# **ASPECTS OF THE CHEMICAL BOND 1996**

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## 1. Introduction

In a preceding essay [1] I outlined the historical, mathematical and physical bases of our present qualitative knowledge about the chemical bond, specifically about covalent binding in simple molecules. An expanded version [2] of that material afforded the opportunity to clarify and to extend the arguments somewhat, and to discuss the reaction to the previously printed version. In the present essay I consider important aspects of chemical binding previously ignored, namely ionic substances, the *transition state* purported to occur between reactants and products during the course of a simple chemical reaction, and a description of the mechanism of an intramolecular rearrangement. As for the covalent bond, these topics evolved largely during three quarters of a century since quantum mechanics was discovered and developed, but involve, more or less implicitly, many ideas based on the classical notion of molecular structure emanating from the nineteenth century. The final section consists of a discussion of the context of quantum chemistry in a contemporary scientific milieu.

## 2. Ionic materials

Whereas some chemical materials with simple stoichiometric descriptions such as  $H_2$ ,  $CH_4$ ,  $CO_2$  and  $H_2O$  are either gaseous or volatile liquid substances under common ambient conditions, other materials with equally simple nominal descriptions such as Be, NaCl and SiO<sub>2</sub> are involatile and refractory solid substances. These properties are supposed to reflect the nature of chemical binding between the atomic centres. In isolated molecules of substances of the former group, there exist strong bonds between adjacent atomic centres, whereas when these substances are condensed into a liquid or solid state only weak binding between atomic centres in separate formula units is observed. In pure solid or liquid phases of substances in the latter group one has difficulty to distinguish atomic centres in explicit sets corresponding to simple formula units. The binding between atomic centres in such distinct units is less weak in the case of H<sub>2</sub>O than in the other cases, consistent with the observation that solid or liquid H<sub>2</sub>O near 300 K is less volatile than  $CH_4$  or  $CO_2$ . Significant spatial attraction (intermolecular interaction) is observable in liquid and solid H<sub>2</sub>O outside the simple formula unit that realistically represents the molecular entity H<sub>2</sub>O in the dilute gaseous phase; likewise small but significant distortions of the geometric structure (defined according to internuclear distance and angle) that is characteristic of the gaseous phase are detectable in ice. Such distortions are much more pronounced for crystalline substances described as inorganic or mineralogical, for which in many cases no compound of the same stoichiometric ratio is characterised in the gaseous phase. The customary description of these substances has been known as the ionic model, but Hyde and O'Keeffe [3] have shown that this description is inadequate; the following discussion on this topic is based largely on a review published by Hyde [4], supplemented with material from subsequent authors. What is offered to replace the ionic model is still essentially a physical model, as quantal treatments of such extended structures remain largely impracticable.

The prototypical example of a binary ionic crystal is that of sodium chloride, described as a virtually infinite array of nominally spherical sodium and chloride ions in three-dimensional space. These ions are described as cations, Na<sup>+</sup>, and anions, Cl<sup>-</sup>; the latter or negative ions are supposed to pack closely in space, with positive ions inserted into appropriate interstices. For NaCl in its normal cubic close-packed form, the cations locate in octahedral interstices, so that each Na<sup>+</sup> has six equidistant adjacent anions; in other crystals cations are found in tetrahedral interstices, accordingly with four anions as immediate neighbours. The coordination at the cationic site is supposed to depend on a purely geometric criterion, the ratio of radii of cation and anion, being in the ranges [0.225, 0.414] for tetrahedral coordination, [0.414, 0.732] for octahedral coordination, and > 0.732 for cubic coordination with eight anionic neighbours.

The vital assumption underlying such a criterion is that an atomic ion of a particular type, classified according to element and to nominal state of oxidation, has a well defined radius that has little or no dependence on the environment, such as the nature or properties of counterions or adjacent atomic centres. Although this assumption, which predates quantum theories, is formally inconsistent with a quantal description of matter, its ramifications with respect to classical geometric and electromagnetic concepts have proved more important in recent practice. A radius of an isolated ion is clearly an arbitrary property, just as even an apparent or effective radius of an atom of a noble gas varies with the nature of the experiment for its measurement, apart from any further dependence on temperature or energy. In contrast the sum of atomic radii of a cation and an adjacent anion in a particular crystalline environment is empirically well defined, just like an equilibrium internuclear distance of a stable diatomic molecule (in an hypothetical state without residual energy). For conventional ions the radii are commonly taken from a list by Pauling [5], and comparison is also made with a more recent compilation [6]; in the (mostly, older) literature such ionic radii are found in several other sets.

