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Molecular Bonding Mechanism for Solid Adhesion

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The purpose of this study is to understand why and how solids can be bonded together with and without an adhesive. Beside van der Waals interactions and chemical bonding, there are some intermediate interactions, such as the Coulombic and charge-transfer interactions. These interactions are also called molecular interactions. Thus, molecular bonding mechanism for solids deals mainly with the formation of an adhesive bond through molecular interactions. The driving forces for molecular interactions are discussed in terms of adhesive energy and separation distance. The functions of electrons are illustrated with molecular orbitals. Moreover, some unique interactions between a molecule and the surface of a solid are demonstrated with the results found by Hoffmann.

KEY WORDS Acceptor; acid; adhesion; adhesive; base; binding energy; donor; electron; molecular bonding; molecule; orbital; separation distance; solid; surface.

1 INTRODUCTION

The total forces of adhesion between two solids are not solely derived from Lifshitz-van der Waals (vdW) and Coulombic attraction.¹ Besides these forces, there are other short-range (<0.3 nm) forces resulting from molecular interactions. The molecular interaction of special interest at the interface (not the interphase as discussed by Sharpe²) is the "intermediate" interaction between the "chemical" reaction of the covalent type and the "physical" interaction of the van der Waals type. Amid all the confusion in the past 15 years, the *intermediate* bonding that we are concerned with in this paper has also been arbitrarily classified as "van der Waals bonding."

Between simple molecules, electrons form a molecular bond through various interactions. Recently, Greenspan³ used the Cray Y-MP/8 supercomputer to establish that electrons can attract even in the same orbital of simple molecules at the ground state. On the basis of his recent simulations, he assumed that two electrons in the same molecular orbital attract, rather than repel, as quantum mechanics implies. His calculations were explored by means of the three-dimensional, supercomputer, molecular-mechanics simulations of H_2^1 , H_2^2 , H^1H^2 , H_2^3 , and H^1H^3 at the ground state. Furthermore, he has also shown that the resulting vibrational frequency and molecular diameter are entirely in agreement with the experiment.

For the adhesion in solids, one of the major molecular interactions has been identified as the donor-acceptor^{4,5} or Lewis acid-base interaction.⁶⁻¹⁴ In this paper, we attempt to treat the subject in broader terms and discuss molecular interactions¹⁵ in terms of bonding between simple molecules by visualizing electrons as a glue. First, we briefly point out theories related to different aspects of molecular bonding and then discuss the adhesive energy-separation distance relationship. Finally, we mention some unique features of molecular interactions on solid surfaces, as proposed by Hoffmann.¹⁶⁻¹⁸

2 THEORIES OF MOLECULAR BONDING

In the following sections, we shall discuss very briefly some calculation methods for molecular orbitals and four of the existing theories about molecular interactions. The first is the interaction energies by Kitaura and Morokuma;¹⁹⁻²¹ the second is the natural bond orbital (NBO) approach;²² the third is the frontier orbitals proposed by Fukui,^{23,24} and the fourth is the perturbation theory by Hudson.²⁵⁻²⁷

2.1 Molecular Orbital Calculations

When two molecules react (or interact), the electrons in molecular orbitals undergo some complicated interactions that are treated quantum-mechanically, starting with the Schrödinger equation. However, because of the presence of the electron-electron repulsion, the Schrödinger equation can not be solved analytically, but has to be solved numerically. For this reason, there have been several approximation methods²⁸ widely employed for the calculations.

For atomic orbitals, there are two common calculation methods: the Hartree-Fock (HF) approximation and the self-consistent field (SCF) approximation. The HF approximation is operated with the assumption of mutually independent one-electron wave functions forming the many-electron antisymmetric wave function which can be expressed as a product of these one-electron orbitals. On the other hand, the SCF approximation consists of a mathematical treatment in which the spatially distributed electron is considered to lie in the average potential field of all the other electrons. A series of iterations is employed to adjust the field mutually consistent within the frame work of Schrödinger equation. Both of these two techniques are complementary to each other.

For molecular orbitals, these two methods have also been used together. The SCF approximation can be applied to molecular orbitals provided that the molecule is assumed to be in the fixed-nucleus approximation. In other words, the electronic motion is assumed to be faster than the nuclear motion.

To determine molecular orbitals, one of the common methods is called the linear combination of atomic orbitals (LCAO). In this method, molecular orbitals are expressed in terms of the summation of atomic orbitals:

$$\Psi_j = \sum_i C_{ij} \chi_i, \quad (1)$$

where Ψ_j is the j th molecular orbital, χ_i is the i th atomic orbital, and C_{ij} is a coefficient in the summation. Several methods are used to determine this coefficient; for example, the SCF methods are based on the iteration.²⁹ In the *ab initio* (first principles) calculation, all electron-electron interactions together with the overlap integrals are explicitly calculated.

On the basis of valence-shell approximations, there have been other semiempirical SCF methods including the complete neglect of differential overlap (CNDO), the intermediate neglect of differential overlap (INDO), the neglect of diatomic differential overlap (NDDO), and the modified neglect of differential overlap (MNDO). For these methods, all valence electrons are explicitly considered.

