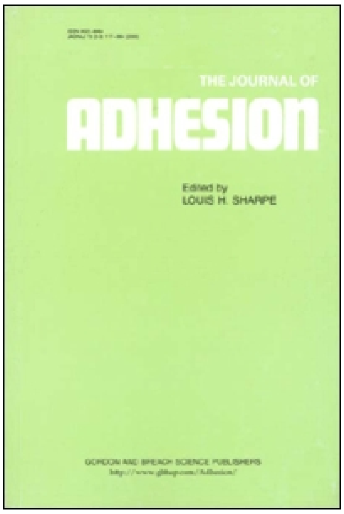

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Relevance of the Hard-Soft Acid-Base (HSAB) Principle to Solid Adhesion*

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In this paper, the acid-base interaction is shown to consist of at least two major components: the electrostatic (or ionic) and charge transfer (or covalent). To complement existing acid-base theories, we further demonstrate the relevance of the density-functional theory to surface interactions and solid adhesion. On the basis of the density-functional theory, two chemical parameters, *i.e.*, chemical potential μ and absolute hardness η, will be shown to govern an acid-base interaction. From these, the number of transferred electrons ΔN can be estimated.

Our findings indicate that the absolute hardness is directly linked to the average energy gap. As ranked by the average energy gaps, all metals are soft, for having narrow gaps; for the same reason, all semimetals and semiconductors are generally soft, and all insulators including polymers are comparatively hard for having wide gaps. Furthermore, to achieve a reasonable rate for an interfacial acid-base interaction or solid adhesion, it is advantageous to consider the HSAB principle: hard bases (or donors) prefer to interact with hard acids (or acceptors) and soft bases (or donors) with soft acids (acceptors).

KEY WORDS Acceptor; charge transfer; chemical potential; coulombic; density-functional; donor; electrostatics; energy gap; hardness; metal; polymer; softness.

1 INTRODUCTION

The donor-acceptor interactions have been studied by Gutmann[1] and Deryagin *et al.*,[2] and the acid-base interactions have been reviewed by Jensen.[3–5] On many occasions, the two terms, though different, have been used interchangeably. In a broader sense, both interactions have been considered as molecular interactions but with different emphases.[6,7] It appears that for a more ionic (or electrostatic) interaction, it is proper to call it the acid-base interaction; while for a more covalent (or frontier orbital) interaction, it is the donor-acceptor interaction.

For polymers, Fowkes,[8–11] Bolger and Michaels,[12] and Bolger[13] have pointed out the important role of the acid-base interaction in the formation of an interfacial bond. The purpose of this paper is to explore the scope and limitations of these interactions. Hence, to apply properly the concept of the acid-base interaction to solid adhesion, we will briefly discuss (1) molecular interactions, (2) the acid-base

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interaction, (3) the hard-soft acid-base (HSAB) principle,[14,15] and (4) the application of the density-functional theory[16] to these interactions and adhesion of solids.

2 MOLECULAR INTERACTIONS

Perturbation Theory

Hudson and Klopman[17] proposed an equation to describe the effect of orbital perturbation of two molecules on chemical reactivity. Their equation for the interaction energy ΔE can be simplified by including only two terms: the Coulombic interaction and the frontier orbital interaction between the *HOMO* (highest occupied molecular orbital) of a nucleophile (or base) and the *LUMO* (lowest unoccupied molecular orbital) of an electrophile (or acid):

$$\Delta E = -\underbrace{\frac{Q_{Nu}Q_{E\ell}}{\epsilon R}}_{\text{(The Coulombic term)}} + \underbrace{\frac{2(C_{Nu}C_{E\ell}\beta)^2}{E_{HOMO}-E_{LUMO}}}_{\text{(The frontier orbital term)}}, \tag{1}$$

where Q_{Nu} and $Q_{E\ell}$ are the total charges of the nucleophile and electrophile, respectively; C_{Nu} and $C_{E\ell}$ are the coefficients of the atomic orbitals Nu and $E\ell$, respectively; β is the resonance integral; ϵ is the permittivity; and R is the distance between Nu and $E\ell$.

For the electrostatic interaction, the first term dominates while, for the electron donor-acceptor (*EDA*) interaction, the second term dominated. Thus, a molecular interaction encompasses chiefly both acid-base and donor-acceptor interactions.

2.2 Critical Interatomic Distance of Molecular Interactions

At this point, it should be emphasized that molecular interactions including the acid-base interaction are insignificant at an interatomic distance greater than 3 Å. For example, the optimum distance is approximately 1.8–2.0 Å for the interaction between borane and ammonia.[18] It has also been reported[19] that the optimum distance for an electrophile-nucleophile interaction is around 2.3–2.7 Å. In the case of solid interactions, this close contact between two solid surfaces is achievable more easily under high vacuum. This may be why the acid-base interaction is not as readily observed for solid-to-solid systems in spite of the fact that it is frequently reported.

