

Overview Lecture

The Lewis acid–base concepts: recent results and prospects for the future

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Abstract—Since many of the applications of the Lewis acid–base concepts to problems in the field of surface chemistry are dependent on the use of the three basic models of Lewis acid–base phenomena introduced in the 1960s (the HSAB principle, the *E & C* equation, and the DN–AN approach), this overview lecture briefly summarizes and comments on the published literature on these models that has appeared since they were last reviewed in 1980. It also comments on the problem of extending them to the multi-site interactions characteristic of polymers and surfaces and suggests some possible directions for future work in this area.

Keywords: Lewis acid–base; HSAB principle; *E & C* equation; donor–acceptor numbers.

1. INTRODUCTION

When asked to give an overview lecture for this symposium in honor of Dr. Fowkes, a number of possible themes suggested themselves. The most obvious choice would have been a review of Dr. Fowkes's own work on the application of acid–base concepts to problems in the field of surface chemistry. However, it is well to remind ourselves that, although we have selected this topic as the theme for this symposium, we are actually celebrating Dr. Fowkes's entire career, and this encompasses far more than just his work with the Lewis acid–base concepts, which, if anything, is merely the most recent entry in a long and distinguished list of contributions. To single out just this aspect would, then, be a distortion and to try and deal with the whole would be an act of hubris on my part, since I am an inorganic chemist, rather than a surface chemist, and I am really not competent to evaluate the significance of Dr. Fowkes's other activities in the field.

A second possible choice would have been to provide an overview of the relevance of the Lewis concepts to problems in the area of surface chemistry and to review recent examples of their successful application. However, given the nature of this symposium, this would be akin to carrying coals to Newcastle, as I would not only be preaching to the already converted (however pleasant that prospect), but performing a redundant service as well, since the proceedings of this symposium will in fact constitute just such a state-of-the-art review.

A third possibility would have been to provide a general introduction to the Lewis acid–base concepts which could serve as a background review for the more specialized papers which follow. Though a pedagogically laudable task, it is also one which I have performed many times in the past [1–7] and, quite frankly, I am tired of listening to myself.

As implied by my title, my final and actual choice is a bit more specialized and presumes some familiarity, not only with the original Lewis acid–base definitions, but with much of their evolution during the last 70 years. My justification for this choice is best seen by first giving a very abbreviated overview of this evolution, which I have divided into four fundamental, and largely non-overlapping, periods (Table 1).

Table 1.

The four fundamental periods in the evolution of the Lewis acid–base concepts

The classical period

- Original definitions (Lewis, 1923, 1938)
- Electrophiles and nucleophiles (Ingold, 1933)
- First monograph (Luder and Zuffanti, 1946)

The quantum-mechanical period

- Quantum-mechanical treatment of charge-transfer complexes (Mulliken, 1951)
- Frontier orbital theory of electrophilic and nucleophilic reactivity (Fukui, 1952, 1954)
- First monograph (Briegleb, 1961)

The quantitative period

- Hard–soft acid–base principle (Pearson, 1963)
- *E & C* equation (Drago and Wayland, 1965)
- Donor and acceptor numbers (Gutmann *et al.*, 1966, 1975)
- Perturbation theory of reactions (Hudson and Klopman, 1967)
- First comparative monograph (Jensen, 1980)

The applied period

- First applications to surface chemistry (Fowkes, 1972)
 - First monograph (proceedings of this symposium)
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The first of these, the classical period, corresponds to the introduction of the original definitions by Lewis in 1923 [8] (and again in 1938 [9], this time with substantially more impact) using the idiom of the localized shared electron-pair bond; the independent introduction of the same concepts in organic chemistry by Ingold in 1933 under the guise of electrophilic and nucleophilic agents [10, 11]; and the publication of the first monograph on the subject by Luder and Zuffanti in 1946 [12].

This was followed in the 1950s by the quantum-mechanical period, which saw a rephrasing of the concepts within the idioms of both valence bond and molecular orbital theory, largely as a result of Mulliken's theoretical treatment of so-called charge-transfer complexes [13] and Fukui's frontier orbital theory of nucleophilic and electrophilic reactions [14]. The first monograph dealing with Mulliken's approach was written by Briegleb in 1961 [15].

The 1960s saw the beginning of what I have called the quantitative period, in which a variety of attempts were made to quantify the Lewis concepts. Foremost among these were the hard–soft acid–base (HSAB) principle of Pearson [16], the *E & C* equation of Drago and Wayland [17], the donor and acceptor numbers of Gutmann and co-workers [18, 19], and the perturbation theory of Hudson and Klopman [20], which was largely an attempt to rationalize quantum-mechanically the HSAB principle. Though all of these authors published books during

the 1960s and 1970s dealing with their particular approaches [21–24], the first comparative monograph was not published until 1980 [3].

The fourth and final period, that of applications, began in 1972 with Dr. Fowkes's first attempts to apply the *E & C* approach of Drago and co-workers to problems in surface chemistry [25] and, until recently, he has remained almost the only person to actively pursue this line of research. However, the large number of participants in this symposium is elegant testimony to the fact that this situation is rapidly changing, and there is little doubt that, when finally published in book form, the resulting symposium proceedings will constitute the first definitive monograph to deal with this aspect of Lewis acid–base chemistry.

Given that each of these periods is dependent on its predecessors and, in particular, that much of the work being done during the applied period is based on the models introduced during the quantitative period, I felt that I, as an inorganic chemist interested in the Lewis concepts, could best serve the needs of those of you who are active in applying them to the field of surface chemistry by critically reviewing some of the basic literature on the Lewis concepts that has appeared since the publication of ref. [3] in 1980, and also by reminding you (in roughly chronological order) of some of the unresolved problems still present in many of the original models. In the process, I will also comment on some potential problems in extending these models, which were largely developed for discrete molecular and ionic species, to the multi-site acid–base interactions characteristic of polymers and surfaces. Lastly, I hope to suggest some new approaches to the ongoing problem of quantifying Lewis acid–base interactions.

2. THE HSAB PRINCIPLE

The most important advance in this area since 1980 is the introduction of the concept of absolute hardness by Parr and Pearson [26–29] in 1983 using the method of density functionals. This defines the electronegativity (χ) of a species as the negative rate at which the energy (E) of the species changes with a change in its electron population (N) at constant potential (v):

$$\chi = -(\partial E/\partial N)_v = (I + A)/2, \quad (1)$$

where I is the ionization potential of the species and A is its electron affinity.