For the later discussion of solid interactions, it is necessary to be acquainted with two more methods: the extended Hückel (EH)³⁰ method and the tight-binding method. In the EH calculations, all overlap integrals of valence atomic orbitals are counted while none of the electron-electron repulsion is explicitly calculated. Thus, the EH method is very approximate; however, if properly employed, it can yield reasonable information about the electronic structure of a molecule because it takes account of all valence electrons, σ and π . One of the EH calculations widely used was developed by Hoffmann.³¹ The solid state analog of the EH is the tight-binding method with overlap. The latter method resembles an MO calculation for a very large molecule, such as the entire solid crystal. In principle, it considers a small repeating piece of crystal assigned as a unit cell. Thus, the total wave function Ψ_i can be expressed in terms of the unit cell orbital Φ_i :

$$\Psi_i(\mathbf{r}, \mathbf{k}) = \sum_j \Phi_i(\mathbf{r} - \mathbf{r}_j) \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}_j)], \quad (2)$$

where the exponential factor, $\exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}_j)]$, introduces the approximate phase relationship between unit cell orbitals located at different lattice positions, \mathbf{r}_j , in the crystal. In a solid, a "band" is an assembly of crystal orbitals (with a common index i) over the allowed range of wavevector \mathbf{k} . In Section 4 of this paper, we shall discuss the interaction between a discrete molecule and a solid surface.

In recent years, a powerful tool developed in the 1960s by physicists has been adopted by some chemists. This method, based on the density-functional theory (DFT),^{32,33} is especially useful for the solid state and materials science. The DFT method is an alternative to the *ab initio* method discussed in the previous section. The *ab initio* method employing the HF technique can solve the Schrödinger equation and predict many chemical parameters rather accurately. However, it involves high computation expenses and presents difficulties in dealing with transition metals and organometallic compounds. On the other hand, the DFT method can be readily applied with much more computational expedience. Actually, this method dealing with electron density instead of wave function can also help solve the Schrödinger equation. Recently, we have successfully applied the DFT to acid-base interactions and solid adhesion.³⁴

With the above brief introduction of some of the MO calculations, we can now proceed to discuss four theories related to molecular bonding.

2.2 Kitaura-Morokuma's Decomposition of Interaction Energies

For a molecular interaction, the energy ΔE_{INT} involved in the interaction is the difference in energy of the molecules before and after the interaction.

$$\Delta E_{\text{INT}} = E_{\text{Complex}} - E_{\text{Isolated molecules}} \quad (3)$$

Kitaura and Morokuma¹⁹⁻²¹ employed the *ab initio* SCF theory to decompose the molecular interaction energy ΔE_{INT} into five components: electrostatic (ES), polarization (PL), exchange repulsion (EX), charge transfer (CT), and coupling (MIX). All components of ΔE_{INT} were calculated by the variational method.

$$\Delta E_{\text{INT}} = \Delta E_{\text{ES}} + \Delta E_{\text{PL}} + \Delta E_{\text{EX}} + \Delta E_{\text{CT}} + \Delta E_{\text{MIX}} \quad (4)$$

The first component, ES, is the electrostatic interaction between the undistorted electron distribution of molecule A and that of molecule B. This interaction may be either attractive or repulsive. The second component, PL, is the polarization interaction which is the effect of the distortion of the electron distribution of A by B, or vice versa, and the higher-order coupling resulting from such distortions. The third component, EX, is the exchange repulsion caused by the exchange of electrons between A and B; this is the short range repulsion due to the overlap of electron distribution of A with that of B. The fourth component, CT, is the charge transfer or electron delocalization to form a dative bond (A→B) between occupied MOs and unoccupied MOs of the two molecules. The charge transfer is different from a true covalent bonding (A—B) which involves the sharing of one electron from each of the two reacting atoms. Finally, the fifth component, MIX, being the coupling (or mixing) term, accounts for higher-order interactions of all the above four components, in some cases including the intermolecular correlation energy or the dispersion component ΔE_{DIS} of vdW interactions. It should be noted that the ES and the PL are considered to be long-range, while the EX and the CT are short-range.

The above four major types of interactions have been schematically illustrated by Isaacs³⁵ (Fig. 1). The dominance of any of the four interactions depends upon the overlapping of atomic orbitals:

Case 1: *Without overlap of atomic orbitals*

$$\Delta E_{\text{INT}} = \Delta E_{\text{ES}} + \Delta E_{\text{PL}} \quad (5)$$

(First order) (Second order)

Case 2: *With overlap of atomic orbitals*

$$\Delta E_{\text{INT}} = \Delta E_{\text{ES}} + \Delta E_{\text{PL}} + \Delta E_{\text{IND}} + \Delta E_{\text{DIS}} + \Delta E_{\text{EX-PL}} \quad (6)$$

(First order) (Second order)

At this point, we can define molecular bonding to be the bonding of molecules through electrons involving electrostatic, polarization, charge transfer, exchange-repulsion and the coupling of all of the above four components. Though the so-called *intermediate* interactions lie in-between vdW interactions and chemical reactions, molecular bonding also overlaps with the vdW interactions. For example, in

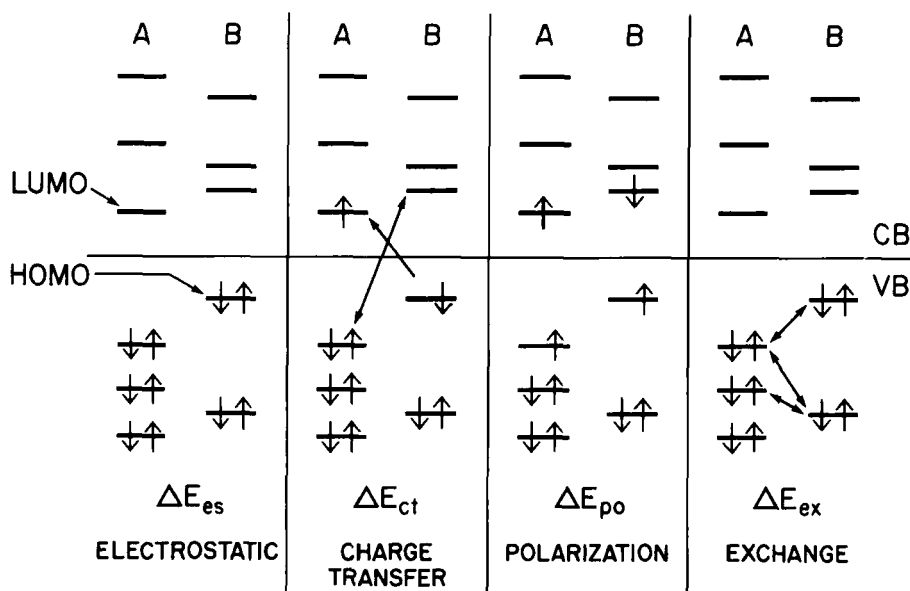


FIGURE 1 Molecular orbital interactions between two closed-shell molecules.