Much evidence inconsistent with this ionic model exists. For instance, in metallic oxides MgO, CaO, SrO and BaO of group 2, the oxide anions can not be closely packed in every case because the distance between adjacent oxide centres varies through a large range, 298 pm for MgO to 391 pm for BaO; likewise the volume per O<sup>2-</sup> varies in the range/10<sup>-29</sup>  $m^3$  from 1.38 for BeO to 4.21 for BaO [7]. Although all four oxides MgO - BaO possess a structure analogous to that of NaCl, ratios of conventional radii of ions in BaO, SrO and possibly also CaO deviate from the range nominally applicable to a close-packed octahedral structure.

The geometry of close packing is also the geometry of open packing [7, 8]. The latter arrangement allows distances between anions and between cations to be a maximum, not a minimum, consistent with the phenomenon of electrostatic repulsion between ions having like charges. The term eutactic, implying well arranged, is devised [8] to signify a spatial order as in close packing. Many structures contain irregular arrays of anions, which are hence not closely packed or eutactic; although these geometries commonly defy description in terms of arrays of anions, or of anionic polyhedra with cations at their centres, in many cases, such as  $Ca_2SiO_4$  to be discussed, the arrangement of cations is regular, according to a familiar geometry.

For some substances, the coordination number is found to be unrelated to the ratio of the ionic radii. For instance Mg has octahedral coordination, denoted  $^{VI}$ Mg, in MgO, but tetrahedral coordination, so  $^{IV}$ Mg, in a mineral spinel, MgAl<sub>2</sub>O<sub>4</sub>, despite its being surrounded by oxygen centres in both cases. In such crystals of  $^{IV}$ Mg $^{VI}$ Al<sub>2</sub> $^{IV}$ O<sub>4</sub>, the larger cation Mg<sup>2+</sup> ( $R = 71|57 \ pm$ ) occupies the smaller, tetrahedral interstice and conversely the smaller cation Al<sup>3+</sup> (67.5|53.5 pm) is located in the larger, octahedral cavities. (Of two values of ionic radius R specified in these cases, the former is listed by Shannon [6] and the latter by Pauling [5].) As an instance of multiple coordination numbers over a greater range, in ternary compounds of oxygen with metals in group 1 and in groups 4 - 12 sodium exhibits coordination to oxide ions numbering from two to twelve [9]; the ionic radius of Na<sup>+</sup> varies almost linearly from about 98 pm at coordination number four to nearly 140 pm at coordination number twelve [6]. The concept of an almost constant ionic radius invariant with coordination number is clearly tested severely under such conditions.

Although measurement of absolute electronic densities in crystals by means of xray diffraction (or other) experiments is problematical, accurate maps of electron density within a unit cell are claimed to be derived with this technique. For lithium fluoride in which the smallest distance between Li and F nuclei is 201 pm, the minimum electronic density along the line between the lithium and fluoride nuclei occurs at a distance  $109 \ pm$  from the latter atomic centre, in contrast with a much larger nominal ionic radius of  $F^{-}$ , 133/136 pm. In crystalline sodium chloride, integration of the density of electronic charge within a sphere of radius corresponding to the minimum electronic density along the line between centres of a cation and of an adjacent anion indicates that the net deficiency of electronic charge within this volume, relative to Na as an electrically neutral atom, is 0.95 electrons, whereas the excess charge within the sphere about the chlorine nucleus is 0.70 electrons. The remaining negative charge, equivalent to 0.25 electrons. is then deduced to locate within the volumes between the spheres; there the electronic density is small, less than  $2 \times 10^{-7}$  electrons  $pm^{-3}$ , compared with  $7 \times 10^{-5}$  and  $1.7 \times 10^{-4}$  electrons  $pm^{-3}$  near sodium and chlorine nuclei respectively [10]. For MgO a minimum electronic density along the line between the atomic centres of Mg and O occurs 91 pm from Mg (compare with the ionic radii specified above); a sphere of this radius contains a net charge +1.9 electrons, but the corresponding sphere about O includes a charge only -0.9 electrons [11]. In this case 1.0 electron per couple of ions (Mg and O) is located in the space between such spheres. This result is consistent with the fact that the electron affinity of an oxygen atom in the gaseous phase is positive for only the first extra electron (*i.e.*  $\Delta U^0 < 0$  for the process  $O + e^- \rightarrow O^-$ , but  $\Delta U^0 > 0$  for the process  $O^- + e^- \rightarrow O^{2-}$ ).