The absolute hardness (η) of a species is, in turn, defined as half the negative rate at which its electronegativity changes with a change in its electron population at constant potential:

$$\eta = -(\partial\chi/\partial N)_v/2 = (\partial^2 E/\partial N^2)/2 = (I - A)/2, \quad (2)$$

where the factor of 1/2 has been arbitrarily introduced in order to create a formal symmetry between the final expressions for electronegativity and absolute hardness when defined in terms of I and A .

Since most chemists are trained to think in terms of orbitals rather than density functionals, Pearson has attempted to translate these results into molecular orbital theory [30, 31]. Within this context, the absolute hardness of a closed-shell species with only doubly occupied orbitals becomes a measure of the

energy separation between its frontier orbitals (i.e. its HOMO–LUMO gap)—a parameter which is large for hard species and small for soft species. This conclusion is essentially identical to the definition of softness given by Jørgensen over two decades ago [32] and also correlates with the polarizability of a species, a property which, in the case of Lewis bases at least, is commonly used as qualitative measure of softness [33]. In the case of open-shell species with a singly occupied orbital, the absolute hardness becomes a measure of intra-orbital electron repulsion. This is large for hard species with small, highly localized orbitals and small for soft species with large, diffuse orbitals.

Using the definition in equation (2), Pearson has also calculated hardness values for a large number of discrete ionic and molecular acids and bases, both in the gas phase and in aqueous solution [31, 34, 35] and later in this symposium Dr. Lee [36] will discuss its possible extension to solids in terms of the energies of their valence and conduction bands.

If one assumes that the degree of charge transfer between an interacting acid and base is a function of the difference in their electronegativities and ceases when these become equal, then the relation between hardness, as defined by equation (2), and the degree of electrostatic vs. orbital perturbation in an acid–base interaction becomes immediately apparent. The electronegativities of species with large values of η are very sensitive to changes in N and will rapidly equalize with only a small degree of charge transfer. In other words, there will be little orbital perturbation and the stability of the resulting hard–hard acid–base complex will depend, for the most part, on the initial net charges and/or dipoles present on the interacting acid and base and will be largely electrostatic in nature. For soft species, the opposite will be true. The low sensitivity of χ to changes in N will result in extensive charge transfer between the acid and base before an equalization of their electronegativities occurs and will lead to extensive orbital perturbation [37].

It should, however, be pointed out that there are many other quantitative softness scales in the literature, including several proposed since 1980 [6, 38–41], which give comparable results and that the absolute hardness concept is not without its problems. These include, in the case of anionic bases, the necessity of applying equation (2) to the neutral atom, rather than to the anion itself, in order to obtain a consistent scale; anomalous η values for Tl^+ vs. Tl^{3+} , for gas-phase vs. aqueous species, and for both H^- and H^+ . In the latter case, there is no value for the ionization potential in equation (2), so η cannot be calculated, though Parr and Pearson have finessed this by arguing that its absence implies that it is really infinite in value.

Interestingly, the H^+ ion, which has been taken as the quintessential example of a hard species, is really atypical in its behavior and also has an anomalous position on many of the other softness scales that have been proposed. Thus, use of the simple criterion that the bonding in hard–hard complexes is largely ionic or polar, whereas that in soft–soft complexes is covalent, would place H^+ , in contrast to the alkali metal ions, in the soft category. Likewise, the use of either gas-phase LUMO energies or orbital electronegativities ranks H^+ as the softest of all the M^+ ions [3]; the use of redox potentials places it between Cu^+ and Tl^+ [3], as does the Pearson–Mawby scale [42]; and the Ahrland scale places it between Cs^+ and Cu^+ [43]. DeKock [44] has also cited several examples of

orbital-controlled electrophilic attack by H^+ , behavior which is again considered to be characteristic of soft, rather than hard, species.

These placement problems reflect a long-standing ambiguity in the phraseology of both the HSAB classification and the HSAB principle. As originally derived from the Edwards equation, softness was intended to be an additional factor in the stabilization of nonprotonic acid–base complexes, as expressed by the relation

$$\log K_{AB} = S_A \cdot S_B + \sigma_A \cdot \sigma_B, \quad (3)$$

where S_A and S_B are the strength parameters of the interacting acid and base, and σ_A and σ_B are their softness parameters. In this relation, H^+ was taken as the arbitrary zero point for σ_A so that

$$\log K_{HB} = pK_a = S_A \cdot S_B. \quad (4)$$

Species which were softer than H^+ would have positive values of σ and experience additional stabilization in their complexes, whereas those which were harder would have negative values and experience destabilization. It was further assumed that the strength parameters could be calculated using an electrostatic model of some sort, whereas the softness parameters would reflect the ability of the species to undergo charge-transfer and orbital perturbations, leading to a significant covalent contribution to the bonding.

The ambiguity in the HSAB classification is the result not only of forgetting that H^+ was intended as an arbitrary zero, rather than as an absolute zero, for the softness scale, but of forgetting that the application of relation (3), in either a qualitative or a quantitative sense, requires that species be ranked according to *both* strength and softness. Indeed, it is a simple matter to show that most scales of so-called softness reproduce Pearson's original qualitative classification only if one uses the ratio σ/S rather than σ alone [3]. The simplest way to do this is to construct a 'sorting map' of species by plotting their S values vs. their σ values. If this is done for ions, using Z/r as the strength parameter, one finds that one must use diagonal lines, rather than vertical lines, to separate the species in the plot into regions corresponding to the hard and soft classification (see Figs 1 and 2). In other words, the classification is a function of σ/S (or S/σ , if you wish to maximize the ratio for hardness rather than softness) rather than σ alone. Thus, H^+ appears in the hard category, in spite of its moderate-to-large σ value on most scales, because it also has a large S value and thus gives a σ/S ratio similar to that of the alkali metal ions, which have inherently smaller values of both σ and S .

The confusion relative to the wording of the HSAB principle itself stems from the fact that relation (3) implies that any statement regarding the stability of acid–base complexes which mentions hardness and softness, but not strength, is incomplete. On the other hand, if such a statement is complete, then the current HSAB classification implies that it is only necessary to know the ratio of σ/S in order to make a prediction about stability, rather than the independent values of S and σ , as implied by relation (3).

