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A further focus on penetration indices of misfit van der Waals crusts

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The recent proposal of the van der Waals crust as the spherical section comprised between the atomic radius and the van der Waals radius of an element generated a commentary by Grochala pointing out some supposed weaknesses of the approach (https://doi.org/10.1039/D3SC90191B). Our inital study is complemented herein by an analysis of the effects of the different size of the two interacting crusts, which shows that the penetration index defined earlier can adequately handle the misfit crust interactions.

In a recent paper published in this journal,[1] we analysed in depth the potential application of a penetration index between the van der Waals crusts of two atoms A and B, p_{AB},[2] as an alternative to the use of raw interatomic distances for the analysis of a variety of bonding situations, from weak van der Waals interactions all the way to strong multiple covalent bonds. The only pieces of information needed are the covalent and van der Waals radii of each of the two elements, r_A, r_B, v_A and v_B, as well as the interatomic distance d_{AB} (Fig. 1a).

The interpenetration of the two crusts is defined as

$$i_{AB} = v_A + v_B - d_{AB} \quad (1)$$

Dividing the interpenetration by the sum of the van der Waals crust widths (w_A and w_B, Fig. 1a and eqn (2)), and multiplying by 100, we obtain the penetration index as a percentage of the sum of the two crust widths (eqn (3)).

$$w_A = v_A - r_A;\ w_B = v_B - r_B \quad (2)$$

$$p_{AB} = 100\frac{i_{AB}}{w_A + w_B} \quad (3)$$

Simultaneously to the appearance of that paper, W. Grochala published a commentary warning about the problems that might arise when using such a penetration index for pairs of atoms with dissimilar sizes and different van der Waals crust widths.[3]

Although we had pinpointed such a possible problem in the text and given a simplified preliminary analysis in an Appendix, we think that the concern expressed by Grochala deserves a more detailed analysis that we present here.

For an AB atom pair, we can differentiate the penetration of atom A into the van der Waals crust of atom B (p_A, eqn (4)) from the penetration of atom B in the crust of atom A (p_B, eqn (5)). Herewith we consider atom A to have a wider crust than atom B, regardless of the values of their covalent and van der Waals radii, *i.e.*, $w_A \geq w_B$.

$$p_A = 100\frac{i_{AB}}{2w_B} \quad (4)$$

$$p_B = 100\frac{i_{AB}}{2w_A} \quad (5)$$

From eqn (4) and (5) it follows that $p_A \geq p_B$ in all cases. Notice also that the two degrees of penetration depend on the crust widths and on the distance, since i_{AB} depends linearly on d_{AB}, not on the atomic radii. Finally, it must be noted that p_A and p_B are calculated relative to the width of one crust each, whereas p_{AB} is calculated with respect to the sum of the two widths, and for that reason we introduce a factor 2 in the denominator of eqn (4) and (5).

To explore the relationships between the three penetration parameters we compare in Fig. 2 their values at some special interatomic distances for the case of two crusts of the same width (left

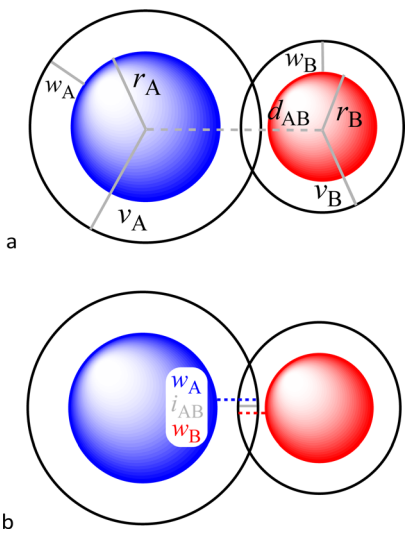

Fig. 1 (a) Definition of the covalent (*r*) and van der Waals (*v*) radii, the width of the van der Waals crust (*w*) and the interatomic distance (*d*) for two nearby atoms A and B. (b) Parameters needed to define the penetration of atom A into the van der Waals crust of atom B and *vice versa* (eqn (4) and (5)).

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column) and for two misfit van der Waals crusts (right column), deduced by introducing the chosen distances into eqn (3)–(5). Notice that the expressions in the right hand column can incorporate the $w_A = w_B$ cases (left hand side) by simply replacing in all the expressions the "<" and ">" symbols by "≤" and "≥", respectively.

