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Hard and Soft Acids and Bases: Atoms and Atomic Ions

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The structural origin of hard−soft behavior in atomic acids and bases has been explored using a simple orbital model. The Pearson principle of hard and soft acids and bases has been taken to be the defining statement about hard−soft behavior and as a definition of chemical hardness. There are a number of conditions that are imposed on any candidate structure and associated property by the Pearson principle, which have been exploited. The Pearson principle itself has been used to generate a thermodynamically based scale of relative hardness and softness for acids and bases (operational chemical hardness), and a modified Slater model has been used to discern the electronic origin of hard−soft behavior. Whereas chemical hardness is a chemical property of an acid or base and the operational chemical hardness is an experimental measure of it, the absolute hardness is a physical property of an atom or molecule. A critical examination of chemical hardness, which has been based on a more rigorous application of the Pearson principle and the availability of quantitative measures of chemical hardness, suggests that the origin of hard−soft behavior for both acids and bases resides in the relaxation of the electrons not undergoing transfer during the acid−base interaction. Furthermore, the results suggest that the absolute hardness should not be taken as synonymous with chemical hardness but that the relationship is somewhat more complex. Finally, this work provides additional groundwork for a better understanding of chemical hardness that will inform the understanding of hardness in molecules.

Introduction

The concept of hard and soft acids and bases remains a subject of intense theoretical interest as well as a very useful guide in experimental studies in areas as diverse as polymerization catalysis and coordination network solids.[1] The application of the hard−soft principle has permitted the a priori design of custom-layered structures and linear coordination polymers and has provided a means of interpreting the interactions in very complex biological structures. Thus, an improved understanding of hard−soft behavior will provide to chemists additional tools, which will permit a more profitable utilization of the chemical property of hardness.

The hard−soft concept was born nearly a half-century ago with the realization by a number of investigators that the strength of an acid or base is dependent on factors extrinsic to itself.[2–4] Although a number of measures of the intrinsic strength of acids and bases have been called intrinsic strength, in this report intrinsic strength is understood to be the contribution to acid or base strength that is independent of the reference acid or base and independent of the molecular environment. The relative strength of an acid may be operationally defined using the displacement reactions

$$A' + A:B \rightarrow A + A':B \qquad (1a)$$

$$B' + A:B \rightarrow B + A:B' \qquad (1b)$$

If these reactions are favorable ($\Delta G < 0$ or $\Delta H < 0$), then it can be said that A′ is a stronger acid than A and B′ is a stronger base than B.[5] One may then ask, “Is the relative strength of the acid dependent of the base used to determine it?” or “Is the relative strength of the base dependent on the acid used to determine it?” There are a number of such

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(1) (a) Silva, R. M.; Gwengo, G.; Lindeman, S. V.; Smith, R. M.; Gardinier, J. R. *Inorg. Chem.* **2007**, *46*, 998. (b) Luo, T. T.; Hsu, L. Y.,; Su., C. C.; Ueng, C. H.; Tsai, T. C.; Lu, K. L. *Inorg. Chem.* **2007**, *46*, 1532. (c) Long, R. J.; Gibson, V. G.; White, J. P.; Williams, D. J. *Inorg. Chem.* **2006**, *45*, 511. (d) Hancock, R. D.; Bartolotti, L. J. *Inorg. Chem.* **2005**, *44*, 7175. (e) Vianelli, R.; Maksic, Z. B. *Inorg. Chem.* **2005**, *44*, 1095. (f) Um, I. H.; Hwang, S. J.; Baek, M. H.; Park, E. J. *J. Org. Chem.* **2006**, *71*, 9191.

(2) (a) Ahrland, S.; Chatt, J.; Davies, N. *Quart. Rev. Chem. Soc.* **1958**, *12*, 265–276. (b) Schwarzenbach, G.; Shellenberg, M. *Helv. Chem. Acta.* **1965**, *48*, 28–46.

(3) Myers, R. T. *Inorg. Chem.* **1974**, *13*, 2040–2041.

(4) Reed, J. L. *J. Phys. Chem.* **1997**, *101*, 7401–7407.

(5) Pearson, R., G. *J. Chem. Educ.* **1968**, *45*, 581–587.

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extrinsic influences, and the concept of hard and soft concerns itself with the influence of the reference base used to determine the strength of acids and the reference acid used to determine the strength of bases. This particular extrinsic influence is called hardness. The name hardness and its compliment, softness, were coined by Pearson, who also proposed the principle of hard and soft acids and bases.[5] This principle in effect defines hard−soft as a property of acids and bases that causes "hard acids [to] prefer to bind hard bases and soft acids [to] prefer to bind to soft bases".[5] To date, the Pearson principle appears to be the clearest and most elegant defining statement about chemical hardness and softness. The Pearson principle not only defines the role of hardness in determining the course of a chemical reaction but also it distinguishes hardness from a variety of other extrinsic influences on acid−base strength and it serves as the jump-off point for any theoretical study of chemical hardness.[4]

This notwithstanding, there have been several interpretations of hard−soft behavior. Whereas one interpretation has considered hard and soft to involve two different properties, one of which dominates in a hard acid or base and the other in a soft acid or base, an alternative considers hard and soft to be the extremes of a single property. In some cases, hard−soft is considered to be a property of the acid or base, and in others it is a property of the acid−base interaction. Most often these distinctions are quite subtle.[4–14] In this report, chemical hardness is considered to be a property of an acid or base, which gives rise to hard−soft behavior. The terms operational chemical hardness and softness will refer to experimental measures of hard−soft behavior as described by the Pearson principle. Also, hardness and softness will be considered to be limiting cases of the same property. To eliminate as many of the other contributions to the extrinsic strength of an acid or base, this report has limited its scope to atoms and their ions.