3 ACID-BASE INTERACTION

The Lewis acid-base interactions[3-5] encompass not only hydrogen-bonding and electron pair donor-acceptor interactions, but also electrophile-nucleophile interactions in organic chemistry.[20] The following general equation describes the Lewis acid-base interaction:

$$\underset{\text{(Acid)}}{A} + \underset{\text{(Base)}}{:B} \rightarrow \underset{\text{(Acid-base Complex)}}{A{:}B} \tag{2}$$

As implied by the perturbation equation [Eq. (1)], both electrostatic (or ionic) and charge-transfer (or covalent) factors are involved in these interactions.

Equilibrium and Kinetics of the Acid-base Interaction-*HSAB principle*

The involvement of two components, electrostatic and charge-transfer, in the acid-base interaction is illustrated best by the hard-soft acid-base (HSAB) principle proposed by Pearson[14] in 1963. This principle describes some basic rules about the kinetics and equilibrium of acid-base interactions in solutions. In this paper, we attempt to extend the HSAB principle to solid interactions with the aid of the frontier orbital method. The HSAB principle will be described as it has evolved in recent years on the basis of the density-functional theory[16,21-23] and the band structures of solids. After the agreement between the HSAB principle and the band structures in the solid state is demonstrated, several examples of adhesion and surface interactions between metals and polymers will be given.

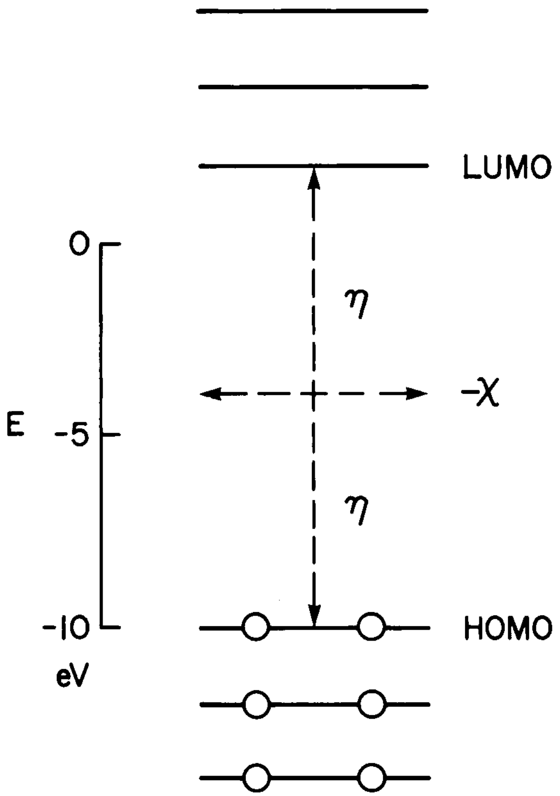

FIGURE 1 Orbital energy diagram for a molecule. HOMO, highest occupied MO; LUMO, lowest unoccupied MO. [After R. G. Pearson, ref. [15]; reproduced with permission.]

The HSAB principle has also been applied for the study of kinetics and equilibrium, and the frontier orbital (Fig. 1) method has been used to illustrate the electrophilic and nucleophilic interactions:[24,25]

- A hard electrophile (or acceptor) has a high-energy *LUMO* (lowest unoccupied molecular orbital) and usually has a positive charge.
- A soft electrophile has a low-energy *LUMO* but does not necessarily have a positive charge.
- A hard nucleophile (or acceptor) has a low-energy *HOMO* (highest occupied molecular orbital) and usually has a negative charge.
- A soft nucleophile has a high-energy *HOMO* but does not necessarily have a negative charge.

For interactions (or reactions), the HSAB rules can be restated as follows:

- A hard-hard interaction (or reaction) is fast because of a large Coulombic attraction as described by the first term of Eq. (1).
- A soft-soft interaction (or reaction) is fast because of large orbital interaction between the *HOMO* of the nucleophile and the *LUMO* of the electrophile as described by the second term of Eq. (1).

These two rules reflect the value of the HSAB principle in establishing the importance of both electrostatic and charge transfer contributions to acid-base interactions.

4 DENSITY-FUNCTIONAL THEORY

4.1 Chemical Potential, Electronegativity and Absolute Hardness

When the HSAB principle was first introduced, the meaning of hardness was not defined theoretically. Certainly, it is not the hardness that measures the resistance against deformation. Then, what is it? It was not until the last few years that the absolute hardness received theoretical support by Parr *et al.* on the basis of the density-functional theory.[16,21-23] However, on the basis of this theory, the absolute hardness alone is indeed incomplete in determining the number of electrons transferred during an acid-base interaction.

