Hardness and Softness in the *Ab Initio* Study of Polyatomic Systems

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A combination of the maximum hardness (MH) principle and the local version of the hard and soft acids and bases (HSAB) principle is tested as a tool to describe the stability and reactivity of polyatomic systems. The local HSAB principle describes regional differences in reactivity whereas the MH principle selects the most stable configuration. This approach is tested using *ab initio* density functional theory techniques. Total-energy calculations fully confirm the validity of both principles.

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Hardness and softness are concepts that have been in the chemical literature for more than two decades [1-3]. Their names were proposed from an empirical correlation with polarizability, and they allowed a classification of the Lewis acids and bases in hard and soft species [1]. The usefulness of these concepts in chemistry is related to the hard and soft acids and bases (HSAB) principle, which establishes that "hard Lewis acids will prefer to interact with hard Lewis bases whereas soft acids will interact with soft bases" [1]. This principle permits the rationalization of a great number of chemical interactions [2]. Moreover, there is evidence that this principle is valid in its local version [4-7], i.e., *given a system with different reactive sites, its hard regions prefer to interact with hard species whereas its soft areas prefer soft attacking groups to react.* This analysis is based on the characteristics of the isolated reactants and therefore, may eventually prove to be helpful in the investigation of complex problems such as surface reactivity.

Recently, it has been shown that the empirical concepts of hardness and softness can be identified in the mathematical structure of density functional theory (DFT) [8-11]. The first step was the identification of hardness η as the second derivative of the total energy E with respect to the number of electrons, or, equivalently, the first derivative of the chemical potential μ with respect to the number of electrons [8]:

$$\eta=\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\mathbf{r})}=\left(\frac{\partial\mu}{\partial N}\right)_{v(\mathbf{r})}. \tag{1}$$

Both derivatives are taken at constant external potential $v(\mathbf{r})$. Softness is defined as the inverse of hardness, $s=1/\eta$ [9]. In addition to s and η which are global properties, one can define local softness $s(\mathbf{r})$ [9] and local hardness $\eta(\mathbf{r})$ [10] as

$$s(\mathbf{r})=\left(\frac{\partial\rho(\mathbf{r})}{\partial\mu}\right)_{v(\mathbf{r})}=\frac{1}{\eta}\left(\frac{\partial\rho(\mathbf{r})}{\partial N}\right)_{v(\mathbf{r})} \tag{2}$$

and

$$\eta(\mathbf{r})=\frac{1}{N}\int d\mathbf{r}'\frac{\delta^2 F[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\rho(\mathbf{r}')\,. \tag{3}$$

These local properties are reciprocals in the sense [10]

$$\int n(\mathbf{r})s(\mathbf{r})d\mathbf{r}=1\,, \tag{4}$$

and reduce to the corresponding global properties by integration [9,10]. In the equations above, $F[\rho(\mathbf{r})]$ is the Hohenberg and Kohn universal functional, and $\rho(\mathbf{r})$ is the charge density.

Incorporation of the concepts of hardness and softness into the structure of DFT has had several important consequences. First, a hardness scale, generated through Eq. (1), that classifies chemical species in accordance with experimental information [12-14] was generated. Second, the HSAB principle could be formally deduced within the framework of DFT [15]. Finally, the existence of the maximum hardness (MH) principle for the ground state of a many-body system has been proved [16]. It has also been shown that the polarizability behaves inversely with hardness, consistent with empirical evidence [17]. These properties reinforce the importance of the concepts of hardness and softness.

At large distances, local hardness becomes proportional to the electrostatic potential generated by the charge distribution of the system [10]; this connection indicates that the hard-hard interaction is mainly related to electrostatic effects. On the other hand, $s(\mathbf{r})$ contains the same local information as the states at the Fermi level (frontier orbitals) [9,18]. Accordingly, soft-soft interactions are driven by covalent (orbital) effects. Notice that Eq. (4) does not imply that $s(\mathbf{r})$ and $\eta(\mathbf{r})$ are reciprocals at each point in space; however, it is expected that regions with low local softness values will be hard regions.

