

The Implications of Symmetry of the External Potential on Bond Paths

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The concept of the chemical bond is of paramount importance to the modern chemical language.^[1] Similar to other unicorns in the chemical world,^[2] like aromaticity, reactivity, or covalency, the chemical bond is a fuzzy entity eluding a precise numerical definition. Guided by the leading role played by the electron density in the Hohenberg and Kohn^[3] theorems, Bader proposed a way to use this observable to generate lines connecting atoms that generally are very well aligned with common chemical sense.^[4–10] Avoiding the highly controversial issue about the interpretation of the zero flux basins that are obtained from the least action principle as the “atoms” of chemistry,^[11] one cannot raise any doubt regarding the existence of the saddle points (critical points) in the region between some nuclei and the corresponding gradient path connecting the nuclei. This is an experimental fact^[27] that in the last 25 years has been widely used to gain a deeper and alternative knowledge about the essence of chemical bonding or, paraphrasing Pauling, the nature of the chemical bond. Despite the uncontroversial physical existence of the gradient paths and critical points, their interpretation as direct manifestations of true chemical interactions has been the source of controversy in the chemical community.^[11–20] The set of critical points and gradient paths, the molecular graph, is a beautiful representation of the structure of the electron density but, its identification with genuine chemical concepts (like a chemical bond) is an interpretation, which like all interpretations, has a degree of

subjectivity and, consequently, any inference drawn from it should be taken with judicious care.

An illustrative example is the interaction between two helium atoms. He₂ is a prototype of a van der Waals dimer, that is, the potential-energy surface of He₂ is repulsive, except for the van der Waals minimum. In this entity, there are two maxima of the electron density at the position of the nuclei, a (3,–1) critical point in halfway between both centers, and a bond path connecting the maxima. Since a minimum always exists between two maxima, this bond path will survive even if the nuclei are separated by 2 or by 20 Å. Certainly, the electron-density value at the (3,–1) critical point is negligible in the latter situation. The central question is the following: Is the existence of a bond path a sufficient condition that proves that two atoms are connected by a bond in the chemical sense of the word? To answer this question, we selected a set of molecules where the number of gradient paths terminating at an atom is chemically meaningless.

Consider the He@C₈H₈ complex.^[21] This endohedral system with *O_h* symmetry is a local minimum on the corresponding potential-energy surface. Using B3LYP/6-311++G(d,p) calculations, we found eight bond paths that connect each carbon atom to helium (Figure 1, top left). As expected, the He–C distances are short (1.480 Å) and, consequently, the value of the electron density at the He–C (3,–1) critical points is relatively high (0.140 a.u., see Table 1). However, the dissociation energy associated to the reaction He@C₈H₈ → He + C₈H₈ is negative (–322.4 kcal mol^{–1}), which indicates that the helium–cubane interaction is destabilizing overall. Note that stability is not the decisive point to define a chemical bond, since also in metastable molecules one can find chemical bonds.

The situation is stranger when a noble gas (Ng) is confined in the C₂₀H₂₀ cage. Evidently, in this case the cavity is larger than in cubane, allowing the inclusion in silico of heavier noble gas atoms than helium. Experimentally, only the helium complex has been characterized,^[22] adopting an *I_h* symmetry, despite the fact that the energy to put the He atom inside dodecahedrane^[22] is 35.5 kcal mol^{–1}. No calculation is necessary to predict that the number of bond paths

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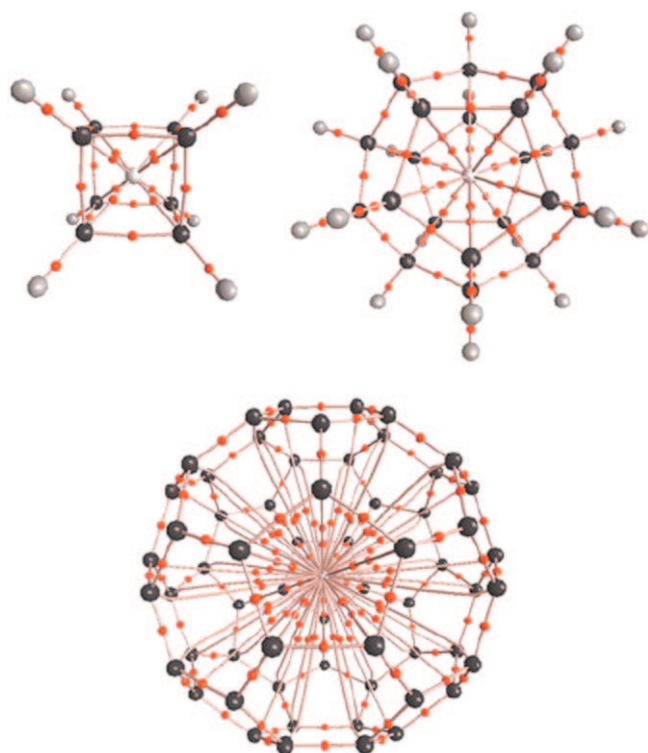


Figure 1. Sets of “bond” paths of He@C₈H₈ (top left), He@C₂₀H₂₀ (top right) and Ng@C₆₀ (bottom; Ng=He, Ne, Ar, and Kr) obtained at the B3LYP/6-311++G(d,p)^[25] level using AIM2000.^[26] Red spheres indicate the position of the (3,-1) critical points.