In the density-functional theory, two basic parameters of importance to chemistry were introduced. According to the theory, any chemical system (atom, molecule, ion, radical) can be characterized by its electronic chemical potential μ and its absolute hardness η. The *chemical potential measures the escaping tendency of an electronic cloud, while the absolute hardness determines the resistance of the species to the loss of electrons*. It should be noted that these two parameters are molecular but not orbital properties. The exact definitions of these two quantities are

$$\mu = (\delta E / \delta N)_v, \tag{3}$$

and

$$\eta = \tfrac{1}{2}(\delta \mu / \delta N)_v = \tfrac{1}{2}(\delta^2 E / \delta N^2)_v, \tag{4}$$

where E is the electronic energy of an atom, a molecule, or an ion; N is the number of electrons, and v is the potential due to the nuclei, plus any external potential (Fig. 2).

For atomic species, the chemical potential is the negative of electronegativity. Unfortunately, the electronegativity has many definitions,[26] including the newest one proposed by Allen.[27] However, this discussion will involve only the definition by Mulliken[28], *i.e.*, the electronegativity, χ^M, is the average of the energy required to remove one electron from an atom, measured as the ionization energy, I, and that released by the gain of one electron, measured as the electron affinity, A. Thus, $\chi^M = \frac{1}{2}(I + A)$.

Hence from Eqs. (3) and (4), operational and approximation definitions give the chemical potential μ

$$\mu \approx -\tfrac{1}{2}(I + A) \approx -\chi^M, \tag{5}$$

and the absolute hardness η

$$\eta \approx \tfrac{1}{2}(I - A), \tag{6}$$

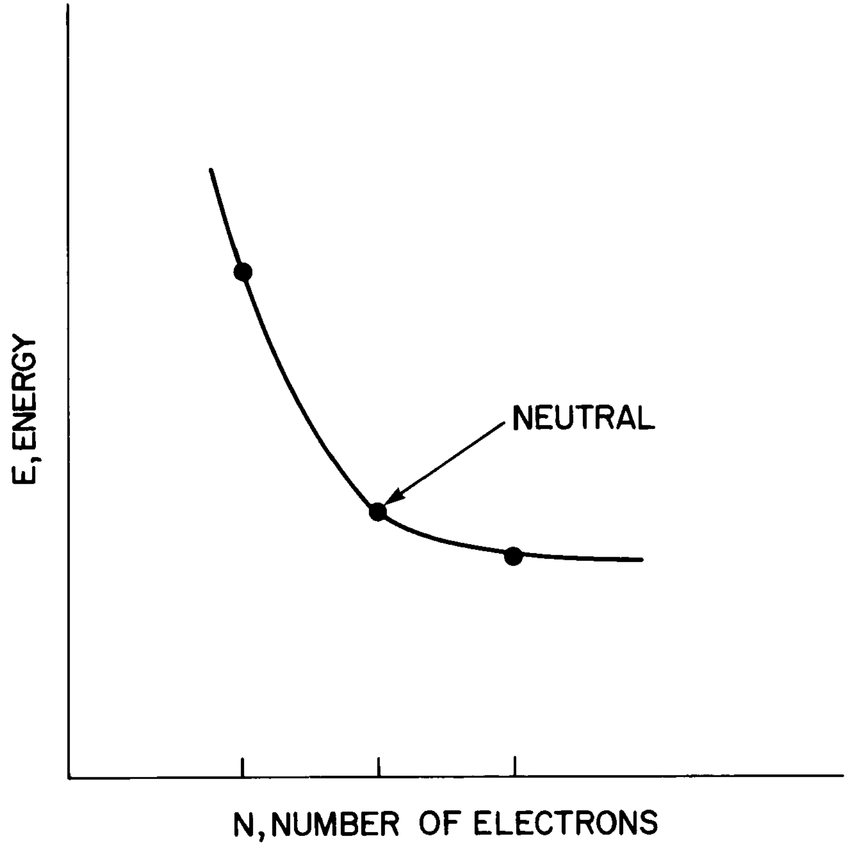

FIGURE 2 Plot of electronic energy vs. number of electrons for a fixed collection of nuclei [R. G. Pearson, ref. [15]; reproduced with permission.]

Since χ^M is the negative of the chemical potential, it deserves to be called the absolute electronegativity; that is, the resistance of the chemical potential to the change in the number of electrons. It should be pointed out that both μ and η are global properties at the ground state in the sense that they characterize the species as a whole. Besides these two properties, there is also the absolute softness, σ, which is the reciprocal of η.