The size of the ion  $\mathrm{Si}^{4+}$  with tetrahedral coordination is listed to be  $40|26 \ pm$ . If the size of this ion is defined as the radius of a sphere containing ten electrons, quantal calculations [12] indicate a radius 61 pm. This value, similar to the value 58 pm for  $\mathrm{Si}^{4+}$  in  $\alpha$ -quartz [13], much exceeds the specified nominal values for coordination of this type. In any case, the idea that anions are necessarily much larger than cations is incorrect; old values of ionic radii are based on theoretical properties of free ions, not of these ions in crystals. In the latter environment anions are subject to a positive site potential (due to the collective electric field of surrounding cations) [14, 15]; this potential, typically 12z V with z being the net charge of the anion in units of the magnitude of the protonic charge, has the effect of contracting the distribution of charge. In this way  $O^{2-}$  appears to become

stable in the crystalline field, whereas the free ion  $O^{2-}$  has indefinite extent. Conversely, cations are subject to a negative potential that has the effect of expanding the distribution of charge. All this evidence indicates that the customary ionic model is gravely deficient.

According to an alternative approach [4], an atomic centre is treated simply as an atom, not as an ion; the terms cation and anion are however retained to distinguish atomic centres of metallic elements from those of non-metallic elements. From a survey of numerous well determined structures of silicates and silica compounds consisting of SiO<sub>4</sub> tetrahedra connected by corners in framework, sheet and chain arrangements, O'Keeffe and Hyde showed that the distances between nearest Si centres lay within a notably narrow range,  $(306 \pm 6) pm$ , with a few outliers at larger separations [16]. Moreover the variation of this range is no greater than for the distribution of lengths of Si-O bonds,  $(164 \pm 6)$  pm; hence the distance between adjacent Si centres varies as little as that between adjacent Si and O centres. This result conforms to what Bragg and Claringbull [17] found earlier, that the distance 305 pm between nearest Si centres in a single chain is invariant in five chains existing in three pyroxene minerals. The distance between nearest Si centres not only in silicate glasses but also in gaseous molecular substances containing the angular moieties Si-O-Si, Si-NH-Si and Si-CH<sub>2</sub>-Si lies also within the range/pm [300, 315], despite the variation of lengths of Si-O, Si-N and Si-C bonds and of interbond angles, 165 pm and 2.56 rad, 170 pm and 2.09 rad, and 188 pm and 1.90 rad in the same order [4]. These data convey the significance that, if silicon atoms in these structures be considered to be in contact, an almost constant atomic radius 153 pm might be ascribed to that interatomic interaction, which is deemed not a chemical bond. Analogous trends prevail in borates (containing the angular moiety B-O-B), phosphates (containing P-O-P) et cetera; the radii are found to be additive, for instance in borosilicates (containing B-O-Si). Such data yield two conclusions. Interactions between atomic centres, between which there is nominally no chemical bond in the traditional sense, that are second-nearest neighbours can play an important role in determining the geometric structure and thermodynamic stability of chemical compounds or materials, in both gaseous and condensed phases. Of these non-bonding interactions those between cations might be more important than those between anions because radii of cations generally exceed those of anions, particularly N, O and F.

Such an approach is proposed to be applicable to small molecules, both organic and inorganic, in the gaseous phase [18]. Extension of this approach to involatile solid compounds is consistent with results of quantal calculations on small isolated molecules in relation to likely structures of solid materials containing similar structural moieties [19, 20, 21]. In their devel-

opment of conformational analysis, organic chemists recognise the importance of non-bonded interactions, and methods to predict and to analyse structures of molecular crystals depend on such phenomena [22]. The latter calculations commonly involve application of functions of potential energy in one dimension, typically of the form  $V(d) = Ae^{-Bd} - C/d^6$  with d as internuclear distance; A, B and C are parameters characteristic of a particular couple of atomic centres. The concept of a hard sphere characterised with a constant radius for a particular atomic centre becomes accordingly replaced for quantitative applications by a distance variable in a range depending on the energy of intermolecular interaction. Although these functions are established for elemental constituents of organic molecular crystals and systems of biochemical importance, within computational approaches named molecular mechanics for instance, they are lacking for nominal cations such as  $Si^{4+}$  and  $O^{2-}$ . This approach involving hard spheres of specified radii nevertheless renders a qualitative understanding of structures of crystalline phases of simple inorganic compounds and minerals. Hence both  $\alpha$ -quartz and cristobalite possess frameworks, topologically distinct but flexible, of SiO<sub>4</sub> tetrahedra connected at corners and collapsed from the most open possible geometries that would be expected if they were truly ionic. The collapse proceeds to the extent that the distance between nearest Si centres is decreased to about 306 pm. SiO<sub>2</sub> consists of tetrahedral SiO<sub>4</sub> moieties rather than octahedral SiO<sub>6</sub> moieties, not because six oxygens can not pack around Si (which occurs in  $^{VI}$ Si $^{IV}$ P $_2$  $^{II}$ O $_7$  for instance), but because more than two silicons must then pack about an oxygen, denoted >IVSi $>IIO_2$ . The minimum condition would then be  $^{VI}Si^{III}O_2$ , which would lead to a distance between nearest silicon atomic centres significantly less than 306 pm, thus an extremely repulsive condition. For comparison, the maximum angle Si-O-Si would be  $2\pi/3 = 2.09$  rad for oxygen coordinating three silicons, whereas this angle in quartz with oxygen coordinating two silicons is 2.56 rad. Great pressure serves to overcome such repulsions, transforming  $SiO_2$  into a structure of the rutile (TiO<sub>2</sub>) type with  $VISi^{III}O_2$ .