Although not explicitly referred to as hard−soft behavior, the fact that the linear free energy relationships that have been used to describe and predict the strengths of acid and base interactions require two parameters rather than one parameter for each the acid and the base, suggesting that at least one extrinsic influence on acid−base strength is in evidence.[5,15,16] Thoughtful examination of these parameters and their interrelationships has suggested the existence of hard and soft acids and bases as well as the principle of hard and soft acids and bases. The hard bases have been characterized as being small, having high electronegativity, being highly polarizable, being difficult to oxidize, and having frontier orbitals of very different energies. Soft bases have a complementary set of properties.[8,14] Hard acids on the other hand have small size, high positive charge and also have frontier orbitals of very different energies.[8,14] Unfortunately, in early investigations it was only possible to classify acids and bases as hard, soft, and borderline.[5]

The physical property that had appeared to best correlate with hard−soft behavior was the polarizability of the acid or base, although this association was not without its difficulties.[3,7,11] Recognizing the absence of a quantitative measure of hardness as a major impediment, Parr and Pearson proposed that the absolute hardness, η_{abs}, be the physical basis of hard−soft behavior and that it should serve as a measure of hardness.[11,12] Rather than being a chemical property or a measure of a chemical property, the absolute hardness is a physical property of atoms and molecules, whose relationship to the chemical behavior and hence chemical hardness is still under investigation.

$$\eta_{\mathrm{abs}} = -\left(\frac{\partial(\chi)}{\partial N}\right)_v = \left(\frac{\partial(\chi)}{\partial q}\right)_v = \left(\frac{\partial^2 E}{\partial N^2}\right)_v = \left(\frac{\partial^2 E}{\partial n^2}\right)_v \tag{2a}$$

where

$$-\chi = \left(\frac{\partial E}{\partial N}\right)_v = \left(\frac{\partial E}{\partial n}\right)_v = \left(-\frac{\partial E}{\partial q}\right)_v \tag{2b}$$

and

$$-\chi_{\mathrm{abs}} = \left(\frac{\partial E}{\partial N}\right)_{v,N=N_0} = \left(\frac{\partial E}{\partial n}\right)_{v,n=n_0} = \left(-\frac{\partial E}{\partial q}\right)_{v,q=o} \tag{2c}$$

where q is the charge on the species. Also, N is the number of electrons and N_0 is the number of electrons in the neutral species. The symbols n and n_0 are the number of valence electrons and the number of valence electrons in the neutral species, respectively. Much of the current work in elucidating the nature of hardness is based on these definitions and assumptions.

Because the energies of atoms and their ions can only be determined for integral charges, the experimental evaluation the derivatives required for absolute hardness is problematic. Thus, in the same article Parr and Pearson proposed the following formulation[11]

$$\chi_{\mathrm{abs}} = \frac{I+A}{2} \tag{3a}$$

$$\eta_{\mathrm{abs}} = I - A \tag{3b}$$

where I and A are the ionization energy and electron affinity, respectively.

Much of this recent work has employed with considerable success the tools supplied by density function theory.[11,12,17–22] These successes notwithstanding, the work

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(6) Pearson, R., G. *J. Chem. Educ.* **1968**, *45*, 643–647.
(7) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539.
(8) Pearson, R. G. *J. Chem. Educ.* **1987**, *64*, 561–567.
(9) Klopman, G. *J. Am. Chem. Soc.* **1968**, *90*, 223–234.
(10) Klopman, G. *J. Am. Chem. Soc.* **1964**, *86*, 1463–69.
(11) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512–7516.
(12) Liu, G. H.; Parr, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 3179–3188.
(13) Pearson, R. G. *Chem. Comm.* **1968**, *65*, 67.
(14) Pearson, R. G. *Inorg. Chem.* **1988**, *27*, 734–740.
(15) Drago, R. S.; Wayland, B. B. *J. Am. Chem. Soc.* **1965**, *87*, 3571–3577.
(16) Edwards, J. O. *J. Am. Chem. Soc.* **1954**, *76*, 1540–1547.
(17) Geerling, P.; DeProff, F.; Langeneaker, W. *Chem. Rev.* **2003**, *103*, 1793–1873.
(18) Rezende, M. C. *J. Braz. Chem. Soc.* **2001**, *73*, 80.
(19) Krishnamurty, S.; Roy, R. K.; Vetrivel, R.; Iwata, S.; Pal, S. *J. Phys. Chem. A* **1997**, *101*, 7253–7257.
(20) Gazquez, J. L.; Martinez, A.; Mendez, F. *J. Phys. Chem.* **1993**, *97*, 4059–4063.
(21) Cong, Y.; Yang, Z. Z.; Wang, C. S.; Liu, X. C.; Bao, X. H. *Chem. Phys. Lett.* **2002**, *357*, 59–64.
(22) Ayers, P. W. *Faraday Discussions* **2007**, *135*, 161–190.
(23) Ayers, P. W. *J. Chem. Phys.* **2005**, *122*−1−3.

of Klopman and others using orbital and perturbation approaches has been able to provide significant insights into the nature of hardness.[3–10,24,25] Furthermore, whereas the language of density function theory is relatively new and has been primarily province of specialists, the orbital and perturbation models are established and are part of the language of most nonspecialists. This report seeks to, by utilizing the Pearson principle and a quantitative measure of chemical hardness, determine the orbital structures and associated properties of acids and bases, that give rise to hard−soft behavior. In so doing, a better guide will be provided to experimentalists for the improved design of such things as new compounds, catalysts, network solids, and structures capable of molecular recognition. Additionally, these results will inform further work on density function theory and other models, which increase our understanding of hard−soft behavior.

The discussion will begin with the determinations of quantitative measures of the chemical hardness of a series of simple atomic acids and bases and with a critical examination of the Pearson principle. To relate the orbital structures of these acids and bases to the quantitative chemical hardness and the physical properties associated with hard−soft behavior, an expanded version of Slater's model for the electronic structure for atoms will be utilized. To reconcile the quantitative chemical hardness and the implications of the Pearson principle with the absolute hardness, some of the properties of the absolute hardness will be examined. A model for the origin of hard−soft behavior will then be proposed.

Computations

The operational chemical hardnesses were computed as the gas-phase enthalpies for the appropriate metathesis reactions using the published heats of formations.[4,26–30] The enthalpies were those for the reactions at 25 °C. The absolute hardnesses and absolute electronegativities were taken from Bratsch's compilation.[31] The computed orbital one-electron energies, relaxation energies, and ionization energies were determined using the expanded Slater's rules as described elsewhere.[32–34]

Results and Discussion

The concept of hardness and softness find their origins in specific chemical behaviors.[1–3] Their chemical origin notwithstanding there should exist a physical basis for hard−soft behavior. This being the case, there should exist within acids and bases electronic structures, which are the origins of these behaviors. Furthermore, there should exist for each of these one or more properties which can be determined, at least in principle, experimentally.[3–8] These having been identified, consideration should be given to how these properties and structures actually give rise to hard−soft behavior. There have been numerous excellent investigations into the source of hard−soft behavior, the most recent of which have used to excellent affect the density functional model. Most of these have cast the physical basis of hard−soft behavior in terms of those properties that arise naturally within density function theory.