This latter problem has been partly tested in an interesting paper published by Arbelot and Chanon in 1983 [45]. Using a purely qualitative version of the HSAB classification, in which species were placed in either the soft, hard, or

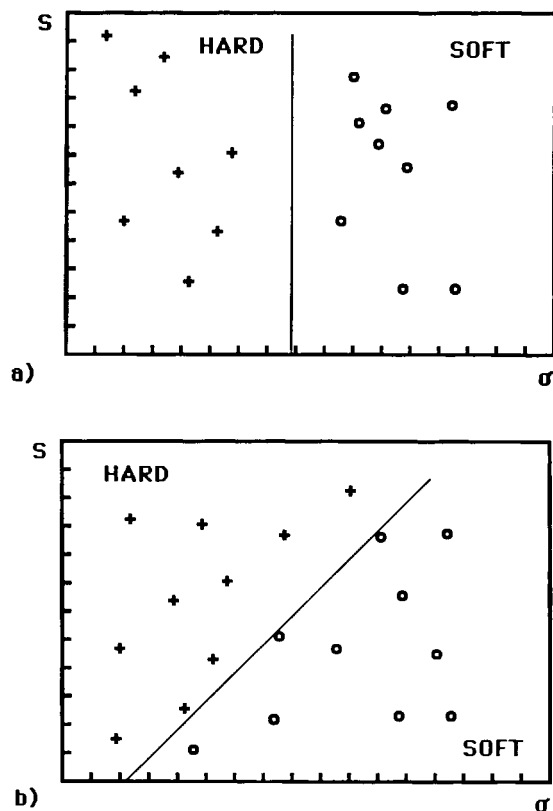


Figure 1. Two limiting cases of an idealized sorting map, based on a plot of the strength (S) vs. the so-called softness (σ) parameters for various species. Circles indicate soft species according to the HSAB classification and crosses indicate hard species. If the classes can be sorted using only vertical lines, as in (a), then σ alone reproduces the HSAB classification. If diagonal sorting lines are required, as in (b), then the classification is really based on some function of σ/S (or S/σ). For more on sorting maps and their uses, see refs [77, 78].

borderline categories, but not ranked within these categories in terms of relative softness, they first showed that such a model could be applied to only 25% of all potential acid–base interactions. That is, one could apply it only to situations in which a clear choice was presented in terms of the three categories (e.g. a hard acid selecting between a hard base and a soft base, but not between two alternative hard bases). Within this 25%, they then tested the version of the HSAB principle that ignores the operation of strength as an independent parameter on 320 example reactions involving gas-phase ionic species, gas-phase molecular species, and aqueous ionic complexes. The principle gave a correct prediction in only 60% of the cases studied, which is barely above random guess.

In order to test the version of the HSAB principle in which softness and strength operate independently, they then established a similar qualitative classification of species as strong, borderline, and weak based on the use of pK_a data. This dropped the number of applicable cases for a purely qualitative model to 9.2% of all possible acid–base interactions, though, within this more restricted set, the success rate of the extended version of the HSAB principle, based on

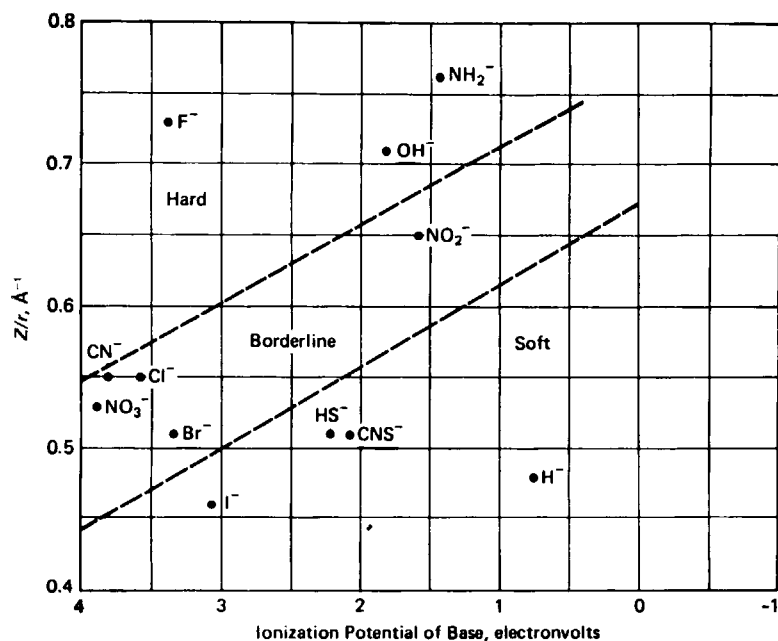


Figure 2. An example of an actual sorting map showing a plot of strength for various ionic Lewis bases, as measured by Z/r , vs. softness, as measured by the first ionization potential. Diagonal lines are required to reproduce the HSAB classification, indicating that it depends on the ratio $I \cdot r/Z$, rather than on I alone (from ref. [3]).

both strength and softness, rose to 86%. Their conclusion was that a purely qualitative classification was much too restricted in its application and that quantitative scales of both strength and softness must be used in conjunction with a relation similar to that in equation (3). In short, the purely qualitative form of the HSAB principle, which refers only to hardness and softness, is wrong.

A similar evaluation of the HSAB principle has been made by Purcell [46] within the limits of the E & C equation. He reported a success rate of 37.7% for the prediction of single displacement reactions and 71.9% for double displacement reactions.

3. THE E & C EQUATION

The E & C equation was introduced by Drago and Wayland in 1965 to predict the enthalpies of formation of one-to-one molecular adducts in the gas phase and in poorly coordinating solvents [17]:

$$-\Delta H_{AB} = E_A \cdot E_B + C_A \cdot C_B, \quad (5)$$

where the E parameters supposedly represent the electrostatic contributions of the acid and base to adduct stability and the C parameters represent the covalent contributions. The parallel between this equation and relation (3) is obvious, and it has proved highly successful for the systems for it was originally designed. The only exception appears to be the E_A and C_A values for $SbCl_5$, which Drago introduced in order to make comparisons with Gutmann's donor numbers (see

next section). As Marcus has recently noted, the predictions for the adducts of this acid agree very poorly with the experimental values reported by Gutmann [47].

