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LETTERS

The Hard and Soft Acids and Bases Principle

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Making use of the approximate expression for the total energy E of a system, in terms of the chemical potential μ and the hardness η, $E[\rho] = N_e\mu - {}^1/_2\, N_e^2\eta + E_{\mathrm{core}}[\rho]$, where N_e is an effective number of valence electrons and $E_{\mathrm{core}}[\rho]$ represents the core contribution to the total energy, it is shown that the interaction between species whose softnesses are approximately equal is energetically favored, relative to the interaction between species whose softnesses are very different from each other.

The statement "hard acids prefer to coordinate to hard bases, and soft acids to soft bases" proposed by Pearson[1] in 1963, and known as the hard and soft acids and bases (HSAB) principle,[2] has been widely used, at a qualitative level, to explain many acid−base reactions.[3] Recently, the definitions of chemical potential[4] (electronegativity) μ, hardness[5] η, and softness[6] S provided by density functional theory,[7]

$$\mu = (\partial E/\partial \mathrm{N})_V \qquad (1)$$

$$\eta = (\partial^2 E/\partial N^2)_V = (\partial\mu/\partial N)_V \quad \text{and} \quad S = 1/\eta = (\partial N/\partial\mu) \qquad (2)$$

(E is the total electronic energy, N is the total number of electrons, and $V(\mathbf{r})$ is the external potential generated by the nuclei), have been used to carry out quantitative studies[8−14] and to derive a theoretical proof of this principle.[15−19] In particular, Chattaraj, Lee, and Parr[16] have established that "among potential partners of a given electronegativity, hard likes hard and soft likes soft".

The object of the present work is to derive an alternative proof that may provide additional support for a better understanding of the HSAB principle. The proof is based on an approximate expression for the interaction energy between two chemical systems A and B, in terms of the chemical potentials and the softnesses of the isolated species, that allows one to establish which is the optimum value of the softness of system B for a given softness of system A.

The starting point makes use of the ground state electronic energy expression[7]

$$E[\rho] = F[\rho] + \int \mathrm{d}\rho\; \rho(\mathbf{r})\, V(\mathbf{r}) \qquad (3)$$

and its associated Euler−Lagrange equation

$$\mu = \frac{\delta F[\rho]}{\delta\rho(\mathbf{r})} + V(\mathbf{r}) \qquad (4)$$

with

$$F[\rho] = T[\rho] + J[\rho] + E_{\mathrm{xc}}[\rho] \qquad (5)$$

where $\rho(\mathbf{r})$ is the electronic density, $F[\rho]$ is the universal Hohenberg−Kohn density functional, and $T[\rho]$, $J[\rho]$, and $E_{\mathrm{xc}}[\rho]$ are the kinetic, the classical Coulomb interaction, and the exchange-correlation energy density functionals.

In order to obtain the dependence of the total electronic energy on the chemical potential and the hardness, it is convenient first to introduce a core density, $\rho_c(\mathbf{r})$, defined by[20]

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$$\rho(\mathbf{r}) = \rho_c(\mathbf{r}) + N_e f(\mathbf{r}) \tag{6}$$

where $f(\mathbf{r}) = (\partial\rho(\mathbf{r})/\partial N)_V$ is the fukui function[21] and N_e represents an effective number of valence electrons (note that since $f(\mathbf{r})$ integrates to 1, then $\rho_c(\mathbf{r})$ integrates to N_c, an effective number of core electrons, $N_c = N - N_e$). This way, multiplying eq 4 by the product $N_e f(\mathbf{r})$, integrating the resulting equation over $\mathbf{r}$, substituting the final equation in eq 3, and using eq 6 leads to

$$E[\rho] = N_e\mu + F[\rho] - \int d\mathbf{r}\, \rho(\mathbf{r}) \frac{\delta F[\rho]}{\delta\rho(\mathbf{r})} + \int d\mathbf{r}\, \rho_c(\mathbf{r}) \frac{\delta F[\rho]}{\delta\rho(\mathbf{r})} + \int d\mathbf{r}\, \rho_c(\mathbf{r})\, v(\mathbf{r}) \tag{7}$$