both of the above cases, the interaction energy involves primarily the electrostatic energy and the vdW energies, such as polarization (induction), dispersion, exchange-polarization, etc. Because of the emphasis of the variational method on the electrostatic component, the charge transfer term ΔE_{CT} is not included in Eqs. (5) and (6). Later, it will be demonstrated that this should not be the case.

The orbital overlap is directly determined by the interatomic distance because it is the critical factor affecting the dominance of each component of the interaction energy. This important energy-distance relationship in simple molecules is illustrated with the complex formed between BH_3 (borane) and NH_3 (ammonia) in Fig. 2 by Isaacs³⁵ on the basis of KM's data.

In this case, ΔE_{ES} is the most dominant. ΔE_{EX} begins to compete strongly at a separation under 2 Å (or 200 pm) and rises steeply but is balanced by the growing polarization (ΔE_{PL}) and charge-transfer (ΔE_{CT}) components. A minimum total binding energy ΔE_b [187 kcal (or -44.7 kcal. mol^{-1})] is reached at 1.8 Å (or 180 pm). In general, for the borane-ammonia interaction, the various components decrease with the increase in distance according to the order: $\Delta E_{ES} > \Delta E_{CT}$ and ΔE_{PL} .

2.3 Natural Bond Orbital (NBO)-Donor-Acceptor Approach

Though the above KM method has enjoyed wide acceptance for many years, the critique²¹ has claimed that the KM method has consistently led to a much smaller estimate of the CT component. The KM treatment of this molecular interaction is based on the electrostatic overlapping charge distribution. On the other hand, an independent method, the natural bond orbital (NBO), considers both bonding and antibonding orbitals. A review of the NBO method has been given by Reed, Curtiss,

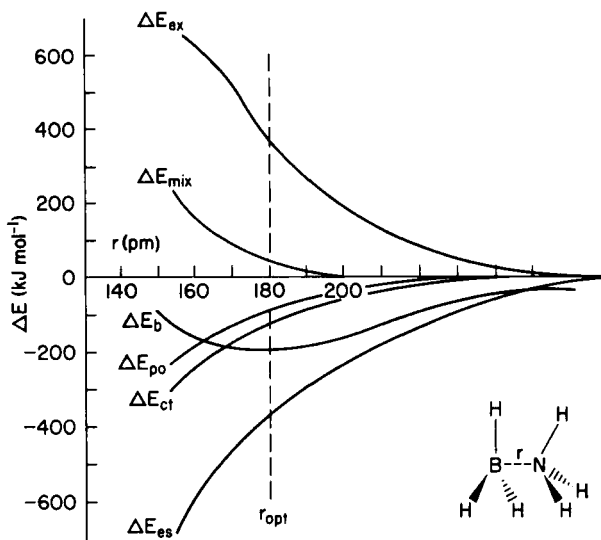


FIGURE 2 Interatomic distances between borane and ammonia. [After N. S. Isaacs, *Physical Organic Chemistry*, p. 59, Longman Scientific and Technical, with Wiley, New York (1987).]

and Weinhold,²¹ and we only attempt to summarize several key concepts related to this method dealing specifically with the H-bonded and other strongly bound vdW complexes.

Originally, the NBO method was developed by Foster and Weinhold³⁶ as an analysis for studying hybridization and covalency effects in polyatomic INDO-SCF-MO wave functions. In fact, the NBO deals with fundamental chemical concepts of localized bonds and lone pairs of electrons in the structure. The NBO analysis, therefore, emphasizes the importance of quantum-mechanical orbital interaction and exchange effects in the vdW regime, distinguishable from classical electrostatic effects. According to the NBO method, a localized σ_{AB} bond can be expressed in terms of orthonormal hybrids h_A and h_B [natural hybrid orbitals (NHOs)]:

$$\sigma_{AB} = c_A h_A + c_B h_B, \quad (7)$$

where c_A and c_B are the polarization coefficients for A and B, respectively, that describe the relative polarity of the bond orbital toward centers A and B. In turn, the NHOs consist of a set of effective valence-shell atomic orbitals (NAOs). The filled NBOs for σ_{AB} of the natural Lewis structure are suitable to describe the covalency of a molecule.

On the other hand, the antibonds are formed from the unoccupied orbitals. As the counterpart of σ_{AB} , σ_{AB}^* is expressed as

$$\sigma_{AB}^* = c_B h_A - c_A h_B. \quad (8)$$

This departure from the idealized Lewis structure is a small correction of the covalency.

As a result, the total energy E can be decomposed into

$$E = E_{\sigma\sigma} + E_{\sigma\sigma^*}, \tag{9}$$

$$= E_{\text{Lewis}} + E_{\text{non-Lewis}}. \tag{10}$$

The symbols σ and σ^* are used in the generic sense referring to filled and unfilled orbitals of the Lewis structure. In fact, σ may be a core orbital (c), a lone pair (n), a σ bond or a π bond, etc., while σ^* may be a σ or π antibond (σ^* or π^*), or an extravalence shell Rydberg (r) orbital, etc. The donor-acceptor interaction as shown in Fig. 3 is an example of the $\sigma \rightarrow \sigma^*$ interactions between filled (donor) and unfilled (acceptor) orbitals. This type of interaction leading to a dative bond ($A \rightarrow B$) has also been called the “charge transfer” or the generalized “Lewis acid-base” interaction.