It has been pointed out that the process of connecting the physical property of absolute hardness to the chemical behavior has yet to be satisfactorily achieved.[22] One of the objectives of the present discussion is to provide a quantitative measure of chemical hardness against which the findings of density function theory can be more profitably be assessed. However, of special interest is to carry out a similar assessment using models, which are more commonly used by those who are not specialists. To limit other extrinsic contributions to acid−base strength and to reduce the electronic complexity, this investigation has been intentionally limited to acids and bases that are atoms and atomic ions in the gas phase. To assist in interpreting the relationship between the relevant orbital structures, their physical properties and hard−soft behavior, an expanded form of Slater's model for atoms, which has been developed in these laboratories, has been utilized.[33–35]

Chemical Hardness: An Operational Chemical Hardness. The Pearson principle can be succinctly described by the generalized metathesis reaction

$$A^sB^h + A^hB^s \rightarrow A^sB^s + A^hB^h \qquad (4)$$

where A and B are acids and bases, respectively, and h and s indicate hard and soft.[4,23] Pearson's principle requires that the change in free energy for this reaction be negative. If it is not, either this reaction is an exception to the Pearson principle or the relative hardness or softness has been incorrectly assigned. Furthermore, although acid and base strengths have both intrinsic and extrinsic components, the course of the metathesis reaction should not reflect the contributions from the intrinsic strengths of the acids and bases.[4]

With this in mind, the molar enthalpies of a series of metathesis reactions have been used to measure the relative hardness and softness of acids and bases.[4] For a number of reasons in establishing this chemical hardness scale, molar enthalpy changes have been used rather than the changes in free energy. This should not pose a problem for the atomic

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(24) Reed, J. L. *J. Phys. Chem.* **1994**, *98*, 10477–10483.
(25) Reed, J. L. *J. Phys. Chem.* **2003**, *107*, 8714–8722.
(26) Stull, D. R.; Prophet, H., *JANAF Thermochemical Tables, National Bureau Standards Circular 37*; National Bureau of Standards: Washington, DC, 1961.
(27) Karapet'yant, M. K.; Karpet'yants, M. L., *Thermodynamic Constants of Inorganic and Organic Compounds*, Ann Arbor-Humphrey Science Publications: Ann Arbor, MI, 1970.
(28) Weast, R. C.; Astle, M. J., Eds. *CRC Handbook of Chemistry and Physics*, 63rd ed.; CRC Press: Boca Raton, FL, 1982; D-52.
(29) Binnerwies, M., *Thermochemical Data of Elements and Compounds*, Wiley-VCH: New York, 1999.
(30) Franklin, J. L.; Dillard, J. G.; Rosenstock, H. MM.; Herron, J. T.; Draxl, K. *Ionization Potenitals, Appearance Potentials and Heats of Formation of Gaseous Positive Ions, National Bureau of Standards Circular 26*; National Bureau of Standards: Washington, DC, 1969.
(31) Shamassundar,; K, R.; Arunan, E. *J. Phys. Chem. A* **2001**, *105*, 8533–8540.
(32) Bratsch, S. G. *J. Chem. Educ.* **1988**, *65*, 34–41.
(33) Slater, J. C. *Phys. Rev.* **1930**, *36*, 57–64.
(34) Reed, J. L. *J. Chem. Educ.* **1999**, *76*, 802–804.
(35) Reed, J. L. *J. Phys. Chem.* **2002**, *106*, 3148–3152.

Table 1. Operational Chemical Hardness of a Series of Anionic and Neutral Atomic Bases and Softness of Their Conjugate Lewis Acids

base	$\Delta H_\eta(Cl^+{-}H^+)/\Delta H_s(Cl^-{-}H^-)$[a]	acid
F^-	75.06 (131.28[b])	F^+
Cl^-	44.14	Cl^+
O^-	36.82	O^+
Br^-	34.27	Br^+
S^-	26.15	S^+
I^-	21.95	I^+
N^-	16.05	N^+
C^-	0.063	C^+
P^-	1.065	P^+
H^-	0.00	H^+
Mg^-	−18.64	Mg^+
Si^-	−18.82	Si^+
Be^-	−40.20	Be^+
B^-	−49.93	B^+
Na^-	−50.99	Na^+
Al^-	−52.23	Al^+
Ca^-	−56.03	Ca^+
Li^-	−58.32	Li^+
K^-	−58.66	K^+
Cs^-	−63.03	Cs^+
F^0	171.54[e]	F^{+2}
Cl^0	54.46	Cl^{2+}
I^0	53.64	I^{+2}
Br^0	22.06	Br^{2+}
B^0	−15.93	B^{+2}

[a] Thermochemical data for computation of $\Delta H_\eta(Cl^+{-}H^+)/\Delta H_s(Cl^-{-}H^-)$ were taken from refs 26, 27, 28, 29, 30, and 31. [b] F^+ and H^+ are used as the discrimination acid.

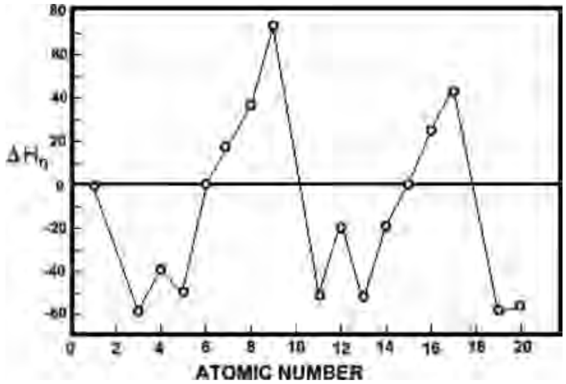

Figure 1. Plot of the operational chemical hardness of the anionic atomic bases versus their atomic numbers.

bases used here, since the entropy changes for such simple species are expected to be small and to have very similar values.[23,36] The enthalpies that are tabulated in Table 1 are called the operational chemical hardnesses, $\Delta H_\eta(Cl^+{-}H^+)$, based on Cl^+ and H^+ as discriminating acids and H^- as the reference base. In other words, Table 1 contains the enthalpies for the reaction

$$HX + ClH \rightarrow HH + ClX \quad \Delta H_\eta(Cl^+{-}H^+) \qquad (5)$$

in which X^- is the base for which the $\Delta H_\eta(Cl^+{-}H^+)$ is being determined. By considering only gas phase reactions, environmental influences have been eliminated and the consideration of only atomic species has eliminated various electronic and structural influences from other atoms that may not involve chemical hardness. One should be mindful, that although these are thermodynamic quantities and thus not the physical basis of hard−soft behavior, they do impose conditions on whatever physical basis for and the interpretation of hard−soft behavior that might be proposed. These will be examined shortly.