The structures of crystals and of even some isolated molecules thus represent a balance between strong attractions affecting nearest neighbours (as chemical bonds) and less strong repulsions between atoms that are second-nearest neighbours about a central atom (between cations about a central anion, and vice versa). The latter, non-bonding repulsions that operate over large distances and involve small electronic densities tend to cause extension (or stretching) of chemical bonds characterised by small distances and large electronic densities. These repulsions are not of primarily electrostatic origin because such conditions fail to explain the observed geometries of flexible structures such as quartz and cristobalite [23], or of structures of CaCl<sub>2</sub> type relative to the topologically identical rutile type [24]. The importance of interactions between second-nearest neighbours, either between two cations or between two anions, depends on not only the relative sizes (pertinent to non-bonded interactions) of atomic centres but also their relative numbers or the stoichiometry of the substance. In a crystalline compound such as  $Li_3N$  repulsions between cations are more important than between anions because cations are preponderant; conversely in AlF<sub>3</sub> the reverse situation pertains. In less extreme cases the relative influences of size and stoichiometry are more subtle. Beside a table of atomic radii Hyde presented [4] a comparison of observed bond angles in cristobalites with those calculated from those radii, which indicates the success of this approach.

# 3. Application of an alternative approach to inorganic structures

Although diamond is an extremely hard and incompressible substance and a thermal conductor superior to metallic copper or silver, it is metastable under normal conditions with respect to graphite. These properties reflect a condition that the distance 252 pm between second-nearest neighbours is about twice the non-bonding radius 125 pm; hence non-bonding contacts are repulsive. If one associates 0.028 aJ with the potential energy of each contact between C atomic centres as second-nearest neighbours in diamond according to the pertinent function V(d) [22], this energy 100 kJ per mole of carbon is comparable with many enthalpies of chemical reactions. Resistance to deformation or to compression of a crystal that necessarily decreases some interatomic distances, with a concomitant greatly increased repulsive energy, explains not only the large bulk modulus, stiffness and thermal conductivity of diamond but also its instability with respect to graphite; in the latter allotropic form atomic centres of carbon within layers, denoted <sup>III</sup>C to indicate the coordination number, experience a greatly decreased energy of repulsion, relative to <sup>IV</sup>C in diamond, because the number of second-nearest neighbours is decreased to a quarter that in diamond. About four fifths of the bulk modulus of diamond arises from these nonbonded repulsions [25], consistent with the concept of stretched bonds and compressed non-bonded contacts. To overcome these repulsions and hence to synthesise diamond, great pressure is required, likewise for boron nitride and silicon carbide in isostructural forms; these three substances are among the least compressible.

For many transformations under great pressure the coordination number increases, as from  ${}^{IV}\text{Zn}{}^{IV}\text{S}$  in a tetrahedral structure to an octahedral structure of  ${}^{VI}\text{Na}{}^{VI}\text{Cl}$  type. In such a case the greatest repulsions involve nearest neighbours, or bonded atomic centres; these repulsions are relieved with an increased coordination number as more numerous bonds imply weaker and longer bonds. As the volume of the unit cell decreases under an applied pressure, the linear dimensions also decrease, about 2.2 per cent for the edge of the unit cell in the case of this phase transformation of ZnS, but the bond length correspondingly increases about 5.6 per cent [4].

In other transformations under pressure, such as for the minerals olivine  $\rightarrow$  spinel with formula unit  ${}^{VI}Mg_2{}^{IV}Si^{IV}O_4$  or for zircon  $\rightarrow$  scheelite with  ${}^{VIII}Zr^{IV}Si^{III}O_4$  [4], no alteration of coordination number is involved. In the former case in which the volume of a unit cell (that contains formula units of the same number) decreases about ten per cent, the oxygen centres have approximately hexagonal eutaxy in olivine but cubic eutaxy in spinel; hence coordination numbers between anions remain invariant. Although the distances between nearest oxide anions decrease on transformation, so that the repulsive energy increases, and correspondingly the distances between magnesium cations decrease, the distances between nearest Mg and Si centres become increased. That this phase change relieves strong repulsions between Mg and Si at the expense of more numerous repulsions between Mg and Mg is consistent with the coordination number of Si by Mg increasing from nine in olivine to twelve in spinel.