In the case of the complex formation of water, the complexation energy ΔE_{COM} , which is the difference between ΔE of the dimer and ΔE of the monomers, can be divided into two components:

$$\Delta E_{\text{COM}} = \Delta E_{\text{CT}} + \Delta E_{\text{NCT}} \tag{11}$$

where CT denotes charge-transfer and NCT no-charge-transfer. For example in the case of water dimer formation through hydrogen bonding, the respective values are -4.1 , -6.5 and $+2.4$ kcal/mol. The no-charge-transfer due to the exclusion repulsion and electrostatic (induction and polarization) interaction appears to dominate the complexation.

In general, the charge-transfer not only results in an increase in binding energy but also allows a significant amount of exclusion repulsion to be overcome, allowing

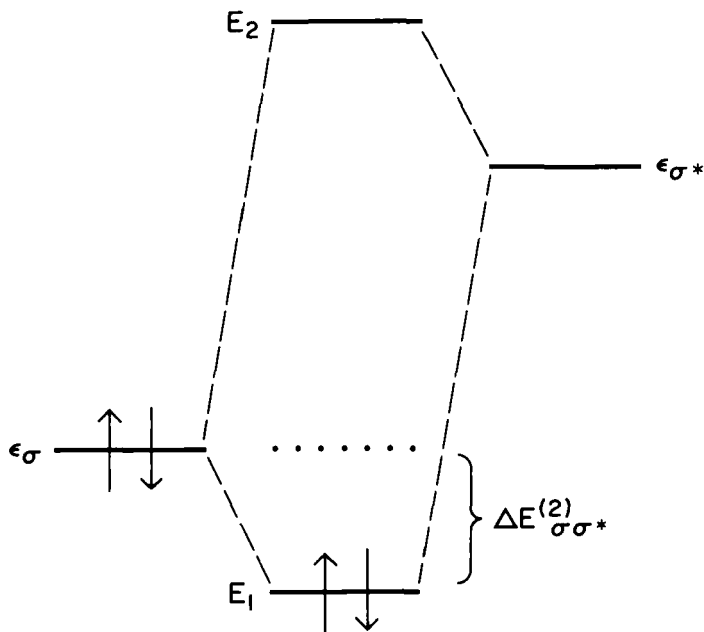


FIGURE 3 Perturbative donor-acceptor interaction, involving a filled orbital σ and an unfilled orbital σ^* .

molecules to approach closer and penetrate significantly into the van der Waals contact distance. It is noteworthy that the vdW penetration distance d_p is actually a criterion for a significant donor-acceptor ("chemical" overlap) character of the bonding:

$$d_p = R_{vdw} - R_{eq}, \quad (12)$$

where R_{vdw} is the vdW radius and R_{eq} the equilibrium radius. For a donor-acceptor interaction to occur, d_p should be appreciably positive, or $d_p \geq 0.1 \text{ \AA}$. Since the empirical vdW radius is related to effective gas-phase collision diameters under ambient conditions ($1 \text{ kT} \approx 1 \text{ kcal/mol}$), one may assume that the donor-acceptor interaction is significant if the complexation energy is 1 kcal/mol or higher.

In brief, the NBO analysis stresses the importance of quantum mechanical orbital interaction and exchange effects in the van der Waals regime. Since these exchange effects are distinguishable from classical electrostatic effects, hydrogen-bonding can be treated more like a donor-acceptor interaction. Of course, customarily hydrogen-bonding has already been treated as an acid-base interaction. Since the charge-transfer component of the total energy as calculated by the NBO model is higher than that by the KM method, the NBO analysis appears to be able to differentiate between hydrogen-bonded and non-hydrogen-bonded species.

2.4 Frontier Orbitals

Similar to the NBO donor-acceptor approach, Fukui²³ has shown that the most important interaction between two molecules is that between the HOMO (highest occupied molecular orbital) of A-molecule and the LUMO (lowest unoccupied molecular orbital) of B-molecule because it will result in the largest drop in energy. These two orbitals are called the frontier orbitals.²⁴ This type of interaction has been also discussed as the donor-acceptor or the acid-base interaction. Other interactions between occupied orbitals and unoccupied orbitals are comparatively secondary and affect only the energetics of transition states.

In terms of the electronic structure in solids, a band is equivalent to an assembly of crystal orbitals. The HOMO is equivalent to the top of the valence band; the LUMO to the bottom of the conduction band. Thus, in terms of energy, the energy of the HOMO is E_v , and that of the LUMO, E_c . The Fermi energy E_F for an intrinsic semiconductor is

$$E_F = \frac{1}{2} (E_{\text{HOMO}} + E_{\text{LUMO}}) = \frac{1}{2} (E_c + E_v). \quad (13)$$

Generally at $T=0$, crystal levels above the Fermi level are unoccupied; while those below the Fermi level are occupied. Furthermore, as stated in the Koopmans' theorem,³⁷ the frontier orbital energies are given by

$$-E_{\text{HOMO}} = I; \quad (14)$$

$$-E_{\text{LUMO}} = A, \quad (15)$$

where I is the ionization potential (or energy) and A the electron affinity.