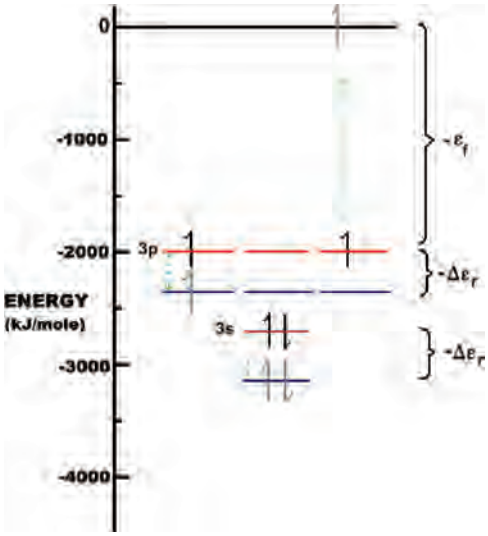

Figure 2. An energy-level diagram for the valence orbitals of a silicon atom undergoing the ionization of a 3p electron and the relaxation of the remaining valence electrons.

Eq 4 can be written in a manner that more explicitly connotes the electron pair donor and acceptor,

$$A^h\subset\leftarrow B^s + A^s\subset\leftarrow B^h \rightarrow A^s\subset\leftarrow B^s + A^h\subset\leftarrow B^h \qquad (6a)$$

However, for the same reaction one might write

$$A^h\rightarrow\supset B^s + A^s\rightarrow\supset B^h \rightarrow A^s\rightarrow\supset B^s + A^h\rightarrow\supset B^h \qquad (6b)$$

Here, ⊂ indicates the electron-pair acceptor and → indicates the electron-pair donor. The enthalpy changes are of course equal for both of these reactions. Now, let the conjugate Lewis acid of a base be the acid that is generated when the donor electron pair is removed from the base. Similarly, let the conjugate Lewis base be the base that is generated when an electron pair is added to the acceptor orbital of a Lewis acid. Finally, let the conjugate Lewis radical be the species formed by removing an electron from the base or adding an electron to its conjugate Lewis acid. For example, NH_3^{2+} is the conjugate Lewis acid of NH_3 and NH_3^+ is its conjugate Lewis radical. As a consequence, the same series of metathesis reactions that is used to determine the operational chemical hardness of a series of bases can be used for their conjugate Lewis acids.

In Table 1 can be found the operational chemical hardnesses for the atomic anions and the enthalpies for the conjugate Lewis acids for elements 1 through 20 (except the noble gases) as well as a number of the heavier elements and several neutral species. The values of the relative operational chemical hardness for the species in Table 1 have a range of 138 kJ/mol, which suggests that the hard−soft preference is indeed a very strong one. For the bases in the table, the discriminating acids are Cl^+ and H^+ of which H^+

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(36) Ritchie, C. D. *J. Am. Chem. Soc.* **1983**, *105*, 7313–7321.
(37) Bromberg, J. P., *Physical Chemistry*, 2nd ed., Allyn and Bacon: Boston, 1984, p 522.

is taken to be a harder acid. The anionic bases in Table 1 are presented in order of decreasing $\Delta H_\eta(\text{Cl}^+{-}\text{H}^+)$. Consistent with the characterization of bases, those having a large $\Delta H_\eta(\text{Cl}^+{-}\text{H}^+)$ are small, of low polarizability, and high electronegativity, and those having a small $\Delta H_\eta(\text{Cl}^+{-}\text{H}^+)$ are large, highly polarizable, and of low electronegativity. Furthermore, they correlate well with the absolute hardness of density functional theory. These same data also yield the enthalpies for the conjugate Lewis acids, $\Delta H_\text{s}(\text{Cl}^-{-}\text{H}^-)$. In this case, the discriminating bases are Cl^- and H^- and H^+ is the reference acid. As expected and consistent with the data in Table 1 for the bases, H^- is assigned as the softer of the discriminating bases. Thus, the relative hardness of the discriminating bases is the reverse of the order for the discriminating conjugate Lewis acids. Because the enthalpy change for reactions 6 are equal for both acids and bases, the order of the relative hardness of the conjugative Lewis acids must be the reverse of that of the bases. Not too surprisingly, this reveals that Cl^+ is a softer acid than H^+, F^+ is also softer than Cl^+, and Na^+ is softer than Cs^+. In fact, the softest acid in the Table is F^+, which is small, compact, of very low polarizability, and very electronegative. Whereas the characterizations of bases have been generally extended to acids in both Pearson's association of hardness with polarizability and with its association with the absolute hardness,[3,7] the values of $\Delta H_\text{s}(\text{Cl}^-{-}\text{H}^-)$ suggest that this should not be the case. Because this result arises not from the experimental data but from the nature of the metathesis reaction itself, it is a general result that the operational chemical hardness correlates negatively with the absolute hardness of density functional theory. Furthermore, the operational chemical hardness of a base is the operational chemical softness of its conjugate Lewis acid. These results have important implications to the density functional analyses as well as for the experimental application of the hard−soft concept.

In Figure 1, $\Delta H_\eta(\text{Cl}^+{-}\text{H}^+)$ has been plotted against the atomic number for 20 of the anionic bases in Table 1. The same plot would of course be obtained if $\Delta H_\text{s}(\text{Cl}^-{-}\text{H}^-)$ were plotted. The regularity in the plot is suggestive of a very well behaved property, and, as one might expect, within each period the anions of the alkali metals constitute the softest bases and the halogen anions constitute the hardest bases. The $\Delta H_\eta(\text{Cl}^+{-}\text{H}^+)$'s are periodic in atomic number. For the nonmetals within each group, there is a consistent decrease in hardness as the atomic number increases, which is again consistent with the association of hardness with polarizability.

It is possible to determine $\Delta H_\eta(\text{Cl}^+{-}\text{H}^+)$ for the neutral forms of five of the anionic bases in Table 1 as well as $\Delta H_\text{s}(\text{Cl}^-{-}\text{H}^-)$ for their conjugate Lewis acids. Because the computations require the enthalpies of formation of molecular cations, it is expected that the uncertainties in the operational chemical hardness and softness will be somewhat larger for these species. With the exception of bromine, as expected, the neutral bases are significantly harder than their corresponding anions. This suggests a modest, but significant, charge dependence for the operational chemical hardness of atoms.