First, we consider the case in which two van der Waals spheres are barely in contact (Fig. 2a). By definition, the three penetration parameters are 0% both for crusts with the same width (Fig. 2a, left) or for misfit crusts (Fig. 2a, right). In a second case (Fig. 2b), the vdW crust of atom A reaches the valence sphere of atom B. The three penetration parameters adopt a value of 50% if the two crust widths are the same (Fig. 2b, left), but for misfit crusts only p_A has that value, while p_B is less than 50% (Fig. 2b, right).

For two misfit atoms, a further approach is required to get the VdW sphere of atom B in contact with the valence sphere of A (Fig. 2b′), giving $p_A >$ 50% and $p_B = 50\%$, while p_{AB} is still less than 100%.

Finally, when the two valence spheres establish contact, *i.e.*, when the interatomic distance is identical to the covalent radii sum (Fig. 2c), the interpenetration index p_{AB} is 100% regardless of the widths of the two van der Waals crusts. The individual penetration p_A reaches values higher than

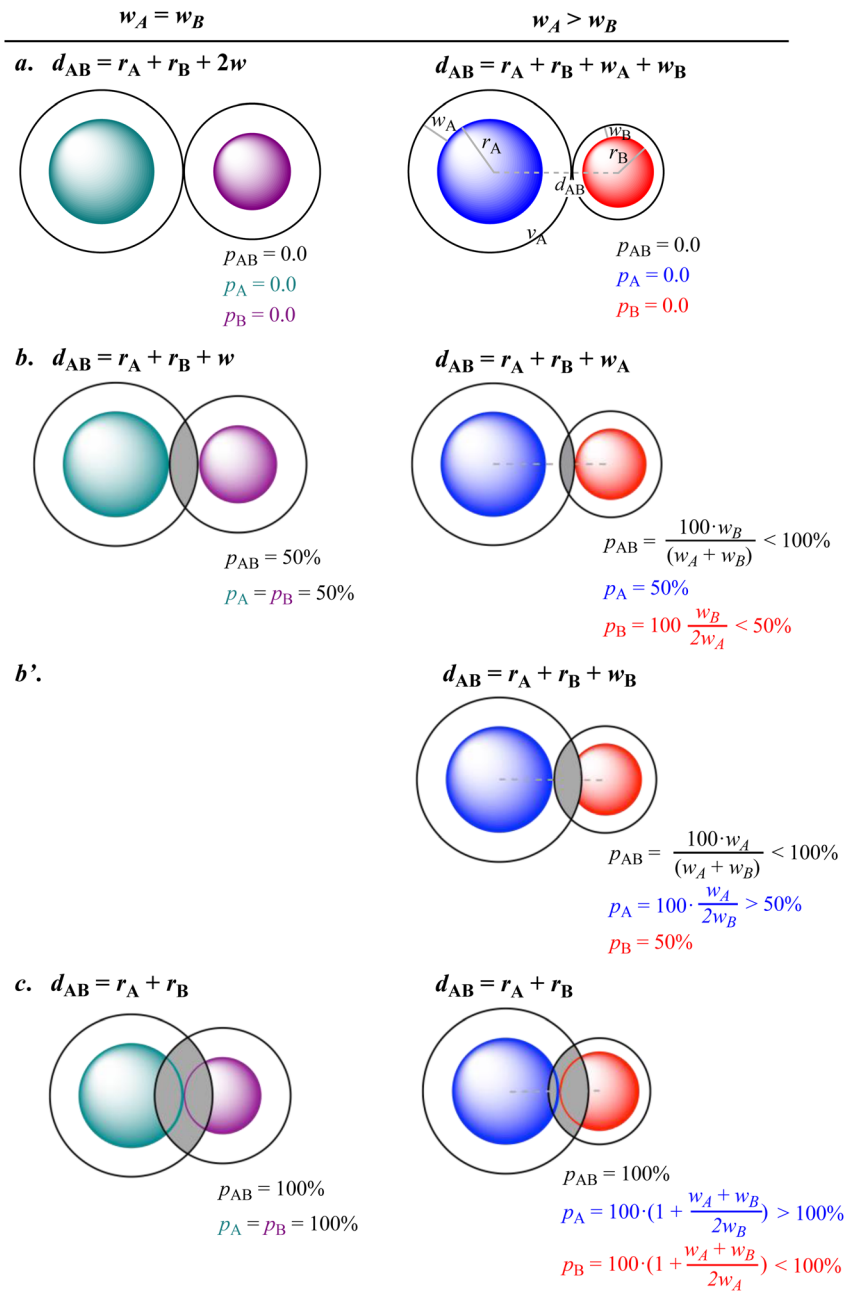

Fig. 2 Values adopted by the individual and diatomic penetration indices at special interatomic distances. The left column shows the case of two atoms of identical curst widths but different atom sizes and the right column a case of two atoms with misfit crust widths.

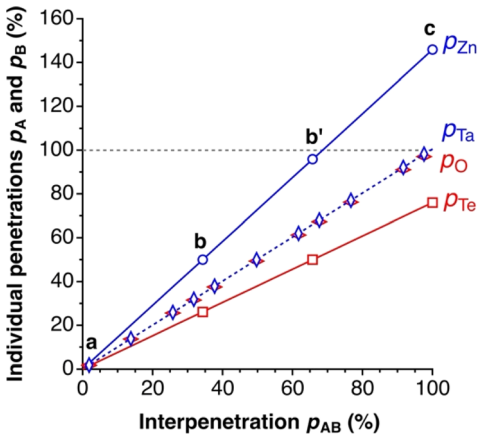

Fig. 3 Dependence of the individual penetration parameters p_A and p_B on the penetration index p_{AB} for the Zn–Te and O–Ta atom pairs, with crust width ratios $w_A/w_B = 1.92$ and 1.01, respectively. The points a, b, b′ and c correspond to the special distances specified in Fig. 2. All values calculated from standard covalent[4] and van der Waals[5] atomic radii at varying A–B distances.

100%, but those of p_B are smaller than 100%.

All in all, it is seen that the evolution of the three penetration parameters as the interatomic distance decreases present each a clearly predictable behaviour. Still more interesting, the individual penetrations p_A and p_B can be obtained from the interpenetration index p_{AB} according to eqn (6) and (7). Conversely, p_{AB} can be obtained from the individual penetrations by means of eqn (8).