2.5 Perturbation Theory

For chemical reactivity, Hudson²⁵ proposed a perturbation theory in place of transition state theory. His hypothesis is that the initial perturbation determines the course of a reaction, or an interaction. Basically, this perturbation method is that on the encounter of two interacting systems (or molecules), the combined wave function of the perturbed system is approximately equivalent to the summation of wave functions of the two unperturbed molecules. In this case, the interaction energy ΔE_{INT} of molecules can be simplified into two terms by neglecting the higher-order terms.^{26,27} The first is the Coulombic (or electrostatic) term consisting of the Coulombic attraction and interelectronic repulsion, and the second is the frontier orbital (or charge-transfer) term describing the contribution from the interaction between the HOMO of a nucleophile (or base) and the LUMO of an electrophile (or acid), and most Lewis acid-base interactions involve both terms:

$$\Delta E_{\text{INT}} = -\frac{Q_{\text{Nu}}Q_{\text{El}}}{\epsilon R} + \frac{2(C_{\text{Nu}}C_{\text{El}}\beta)^2}{E_{\text{HOMO}} - E_{\text{LUMO}}}, \quad (16)$$

(The Coulombic term) (The frontier-orbital term)

where Q_{Nu} , Q_{El} are the total charges for the nucleophile and electrophile, respectively; C_{Nu} and C_{El} are the coefficients of the atomic orbital Nu and El , respectively; β is the resonance integral, $\langle \Psi_1 | H | \Psi_2 \rangle$; ϵ is the permittivity, and R is the distance between Nu and El .

This equation also contributes to the understanding of the hard-soft acid-base (HSAB) principle.³⁸⁻⁴³ For the ionic (hard) electrostatic interaction, the first term dominates, while for the covalent (soft) electron donor-acceptor (EDA) interaction, the second term prevails. It is noteworthy that the Coulombic term, which is long-range, is inversely proportional to the distance, while the second term, which is short-range, is inversely proportional to the energy gap between the HOMO and the LUMO of two respective molecules. This energy gap has been equated to the absolute hardness of the HSAB principle.⁴⁴⁻⁴⁷ When two reacting molecules start to approach each other, their orbitals perturb and interact. As a result, two transition orbitals are formed, i.e., bonding and antibonding as described in the above NBO approach. The formation of the former is accompanied by the evolution of heat; hence the reaction is exothermic. On the other hand, the formation of the latter requires the absorption of heat; hence the reaction is endothermic because two electrons must go into the antibond.

3 ADHESIVE ENERGY AND SEPARATION DISTANCE

3.1 Universal Adhesive Energy-Separation Distance Relationship

For a molecular interaction, the system does not involve an external adhesive. The adhesion is achieved by bringing both molecules close enough because the adhesive energy is a function of the binding energy and separation distance. Ferrante *et al.*⁴⁸⁻⁵⁰ calculated the adhesive energy for clean bimetallic interfaces using a

quantum-mechanical jellium model and found the universality of the adhesive energy E_{ad} versus the interatomic separation, a , between the surface of metals. Most metals when adhered follow the universal relationship between the scaled adhesive energy, $E_{ad}^*(a^*)$, and the scaled separation, a^* :

$$E_{ad}(a) = \Delta E \cdot E_{ad}^*(a^*), \quad (17)$$

where $E_{ad}(a) = [E(a) - E(\infty)]/2A$; A is the cross-sectional area; $a^* = (a - a_m)/\ell$, and

$$\ell_{(\text{scaling length})} = \left[\frac{\Delta E}{(d^2 E_{ad}(a)/da^2) a_m} \right]^{1/2}, \quad (18)$$

ΔE the equilibrium binding energy or the magnitude of $E_{ad}(a)$ at the respective minima of the curves,

$E_{ad}^*(a^*)$ a universal energy relation,

a_m the equilibrium separation, and

a the atomic separation from the equilibrium value a_m .

When two metals are identical, ΔE becomes the surface energy of the metal.

Interestingly, the universality of this fundamental relationship is not limited to solids; thus, subsequently it has been extended by Rose *et al.*⁵¹ into a nuclear equation of state. For nucleons, the \bar{V}_{14} potential is averaged from the spin-isospin-dependent s- and p-wave components to represent nuclear matter. In the region of strong bonding, the \bar{V}_{14} potential is virtually indistinguishable from the universal

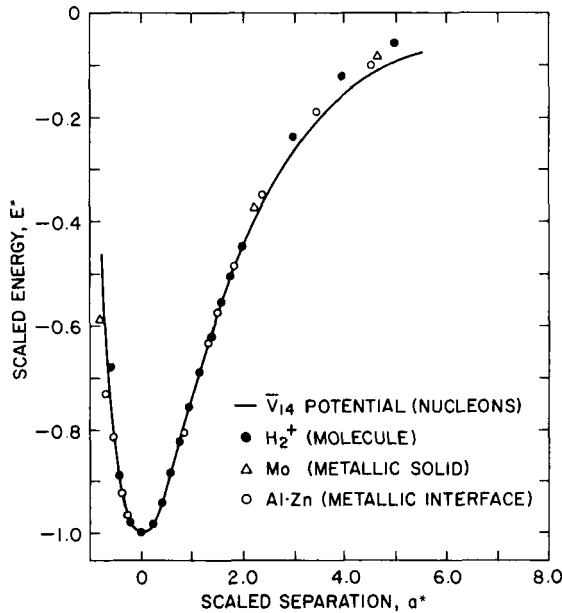


FIGURE 4 Comparison of a scaled two-nucleon (\bar{V}_{14}) with scaled binding energy relations for the molecule H_2^+ , the bulk metal Mo, and the bimetallic interface Al-Zn. [After J. H. Rose, J. P. Vary and J. R. Smith, *Phys. Rev. Lett.* 53 (4), 344, (1984), reproduced with permission.]

binding-energy relation of solids as shown in Fig. 4. Consequently, it has been established that the surface and cohesive energies of nuclei can also be related to the nucleon separation as in the case of metals and the electron-hole liquids.