It should also be noted that, in spite of the names assigned to the parameters and their implied basis in bonding theory, there is, to the best of my knowledge, no evidence that they in fact reflect the relative electrostatic and covalent contributions to the bonding in the resulting adducts. That is, they have not been shown to correlate with either a physical property (e.g. dipole moment, ionization potential, etc.) or with a quantum-mechanically calculated index thought to parallel such contributions. This observation, of course, does not damage their value as a purely empirical method of calculating enthalpies of formation for molecular adducts; it is merely intended to warn users that they should not take the implied theoretical basis too literally.

The original E & C equation was designed to deal with enthalpies of gas-phase acid–base interactions and, by implication, with bond energies. However, in the last decade, Drago and co-workers have attempted to explore its relationship to other acid–base scales, most of which are based either on spectral shifts or on free-energy data, using the modified equations [48]

$$\Delta X + W = E_A^* \cdot E_B + C_A^* \cdot C_B \quad (6)$$

and

$$\Delta X + W = E_A \cdot E_B^* + C_A \cdot C_B^*, \quad (7)$$

where ΔX is the change in the property in question (and is equal to $-\Delta H_{AB}$ in the case of the original gas-phase enthalpies), W is any constant contribution to the interaction when a given acid interacts with a series of bases [equation (6)] or a given base interacts with a series of acids [equation (7)] and is equal to zero in the case of the gas-phase enthalpy data correlated by the original equation, and the starred E and C parameters are the original unstarred values modified to incorporate the necessary conversion factors between the units of enthalpy and those of the new property, ΔX , (i.e. frequency shift, $\log K$, etc.) being correlated. Using these relations, they have established correlations between the E and C model and such properties as the Hammett substituent coefficients [49], the Soret band [50] and IR frequency shifts which accompany acid–base adduct formation [49], the Kamlet–Taft β parameter [51], and the theoretical basis of linear free-energy correlations in general [52]. Correlations between the E and C model and both cobalt–carbon bond strengths [49] and metal–metal bond strengths [53] have also been established.

An attempt to extend the original E & C model in yet a second direction was made by Kroeger and Drago in 1981 [54]. They proposed a revised six-parameter equation:

$$-\Delta H_{AB} = e_A \cdot e_B + c_A \cdot c_B + t_A \cdot t_B, \quad (8)$$

in which the e and c parameters again represent the (redetermined) electrostatic and covalent contributions of the acid and base, and the additional t parameters reflect their ability to undergo charge transfer. It was hoped that this extended equation would allow ion–ion adducts and ion–molecule adducts, as well as the molecule–molecule adducts covered by the original E & C equation, to be

incorporated within a single model. However, as far as I know, there has been no further development of this approach, though more recently a third proposal has been made which is apparently able to deal with gas-phase enthalpies for neutral molecule–ion interactions [55, 56].

The original *E* & *C* equation has been the model of choice for Dr. Fowkes in his work on the application of Lewis acid–base theory to surface chemistry, and he has attempted to determine *E* and *C* parameters for both polymers and surfaces [57]. The only potential problem with such extensions lies in the fact that the *E* & *C* equation implicitly assumes that a molecule is either a Lewis acid or a Lewis base. In reality, most molecules have both donor and acceptor sites, though usually one of these functions clearly dominates the molecule's chemistry. Nevertheless, when we are dealing with bulk liquids, in which self-association of the molecules plays an important role, this amphoteric behavior is potentially important.

4. DONOR AND ACCEPTOR NUMBERS

The donor number (DN), as a measure of Lewis basicity, was introduced in 1966 by Gutmann, Steininger, and Wychara [18], and was defined as the negative of the enthalpy of formation for the adduct formed between the base in question and the reference Lewis acid, antimony pentachloride:

$$\text{DN}_B = -\Delta H(\text{SbCl}_5\text{-B}). \quad (9)$$

This was supplemented in 1975 by the introduction of the acceptor number (AN) as a potential measure of Lewis acidity for a species [19]. This was defined as the relative ^{31}P -NMR shift induced in triethylphosphine oxide (Et_3PO) when it was dissolved in the species in question. This was further scaled by assigning a value of 0 to the shift induced by hexane and a value of 100 to the shift produced by SbCl_5 upon interacting with Et_3PO in a dilute 1,2-dichloroethane solution.

Gutmann further proposed that the enthalpy of a given acid–base interaction could be approximated by a two-parameter equation of the form

$$-\Delta H_{AB} = \text{AN}_A \cdot \text{DN}_B / 100, \quad (10)$$

where the factor of 100 converts the AN value from a percentage of the SbCl_5 value to a decimal fraction.

Some comments on both scales and on the interaction equation itself are in order. First, it is important to realize that many reported DN values are only approximate, as they have been determined indirectly by means of linear correlations with other reported measures of Lewis basicity, rather than being directly measured in the laboratory via equation (9). Thus, of the 171 values given by Marcus in 1984 [47], only 50 were determined calorimetrically. Indeed, for some of the so-called 'bulk' donicity values given in the literature, Marcus reported that he was unable to track down the origins of the original approximations. Even in the case of those values that were determined experimentally, there is evidence of errors of the order of ± 3 kcal in the reported values, due in part to the limitations of the original calorimetric procedure used [58, 59].

In 1985 Maria and Gal [59] reported a parallel measure of donor ability based on the enthalpy of interaction with the reference acid BF_3 . Rather surprisingly, they found that their values correlated only moderately well with those based on

the Gutmann SbCl_5 scale and that they gave a family of lines when correlated with the Kamlet–Taft β parameter, which measures basicity relative to the H-bonding ability of the base. They have suggested, via the classic research of Brown, that steric strain may be involved. This was also suggested earlier by Drago and Lim relative to the adducts of SbCl_5 [47] and would imply a further modification of equation (3), via the addition of a steric parameter (s), to give a so-called triple s correlation (strength, softness, and steric strain) for the prediction of acid–base interactions:

$$\log K_{\text{AB}} = S_{\text{A}} \cdot S_{\text{B}} + \sigma_{\text{A}} \cdot \sigma_{\text{B}} + s_{\text{A}} \cdot s_{\text{B}}. \quad (11)$$

An equation of this form has actually been developed for aqueous ionic complexes by Handcock and Marsicano [41]:

$$\log K_{\text{AB}} = E_{\text{A}}^{\text{aq}} \cdot E_{\text{B}}^{\text{aq}} + C_{\text{A}}^{\text{aq}} \cdot C_{\text{B}}^{\text{aq}} - D_{\text{A}} \cdot D_{\text{B}}, \quad (12)$$

where, in analogy with the Drago E & C equation, the E^{aq} and C^{aq} parameters reflect the electrostatic and covalent contributions to complex formation (but are numerically different from Drago’s values), and the D parameters are thought to reflect desolvation phenomena, which are related, in turn, to both steric hindrance and specific solvation effects accompanying complex formation. It is also of interest to note that these authors have found, in keeping with our earlier discussion, that the HSAB classification correlates with the $C^{\text{aq}}/E^{\text{aq}}$ ratio of the species rather than with C^{aq} alone.