Furthermore, according to Koopmans' theorem,[29] the frontier orbital energies are given by

$$-E_{HOMO} = I; \ -E_{LUMO} = A, \tag{7}$$

However, any definition based on E_{HOMO}-E_{LUMO} should be used with care because LCAO/SCF calculations place the virtual orbitals too high in energy. According to the frontier orbital method,[24] the relationship between η and the energies of *LUMO* and *HOMO* is clearly shown in Fig. 1. Thus, from Fig. 1,

$$\eta \approx -\tfrac{1}{2}(E_{HOMO} - E_{LUMO}). \tag{8}$$

Here χ^M is the horizontal broken line in the middle of the energy gap, and the energy gap E_g is twice the absolute hardness η. Moreover, a hard molecule has a wide energy gap, while a soft molecule has a narrow gap. It will be demonstrated that the energy gap is an important link between chemistry and physics in the solid state.

4.2 Number of Transferred Electrons

The apparent success of the density-functional theory is to provide two chemical parameters from which we can calculate the number of electrons transferred resulting mainly from the charge transfer between the two molecules. Since charge (or electron) transfer is one of the major mechanisms of molecular interactions, when two systems, A and B, are brought together, electrons will flow from that of lower χ to that of higher χ, until the chemical potential reaches an equilibrium. This follows the electronegativity equalization principle introduced by Sanderson.[30] According to this principle, when atoms (or other combining groups) of different chemical potentials unite to form a molecule with its own characteristic chemical potential, to the extent that the atoms (or groups) retain their identity, their chemical potentials must equalize.

Usually, but not always, there are electrons flowing in both directions. As a first approximation, the (fractional) number of electrons transferred, ΔN, is given by [31]

$$\Delta N \approx (\mu_B - \mu_A) / 2(\eta_A + \eta_B) \approx -\Delta\mu / 2\Sigma\eta, \tag{9}$$

or

$$\Delta N \approx (\chi_A - \chi_B) / 2(\eta_A + \eta_B) \approx \Delta\chi / 2\Sigma\eta. \tag{10}$$

Thus, the electron transfer is driven by $\Delta\chi$, but resisted by the sum of η's. Since molecular interactions involve other interactions besides electron transfer, ΔN is not the total change of electrons,[32] but is still useful in determining the initial orbital interaction between A and B, and in serving as an approximation for the bond strength. Equation (10) also suggests that when $\Delta\chi \rightarrow 0$, there is no electron transfer. Since η's for metal atoms never approach zero, $\Sigma\eta \neq 0$. For the hard-hard interactions $\Sigma\eta$ can be very large, thus ΔN becomes too small, and the interaction will be dominated by the electrostatic interaction, instead of by electron transfer. On the other hand, for the soft-soft interaction, $\Sigma\eta$ can be rather small, and ΔN will be large. As expected, the interaction will be accompanied by polarization; however, it may not affect ΔN significantly. Besides these extreme cases, generally ΔN is a fractional number of transferred electrons.

5 ACID-BASE INTERACTIONS IN SOLIDS

In the literature, there have not been many discussions about acid-base interactions in solids. Recently, Lee[33-38] has demonstrated that the extension of the HSAB principle to solid interactions is feasible in view of the electronic band structures. In the following, the physical meaning of the absolute hardness will be discussed in terms of the average energy gap.

5.1 Electronic Band Structures of Solids

Solids can be classified as metals, semimetals, intrinsic semiconductors, and insulators. The band structures of solids are illustrated in Fig. 3. Monovalent metals,[39] *e.g.*, Na^0, have a partially filled valence band, the lower half of which is occupied. The Fermi level is in the valence band but at the top of the occupied orbitals. Furthermore, there is still an energy gap between the valence band (occupied *MO*)