That repulsions between cations are more important than those between anions is consistent with the fact that arrays of cations in many crystalline structures exhibit regularity whereas associated arrays of anions lack such regularity. A few notable instances include La<sub>2</sub>O<sub>3</sub>, BaSO<sub>4</sub>,  $\beta$ -K<sub>2</sub>SO<sub>4</sub> and Ca<sub>2</sub>SiO<sub>4</sub> [4]. In the latter case, for which five phases exist at various temperatures, in three polymorphs only Ca and Si cations display a regular array, recognised to be of the Ni<sub>2</sub>Si or PbCl<sub>2</sub> type, as is indeed the separate compound Ca<sub>2</sub>Si; the molar volumes 51.8 mL mol<sup>-1</sup> of these silicates and 49.9 mL mol<sup>-1</sup> of the silicide are notably comparable [26].

The stoichiometry of binary fluorides, oxides and nitrides confirms the validity of this approach. For oxides of alkali metals, apart from peroxides with O-O bonds and suboxides with M-M bonds, the normal formula unit  $M_2O$  implies twice as many large cations M as small anions (O<sup>2-</sup>). All these oxides have an *antifluorite* structure-tetrahedral coordination of the cations and eight cations about each anion, so  ${}^{IV}M_2{}^{VIII}O$ . Hence the coordination number of the large cation is small and that of the small anion is large, a condition inconsistent with traditional rules about the ratios of radii. These oxides are prepared only with great difficulty: the peroxides  $M_2O_2$  and, with more massive alkali atoms, even superoxides  $MO_2$  form readily instead. Even when a normal oxide forms it is reactive with atmospheric  $H_2O$ ,  $CO_2$  et cetera, indicating a modest enthalpy of formation and weak bonds. This poor stability is attributed [4] to large repulsions between cations in the normal binary compound. The effect is less severe with oxides of alkaline-earth metals (group 2) because a smaller stoichiometric ratio ac-

companies increased charge on cations. Conversely the stoichiometric ratio is decreased for alkali metals with fluorides as anions, in which binding is correspondingly stronger [27].

Analogously, if the anion carries a greater negative charge, the problem relative to normal alkali oxides is expected to be exacerbated, as there are then even more numerous cations per anion. Such a condition arises for nitrides of alkali metals,  $M_3N$ . For the more massive atoms of elements in group 1 these compounds have not been prepared: only Li<sub>3</sub>N is known. Instead of nitrides, azides  $MN_3$  are formed, of which  $NaN_3$  has considerable stability. These polyanions  $N_3^-$  are obvious extensions of peroxides  $O_2^{2^-}$ . For carbides no binary compound  $M_4C$  of group 1 is known, and only Be<sub>2</sub>C of group 2, but Al<sub>4</sub>C<sub>3</sub> and boron carbides of group 3. The stable compounds consist instead of ethynides, for instance CaC<sub>2</sub>, containing  $C_2^{2^-}$ , or polycations in Ca<sub>2</sub>N and Ca<sub>11</sub>N<sub>8</sub>.

The traditional ionic model in chemistry, with its emphasis on relatively large anions, is thus obsolete: many properties and phenomena in the chemistry and physics of the solid state, and in mineralogy, are readily explained [4] as a natural consequence of repulsion between cations.

Measurements of density of electronic charge within the unit cell of crystals by means of xray diffraction can illuminate the nature of chemical binding. Although chemists might retain an impression that charge flows extensively in the formation of a covalent bond from two atoms, so as to accumulate in the region between closely adjacent atomic centres at the expense of electronic density in other directions, accurate measurements of charge density indicate that, for instance, approximately one tenth of an electron is displaced into the overlap region between two carbon atomic centres separated about 150 pm [28]. Formation of a covalent chemical bond nominally involving sharing of electrons remains consistent with a minimum of electronic density along the line of that bond between the nuclei. Such experimental results conform to those from calculations. The distribution of electronic charge associated with an isolated atomic centre hence alters little on formation of a covalent bond. Even though the extent is small, it is significant: nuclei are thereby held near their equilibrium separations. For instance, in the case of HCl at the equilibrium separation the internuclear repulsion is forty times as great as the binding energy or strength of the chemical bond. In preceding essays [1, 2] there was reported an interpretation [29] of electronic density within unit cells, by means of xray diffraction measurements, that for electronic charge to accumulate in the region between two nominally bonded atomic centres might not necessarily accompany formation of a bond [30]. That approach, combined with other work [31], depends on plots of the difference of electronic density between an experimental distribution and a quasi-classical density postulated for

spherically averaged atoms, whether with or without allowance for atomic vibrations. Such an hypothetical distinction is fraught with risks of incorrect and unwarranted conclusions concerning covalent chemical bonds [32], but the choice of a reference state alternative to that of a spherical atomic centre for the comparison of experimental electronic densities is even more arbitrary [33].