More recently, Riddle and Fowkes have raised some problems relative to the AN scale [60]. They have shown that dispersion-only liquids, such as hexane, produce a significant ^{31}P shift in Et_3PO and that consequently AN values should be corrected for this dispersion effect. In many cases, this correction is quite substantial. Thus, 13.7 of the original 14.2 AN units assigned to pyridine appear to be due to dispersion rather than to specific electron-pair donor–acceptor interactions, lowering its measure of ‘true’ Lewis acidity from 14.2 to 0.5. These authors have also found that these dispersion-corrected AN values correlate with the enthalpies of formation of the actual adducts formed between Et_3PO and the acid in question, and have suggested that this enthalpy be taken as the true measure, AN^* , of Lewis acidity for a species, thus giving both the DN and AN scales the same units. The relation between these various scales is given by the equation

$$\text{AN}^* = -\Delta H(\text{A-Et}_3\text{PO}) = 0.288(\text{AN} - \text{AN}^{\text{d}}), \quad (13)$$

where the AN values are the original values reported by Gutmann, and AN^{d} are the dispersion contributions reported by Riddle and Fowkes.

As for the two-parameter interaction equation in equation (10), this is known, on the basis of Gutmann’s own work, to be incorrect. In his original work on the DN scale, he found that the enthalpies of adduct formation for a given acid linearly correlated with the DN values of the bases (Fig. 3):

$$-\Delta H_{\text{AB}} = a \cdot \text{DN}_{\text{B}} + b. \quad (14)$$

This implies the necessity of a three-parameter, rather than a two-parameter, equation, with one parameter characteristic of the base (DN) and two characteristic of the acid (a and b , the slope and intercept of the line, respectively).

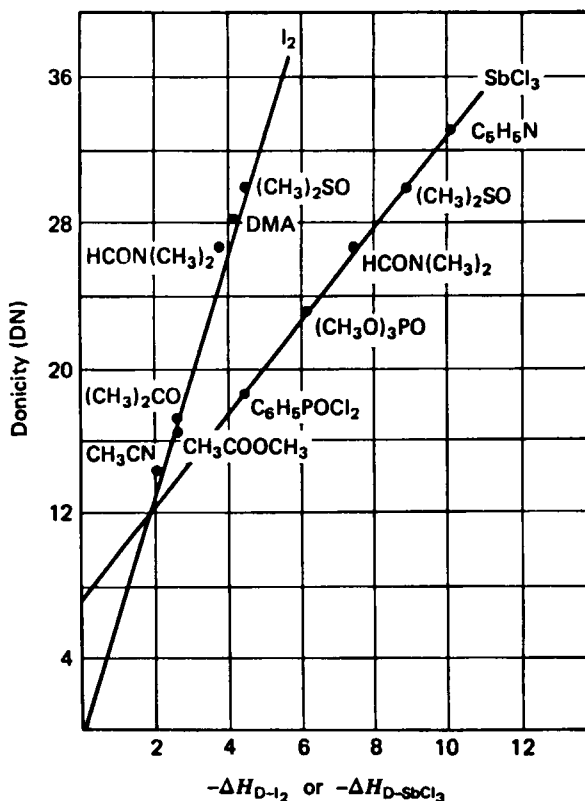


Figure 3. Two examples of a DN_B vs. $-\Delta H_{AB}$ plot. The fact that each acid gives a line with its own characteristic slope and intercept shows the necessity of using at least a three-parameter equation to correlate enthalpies of adduct formation.

Interestingly, about the same time, Satchell and Satchell [61, 62] found similar three-parameter linear correlations in their studies of adduct formation using metal halides as the Lewis acids and pK_a values as a measure of Lewis basicity:

$$\log K_{AB} = a \cdot pK_a + b. \quad (15)$$

These three-parameter correlations can be understood as an approximation to the four-parameter correlations implied by equations (3) and (5) by using the E & C equation. The bases used by both Gutmann and the Satchells are almost exclusively N and O donors, i.e. they are relatively hard, and an examination of the 39 N and O bases in Drago's list shows that the variations in their E_B values are quite small compared with the variations in their C_B values. Thus, the E_B values vary from 1.52 to 0.70, or less than one unit, whereas the C_B values vary from 13.2 to 0.53. (I have used the list of E and C parameters listed in ref. [63].) This is shown graphically in Fig. 4. Hence for this set of bases one can approximate the full E & C equation with the relation

$$-\Delta H_{AB} = 1.12 E_A + C_A \cdot C_B, \quad (16)$$

where 1.12 is the average value of E_B . Like equations (14) and (15), this now

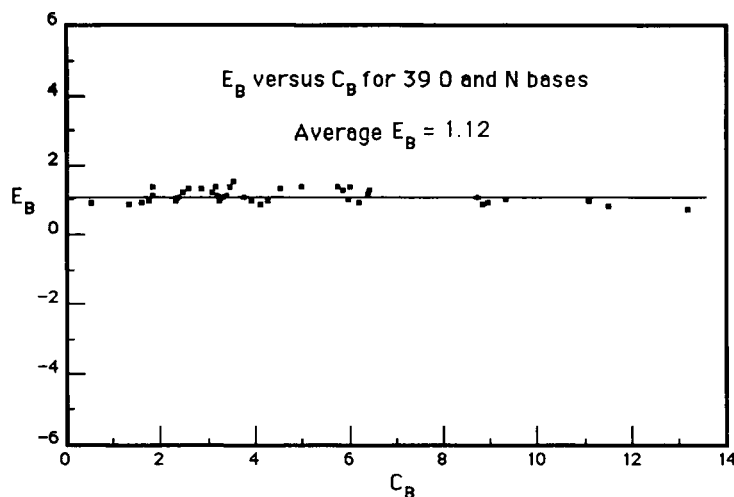


Figure 4. A plot of E_B vs. C_B for the 39 N and O donors in Drago's data set.