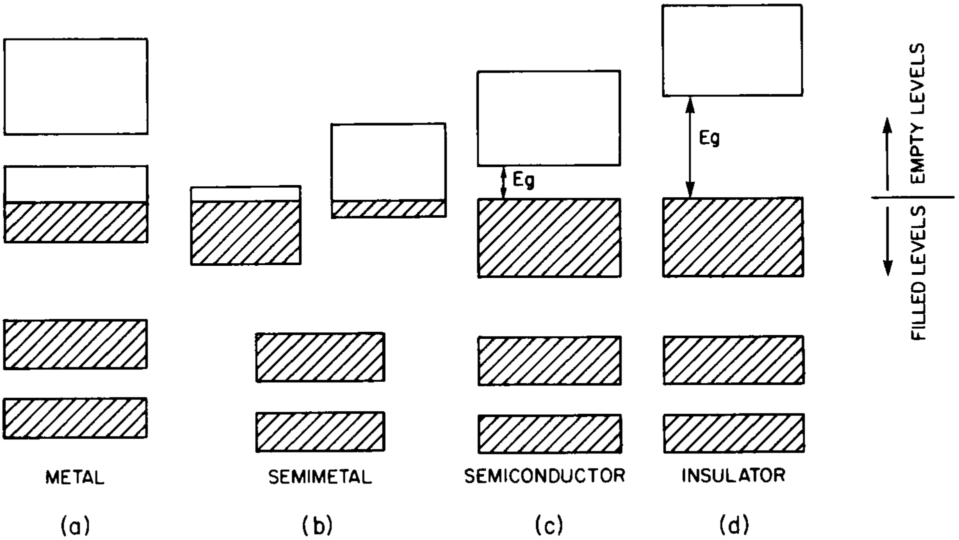

FIGURE 3 Band structures of solids: (a) metal; (b) semimetal; (c) semiconductor; (d) insulator. [A. J. Epstein, and J. S. Miller, ref. [40], adopted with permission.]

and the conduction band (unoccupied *MO*). In some metals, such as the bivalent metals, the valence band is full but overlaps with a higher unoccupied conduction band. In this case, the Fermi level is between the conduction band and the overlapped valence band.[40] Thus, the electrons close to the Fermi level are still free to move as the extra bands supply the unoccupied states. In the latter case, there appears to be no minimum energy gap, $E_g{}^o$, a parameter which is generally reported in the literature [*e.g.*, *Handbook of Chemistry and Physics,* CRC Press, Florida (1989–1990)]. However, it is not obvious that there will always be an average energy gap $E_g{}^{Av}$, especially in metal atoms, which will be discussed later.

In addition to metals, there are semimetals,[41] such as graphite, whose valence band and conduction band can overlap. In general, their minimum energy gaps are very narrow. The third class of solids is the intrinsic semiconductor; its minimum energy gap $E_g{}^o$ is generally below 3 eV. Thus, the thermal excitation alone can create an electron-hole pair to enhance conduction. The Fermi level of the intrinsic semiconductor[39] lies between the valence band (*HOMO*) and the conduction band (*LUMO*). Hence,

$$E_F = \tfrac{1}{2}(E_{HOMO} + E_{LUMO}) = \tfrac{1}{2}(E_c + E_v), \tag{11}$$

where E_F is the energy of the Fermi level. The fourth class of solids is the insulator, including most nonconducting polymers. Generally, the minimum energy gap of an insulator is above 3 eV. Therefore, the thermal excitation alone cannot enhance the conduction of electricity.

5.2 Phillips' Ionic and Covalent Components of the Average Energy Gap

Let us now return to our familiar theme of dual components—electrostatic (ionic) and charge transfer (covalent). The average energy gap $E_g{}^{Av}$ [42–44] is defined as the difference in energy between the bottom of the conduction band and the top of the valence band.

$$E_g^{Av} = -(E_{HOMO} - E_{LUMO}) = -(E_v - E_c). \tag{12}$$

Interestingly, according to Phillips[42,43], $E_g{}^{Av}$ also contains both a covalent (homopolar) component E_h and an ionic (heteropolar) component C:

$$(E_g^{Av})^2 = (E_h)^2 + (C)^2. \tag{13}$$

Equation (13) resembles the Hückel relation, and C is similar to $\Delta\chi$.

For $A^N B^{8-N}$ compounds, $E_g{}^{Av}$ can be determined from the high frequency dielectric constant ϵ_∞ according to the following equation:

$$\epsilon_\infty = [1 + (\hbar\Omega_p)^2 / (E_g^{Av})^2], \tag{14}$$

where Ω_p is the plasma frequency of the valence electron. Thus, the average energy gap is a fundamental physical parameter. From these two components, Phillips also defines ionicity f_i (or fractional ionic character) as follows:

$$f_i = C^2 / (C^2 + E_h^2). \tag{15}$$

On the basis of the density-functional theory, discussed in Section 5.2, it is insufficient to use $\Delta\chi$ (or f_i) alone to estimate the number of electrons ΔN from Eq. (10)

involved in the electron transfer. According to the theory, another measure, the absolute hardness, has to be taken into account. Here, η is related to the average energy gap:

$$E_g^{Av} \approx 2\eta. \tag{16}$$

5.3 Average Energy Gap and Absolute Hardnesses of Metals

Now let us examine again the band structures of the solids in Fig. 3. In Fig. 3a, the structure of metals with zero or low E_g signifies that all bulk metals are "soft" as implied by $A = I$ for the finite-difference approximation. However, different metals have different softnesses, all large, but not infinite,[45] and metal atoms are as "soft" as the low finite η values calculated from the A-I data (Table I). Indeed, metals have been classified as amphoteric materials. Most of the metals are "soft" acids, and some of them "soft" bases. When two metals are brought together into close contact, one of them becomes an acid and the other a base. Cain *et al.*[46] showed the reaction at the Cu^0-Cr^0 interface to be an acid-base interaction. In this case, a soft base Cu^0 and a soft acid Cr^0 react preferentially. In fact, the Cr atom ($\eta = 3.1$ eV) is as soft as the Cu atom ($\eta = 3.3$ eV).