A claim to detect orbitals (that lack physical existence) by means of experiments with scattered xrays would be astounding, but to compare experimental densities of electronic charge with those calculated accurately is intrinsically unobjectionable. For a complex of iron with tetraphenylporphyrin derivatives, a pattern of electronic density near the iron atomic centre was interpreted to indicate varied occupancy of d orbitals [34]; this pattern agrees with results of calculations [35] according to an extended Huckel method that involve an approximate one-electron hamiltonian and an inadequate Mulliken population analysis. As this method is inherently unreliable because of its lack of theoretical foundation, gross approximations, and neglect of important electronic interactions such as correlation [35], any agreement with experimental results is regarded as fortuitous. Improved calculations of electronic density according to superior procedures are required before such comparison with experimental data can be regarded as meaningful, but perhaps such crude calculations are required [36] to confer such alleged properties of nonexistent orbitals. In that crystallographic analysis [34], hydrogen atomic centres were eventually located directly, rather than being placed at idealised positions relative to adjacent atomic centres associated with greater electronic density on the basis of preconceived structural notions; the latter practice is common in experiments in which measurement of the diffraction pattern is less thorough. When crystallographic analyses based on xray diffraction enable detection of hydrogenic atomic centres at separations from more massive nuclei consistent with accurate distances inferred with other experimental techniques, a claim to detect electronic density associated with specific features of a basis set in a theoretical calculation might be more seriously entertained.

In an ionic material the minimum electronic density at some point along the line connecting the nuclei of a cation and an adjacent anion was found to be small [10]. In crystalline lithium hydride that has a structure analogous to that of NaCl, the internuclear distance between Li and adjacent H is  $204 \ pm$ , compared with about 160 pm for the isolated diatomic molecule in the gaseous phase [37]. The measured electric dipolar moment of the latter free LiH molecules corresponds to nominal transfer of about 0.75 electron from lithium to the hydrogen atomic centre [37], indicating a strongly polar bond. For such an ionic (or, more properly, strongly polar) bond in a crystalline environment there might appear to occur a much greater transfer of electronic density from the region of one atomic centre to another than actually occurs in a covalent bond such as between carbon atoms mentioned above. Whether the electronic density in inorganic crystals is consistent with superposition of ions or of atoms becomes a pertinent question [33]. A careful analysis of crystalline  $\text{Li}_2\text{BeF}_4$  according to both atomic and ionic models yielded almost identical indices of the goodness of fit of 6435 independent reflections of xrays, but supplemental measurements on only 22 weak reflections more sensitive to the electronic distribution indicate that charge density far from atomic centres is slightly better represented on a basis of neutral atoms than of ions [38]. As scattering of xrays in a crystal of  $\text{Li}_2\text{BeF}_4$  is dominated by the electronic density present near the fluorine atomic centres, of which most electronic density is insensitive to the environment, a superior test to distinguish ions and atoms might be made with a crystal of LiH.

In conclusion of this discussion of chemical binding in inorganic species, the question whether crystals traditionally considered ionic consist of atomic ions or of nearly electrically neutral atomic centres remains generally unresolved. For the same reason the energy of an ionic bond appears not to differ greatly from that of a covalent bond at comparable internuclear separations typical of structures in these crystalline environments. Consistent with this condition, calculations of metallic lithium and sodium-and even methane-according to an ionic model provide moderate agreement with experimental measurements of cohesive energy [39], despite these substances being regarded as not ionic.

The problem of locating hydrogen atomic centres within unit cells of crystals by means of xray diffraction contrasts with the ease of calculating electronic structure and properties of  $H_2^+$  and  $H_2$ . The latter systems have been favoured vehicles to test the virial theorem [40] in relation to relative contributions of kinetic and potential energies of electrons to the net binding energy, commonly as a function of internuclear distance. According to such calculations one can readily demonstrate that Bader's attribution [41] of the phenomenon, that accumulation of electronic charge in the internuclear region causes the potential energy of a system to increase rather than to decrease, only to a system that fails to obey the virial theorem is inaccurate. His definition of an atom, or functional group, within a molecule is not unique, despite his profound reflections on this subject [42]; other definitions would yield atoms of varied size and shape, as any partition of electronic density within a molecule is fundamentally arbitrary. If the electronic density about any isolated atomic centre were to show a radical alteration on formation of a chemical bond, in contravention of the argument above, the atomic centre most likely to exhibit such effects would be hydrogen. For such a reason, just as to extrapolate from results for an H atom (for which Schrodinger's equation is solved exactly as an atomic system with one electron-two bodies in total) to atoms with many electrons is invalid, so to infer much about another chemical bond from effects that one readily calculates for  $H_2$  is unwise: the hydrogenic atomic centre is special in involving only a *valence* electron.