So far the attempts to employ the MH principle and the local version of the HSAB principle have used Hartree-Fock rather than DFT approaches [4-7,19,20]. Here we test the applicability of these principles in the context of the theory in which they were defined by calculating global and local softness of a test system from *ab* *initio* DFT. The results are used to predict the stability and reactivity of the system according to the MH and HSAB principles. Total-energy calculations of the interaction energy of isolated atoms with the test system are also performed and show excellent agreement with the predictions of the HSAB principle.

The test system selected is a Si_4 cluster. This system was chosen for the following reasons: (a) It is a stringent test case for local reactivity criteria because it is built up from the same basic units. Consequently, it is very difficult to describe local differences in chemical reactivity by simply referring to the properties of the isolated basic units. (b) Its ground-state configuration is a high symmetry structure [21], so that the mapping out and analysis of local softness is more tractable. (c) It can be molded in several alternative structural geometries which is important for testing the usefulness of the MH principle in the selection of the true ground-state configuration.

We calculate global hardness and local softness using Janak's extension for fractional occupancies of the Kohn-Sham formalism [22]. To calculate η and $s(\mathbf{r})$, we use the second equalities of Eqs. (1) and (2), respectively. For both η and $s(\mathbf{r})$ there are two different cases one must consider. These are related to processes in which electronic charge is transferred *to* the system $[\eta^-, s^-(\mathbf{r})]$, and processes in which it is *removed* from the system $[\eta^+, s^+(\mathbf{r})]$. For closed-shell systems (systems with a gap), $\eta^+ \neq \eta^-$ and $s^-(\mathbf{r}) \neq s^+(\mathbf{r})$, whereas for open shell (gapless) systems, $\eta^+ = \eta^-$ and $s^-(\mathbf{r}) = s^+(\mathbf{r})$. To analyze the stability of the system, the relevant quantity is the average, $\eta^0 = \frac{1}{2}(\eta^+ + \eta^-)$, because it contains the information of both directions of charge transfer. To examine the usefulness of $s(\mathbf{r})$ as a local reactivity parameter, processes in which charge is transferred to the cluster are considered. This is done purely for simplicity and without loss of generality. Therefore the relevant quantity that we shall focus on is $s^-(\mathbf{r})$.

To solve the Kohn-Sham equations, total-energy pseudopotential calculations [23] were performed with a Perdew and Zunger form of the exchange and correlation potential [24]. Norm-conserving nonlocal Kleinman-Bylander pseudopotentials were generated as described by Rappe *et al.* [25]. To perform the geometry optimization of the isolated cluster, a cubic supercell of length 10 Å was used, while for the interaction of the cluster with an additional atom we used a supercell of dimensions 10 Å × 10 Å × 18 Å. This choice assures that the interaction between cells can be neglected. Recently, this methodology was successfully applied to molecules [26]. Plane-wave basis functions up to a cutoff energy of 12 Ry, and the Γ point for $\mathbf{k}$ integration were used throughout this work.

Test of the MH principle.—In Table I, the results obtained for geometrical structures of Si_4 are displayed. The minimum energy of each symmetry configuration was determined through simulated annealing [27] by using high cooling speeds. The final structures are very similar to those previously reported from Hartree-Fock calculations [21] and from molecular dynamics techniques [28].

Even though the MH principle has been rigorously proved under conditions of constant chemical potential [16], it appears that for our particular case it is valid without that restriction (see the values of electronegativity in Table I). If this turns out to be true in general, it would be extremely useful because one could now search for the ground state without calculating the total energy. Although the difference in hardness between the optimized square and tetrahedral structures is small, it is clear that the most stable configuration has the highest global hardness among the three structures. Of course one test case is not sufficient to set the rule. Here we present it only as a very intriguing possibility.

Calculation of local softness.—Now, let us focus our attention on the local softness of the ground-state configuration of Si_4. In Fig. 1 we present calculations of $s^-(\mathbf{r})$ in different planes of the molecule. Various potential reactive sites of the cluster are clearly distinguished. In the molecular plane, the softer regions are those located in the outer regions of the corners of the rhombus structure. There are hard channels for hard attacking groups, such as the one marked with α in Fig. 1(a). In the perpendicular plane we can see that the softest regions in the cluster are those located at the atoms which are along the longer diagonal, above and below the molecular plane. There is a hard pathway in the center of the rhombus [see β in Fig. 1(b)]. Figure 2 shows the softness values along the α and β channels. In this figure only the values of $s^-(\mathbf{r})$ between 1 and 4 Å are displayed because the attacking groups are more sensitive to the outer regions of $s^-(\mathbf{r})$. In Fig. 2 we can identify the presence of "softness barriers" for hard attacking groups. At distances longer than 1.5 Å, channel α is softer than the β channel. In contrast, channel α is harder at short distances as a consequence of the presence of a silicon

TABLE I. Hardness, relative energy, and electronegativity for selected symmetries of Si_4.