5.4 Average Energy Gaps and Absolute Hardnesses of Semiconductor Elements

Figures 3b and 3c show that both semimetals[47] and semiconductors should be rather "soft," because of relatively low E_g^0 and E_g^{Av} values (most of η's<3.0 eV). Semiconductors generally react readily with metals even at ambient temperatures.[50] Thus, the interaction takes place as a "soft" acid (metal) with a "soft" base (semicon-

TABLE I
Average energy gaps and hardness values for transition metal atoms (eV)

Metal	I (a	A (b	χ^M	η (c	E_g^{Av} (calc.) (d
Ti	6.82	0.08	3.45	3.4	6.8
V	6.7	0.5	3.6	3.1	6.2
Cr	6.77	0.66	3.72	3.1	6.2
Mn	7.44	0	3.72	3.7	7.4
Fe	7.87	0.25	4.06	3.8	7.6
Co	7.8	0.7	4.3	3.6	7.2
Ni	7.64	1.15	4.4	3.3	6.6
Cu	7.73	1.23	4.48	3.3	6.6
Mo	7.10	0.75	3.9	3.2	6.4
Ru	7.40	1.5	4.5	3.0	6.0
Pd	8.34	0.56	4.45	3.9	7.8
Ag	7.58	1.30	4.44	3.1	6.2
Pt	9.0	2.1	5.6	3.5	7.0
Au	9.23	2.31	5.77	3.5	7.0

[a] From ref. [48].
[b] From ref. [49].
[c] From ref. [45].
[d] E_g^{Av} is calculated from η obtained from A-I values.

TABLE II
Minimum and average energy gaps and absolute hardness values for elements (diamond structure) (eV)

	E_g^o [a]	E_g^{Av} [a]	η^{Av} [b] (cal'ed)	η [c]
C	5.4	13.6	6.8	5.0
Si	1.1	4.8	2.4	3.4
Ge	0.7	4.3	2.2	3.4
Sn	0	3.1	1.6	3.1

[a] E_g^o and E_g^{Av} are from ref. [47].
[b] η^{Av} is calculated from E_g^{Av}.
[c] η is the value obtained by Pearson, ref. [45].

ductor). Both chemical reaction and inter-diffusion[51] jointly create a diffused "interphase" instead of an abrupt "interface."

For comparison, both E_g^o and E_g^{Av} for several elements (diamond structure) are listed in Table II. In general, E_g^{Av} is always larger than E_g^o. From Table I, the η^{Av} values calculated from E_g^{Av}'s are rather close to those calculated from the *A-I* data; however, the agreement is still not good enough.

5.5 Local Hardness

It is important to remember that the hardness of one material with respect to another depends on its η. The one with a lower η value is "softer" than the one with a higher η though they both can be "hard." Even in the same material, one functional group can be harder than the other. In this case, a new term, the local hardness, $\tilde{\eta}$,[15] has been introduced to signify the relative hardness of each functional group.

In Fig. 3d, it is noted that the band structure of an insulator contains a large gap. Thus, most insulators, regardless of whether they are organic or inorganic, are considered to be comparatively "hard" on the basis of the energy gap alone. Generally, they are harder than metals, semimetals, and semiconductors.

6 APPLICATIONS OF THE DENSITY-FUNCTIONAL THEORY TO SOLIDS

6.1 Number of Transferred Electrons, ΔN, Calculated from the Electronegativity and Average Energy gap

On the basis of the relation between η and χ, we propose to express ΔN in terms of the average energy gap of a solid:

$$\Delta N \approx (\chi_A - \chi_B) \,/\, (E_{g_A}^{Av} + E_{g_B}^{Av}), \tag{17}$$

or

$$\Delta N \approx \Delta\chi \,/\, \Sigma E_g^{Av}. \tag{18}$$

This derived equation (18) is very important with regard to the molecular interaction. Now, if we know the difference in electronegativities of A and B molecules and the average energy gaps, we can estimate the extent of electron transfer for the interaction. This equation is especially useful for semiconductor compounds for which both χ and E_g^{Av} are available in the literature.

6.2 Electronegativities and Work Functions of Solids

In a solid, the chemical potential can be represented by the negative of the work function. Steiner and Gyftopoulos[52] have shown that the work function ϕ for a metal surface is equal to the neutral electronegativity of the surface atoms. Thus

$$\phi = \chi^M. \tag{19}$$

Here again, the electronegativity of Mulliken has the best fit with the work function.