An Expanded Slater Model for Atoms. Although most of the current advances in our understanding of absolute hardness have utilized the density functional model, the simple model proposed by Slater[33] for the structure and energetics of atoms and their ions can provide quite significant insights into absolute hardness and hard−soft behavior. Recently Slater's original model has been expanded to better reflect the energetics of atoms and has been shown to have a number of applications.[4,34,35] In the original Slater model, the electronic structure of the atom or ion is described simply by its configuration. However, rather than considering explicitly the pairwise electron−electron interactions, the nuclear charge experienced by each electron is approximated as shielding by each of the remaining electrons. This model has been recently refined, and the one-electron energies of the representative elements through iodine can be obtained using only four empirically determined shielding constants.[34,35] An additional four constants are required for elements in the first two transition series. The effectiveness of the model was demonstrated by its ability to very reasonably reproduce the electronic energies for chlorine and its ions, Cl^0 through Cl^{14+}. The average absolute error between the experimental electronic energies and those computed using the expanded Slater model is 4.5% for these ions. In addition, the model has been shown to provide excellent estimates for the ionization energies of atoms and their ions as well as the core ionization energies of atoms and ions. Furthermore, the model provides an excellent explanation for such things as the manner by which the valence shell electrons are able to influence the 1s core ionization energies of atoms and why potassium is not a transition element although the 3d orbital has a more negative one-electron energy than the 4s orbital.[35]

In Slater's model, the electronic energy of the atom or atomic ion is simply taken to be the sum of the one-electron energies, ϵ_i, of each of its electrons,

$$E = \sum_\text{i} \varepsilon_\text{i} + E_\text{pairing} \tag{7}$$

where E_pairing is an additional energy for paired electrons. The one-electron energy however is obtained using the equation for the orbital energies of the hydrogen-like atoms, in which the nuclear charge has been replaced by an effective nuclear charge (Z^*),

$$\varepsilon_i = -1312\ \text{kJ/mole}\left(\frac{Z_\text{i}^*}{n_\text{i}}\right)^2 \tag{8}$$

where n_i is the principle quantum number. The effective nuclear charge is the nuclear charge minus the shielding (c_ij) by each of the remaining electrons.

$$Z_\text{i}^* = Z - \sum_{\text{j}\neq\text{i}} c_\text{ij} \tag{9}$$

The summation is over all of the remaining electrons. The interaction of electrons paired in the same orbital is greater than the interaction of similar unpaired electrons. This difference may be treated as the pairing energy that appears in equation 7, or equivalently incorporated in the form of different shielding constants for paired and unpaired electrons. The values of the shielding constants may be found elsewhere and are not used explicitly in this report.[4,34] The Slater model is especially suited for this investigation not only, because it provides a simple and familiar interpretation of atomic energetics, but also because it casts it in terms of the commonly recognized electronic structures.

The valence shell is the most cited electronic structure of atoms, and among its associated properties are the electron affinity and the ionization energy. The core however has only an indirect impact on acid−base chemistry. The valence shell can be thought of as being formed from two substructures, the frontier electrons and/or virtual orbitals and the valence electrons that are not frontier electrons, which will be called the responding electrons. Using the expressions generated by eq 7 for the electronic energy of the anion, neutral, and cation of an atom, the following expressions have been generated for the electron affinity and the ionization energy of an atom having n valence electrons,

$$I = -(n-1)\Delta\varepsilon_r - \varepsilon_f \tag{10a}$$

$$-A = (n+1)\Delta\varepsilon_r + \varepsilon_f \tag{10b}$$

where ϵ_f is a frontier electron one-electron energy and ϵ_r is the one-electron energy for the responding electrons. Because eqs 10a and 10b are for interpretation purposes only, to maintain simple expressions the orbital energies are the average for the relevant orbitals. The term $\Delta\epsilon_r$ is called the orbital relaxation energy and is equal to ϵ_r for the more positive species subtracted from ϵ_r for less positive species. This number is positive.

The roles of both substructures in the charge transfer processes are more clearly illustrated in Figure 2, which illustrates the role that each structure plays in the ionization process. Whereas the frontier electron is being removed, it undergoes an energy change of $-\epsilon_f$ and the responding electrons undergo a relaxation with a change in energy for each electron of $-\Delta\epsilon_r$. In addition, as the responding electrons undergo relaxation, their orbitals decrease in size as a result of an increase in the effective nuclear charge that they experience.

To interpret the electronegativity and absolute hardness in the Slater model, these expressions for ionization energy and electron affinity (eqs 10a and 10b) are substituted into eqs 3a and 3b to yield,

$$\chi = -(\varepsilon_f + n\Delta\varepsilon_r) = -(\varepsilon_f + n_0\Delta\varepsilon_r) + q\Delta\varepsilon_r \tag{11a}$$

$$\chi_{abs} = -(\varepsilon_f + n_0\Delta\varepsilon_r) \tag{11b}$$

$$\eta_{abs} = 2\Delta\varepsilon_r \tag{11c}$$

The electronegativity has been also written in terms of the atomic charge, q, which has the form of the experimental electronegativity function.[9,10,32] Thus, in addition to the single-electron relaxation energy being half of the absolute hardness, it is also the charge coefficient in the experimental electronegativity function. The Slater interpretation of the absolute hardness provides a number of insights of interest to the hard−soft discussion. The absolute hardness is a property of a single electron. The absolute hardness is the relaxation of this electron, which arises from the transfer of a single frontier electron. The absolute hardness in the Slater interpretation has no explicit dependence on the charge of the atom.

It is convenient to discuss the physical basis of hard−soft behavior in terms of the set of atomic orbials and the properties that have been associated with them. Among the relevant sets of atomic orbitals are the frontier orbitals, the responding electrons, and the whole valence shell. Associated with each of these structures are properties, which have over the years been linked to hard−soft behavior.