3.2 Optimum Separation Distance and Solid Adhesion

To facilitate electrons functioning as a "glue," it is of utmost importance that electrons in the orbitals are close enough to undergo various interactions. For example, it is much easier for clean metals to cling together under ultrahigh vacuum. However, for contaminated metals or rough surfaces, adhesion, if it exists at all, drops off considerably. There appears to be a critical distance necessary for a metal to achieve adhesion.

Ferrante and Smith⁵² have stated that it is the kinetic energy that initiates the bonding, but it is exchange-correlation energy that determines the strength of adhesive bond at the bimetallic interface. The range of strong bonding is about 2 Å (or 0.2 nm) for the Al (111) – Mg (011) contact. It should be noted that the electrostatic energy is repulsive at small separations but attractive at large distances. Thus, the dominant repulsive term is the kinetic energy at small separation. Indeed, the decomposition of energies for the bimetallic adhesion has been shown to be similar to that by the KM method. The optimum separation discussed here is also similar to that (1.8 Å) for the acid-base $\text{BH}_3 - \text{NH}_3$ complex.³⁵ Interestingly, the optimum distance for an electrophile-nucleophile interaction⁵³ has also been found to be 2.3–2.7 Å.

A recent work by Holubka *et al.*⁵⁴ using the MNDO method shows that the interaction of Al_2O_3 with acrylates is much more favorable in forming the complex than that with methacrylates merely due to a closer distance and less steric hindrance of the former. In brief, the separation for a molecular interaction should be below 3 Å, but the optimum distance is generally around 2 Å.

4 MOLECULAR BONDING ON SOLID SURFACES

In the above sections we discuss molecular bonding as a whole. In this section, we examine 1) the interactions between two discrete molecules and 2) interactions between a molecule and a solid surface. We intend to point out that there is a subtle difference between these two cases.

4.1 Interactions between Two Discrete Molecules

In 1964, Blyholder⁵⁵ first applied the orbital concept for the study of solid surfaces. In recent years, Hoffmann¹⁶⁻¹⁸ employed the frontier orbital concept^{23,24} and the extended Huckel method for the study of solid interactions. He categorizes solid interactions according to the number of electrons exchanging intermolecularly:

- 1) two-electron interaction involving an electron pair,
- 2) four-electron exchange, and
- 3) no-electron exchange.

In the diagram (Fig. 5a), a is shown in interactions ① and ②; b in interaction ③, and c in interaction ④. Interactions ① and ② result in a true covalent or dative bonding; thus its overall effect is the stabilization of the system by lowering of energy. If it is a complex formation, the bond is dative in nature involving a donor and an acceptor of the electron. This is what we discussed in earlier sections. Interaction ③ is the exchange that is repulsive in nature. When the overlap of orbitals takes place, the antibonding level rises and the bonding level lowers. Thus, the energy for going up is more than that for coming down. However, the total energy¹⁵⁻¹⁷ of the overlapped orbitals is higher than that of separately isolated orbitals.

Finally, the interaction ④ which involves no electron from each of the unoccupied orbitals produces no net gain or loss in energy. In other words, this is the effortless combination of orbitals for a pair of molecules.

4.2 Interactions between a Molecule and a Solid Surface

If one of the interacting pair is not a discrete molecule but a solid (Fig. 5b), Hoffmann¹⁶⁻¹⁸ points out a new concern that interaction ③ may prevent interactions ① and ② from happening. The reason is that the antibonding level of the molecule may rise above the Fermi level of the solid. Then, unexpectedly, electrons may flow from the antibonding level to the Fermi level of the solid, and consequently the stabilization effect is reduced.

For a metal surface that is nearly a continuum, one more interaction can be realized, i.e., interaction ⑤. Here, the Fermi level is at the top of the valence band (or the occupied level), and electrons (or holes) will flow in the surface and in the

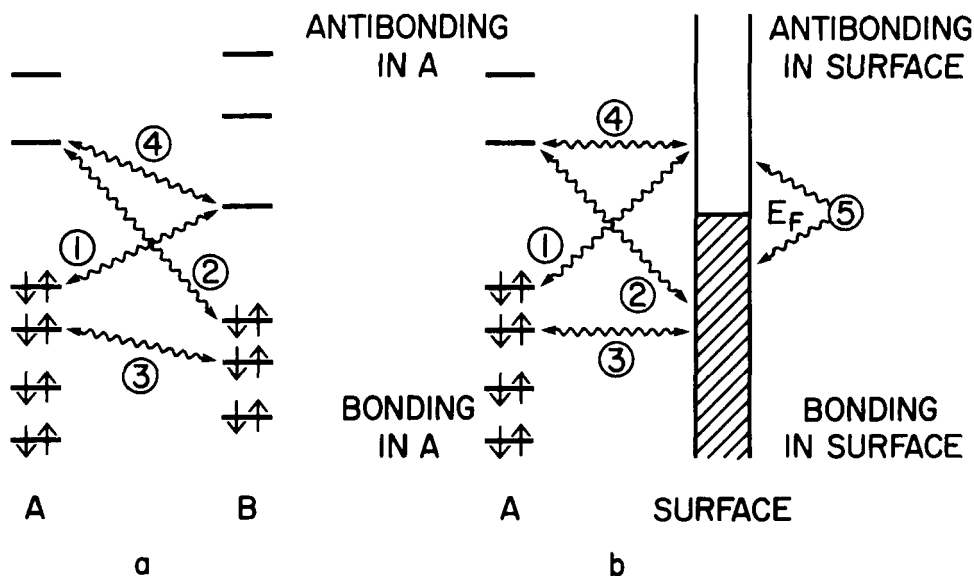


FIGURE 5 Comparison of orbital interactions: (a) between two discrete molecules and (b) between a molecule and a solid surface. [After R. Hoffmann, *Rev. Mod. Phys.* **60** (3), 601 (1988), reproduced with permission.]

bulk beneath it in an attempt to balance the interactions. This particular interaction has a sort of house-cleaning effect. Thus, all four first-order interactions (① → ④) will move the metal's level up and down, but interaction ⑤ influences only the second-order energetics and bonding resulting from the shift of electron density around the Fermi level.