Without exception, electrons tend to flow from a metal of low ϕ to one of high ϕ. Hence, the difference of ϕ forms a contact potential V_c at the interface:

$$V_c = e(\phi_A - \phi_B) = e\Delta\phi, \tag{20}$$

where e is the electronic charge.

6.3 Number of Transferred Electrons Calculated from the Work Function and Energy Gap

Instead of chemical parameters, the number of transferred electrons can also be determined from physical properties, such as the work function and the average energy gap of a solid. Substituting Eq. (19) into Eq. (18), we obtain an important relation for solids:

$$\Delta N = \Delta\phi \,/\, \Sigma E_g^{Av}. \tag{21}$$

This equation somewhat resembles Ohm's law, which states that the electric current is directly proportional to the voltage (or potential) and inversely proportional to the resistance. Besides metals, work functions of several polymers are available in the literature;[53,54] otherwise the contact potential can be determined between a metal and another solid and by substituting it into Eq. (21) gives

$$\Delta N = V_c \,/\, (e\Sigma E_g^{Av}). \tag{22}$$

If ΣE_g^{Av} approaches zero in the case of bulk metals, ΔN may go to infinity for the metal-to-metal contact, as in the case of cold-welding of metals under ultra-high vacuum or in outer space.[55] The interesting point about Eqs. (21) and (22) is that instead of the two basic chemical parameters, we can now use two equivalent physical properties, *i.e.*, the work function or contact potential and the energy gap to estimate ΔN for any molecular interaction. These two equations signify the eventful result in the meeting of chemistry and physics in the solid state.

7 APPLICATIONS OF THE DENSITY-FUNCTIONAL THEORY TO ADHESION AND INTERFACIAL INTERACTIONS BETWEEN METALS AND POLYMERS

The interactions between metals and polymers are good examples of the applications of the HSAB principle to solids. When Cr° is deposited on pyromellitic dianhydride-oxydianiline polyimide (PMDA-ODA PI), there appears to be some chemical bonding between the Cr atom and PI. In this case, the Cr atom is a "soft" acid, and PI is a "hard" base. How can the bonding take place? According to Ho *et al.*[56,57], presumably, the reaction does not proceed in the manner of the Cr atom attacking one of the carbonyl groups (nucleophiles). What probably happens is that the Cr atom delocalizes and forms a charge transfer (or acid-base) complex with the PMDA unit of the PI. In the frontier orbital terminology, stabilization of the complex is achieved through the transfer of electrons from the d-states of the Cr atom (*HOMO*) to the *LUMO* of the π-system of the PMDA unit of PI. In this manner, PI acts as a "soft" acid by accepting the electron and the Cr atom ($\eta = 3.1$ eV) becomes a "soft" base by donating the electron. However, there are other works indicating that the metal atom, such as Cr, may indeed bond to the carbonyl.[58-60] It is likely that the Cr-PI complex is a transition state which leads to the final product between Cr atoms and the carbonyls. Other transition metals, *e.g.* Ti ($\eta = 3.4$ eV),[61] are also very reactive with PI. The general reaction presumably follows paths similar to the acid-base interaction.

One of the exceptions is Cu^{o},[62] which does not interact with PI after the deposition and gives rise to a much weaker complex. Cain *et al.*[63,64] used the tight binding calculations of the extended Hückel type to find the relative acid strengths of Cu compounds in the following decreasing order: $CuF_2 > CuO > CuF \approx Cu_2O > Cu^{o}$. Indeed, the Cu ions react faster than Cu^{o} with functional polymers. The Cu^{2+} ion has a Fermi level lying below the top of the Cu 3d band, and some of the Cu 3d orbitals are unoccupied and thus able to accept electron pairs by acting as an acid. In the HSAB terminology, Cu becomes a "hard" acid in the form of Cu^{2+} ion because the hardness for the Cu atom is 3.3 eV, and that for Cu^{2+}, 8.3 eV.

Generally, many transition metals react well with polymers, ceramics,[65] *etc.*, partly because of the ease of oxidation and partly because of the availability of d-orbitals. Buckley and Brainard[66] have found that metals react with PTFE (Teflon) and PI during their pin-and-disc experiments under high vacuum. With PTFE, the adhesion forces are three times the applied load. For this case, these interactions may also be explained by the HSAB principle. In the literature, there are numerous examples of interfacial interactions that can be classified as the acid-base interaction. However, we are unable to discuss them all in this paper. One of the reasons is that absolute hardness values for polymers have yet to be determined indirectly. We are planning to publish the calculated values in the future.