#### 4. Mechanisms of reactions

A theory of absolute rates of chemical reactions based on purported thermodynamic properties of an energised species (formerly activated complex) is of long standing [43], but severe and convincing criticisms of that theory are of equal longevity [44]. The quintessential equation of this theory is expressed as

$$k' = \kappa (k_B T/h) e^{-\Delta H^{\frac{1}{4}}/(R_g T)} e^{\Delta S^{\frac{1}{4}}/R_g}$$
(1)

in which k' is the coefficient of the rate of a bimolecular reaction between reactants A and B in solution at temperature T [45]:

$$A + B \rightarrow products$$
 (2)

a transmission coefficient  $\kappa$  measures the efficiency of passage of the energised species through a transition state to yield the products, although  $\kappa$ is almost invariably accorded a value unity;  $k_B$  is the Boltzmann constant (the ideal-gas constant  $R_g$  divided by the Avogadro constant  $N_A$ ), h is the Planck constant, and  $\Delta H^{\ddagger}$  and  $\Delta S^{\ddagger}$  are respectively the standard molar changes of enthalpy and entropy for the conversion of reactants into the activated complex  $AB^{\ddagger}$ . The latter species, purported to be in equilibrium with the reactants, proceeds somehow to form the eventual products; confusion between a thermodynamic equilibrium and a steady state (if  $\kappa$  is unity) failed to daunt the originators of this approach. As  $k_B$  pertains to molecules rather than to moles, the dimensions of k' are the product of the reciprocal of a concentration of molecules per unit volume and a reciprocal of time [46]. The reaction of A and B is characterised empirically with an activation energy  $E_a$  according to an equation

$$k = A e^{-E_a/R_g T} \tag{3}$$

that Arrhenius attributed to van't Hoff, in which the coefficient k pertains to an overall rate of reaction according to a defining rate law

$$-d[A]/dt = v = k[A][B]$$

$$\tag{4}$$

for the velocity v of the reaction at time t. The dimensions of k are therefore those of reciprocal of concentration and of reciprocal of time. To make the latter two equations consistent with the former one, one must include a volume in that equation. If one considers both equations in terms of molecules, instead of moles, per unit volume  $(m^3)$ , one writes

$$k' = (k_B T/h) V^{\ddagger} e^{-\Delta H^{\ddagger}/(R_g T)} e^{\Delta S^{\ddagger}/R_g}$$
(5)

$$k' = (1/N_A)Ae^{-E_a/(R_gT)}$$
(6)

Then if we assume, for the purpose of estimating an order of magnitude of the pertinent quantity, a spherical volume  $V^{\ddagger} = \frac{4}{3}\pi R^3$ , that volume is identified with  $(1/N_A)$ . Hence the radius R of the energised species is  $\approx 7 \times 10^{-9} m$ , the same for all reactions [46]! From the combination of the latter two equations under these circumstances,  $-\Delta S^{\ddagger}/J K^{-1} mol^{-1}$ lies in the range [0, 200] for selected reactions [46], but such values are meaningless as they depend on the invariance of  $V^{\ddagger}$ .

This theory of the absolute rate of reactions is fundamentally spurious [46]; its parameters  $\Delta G^{\ddagger}, \Delta H^{\ddagger}, \Delta S^{\ddagger}, V^{\ddagger}$  et cetera have no meaning outside this context. Despite this severe failure, Gibbs energies, enthalpies and entropies of activation are commonly reported for reactions in solution, even though this theory takes no account of the influence of the solvent (or environment) on the mechanism; the research field called physical organic chemistry that had as its objective to investigate and to characterise reactions in solution according to such tenets is practically moribund. Within the classical concept of molecular structure, a reaction takes place on a hypersurface of potential energy: no hypersurface of Gibbs energy G is definable.

Moreover even the justification of the classical concept of molecular structure by means of the approach of Born and others is precariously applied to an energised species. The transition state of which some authors undertake unremittingly to calculate directly the geometry with computer programmes for molecular electronic structure is neither a quantum state nor a thermodynamic state: the result of such calculation can best be called a transition structure; as such a structure generally implies a point on a hypersurface of potential energy at which (adiabatic) electronic states might intersect or interact strongly, the approximation due to Born and Oppenheimer is least valid in these conditions. For some small stable molecules having nearly the minimum energy (relative to unexcited atoms) and with due account of perturbations (adiabatic and nonadiabatic effects that are artifacts of the approximate separation of electronic and nuclear motions) [47], the concept of molecular structure is demonstrated to be practicable; the corresponding experimental justification and detailed evaluation of a definable structure of any postulated transition state or of an effective structure within an actual quantum state of the energised species remains a worthy but formidable objective, to which experiments are currently directed. To the extent that such a species has necessarily only transient existence, the experimental evaluation of its intrinsic properties becomes correspondingly hampered, in accordance with Heisenberg's principle of indeterminacy. Improved theories of reaction kinetics that retain the notion of a transition state are based on a potential-energy surface [48, 49].