contains three parameters, one characteristic of the base (C_B) and two characteristic of the acid ($1.12 E_A$ and C_A , corresponding to the intercept and slope, respectively, of a plot of $-\Delta H_{AB}$ vs. C_B). An example plot is shown in Fig. 5 for the case of iodine adducts, for which $E_A = C_A = 1.00$, and for which equation (16) becomes

$$-\Delta H_{AB} = 1.12 + 1.00 C_B. \quad (17)$$

Obviously, the larger the E_A value of the acid, the greater the scatter will be in the corresponding graph.

Actually, the failure of the two-parameter interaction equation in equation (10) is not serious, as few authors have made use of it in their work, preferring instead

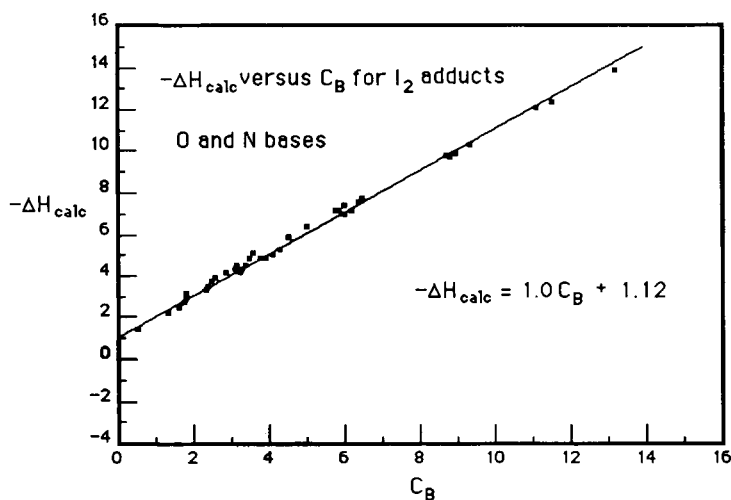


Figure 5. A plot of $-\Delta H_{AB}$ for adducts of I_2 vs. C_B of the base ($-\Delta H_{AB}$ calculated using the full E & C equation).

to use DN and AN values as empirical parameters within some more general linear regression correlation. For example [7],

$$P = P_0 + \alpha \cdot \text{DN} + \beta \cdot \text{AN} + \gamma \cdot \delta_d, \quad (18)$$

where P is the property whose value is varying as a function of the solvent, P_0 is the value of the property for the reference system, α measures the sensitivity of the property to solvent basicity, β measures its sensitivity to solvent acidity, and γ measures its sensitivity to dispersion interactions as measured by the dispersion-only solubility parameter, δ_d .

One final result of interest to the donor and acceptor number approach is a paper published by Sabatino, La Manna, and Paoloni in 1980 [64] which reported linear correlations between a variety of experimental parameters as a function of change in solvent (e.g. rates and activation energies for substitution processes, free energies of solvation and transfer for ions, etc.) and the corresponding calculated *ab-initio* HOMO and LUMO energies for the solvents in question. Since similar linear correlations could be made between the properties and the DN and AN values of the solvents, the authors implied that the calculated energies of the frontier orbitals directly paralleled these parameters, though for some unknown reason they did not perform the obvious act of directly correlating them with one another. If this identification is correct, then it is of interest to note that the Parr–Pearson definitions of absolute hardness and electronegativity imply that for these solvents

$$\chi = f(\text{DN} + \text{AN}) \quad (19)$$

and

$$\eta = f(\text{DN} - \text{AN}), \quad (20)$$

though the exact details of the functional dependence are unknown.

5. PROSPECTS FOR THE FUTURE

As can be seen from the above comments, though there have been some interesting developments since 1980, these have not resulted in a major revision of the original quantitative models introduced in the 1960s, most of which are now more than 25 years old. This observation raises the question of whether there are any other serious alternatives, aside from basic quantum-mechanical calculations, that might be developed in the next decade. One obvious possibility is, of course, the development of more complex multi-parameter empirical equations. The six-parameter equation of Kroeger and Drago [equation (8)] has already been mentioned and the six-parameter strength, softness, steric strain relations in equations (11) and (12) are yet another possibility.

A third serious candidate is the so-called ‘universal solubility equation’ of Kamlet, Taft, *et al.*, which has received a good deal of publicity in recent years [65–68]. Like equation (18), this is designed to predict the way in which a change in solvent will affect a given physico-chemical property, P , the most important of which is the solubility, measured as $\log K_{\text{sol}}$:

$$P = P_0 + A\delta_1^2 \cdot V_2 + B\pi_1^* \cdot \pi_2^* + C\alpha_1 \cdot \beta_2 + D\alpha_2 \cdot \beta_1. \quad (21)$$

The various terms in this equation are defined in Table 2. Several authors have reported good success with this relation and have indicated a preference for the Kamlet–Taft β measure of basicity over that provided by the DN scale [69]. My first reaction is that this success is hardly surprising, given that equation (21) contains at least 17 parameters, if one counts the correlation coefficients, the hidden correction parameters, and the alternative values of α and β . Indeed, one is tempted to paraphrase Cauchy’s famous remark that he could graph an elephant, if given enough disposable parameters, and, if given two or more, he could make it wag its tail.

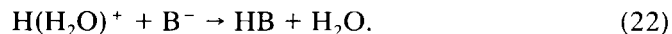
Table 2.
Definitions of the parameters in the universal solubility equation [67]

$\delta_1^2 V_2$	Product of the solubility parameter and molar volume
π^*	Polarity; may have to be modified with polarizability δ
α	H-bonding ability of the acid; may have to be modified as α_m
β	H-bonding ability of the base; may have to be modified as β_m

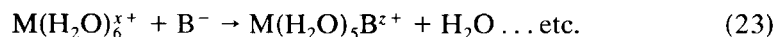
Actually, this is really not a fair comment, as equation (21) does not model simple acid–base adduct formation, but rather a more complex acid–base competition between solvent and solute, and a similar modeling of solubility using the conventional Lewis approach would be almost as complex. The real problem with the Kamlet–Taft approach is their denial of the usefulness of the Lewis concepts and their claim that at least three kinds of acidity exist: Lewis acidity, conventional Brønsted acidity as measured by pK_a values, and H-bonding acidity as measured by their α and β parameters [68]. This, of course, subverts the basic insight of the Lewis concepts relative to the fundamental identity of the electron-pair donor–acceptor mechanism underlying all of these phenomena.