$$p_A = \frac{p_{AB}}{2} \times \left(1 + \frac{w_A}{w_B}\right) \quad (6)$$

$$p_B = \frac{p_{AB}}{2} \times \left(1 + \frac{w_B}{w_A}\right) \quad (7)$$

$$p_{AB} = 2\frac{p_A\, p_B}{p_A + p_B} \quad (8)$$

Those relationships are illustrated in Fig. 3, where we plot the individual penetration parameters p_A and p_B as a function of the interpenetration index p_{AB}, for two atom pairs: one with practically identical crust widths, Ta–O (w_{Ta} = 0.83, w_O = 0.84 Å), and one with very different widths, Zn–Te (w_{Zn} = 1.17 Å, w_{Te} = 0.61 Å). In the first case (Fig. 2, left column), the individual penetrations p_A and p_B are equal to the interpenetration index p_{AB} at any interatomic distance, whereas for atom pairs with different crust widths (*e.g.*, Zn and Te) p_A increases at a higher rate than p_B as the interatomic distance decreases (*i.e.*, as p_{AB} increases).

Conclusion

Even for misfit van der Waals crusts the interpenetration index p_{AB} carries information on the different left-right (p_A) and right-left (p_B) penetrations. Those differences depend only on the relative widths of the two interpenetrating crusts (w_A and w_B), but not on the atomic sizes (r_A, r_B, v_A and v_B), as seen in eqn (6)–(8).

$$\frac{p_A}{p_B} = \frac{w_A}{w_B} \quad (9)$$

The deviation of the p_A and p_B values from p_{AB} for an AB atom pair with misfit van der Waals crusts can be expressed by their quotient, which is found to be identical to the quotient of the crust widths (eqn (9)).

For those reasons, we think that it is advisable to use preferentially the interpenetration index p_{AB}, which is conceptually clearer, implies no loss of information on the individual penetration indices p_A and p_B, and is simpler to use.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this comment.

Author contributions

Both authors contributed to the discussion, writing and revision of the original draft.

Conflicts of interest

There are no conflicts to declare.

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