As a mechanism of a specific chemical reaction, we consider briefly a stereospecific electrocyclic process, namely the conversion of buta-1,3-diene to cyclobutene. Woodward and Hoffmann [50] postulated that the stereochemical course of electrocyclic closure to form a ring of carbon atoms is set according to the symmetry of a particular molecular orbital, that of greatest energy with which electrons are associated, in the acyclic precursor. Support for this generalisation came from calculations based on an extended Huckel theory (disreputable for reasons stated above), which also indicates application to reactions in which such a ring of carbon atoms was opened. Such an explanation is unsatisfactory because the structure of the product of the reaction of ring opening, rather than the structure of the reactant, appears to govern whether the reaction is conrotatory or disrotatory, apart from the problems of reliability associated with extended Huckel theory in supporting predictions of a rule based on the symmetry of a single hypothetical molecular orbital. As any orbital, atomic or molecular, is an artifact of a particular mathematical method, and as in a thorough calculation of electronic structure including electronic correlation no orbital remains at the end of the calculation, such an approach is inherently suspect.

Longuet-Higgins and Abrahamson developed an alternative and more systematic procedure by considering the symmetry of electronic states, hence generating correlations along the entire course between reactants and products, without engaging in numerical calculations [51]. In this way predictions eventuated for not only the interconversion of cyclobutene and buta-1,3-diene but also of cyclopropyl radical, cation and anion and each corresponding allyl species. Although the latter authors maintained reliance on atomic and molecular orbitals to produce the symmetries of electronic states, these symmetries can be in principle determined on analysis of rotational fine structure in molecular spectra; in that sense symmetries are observable properties. The so called conservation of orbital symmetry lacks physical foundation as it relies on constituents of a basis set that one can in principle select arbitrarily, without even regard for the accuracy of an ultimate energy that might result from an actual calculation employing them according to a conventional procedure.

# 5. Conclusion

In this essay I extend the discussion of chemical binding to include what are conventionally called ionic compounds and inorganic crystals, and summarise aspects of mechanisms of chemical reactions. If as a consequence of perusing this essay and its predecessor [2] the reader acquires a pessimistic view of the present status of understanding of fundamental chemical phenomena and properties, he might appreciate the paradox that, although "chemistry is demanding on the intellect, it is increasingly anti-intellectual" [52]. "Terms such as electronegativity, hybridisation and orbitals are used in meaningless explanations (in chemistry), devoid of intellectual content" [52]. Selinger's reflections in 1982 on the dichotomies between teaching and research in chemical science, between the lip-service to quantum mechanics as the basis of chemical science and the selective use of quantal terms in circular arguments to rationalise essentially classical observations, remain valid. As an imminent advance in quantum theory, or its total replacement due to obsolescence on the emergence of a successive theory at once more readily understandable and easily applicable, seems unlikely, what is needed to improve the internal consistency of chemical theory is a thorough reassessment of essential chemical knowledge worthy at each successive stage of the educational process.

Does the nature of the chemical bond matter [53]? "The most useless part of chemistry-theoretical-is widely taught, seldom understood or appreciated and its redeeming feature (its profound philosophical implications) ignored" [52]. In such grossly exaggerated claims as "great successes of quantum chemistry [actually quantum-chemical computations] that super high accuracy predictions can now be made" [54], the practitioners of calculations, so called ab initio (despite their calibrated basis sets) - or perhaps more accurately ad nauseum? - delude themselves as they seek to mislead their readers. The accuracy claimed for bond lengths is a few parts in  $10^{-13}$  m [54]; as a length of a typical C-H or O-H bond is about  $10^{-10}$  m, the ratio of this error is about one part in 400. In contrast the order of adiabatic effects in bond lengths is the ratio of an electronic to a nuclear mass [37], so a maximum about one part in 1800 in the case of the mass of a proton. Hence the errors of such computations of bond lengths are still typically at least a few times the magnitudes of the corresponding adiabatic effects, whereas nonadiabatic effects are entirely ignored despite having magnitudes comparable to those of adiabatic effects for small molecules [37], and these errors amount to a thousand times the meaningful uncertainties of equilibrium bond lengths and properties of small molecules [55]. If the nature of the chemical bond matters, we should expend a serious effort to ensure that during the teaching of chemistry as an "indoctrination of the student with current paradigms-the behavioural code of normal science" [52] chemical binding in gaseous and crystalline matter is provided a more firm foundation than the confused collection of empty rhetoric abounding in the present chemical literature.

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