The size of the species, its frontier orbital energy, and its frontier orbital energy gap are among the relevant properties of the frontier orbitals. The importance of frontier electrons and frontier orbitals is implied in the Lewis definition, thus frontier orbitals were among the first electronic structures to be identified with acid−base behavior. The size of the occupied frontier orbital dictates the size of an atom. A reasonable and simple indicator of the relative size of an atom or ion is provided by the average distance of this electron from its nucleus. This may be obtained for a hydrogenic atomic orbital (table 2) and is found to be inversely related to ϵ_f. Pearson has also associated the gap in the energies of the occupied frontier orbital and the unoccupied frontier orbital, $\Delta\epsilon_f$, which is the difference in the energy of the frontier electron and the lowest-energy virtual electron, with the absolute hardness. In the Slater

Table 2. Relevant Electronic Structure and Their Associated Properties

structure	properties	Slater interpretation
frontier orbital	size	$n_{QN}^2 C/\sqrt{-\varepsilon_f}\left\{1 + 1/2\left[1 - l(l+1)/n_{QN}^2\right]\right\}^a$
	orbital energy	ε_f
	energy gap	$\Delta\epsilon_f = \Delta\varepsilon_r$
responding electrons	absolute hardness	$2\Delta\epsilon_r$
	relaxation energy	$\pm(n-1)\Delta\epsilon_r$
valence shell	atomic charge	$n_0 - n$
	electronegativity	$-\epsilon_f - n\Delta\epsilon_r$
	absolute electronegativity	$-\epsilon_f - n_0\Delta\epsilon_r$
	polarizability	$\sim n\Delta\epsilon_r$
	ionization energy	$-(n-1)\Delta\epsilon_r - \epsilon_f$
	electron affinity	$-[(n+1)\Delta\epsilon_r + \epsilon_f]$

[a] Ref 37 $C = a_o\sqrt{R}$ where a_o is the Bohr radius, R is the Rydberg constant, n_{QN}, the principle quantum number, and l is the angular momentum quantum number.

model as suggested by Pearson, $2\Delta\epsilon_r$ is also equal to $\Delta\epsilon_f$ for atoms.

The role of the responding electrons, although not described as such, has dominated the hard−soft discussions. The absolute hardness and the relaxation energy are the relevant properties of the responding electrons. Whereas the absolute hardness is the energy associated with the response of a single electron and is always positive, the relaxation energy is a measure of the response of all of the responding electrons and may be positive or negative depending or whether the species is an acid or a base. Moreover, unlike the absolute hardness it is a charge-dependent property.

Most atomic properties actually involve all of the valence electrons, however. The atomic charge is of course determined by the number of valence electrons. The ionization energy, electron affinity, and electronegativity are all combinations of the frontier orbital energy and the relaxation energy (Table 2). Polarizability is a property associated primarily with the valence-shell electrons, and it is a measure of the ease with which the electron cloud deforms in an external electric field. The orbital relaxation energy and by extension the absolute hardness is a measure of the energy involved in the deformation of the valence-electron cloud when subjected to a change in the internal electric field. Thus, although polarizability and absolute hardness are not necessarily proportional, it is expected that they exhibit very similar behaviors and exert similar influences.[11,36] These structures and properties have been summarized in Table 2. A number of simplifying approximations have been made in arriving at the Slater interpretations. However, because the resulting expressions are for interpretation purposes rather than for computations, these seem reasonable.

It is evident from the entries in Table 2 that all of the relevant atomic properties are combinations of ϵ_f, $\Delta\epsilon_r$, and n. One of the results of this is that most of these atomic properties are highly correlated, which helps explain why so many of them have been associated with hard−soft behavior. Although these relevant structures and properties have been identified, in the absence of a quantitative measure of chemical hardness, this analysis would be of limited use in understanding the orgin of hard−soft behavior. As recently pointed out by Ayers,[22] the proposal by Parr and Pearson[11] that the absolute hardness be one such measure is limited by the fact that hardness is a chemical property and absolute hardness is a physical property, and it has yet to be established that these properties are in fact synonymous. Having at hand experimental measures of chemical hardness and a model for interpreting its properties, the absolute hardness can be examined.

The Absolute Hardness of Atoms. Although over the past half century numerous atomic and molecular properties have been identified as the basis for hard−soft behavior, the absolute hardness of Parr and Pearson has dominated the current investigations.[11,17,23] This property has proven to be equally at home in both the orbital and density functional models. This being the case, the absolute hardness will be considered in detail before proceeding with the analysis. In addition, the word electronegativity will refer to the property that is formulated in eq 2b, and for atoms it is a function of absolute hardness and charge. Absolute electronegativity, χ_{abs}, will refer to the electronegativity of the neutral atom.[11]

Because the differentiations in eqs 2a, 2b, and 2c cannot be carried out on atoms; they have been approximated as eqs 3a and 3b. These approximations have been referred to as finite difference approximations. This designation has been unfortunate, however. In the strict mathematical sense, the application of the finite difference approximation to the electronegativity and hardness in eqs 2a and 2b become eqs 12a and 12b.

$$\chi = -\left(\frac{\Delta E(N)}{\Delta N}\right)_v \tag{12a}$$

$$\eta = \left(\frac{\Delta \chi}{\Delta N}\right)_v \tag{12b}$$

Eqs 3a and 3b are excellent approximations for the electronegativity and absolute hardness of atoms. This is because these equations are not finite-difference approximations. Rather, they are exact formulations of eqs 2a, 2b, and 2c, provided that the energy is a quadratic function of the number of electrons (eq 13),

$$E = \frac{1}{2}\eta_{abs}n^2 + (-\chi_{abs} - \eta_{abs}n_o)n = \frac{1}{2}\eta_{abs}q^2 + \chi_{abs}q + c \tag{13}$$

where c adjusts the reference state to that of the neutral atom. This being the case, eqs 3a and 3b might be more properly named the quadratic approximations.

Chlorine and its ions provide an excellent illustration of these things. Using the experimental ionization energies of Cl^0 through Cl^{14+}, which are known with great accuracy,[38] the electronic energies of these ions can be computed. When these electronic energies are plotted against the number of electrons in the outer shell, n, an excellent fit to eq 13 results. A least-squares fit of this data to this expression for the species Cl^0 through Cl^{7+} yields η_{abs} equal to 440.9 kJ/mol, and the average relative error between the experimental energies and those computed from the eq 13 is less than 5%. For Cl^{7+} through Cl^{14+}, η_{abs} equals 1681.6 kJ/mol and the average relative error is less than 0.3%. Furthermore, differentiation of eq 13 yields expressions for χ_{abs} and η_{abs} (eqs 2). The faithfulness with which eq 12 reproduces the experimental energies suggests that a high level of confidence should be placed in the values of χ_{abs} and η_{abs} obtained via eqs 3a and 3b.

There are several important conclusions that are suggested by these results. First, as already noted, the absolute hardness of atoms and atomic ions can be known to a high degree of confidence. Also eqs 3a and 3b are not good approximations for either electronegativity or absolute hardness, if the electronic energy is not a quadratic function of the number of electrons for the species under consideration. In addition, it would appear that the absolute hardness of the atom and ions, Cl^0 through Cl^{7+} (third shell) are all essentially equal as is the case for the ions Cl^{7+} through Cl^{14+} (second shell).