In Fig. 6, interaction ④ is compared to (a) two discrete molecules and (b) a molecule and a solid surface. As mentioned previously, for two discrete molecules, interaction ④ produces no net change in energy. However, in the case between a discrete molecule and a surface, the situation is different. In a solid, there is a continuum of levels, the bonding of the interacting levels may fall below the Fermi level of the solid (Fig. 6b). After becoming filled, it will promote the fragment A-surface bonding. Moreover, the surface may supply the electrons to fill that level. Therefore interaction ④ may produce a change in energy only between a discrete molecule and a solid surface but not between two discrete molecules.

4.3 Chemisorption on Solid Surfaces

What happens if there is chemisorption on the solid surface? The net result is that the metal-adsorbate bond is strengthened at the expense of the bonding of the adsorbate within the bulk. This somewhat resembles that push-and-pull mechanism in organic chemistry, and there appears to be an overall conservation of energy. This interesting aspect of chemisorption has been applied to surface interactions between gas molecules and solids. We believe that some of those aspects may be related to solid adhesion. However, we do not intend to elaborate the subject in this section.

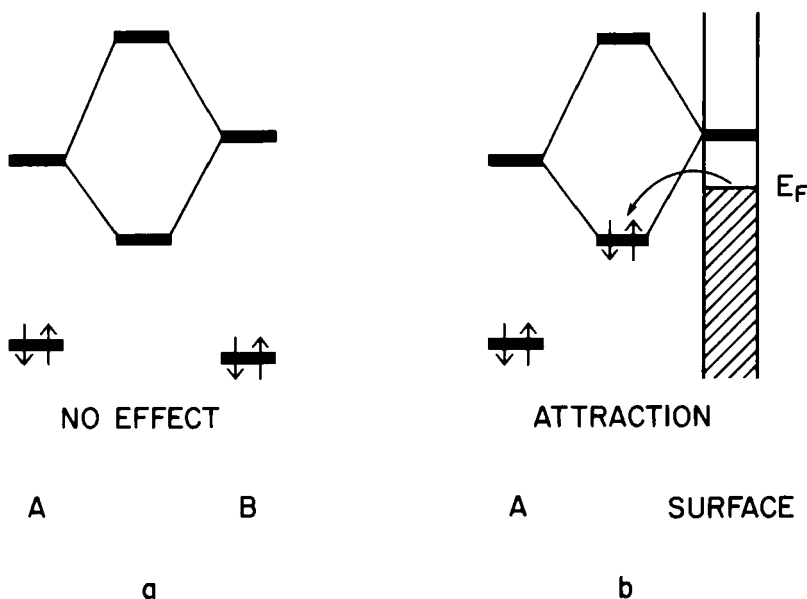


FIGURE 6 Comparison of interaction (4): (a) between two discrete molecules and (b) between a molecule and a solid surface. [After R. Hoffmann, *Rev. Mod. Phys.* **60** (3), 601 (1988), reproduced with permission.]

4.4 Impurity and Contamination on Solid Surfaces

Why do some solids not adhere to each other? Besides surface asperities, adsorbates, impurities and contaminations are the worst obstacles to adhesion. Both of them can keep real surfaces apart. As a result, the intermolecular distance can be much greater than 100 Å, and at such a distance even the Lifshitz-van der Waals interactions are weak, and, beyond any doubt, the molecular interaction does not exist.

Smith and Cianciolo⁵⁶ have found that impurities on the solid surface can adversely affect the adhesive binding energy ΔE . At low temperatures, if it is energetically more favorable for impurities to segregate on the surface, then ΔE will decrease. However, the converse is also true; if the surface segregation is endothermic, ΔE should increase. For the latter case, impurities tend to segregate at the grain boundary. In either cases, impurities are detrimental to adhesion.

4.5 Avalanche on Clean Solid Surfaces

The work on the effect of impurities suggests that it is of utmost importance in keeping solid surfaces clean. If the intermolecular distance falls below a critical distance, Smith *et al.*⁵⁷ have observed that an avalanche takes place on the surfaces as shown in Fig. 7. This kind of surface collapse resembles “cold-welding” of metal surfaces under ultrahigh vacuum or in outer space.