The density-functional theory indicates that both chemical parameters are required to determine the number of electrons transferred for the interaction between A and B molecules. Thus, the absolute hardness alone is insufficient to predict the extent of the interaction. It is important to point out that although absolute hardness values are rather similar for all metals, all metals have different electronegativities or work functions. Hence, they do not react in the same way or at the same rate with polymers. For example, the work function of Cu^{o} is 4.65 eV, and that for Cr^{o} 4.50 eV. In the case of polyimide ($\phi = 4.36$ eV),[53] one may expect that both Cu^{o} and Cr^{o} should react in the same manner. However, the experimental results show otherwise, thus we also need to compare the Fermi levels of both metals. According to Hoffmann,[67,68] the interaction between a molecule and the surface of a metal is different from that between two different molecules, and this type of interaction depends greatly on the Fermi level of the metal involved. For example, since the Fermi level of Cr^o is significantly higher than that of Cu^o, a molecule that can readily react with Cr^o may not react with Cu^o.

Since all metals are "soft" and most polymers are "hard," the metal-polymer reaction or adhesion, unlike the exceptional Cr-PI reaction mentioned above, is generally difficult to achieve. To circumvent this situation, most metals have to be transformed into harder counterparts, *e.g.*, related oxides of higher absolute hardness values. This is exemplified by the cited case about Cu^{2+} ions[63,64] which are harder than the metal atoms, Cu^o. Consequently, the reactivities of the metal-polymer interactions are also determined by the ease of the formation of oxides, and that ease is, in turn, controlled by the heat of formation H_f of the oxides.[69] In theory, the more negative the H_f, the more reactive the interaction. For the same reason, Au^o is always nonreactive because of its high work function. We have explored in detail the metal-polymer adhesion in a separate paper on the chemistry and physics of solid adhesion.[70]

8 SUMMARY

In this paper, we have attempted first to discuss the acid-base interaction, from a broader perspective, in terms of the molecular interaction. Two major terms were pointed out to be involved in the interaction: the Coulombic and the frontier orbital terms. It is important to note that there is a critical interatomic distance for a molecular interaction, *i.e.* approximately 3 Å. However, the optimum distance is about 2.0 Å.

The focal point of this paper is the application of the density-functional theory to molecular interaction in solids. For an acid-base interaction, one needs to consider first the HSAB principle based on absolute hardness. Otherwise, without matching the hardness of both species the interaction may be too slow to be detected. Theoretically, on the basis of the density-functional theory, two basic chemical parameters should be considered simultaneously: the chemical potential and the absolute hardness, from which a more fundamental parameter, ΔN, the (fractional) number of electrons transferred from molecule A to molecule B, can be estimated.

The extension of the HSAB principle and the frontier orbital concept to solid interactions has been demonstrated. For the HSAB principle, the absolute hardness has been discussed along with the average energy gap in a solid. The average energy gap also consists of two components: ionic and covalent. Through the energy gap, we found a bridge between chemistry and physics in the solid state. Furthermore, we can interpret a molecular as well as an acid-base interaction on the basis of well-defined physical properties instead of the chemical parameters derived from the density-functional theory. For example, in the case of metals or polymers, ΔN can be estimated from two physical properties, *i.e.* the work function and the energy gap, instead of chemical parameters. Although we have not supplied any direct experimental evidence in this paper, we believe that our findings have a theoretical basis and should be helpful to those carrying out research on interfacial interactions and solid adhesion.

NOMENCLATURE

A	Electron affinity
C	Ionic (heteropolar) component of the average energy gap
C_{El}	Coefficient of the atomic orbital of the electrophile
C_{Nu}	Coefficient of the atomic orbital of the nucleophile
e	Electronic charge
ΔE	Interaction energy
E	Electronic energy of an atom, a molecule, or an ion
E_c	Energy of the conduction band edge
E_F	Energy of the Fermi level
E_g^o	Minimum energy gap
E_g^{Av}	Average energy gap
E_h	Covalent (homopolar) component of the average energy gap
E_{HOMO}	Energy of the highest occupied molecular orbital
E_{LUMO}	Energy of the lowest unoccupied molecular orbital
E_V	Energy of the valence band edge
f_i	Phillips ionicity or fractional ionic character
I	Ionization potential
ΔN	Number of electrons transferred
Q	Total electronic charge
R	Distance between an electrophile and a nucleophile
v	Potential due to nuclei, plus any external potential
V_c	Contact potential

Greek letters

β	Resonance integral
ϵ	Permittivity
ϵ_∞	High-frequency dielectric constant
η	Absolute hardness
$\tilde{\eta}$	Local hardness
μ	Chemical potential
σ	Absolute softness
$\tilde{\sigma}$	Local softness
ϕ	Work function
χ^M	Electronegativity (Mulliken)
Ω_p	Plasma frequency of the valence electron

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