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(38) Huheey, J. E., *Inorg. Chem.*, 2nd ed.; Harper & Row: New York, 1983; p 42.

More generally, the absolute hardness is constant for atoms and ions over those ranges, over which the electronic energy is a quadratic function of charge. Thus, the absolute hardness of atoms is a charge-independent quantity. This particular result is troubling because it is generally believed that chemical hardness is a charge-dependent property, which increases significantly as the charge increases, although exceptions have been noted.[3–5] Furthermore, the results in Table 1 demonstrate quantitatively the dependence of the operational chemical hardness on the charge. Finally, because the energy of atoms and ions having noble-gas configurations are equally well described by the quadratic energy function (eq 13) generated using lesser-charged species (i.e., Cl^0 through Cl^{7+}) as species having a greater charge (i.e., Cl^{7+} through Cl^{14+}), such species have two absolute electronegativities and two absolute hardnesses, as determined from the experimental energy data. The fact that atomic species having noble-gas configurations are expected to exhibit two different experimental hardnesses is not generally appreciated, and this property must also be a characteristic of the physical basis of hard−soft behavior.[8,11]

Orbital Structures and Chemical Hardness. If the Pearson principle is taken to be a defining statement about chemical hardness and the metathesis reaction is taken to yield an operational measure of this property, certain conditions are automatically placed on the relevant structures, which in the orbital model consist of subsets of the atom's orbitals. Therefore, the goal is to identify the subset of the atom's orbitals, which is the source of hard−soft behavior. Furthermore, these atomic orbitals must be able to give rise to properties that correlate with the operational chemical hardness, as well as reflect the dependence of chemical hardness on the charge of the acid or base. In addition, as has already been noted, the operational chemical hardness for a base is numerically equal to the operational chemical softness of its conjugate Lewis acid. This would seem to suggest that the same structure controls the hard−soft behavior of both the base and its conjugate Lewis acid and that it must influence the hardness of the base in a manner opposite to its influence on its conjugate Lewis acid. Put another way, if a change in a relevant structure causes the base to become harder, the same change in the conjugate Lewis acid will cause it to become softer by the same amount.

This influence on hard−soft behavior is a manifestation of the contribution of these orbital subsets to the energetics of the acid−base interaction, which is reflected in the change in energy caused by the transfer of a small increment of charge, δn, during this interaction. For an acid let δn be positive then for a base the increment is -δn. Over the years there have been a number of properties derived from the atomic orbital subsets that have been identified with hard−soft behavior and a number of these have been included in Table 2. Foremost among these are the electronegativity, polarizability and ionization energy, which are associated with the atom's entire valence shell. However, in conflict with the requirement that the same substructure be operative in a base and its conjugate Lewis acid, the valence shell of a base and its conjugate Lewis acid are very different. Furthermore, the analyses in Table 2 suggest that the transfer of an increment of charge would not result in a contribution to the energetics that would be consistent with chemical hardness, which is that δn results in a change in energy that is equal in magnitude but opposite in sign for a base and its conjugate Lewis acid. This is reflected in the explicit dependence on n.

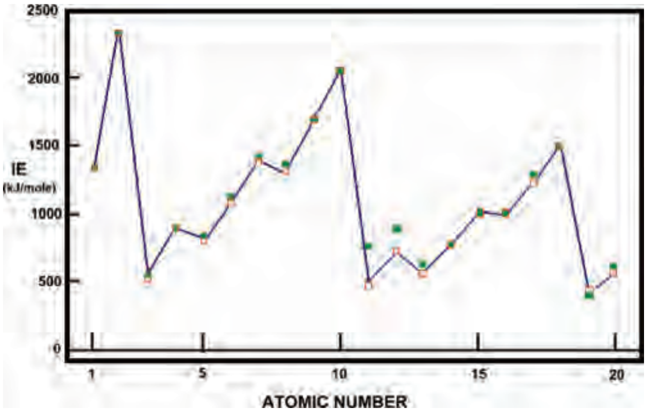

Figure 3. Plot of the (■) computed ionization energy, () experimental ionization energy versus their atomic number.

Of the properties derived from the valence-shell, polarizability has been most closely associated with chemical hardness.[5–8,11] Polarizability allows an electron cloud to deform in an electric field but the deformation results in stabilization ($\Delta\epsilon < 0$) for both acids and bases. These observations seem to suggest that it is unlikely that hard−soft behavior finds its origins in the valence shells of the base or its conjugate Lewis acid.

The Lewis definition of acids and bases associates the frontier orbitals with acid−base behavior. Although the occupied frontier orbital of a base is the same orbital as the unoccupied frontier orbital of its conjugate Lewis acid, the energies of these orbitals, ϵ_f, are quite different due to differences in the effective nuclear charges. The contribution of these orbitals to the energetics of an acid−base interaction would be $\pm \epsilon_f \delta n$, which would not meet the energy requirements for the contributions to hard−soft behavior as described above.

The plot of the operational chemical hardness and softness versus the atomic number (Figure 1) is very similar to that of the first ionization energy versus atomic number of the same elements. In Figure 3 are plotted both the experimental first ionization energies and for comparison those computed using Slater's model (eq 10a). The correlation of the experimental ionization energy with $\Delta H_\eta(Cl^+{-}H^+)$ yields a correlation coefficient of 0.91. It is, however, of special interest to note that the periodicities of $\Delta H_\eta(Cl^+{-}H^+)$ and hence $\Delta H_s(Cl^-{-}H^-)$ are in phase not with the ionization energies of the actual acid or base species (the anions and cations) but with that of the conjugate Lewis radical. The periods for the ionization energies of the anionic and cationic species are out of phase with $\Delta H_\eta(Cl^+{-}H^+)$ by plus and minus one atomic number, respectively.

This would seem to suggest that $\Delta H_\eta(Cl^+{-}H^+)$ derives from an orbital substructure that is common to both the anion and cation. The analyses in Table 2 show that the ionization energies derive from $\Delta\epsilon_r$, ϵ_f, and n, of which only $\Delta\epsilon_r$ is common to a base and its conjugate Lewis acid. The orbital subset common to the base and the conjugate Lewis acid is the set of responding electrons of the conjugate Lewis radical. This would suggest that chemical hardness derives from this orbital substructure.