	Rhombus	Square	Tetrahedron
Hardness (η^0) (eV)	1.67	1.52	1.50
Relative energy (eV)	0	1.98	2.27
Electronegativity (eV)	4.57	3.70	5.05
Optimized geometry (Å)	Diagonals: 3.929,2.383	Side: 2.296	Bond length: 2.448

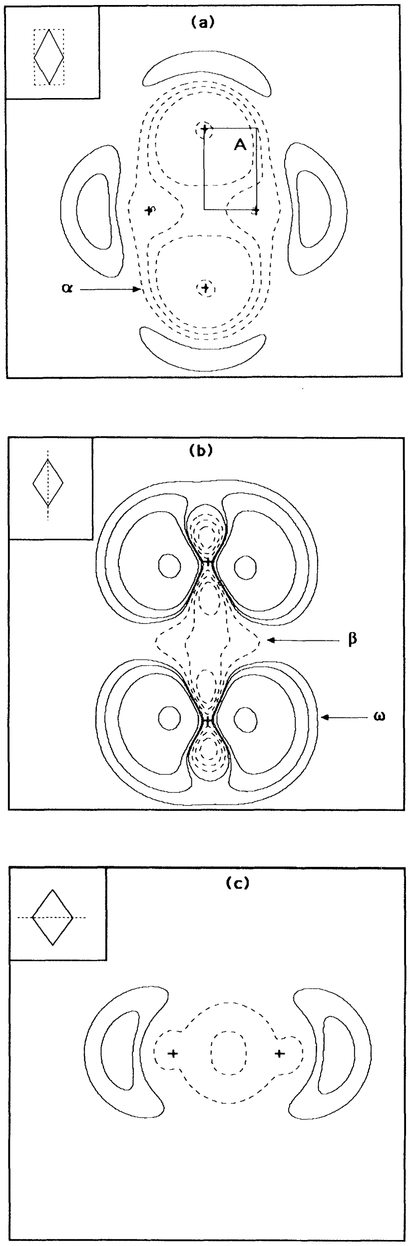

FIG. 1. Contour plots of local softness $s^-(\mathbf{r})$ in three planes: (a) the molecular plane, and (b),(c) two perpendicular planes, as indicated in the upper left corner of each figure. Dashed contours are for negative values and solid lines are for positive. The contour values for (a) are −6.0, −3.0, −0.6, 1.8, 3.0 in $(\mathrm{keV})^{-1}$ Å^{-3}; the small negative contours surrounding the atomic positions correspond to −6.0 for the atoms along the large diagonal and to −0.6 for atoms on the short diagonal. For (b) the contours are −6.0, −3.0, −0.6, 1.8, 3.0, 6.0, 30.0 $(\mathrm{keV})^{-1}$ Å^{-3}. For (c) they are −3.0, −0.6, 1.8, 3.0 $(\mathrm{keV})^{-1}$ Å^{-3}. The channels for hard attacking groups are indicated by α and β whereas ω identifies the preferred sites for soft attacking species. The region labeled A is a projection of the plane 3 Å above the molecule which contains the probe atoms.