In saying this, I do not wish to deny the uniqueness of H^+ relative to its electron-pair acceptor properties. Some of these idiosyncrasies were referred to earlier in our discussion of the HSAB classification, and they are in many ways a result of the unique position of hydrogen in the periodic table (Fig. 6). However, I do not believe that they are of such a magnitude as to necessitate a separate and unique vocabulary for describing both the reactivity and the composition of hydrogen compounds, as required by the Arrhenius and Brønsted approaches.

At this point it is perhaps worthwhile being a bit more explicit about these peculiarities and their bearing on the Lewis concepts. In contrast to other ionic Lewis acids, the H^+ ion is unique in that it is monobasic, each ion requiring only one unit of base for its neutralization:



Consequently, in keeping with the classic characteristic of acids and bases, it can be titrated with solutions of monodentate bases and displays sharp end-points. Metal ions, on the other hand, typically have coordination numbers of 4, 6, or greater and require more than one unit of a monodentate base for their neutralization:



G P	S1	S2
1	H	He

G P	P1	P2	P2	P3	P4	P5	P6	P7	P8
2	Li	Be		B	C	N	O	F	Ne
3	Na	Mg		Al	Si	P	S	Cl	Ar
4	K	Ca	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	112	113	114	115	116	117	118

G P	D3	D4	D5	D6	D7	D8	D9	D10	D11
4	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
5	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
6	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au
7	Lr	104	105	106	107	108	109	110	111

G P	F3	F4	F5	F6	F7	F8	F9	F10	F11	F12	F13	F14	F15	F16
6	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
7	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

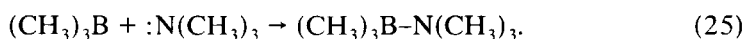
Figure 6. A 'four-block' periodic table emphasizing the unique position of hydrogen. Elements in the S-block (H and He) use only filled and/or empty *s* orbitals in their bonding. Elements in the P-block use filled and/or empty *s* and *p* orbitals; elements in the D-block use filled and/or empty *s*, *p* and *d* orbitals; and elements in the F-block use filled and/or empty *s*, *p*, *d* and *f* orbitals. This is a modification of the three-block table originally proposed by Sanderson. The smaller G/P symbols in the upper left of each block stand for group and period, respectively.

The result is a multi-step neutralization process and a smearing of the end-points, leading to an inability to determine metal ion concentrations in this manner. However, once the nature of this difference between the proton and other metal ions was understood, it became possible to design multidentate bases, such as EDTA, which could effect the neutralization of metal ions in a single step and so allow one to apply the conventional techniques of acid–base titration to their determination:



As the classic book by Tanabe shows [70], similar problems exist with the multiple donor and acceptor sites present on surfaces and polymers. Indeed, in the case of the latter especially, one would expect that the number of operative donor–acceptor sites would vary with temperature and so make the assignment of specific AN and DN values, or *E* and *C* parameters, difficult.

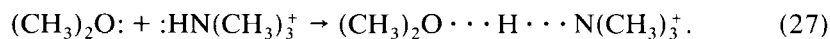
In contrast to metal ions, many molecular Lewis acids are, like the proton, monobasic. In this case, the difference between these species and the proton, as Brown pointed out long ago, lies in the possibility of developing steric strain in the resulting molecule–molecule adducts [71, 72]:



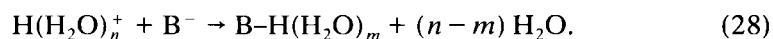
As long as we have a complete transfer of the proton to the base, steric strain should be at a minimum in the corresponding proton adduct, since the proton is the smallest possible acceptor site and has no attached groups to interfere with the groups attached to the donor site:



If, however, we are looking not at a complete transfer of the proton, but at an incomplete displacement of one base by another, as in the case of hydrogen bonding, then the exact opposite may be true. Here the small size of the proton, in contrast to larger acceptor sites, will maximize the crowding of the two bases and thus maximize the potential for steric strain in the resulting H-bonded complex:



This is, at least, what Handcock and Marsicano [41] have concluded, via the use of equation (12), to describe the formation of ionic complexes in water, and it might also account for the conclusions of Kamlet, Taft *et al.* that Brønsted basicity (complete proton transfer, minimum steric strain), as measured by pK_a values, appears to be different from H-bonding basicity (incomplete proton transfer, maximum steric strain), as measured by their β parameter. Drago, on the other hand, maintains that in aqueous solution there never is complete proton transfer and that equation (22) should be explicitly written as



In other words, the proton is always H-bonded and pK_a values simply measure a change in the H-bonding partners, in which case it becomes difficult to understand the basis of the distinction between β and pK_a , save, perhaps, as a function

of reaction stoichiometry (i.e. the difference between a simple addition reaction and a displacement reaction).

The importance of the steric problem for surface phenomena is that the potential for steric strain (this time between similar molecules adsorbed on adjacent sites) should increase as the degree of surface coverage increases, leading to a variation in the effective acidity or basicity of the surface as a function of the degree of surface neutralization.

In closing, I would like to make one final suggestion for future work and that is the possibility of calculating Lewis acid–base parameters by means of topological indices, rather than experimentally measuring them. It is a fundamental postulate of chemistry that the specific or intrinsic properties of materials, i.e. those properties that are independent of sample size, shape, and function, and which we use to characterize specific kinds of matter or substances, are a function of molecular composition, structure, and interaction:

$$\text{intrinsic properties} = f(\text{molecular composition, structure, interaction}). \quad (29)$$

This formulation is actually slightly redundant, as the degree of molecular interaction itself also depends, in part, on molecular composition and structure, as well as on extrinsic factors, such as concentration (c) and temperature (T); so that it is perhaps more accurate to write

$$\text{intrinsic properties} = f(\text{molecular composition, structure, } c, T). \quad (30)$$

Since the advent of the electronic theory of matter, chemists have largely ignored this level of functional dependence and have instead pursued a more reductionistic program:

$$\text{intrinsic properties} = f(\text{electronic composition and structure}). \quad (31)$$

However, the complexity of rigorous quantum-mechanical calculations has resulted in a movement to reconsider the more classical proposition in equation (30). For quantitative work, this requires the development of algorithms for reducing the classical composition and structure of a species to characteristic numerical indices which can then be used, in combination with linear regression analysis, to correlate and predict molecular properties.