The absolute electronegativity, which has a long association with chemical hardness, derives form the valence shell of neutral species. Furthermore, the absolute electronegativity also correlates with $\Delta H_\eta(\mathrm{Cl^+{-}H^+})$, and its correlation coefficient is somewhat better at 0.95. In an acid−base interaction upon the transfer of $\pm\delta n$ charge the contribution of the absolute electronegativity is $\pm\delta n(\epsilon_f + n_0\Delta\epsilon_r)$, which is in fact equal in magnitude and opposite in sign for a base and its conjugate Lewis acid. However, the absolute electronegativity is a charge-independent quantity as indicated in Table 2. In addition, it does not arise from a structure common to both the base and its conjugate Lewis acid.

The absolute hardness makes an implicit contribution to the energy, resulting from the transfer of $\pm\delta n$ charge via the electronegativity, which has already been discussed (eq 13). The explicit contribution arises from the quadratic term. This contribution to the energy is $^1/_2\eta_{abs}(\pm\delta n)^2$, which is positive for both the base and its conjugate Lewis acid. Thus, it does not meet the requirement of the transfer of the charge, yielding an equal in magnitude but opposite in sign contribution to the energetics for both $+\delta n$ and $-\delta n$. Furthermore, the correlation coefficient for the correlation of the absolute hardness of the anionic bases with the operational chemical hardness is only 0.87. The absolute hardness of all of the representative elements have been evaluated using eq 3 and its variants.[32,39,40] The analyses in these reports and the chlorine example cited earlier strongly suggest that the absolute hardness itself should have no significant charge dependence for configurations arising from the same valence shell. In contrast, the chemical hardness is a charge-dependent property. These results would seem to suggest that the absolute hardness cannot itself be identified as being equivalent to chemical hardness as has often been the practice.

The absolute hardness derives from the relaxation of a valence electron during charge transfer in an acid−base interaction. In most cases, more than one electron undergoes relaxation during the interaction, and this should be a factor in the hard−soft contribution to the reaction energetics. The observation that the plots of operational chemical hardness and softness versus atomic number are in phase not the ionization energies of the actual acids and bases but with the ionization energies of the conjugate Lewis radicals supports the idea that the responding electrons of interest are those of the conjugate Lewis radicals of the acids or bases. This is in contrast to the intrinsic strength and those properties closely associated with it such as electronegativity, for which the plots would be in phase with the ionization energies of the acid and base species themselves. If the number of valence electrons on the conjugate Lewis radical is n_r, then there are $n_r - 1$ responding electrons in the base and conjugate Lewis acid, which would constitute the structure that would give rise to chemical hardness in atoms. For a base, this relaxation energy is $-\delta n(n_r - 1)\Delta\epsilon_r$ and for an acid it is $+\delta n(n_r - 1)\Delta\epsilon_r$. Thus, as required there is a common structure in the base and its conjugate Lewis acid that gives rise to hard−soft behavior. The impact on the energetics is equal in magnitude but opposite in sign for a base and its conjugate Lewis acid. Because n_r itself is a charge-dependent quantity, this structure should give rise to a charge-dependent chemical hardness. The relaxation energy of these responding electrons is $\pm\delta n(n_r - 1)\Delta\epsilon_r$ and it is proportional to $\pm\delta n(n_r - 1)\eta_{abs}$, in which η_{abs}, absolute hardness, has been evaluated experimentally.[32,38,39] The quantity $(n_r - 1)\eta_{abs}$ does in fact correlate with $\Delta H_\eta(\mathrm{Cl^+{-}H^+})$ and has a correlation coefficient of 0.95, which further supports the responding electrons as the source hard−soft behavior.

In Closing. Although the principle of hard and soft acids and bases continues to be utilized in many chemically meaningful ways, over the years the theoretical discussions of hardness seem to have shifted from a discussion of a physical basis of a chemical behavior described by the Pearson principle to a discussion of a well-defined physical property that may or may not give rise to hard−soft behavior. The absolute hardness, which has been the focus of much of the current work, has been often assumed to be synonymous with chemical hardness. In this report, the Pearson principle has been used as a defining statement about chemical hardness, and with this in mind an operational chemical hardness for a series of atomic acids and bases have been determined. The quantitative measurement of chemical hardness has revealed a well-behaved periodic property that makes a quite substantial contribution to the energetics of acid−base interactions. The magnitude of its contribution to the strength of an acid−base interaction is such that it should compete effectively with a number of other extrinsic contributors to acid−base strength, yet its magnitude is such that it is expected to be generally a perturbation to the intrinsic strength of acids and bases. All of these expectations are consistent with observed chemical behaviors.

In an orbital model, it is reasonable to expect that the source of hard−soft behavior should lie in one of the orbital subsets and that there should be one or more properties of this orbital subset that provide clues to how the subset gives rise to hard−soft behavior. In addition, there appears to be an intimate relationship between the chemical hardness of a base and that of its conjugate Lewis acid, which ascribes specific properties to the orbital subset, giving rise to hard−soft behavior. It appears that hard−soft behavior derives from the response of the responding electrons to an acid−base interaction and that the associated energy is substantial.

It would appear that hard−soft behavior finds its origins in the relaxation of the responding electrons during the transfer of charge in an acid−base interaction. In the acid during the acid−base interaction, the energy of its responding

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(39) Ickowski, R. P.; Margrave, J. L. *J. Am. Chem. Soc.* **1961**, *83*, 3547.
(40) Mulliken, R. S. *J. Chem. Phys.* **1934**, *2*, 782–793.

valence electrons increases as their orbitals expand, whereas in the base these electrons decrease in energy as the orbitals contract. Among the perhaps unexpected results is that, although from the earliest discussions the hardness of acids and bases has been associated with low polarizability and softness with high polarizability, this appears not to be the case for acids. The soft acids appear to actually have the lowest polarizabilities, and the hard acids appear to have higher polarizabilities. Similarly, acids having a large absolute hardness appear to be chemically soft, and acids having a low absolute hardness appear to be chemically hard. The relationship between absolute hardness and the operational chemical hardness is nonlinear, and the failure of simple models based on an often assumed linear dependence on the absolute hardness is unsurprising. Finally, it appears that, rather than the absolute hardness, the relaxation energy, which is closely related to the absolute hardness, appears to best correlate with chemical hardness. Because in fact the absolute hardness is a component of the relaxation energy, it would appear that this and the identification of the structure and behavior that gives rise to hard−soft behavior in atoms will inform further experimental and theoretical investigations into hard−soft behavior in molecules.

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