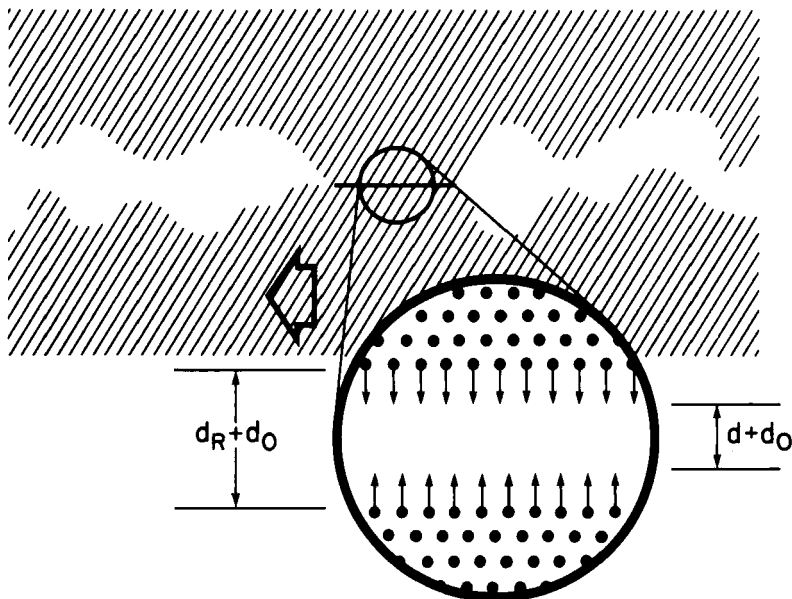


FIGURE 7 Cross section of sliding surface. Inset: Region that has avalanched together, with arrows showing the displacements of the atoms in the surface layers due to avalanche. Also shown are the rigid interfacial separation, $d_R + d_0$, and the relaxed interfacial separation, $d + d_0$, where d_0 is the bulk interplanar spacing. [After J. R. Smith, *et al.*, *Phys. Rev. Lett.* **63** (2), 1269 (1989), reproduced with permission.]

A similar phenomenon has been observed⁵⁸ between a Ni tip for an atomic force microscope (AFM) and a clean Au surface under high vacuum. For various interactions, Au atoms from the metal surface can swarm onto the Ni tip and adhere strongly to form an “adhesive neck,” and the remaining Au surface deforms due to the local ductile extension upon the separation of the adhered Ni tip.

5 SUMMARY

This study shows us that indeed solids can be bonded together even without an adhesive by a molecular bonding mechanism. In general, we may consider that there are clear-cut adhesion mechanisms, such as the acid-base interaction (dative bond), adsorption (physical), chemical covalent bonding, diffusion, electrostatic, mechanical interlocking, etc. However, throughout this simplistic study, it is clear that except for chemical covalent bonding, there is no clear-cut mechanism, especially for molecular bonding. Molecular interactions through electrons can involve electrostatic (ES), polarization (PL), charge-transfer (CT), exchange-repulsion (EX), and the coupling (MIX) of any of these four components. For an ionic material, the charge-controlled Coulombic interaction dominates, while for a covalent material, the frontier-orbital-controlled charge-transfer prevails. Above all, in the background, there are always some secondary vdW interactions⁵⁹ which are generally associated with physical adsorption. That is why there has been constant confusion about adhesion mechanisms, for example, the acid-base interaction.

Though electrons are directly involved in the molecular bonding, we can not equate this broad mechanism to the electrostatic (or electronic) mechanism involving a long-range electrical double layer (EDL) as proposed by Deryaguin *et al.*⁶⁰ It has been shown that the adhesive strength derived from the electrostatic mechanism as proposed is no more than 10% of the total.^{61–63} Indeed, for the molecular bonding mechanism, the interaction energy has at least three other components beside the ES interaction. Though this study may provide the electrostatic mechanism with some support at the molecular level, the electrostatic interaction is definitely not the only mechanism for molecular adhesion.

Finally, this type of molecular orbital study appears to lead us to a broad perspective about solid adhesion. It has been demonstrated that molecular interactions are related to the intermolecular distance. It has been shown that the adhesive energy is a function of binding energy and separation distance. Furthermore, there are long-range interactions, such as Coulombic and vdW and short-range interactions, such as charge-transfer and exchange repulsion. For Coulombic, the range can be as short as nuclear and as long as those beyond several hundred Angstroms; for vdW, it has an optimum at 4 Å, and the non-retarded microscopic interaction energy inversely proportional to the sixth power of distance falls off very rapidly. For most charge-transfer interactions, the range is below 3 Å, and the optimum is approximately 2 Å; for the transfer interaction. The exchange repulsion increases rather fast below 2 Å. Thus, the separation distance can reflect how much adhesive energy is involved. In achieving optimum molecular adhesion, it is beyond any doubt that a solid should be cleaned from adsorbates, impurities and contaminations.

We should also point out that though solids like small molecules can be bonded by electrons, solids are never as simple as small molecules. Many other factors, such as crystal structure and physical properties, can all affect adhesion. Moreover, the interactions between two discrete molecules are different from those between a discrete molecule and a solid surface. On a solid surface, there is a different type of electronic interaction that can affect both adhesion and chemisorption.

NOMENCLATURE

a^*	Scaled separation
A	Electron affinity
c	Polarization coefficient
C_{Et}	Coefficient of the atomic orbital of the electrophile
C_{ij}	Coefficient of the summation
CT	Charge transfer
C_{Nu}	Coefficient of the atomic orbital of the nucleophile
d_p	Penetration distance
DIS	Dispersion component
ΔE_b	Binding energy
ΔE_{INT}	Interaction energy
$E_{ad}^*(a)$	Scaled adhesive energy
E_c	Energy of the conduction band edge
E_{COM}	Complexion energy
E_F	Energy of the Fermi level
E_{HOMO}	Energy of the highest occupied molecular orbital
E_{LUMO}	Energy of the lowest unoccupied molecular orbital
ES	Electrostatic Component
E_V	Energy of the valence band edge
EX	Exchange repulsion
h	Hybrid orbital
H	Hamiltonian
I	Ionization potential
\mathbf{k}	Wavevector
ℓ	Scaling length
MIX	Coupling component
NCT	No charge-transfer
PL	Polarization
Q	Total electronic charge
\mathbf{r}_j	Lattice position
R	Distance between an electrophile and a nucleophile
R_{eq}	Equilibrium radius
R_{vdW}	vdW radius

Greek letters

β	Resonance integral
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ϵ	Permittivity
σ	Sigma bond
σ^*	Sigma antibond
ϕ	Unit cell orbital
χ	Atomic orbital
Ψ	Molecular orbital

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