Table 1. The Ng–C distances ($r(\text{Ng}-\text{C})$ [Å]), the electronic density ($\rho(\mathbf{r})$ [a.u.]) at Ng–C (3,-1) critical points, the Laplacian of the density ($\nabla^2\rho$ [a.u.]) at Ng–C (3,-1) critical points, and the dissociation energies associated to the reactions He@Cage \rightarrow He + Cage (ΔE [kcal mol⁻¹]) of the selected endohedral complexes.

	$r(\text{Ng}-\text{C})$	ρ	$\nabla^2\rho$	ΔE
He@C ₈ H ₈	1.480	0.140	0.160	-322.4
He@C ₂₀ H ₂₀	2.190	0.023	0.033	-35.5
He@C ₆₀	3.545	0.002	0.002	-1.2
Ne@C ₆₀	3.544	0.002	0.003	0.8
Ar@C ₆₀	3.546	0.005	0.005	-5.8
Kr@C ₆₀	3.547	0.007	0.006	-11.5

connecting the noble gas atom to the carbon atoms will be vast. In fact, calculations show the presence of twenty He–C bond paths (See Figure 1, top right). Given that the He–C distances are larger than in the He@C₈H₈ case (2.190 Å), the electron density values at the He–C (3,-1) critical points are one order of magnitude smaller than the corresponding values in He@C₈H₈. The topology of the electron density suggests that the noble gas atom in He@C₂₀H₂₀ is twenty-coordinate. How can one reconcile this result with chemical sense?

What is the maximum number of bond paths terminating at an attractor? Let us propose another example: Ng@C₆₀ (Ng=He–Kr), in particular Ar@C₆₀.^[23] We found that this system is a minimum on its corresponding potential-energy surface. The Ar–C distances are 3.546 Å and the dissociation

energy is slightly lower than 6 kcal mol⁻¹. The set of bond paths for this complex is depicted in Figure 1 (bottom). It is apparent that the number of trajectories that terminate at the central attractor is huge and it is evident that this number is a consequence of the high symmetry adopted by the complex. In the I_h Ar@C₆₀ complex as any I_h Ng@C₆₀ system, sixty bond paths connect the central noble gas atom, one to each carbon. In this sense, the noble gas atom is a sixty-coordinate atom! Are these contacts “genuine” chemical bonds? Let us remember the definition of chemical bond provided by IUPAC: “there is a chemical bond between two atoms or groups of atoms in the case that the forces acting between them are such as to lead to the formation of an aggregation with sufficient stability to make it convenient for the chemist to consider it as an independent ‘molecular species’”.^[24] Since the properties exhibited by Ar@C₆₀ are essentially the same as those of free C₆₀ from the chemical point of view none of the Ar–C bond paths is a “genuine” chemical bond.

Finally, let us extrapolate this situation to an extreme example in which the Ng atom is confined inside a continuum potential that resembles the confining potential produced by the molecular cage. The schematic plot of the electron density with respect to the distance is depicted in Figure 2. For

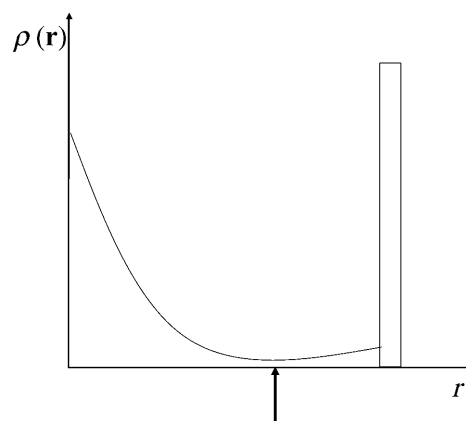


Figure 2. Schematic representation of the electron density with respect to the distance of the center of the cage by using an electron attractive potential.

an electron attractive potential, there is a minimum at the radius indicated in the figure by the arrow and, more importantly, the presence of this critical point happens at every angle. Thus, it will be a continuum of critical points. Is this contradicting chemical reasoning? Yes. Is this contradicting physics? No. The electron density is adapting to the nature of the restrictions, symmetry among them, imposed by the external potential. This extreme example shows that the one-to-one mapping of gradient path/chemical bond or interaction can be misleading. Remember that the electron density will always follow the symmetry imposed by the external potential, a fact that should not be surprising if one recalls the first theorem of Hohenberg and Kohn.^[3] There-

fore, some potential or boundary conditions can lead to situations in which the electron density will have critical points, which cannot be disputed on physical grounds, but can also be over-interpreted on chemical basis. Thus, it is risky to make the one-to-one analogy between a bond path and a chemical bond in the usual chemical sense of the word.

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