</sup> for each of the increased-valence structures than does occur in any of their component Lewis structures. Therefore all increased-valence structures are electronically hypervalent.

## Note added in proof

For PCl<sub>5</sub>, an increased-valence analogue of structure **1a** is obtained *via* the delocalization of two electrons from the Cl<sup>-</sup> of the Kekulé structure **1c** rather than one (as in structure **1c**), to give two 1-electron P-Cl bonds, a fractional equatorial 2c-2e P-Cl bond as well as the fractional axial 2c-2e P-Cl bond of structure **1d**.

## Acknowledgements

We thank Dr Margaret-Jane Crawford for drawing the valence bond structures. We also thank and appreciate the Reply by Durrant to our Comment.

## Notes and references

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- 4 Schleyer<sup>5</sup> has made the distinction between geometric hypervalence or hypercoordination, and electronic hypervalence. Cowley<sup>2a</sup> has written: Traditionally, hypervalence describes any atom that breaks the octet rule (or duet rule for hydrogen) by bonding to more neighbouring atoms than its valence electrons should allow. This point of view is adopted here. See for example, ref. 6 and 7 for discussions on hypervalence with<sup>6</sup> and without<sup>7</sup> increased-valence. Some of the discussions of ref. 7 assume that resonance between all of the ionic structures, such as structure **1c** for  $\text{PCl}_5$ , generates hypervalence for hypercoordinate systems.
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- 10 See for example: (a) P. C. Hiberty, *Isr. J. Chem.*, 1983, **23**, 10–20; (b) B. Braida, C. Walter, B. Engels and P. C. Hiberty, *J. Am. Chem. Soc.*, 2010, **132**, 7631–7637; (c) R. D. Harcourt and T. M. Klapötke, (i) *J. Fluorine Chem.* 2006, **127**, 712–718 for  $\text{PF}_5$  calculations. (ii) *Z. Naturforsch., B: J. Chem. Sci.*, 2012, **67**, 935–943.
- 11 C. A. Coulson and I. Fischer, *Philos. Mag.*, 1949, **40**, 386–393.
- 12 R. D. Harcourt, ref. 9b, pp. 277–280 and ref. 14a–l and 15 therein. Missing fishhook arrows in the  $\text{S}_{\text{N}}2$  mechanisms on pages 277 and 279 are included in Fig. 21-4 on page 278. On pages 85 and 202, change  $y + b + kb$  and  $y + b - k*b$  to  $y + b + ka$  and  $y + b - k*a$ , and change The  $V_{\text{ab}}$  of Eqn. (28) to The  $V_{\text{ab}}$  of Eqn. (30).
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- 16 For the increased-valence structure  $\bullet\text{X} \bullet \text{A}-\text{Y}$ , the orbitals are<sup>13</sup>  $x$ ,  $x + 1/2ka$ ,  $y + 1/2ka$  and  $ka + y$ . For the increased-valence structure  $\text{X}-\text{A} \bullet \text{Y}$ , the orbitals are<sup>13</sup>  $ka + x$ ,  $x + 1/2ka$ ,  $y + 1/2ka$  and  $y$ .
- 17 R. D. Harcourt, ref. 9b, 318–319.
- 18 R. D. Harcourt, *J. Mol. Struct.*, 1991, **229**, 39–62.
- 19 The  $\gamma$  parameter of ref. 1 provides ‘the formal shared electron count at a given atom, obtained by any combination of ionic and covalent resonance forms<sup>20</sup> that reproduces the observed charge distribution<sup>1</sup>’.
- 20 Whether or not an O, S or N atom expands its valence shell expansion to form the additional 2c–2e bond in each of the covalent structures **2c**, **4c**, **5c** and **6c** will determine the nature of the covalent structure (for example  $\text{X}-\text{A}-\text{Y}$  and  $\text{X}-\text{A}-\text{Y}$  without and with fractional 2c–2e bonds) that may be used to calculate  $\gamma(\text{A})$ . Here we use  $\text{X}-\text{A}-\text{Y}$ , as has Durrant<sup>1</sup>
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