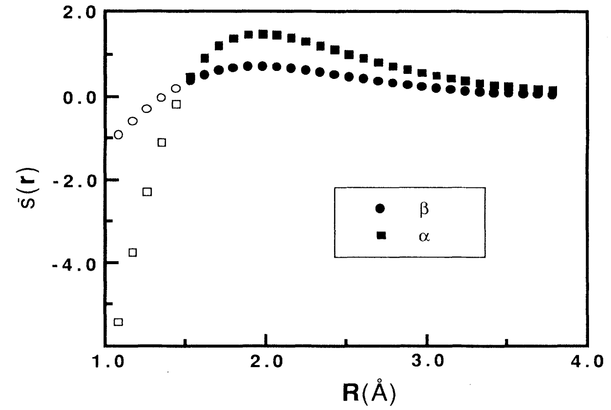

FIG. 2. Local softness for nucleophilic attacks, $s^-(\mathbf{r})$, along the α and β trajectories of Fig. 1. The horizontal axis corresponds to the perpendicular distance, measured from the largest diagonal of the rhombus. The zero of the horizontal scale is a point along α and β that lies on that diagonal. The solid symbols correspond to physically meaningful values of softness for the two trajectories.

atom at $R=0$ on this channel. In Fig. 2 the smaller softness barrier is that of the β channel, indicating that this is a convenient trajectory for hard reactants. It is also concluded from Fig. 1, that the preferred trajectory for soft-soft interactions is the one marked with ω.

Test of the local HSAB principle.—The predictions outlined above were tested by performing "theoretical experiments" through the use of "probe atoms." To assure that the charge is transferred to the cluster and that $s^-(\mathbf{r})$ is the pertinent quantity to analyze cluster chemical reactivity, the probe atoms selected have lower electronegativities than the cluster. In addition, the probes should have different hardness to allow the study of the differences between hard-hard and soft-soft interactions. Two atoms that satisfy those requirements are Si and Ga; Si presents an electronegativity of 4.05 eV and a hardness of 2.99 eV, and Ga has an electronegativity of 2.61 eV and a hardness of 2.09 eV.

Interaction energies, defined as the energy difference between the coupled system and the isolated parts, were determined on a mesh of 25 points for the $\mathrm{Si_4}$-Si and $\mathrm{Si_4}$-Ga systems. The probe atoms were moved on a region parallel to the molecular plane located 3 Å above it while the cluster configuration remained fixed. Figure 3 shows the constant-energy contour curves for the interaction energy. Our results (Figs. 1 and 3) agree with the predictions of the local HSAB principle, i.e., softer regions in the cluster present strong interaction with the softer atom (Ga) and hard regions present strong interaction with the hard atom (Si). This distinction of regional reactivities presents the first demonstration of the local HSAB principle in action.

In conclusion, we have corroborated the applicability of

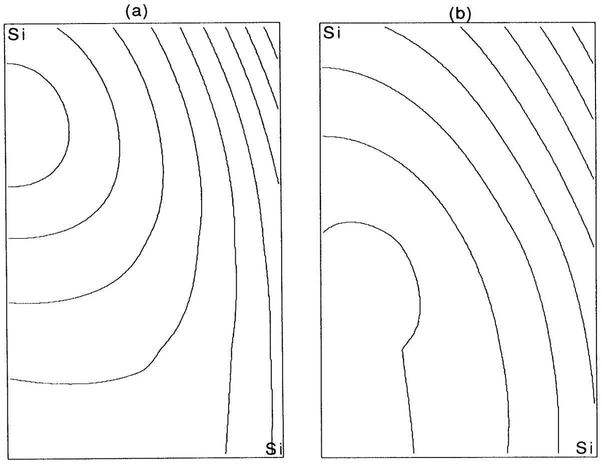

FIG. 3. Constant-energy curves for the interaction of Si_4 with (a) Si and (b) Ga. Probe atoms were moved around on a plane located 3 Å above the molecular plane corresponding to the projection A in Fig. 1(a). In both cases, the weaker interaction corresponds to the contour in the upper right corner of the figure. The orientation of the plane is identified by the positions of silicon atoms located on the molecular plane (upper left and lower right corners). The contour values (in eV) for (a) range from −1.41 to −1.65 with a constant step of −0.03, and for (b) range from −2.29 to −2.85 in steps of −0.08.

the global hardness to select the most stable configuration of a system (relaxing the restriction of constant chemical potential), and we have verified the validity of the HSAB principle in a local sense. The combination of these reactivity criteria gives a unified approach in which it is possible to study the stability and the reactivity of a system by using well-defined DFT ground-state properties of the isolated reactants. Furthermore, $s(\mathbf{r})$ allows us to include in the same description, reactions which are driven by electrostatic effects (hard-hard interactions) and those related to orbital effects (soft-soft interactions).

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