Several popular reviews of this subject have appeared in recent years, the most accessible being those of Rouvray [73] and Seybold *et al.* [74], as well as a variety of topological algorithms, the most flexible of which has been the so-called Randic index, which has been extensively developed by Kier and Hall [75, 76]. In the Randic approach, each atom is assigned a characteristic ‘valence’ value, defined in one of two ways:*

$$\delta_i = \text{number of bonded atoms} - \text{number of bonded hydrogens} \quad (32)$$

$$\delta_i^v = \text{number of valence electrons} - \text{number of bonded hydrogens}. \quad (33)$$

These valence values are then combined in various ways to generate characteristic numerical indices that reflect various aspects of a molecule’s composition

*The definition of δ_i^v given here is for period 2 elements. A more general definition can be found in ref. [76].

and structure. The first of these, the 0th-order ${}^0\chi$ and ${}^0\chi^v$ indices, essentially reflect only composition:

$${}^0\chi = \sum(\delta_i)^{-0.5} \quad (34)$$

$${}^0\chi^v = \sum(\delta_i^v)^{-0.5}. \quad (35)$$

The sums are over all atoms, except the hydrogen atoms, which serve as an arbitrary zero point for the indices, and the χ and δ 's should not be confused with those used in earlier equations for electronegativity and the dispersion-only solubility parameter. The sum, ${}^0\chi + {}^0\chi^v$, has been shown to correlate with the molecular volume, whereas the difference, ${}^0\chi - {}^0\chi^v$, reflects the number of π and lone-pair electrons in the molecule and correlates with valence-state electronegativities.

First-order indices, which are summed over the bonds in the molecule, reflect information about both the composition and the molecular topology and distinguish between various topological isomers (see Fig. 7 for an example calculation for 1-propanol and 2-propanol):

$${}^1\chi = \sum(\delta_i\delta_j)^{-0.5} \quad (36)$$

$${}^1\chi^v = \sum(\delta_i^v\delta_j^v)^{-0.5}. \quad (37)$$

Higher-order indices can also be defined which are summed over larger fragments of the molecule:

$${}^2\chi = \sum(\delta_i\delta_j\delta_h)^{-0.5}. \quad (38)$$

The physical interpretation of these is not always apparent, though some are thought to reflect such properties as molecular flexibility for the region of the molecule in question.

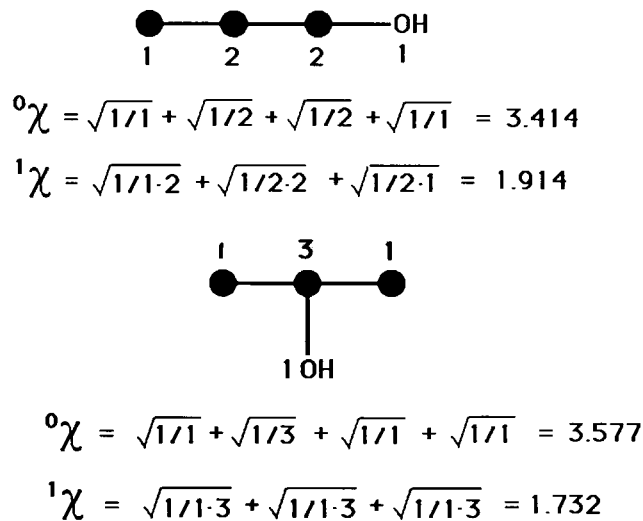


Figure 7. An example showing the calculation of the ${}^0\chi$ and ${}^1\chi$ indices for 1-propanol and 2-propanol. The H atoms are not shown, except on the OH group for ease of identification. Atoms are numbered with their δ values.

Kier and Hall, in their two monographs on this subject [75,76], have summarized an impressive array of physical and biological properties which can be correlated with these indices, some examples of which are listed in Table 3. Of particular interest to the Lewis acid–base concepts is a reported correlation between the ionization potentials, IP, of a mixed list of alcohols, amines, and ethers and the 0th- and 1st-order indices:

$$\text{IP (eV)} = 5.014 ({}^0\chi - {}^0\chi^v) + 5.166 ({}^1\chi - {}^1\chi^v) + 5.341, \quad (39)$$

where $r = 0.955$, $s = 0.299$, and $n = 24$. Likewise, the chromatographic retention times, RI, of alcohols can be correlated with ${}^1\chi$ and ${}^1\chi^v$:

$$\text{RI} = 486 {}^1\chi - 293 {}^1\chi^v + 44.9, \quad (40)$$

where $r = 0.995$, $s = 10.1$, and $n = 32$. Since ionization potentials are related to donor ability and several authors have attempted to correlate chromatographic retention times with solvent basicity and acidity, these results strongly suggest that it should also be possible to correlate such parameters as DN, AN, S , σ , s , or even $\log K_{AB}$ with such indices, thereby allowing one to calculate them solely from a knowledge of the classical structure and composition of the molecule in question.

Table 3.

Example properties successfully correlated by means of topological indices^a

Boiling points	Solubilities
Densities	Partition coefficients
Heats of atomization	Heats of formation
Solvent polarities	Anesthetic activity
Narcotic activity	Hallucinogenic activity
Toxicity	Sweet and bitter taste

^aBased on refs [75, 76].

In fairness, it should be pointed out that there are still a large number of unsolved problems connected with this approach. For example, there does not seem to be a systematic way of selecting ahead of time which combination of indices to use in a particular correlation. Likewise, there is at present no way of indicating higher-order geometric differences (and thus of distinguishing, for example, between *cis*- and *trans*-isomers), though it seems to me that it should be possible to develop such an algorithm based on the molecule's symmetry elements. There is also some debate as to how to extend the approach to non-molecular solids and thus, by implication, to surfaces.

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