It is convenient to introduce in eq 7 the functional expansions of $F[\rho]$ and of $\delta F/\delta\rho(\mathbf{r})$ in terms of their functional derivatives, that is[20,22,23]

$$F[\rho] = \int d\mathbf{r}\, \rho(\mathbf{r}) \frac{\delta F[\rho]}{\delta\rho(\mathbf{r})} - {}^1\!/_2 \int\!\!\int d\mathbf{r}\, d\mathbf{r}'\, \rho(\mathbf{r})\, \rho(\mathbf{r}') \frac{\delta^2 F[\rho]}{\delta\rho(\mathbf{r}')\, \delta\rho(\mathbf{r})} + {}^1\!/_6 \int\!\!\int\!\!\int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''\, \rho(\mathbf{r})\, \rho(\mathbf{r}')\, \rho(\mathbf{r}'') \frac{\delta^3 F[\rho]}{\delta\rho(\mathbf{r}'')\, \delta\rho(\mathbf{r}')\, \delta\rho(\mathbf{r})} + \ldots \tag{8}$$

and

$$\frac{\delta F[\rho]}{\delta\rho(\mathbf{r})} = \int d\mathbf{r}'\, \rho(\mathbf{r}') \frac{\delta^2 F[\rho]}{\delta\rho(\mathbf{r}')\, \delta\rho(\mathbf{r})} - {}^1\!/_2 \int\!\!\int d\mathbf{r}'\, d\mathbf{r}''\, \rho(\mathbf{r}')\, \rho(\mathbf{r}'') \frac{\delta^3 F[\rho]}{\delta\rho(\mathbf{r}'')\, \delta\rho(\mathbf{r}')\, \delta\rho(\mathbf{r})} + \ldots \tag{9}$$

Thus, using eqs 8 and 9 in eq 7 and keeping terms up to second order, one finds that

$$E[\rho] = N_e\mu - {}^1\!/_2 \int\!\!\int d\mathbf{r}\, d\mathbf{r}'\, [\rho(\mathrm{r})\, \rho(\mathbf{r}') - 2\rho_c(\mathbf{r})\, \rho(\mathbf{r}')]\, \eta(\mathbf{r},\mathbf{r}') + \int d\mathbf{r}\, \rho_c(\mathbf{r})\, v(\mathbf{r}) \tag{10}$$

where $\eta(\mathbf{r},\mathbf{r}') = [\delta^2 F[\rho]/(\delta\rho(\mathbf{r}')\, \delta\rho(\mathbf{r}))]$ is the hardness kernel. By recalling that the softness kernel, $S(\mathbf{r}, \mathbf{r}')$, is the inverse of the hardness kernel, and that the integral of the softness kernel over $\mathbf{r}'$ leads to the local softness $S(\mathbf{r})$, which in turn is the product of the fukui function $f(\mathbf{r})$ and the global softness S (the inverse of the hardness), one can show that[24]

$$\eta = \int d\mathbf{r}'\, f(\mathbf{r})\, \eta(\mathbf{r},\mathbf{r}') \tag{11}$$

Thus, substituting eqs 6 and 11 in eq 10 one finds that, to second order,

$$E[\rho] = N_e\mu - {}^1\!/_2\, N_e^2 \eta + E_{\mathrm{core}}[\rho] \tag{12}$$

where

$$E_{\mathrm{core}}[\rho] = \int d\mathbf{r}\, \rho_c(\mathbf{r})\, v(\mathbf{r}) + {}^1\!/_2 \int\!\!\int d\mathbf{r}\, d\mathbf{r}' \frac{\rho_c(\mathbf{r})\, \rho_c(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + {}^1\!/_2 \int\!\!\int d\mathbf{r}\, d\mathbf{r}'\, \rho_c(\mathbf{r})\, \rho_c(\mathbf{r}') \frac{\delta^2 (T[\rho] + E_{xc}[\rho])}{\delta\rho(\mathbf{r}')\, \delta\rho(\mathbf{r})} \tag{13}$$

represents the core contribution to the total electronic energy. Equation 5 has been used in eq 13.

Now, let us consider the interaction energy between two systems A and B, $\Delta E_{\mathrm{AB}} = E_{\mathrm{AB}} - E_{\mathrm{A}} - E_{\mathrm{B}} + E_{\mathrm{AB}}^{\mathrm{NN}}$, where $E_{\mathrm{AB}}^{\mathrm{NN}}$ is the nuclear−nuclear repulsion energy. According to eq 12 one finds that

$$\Delta E_{\mathrm{AB}} = N_{e\mathrm{AB}}\mu_{\mathrm{AB}} - {}^1\!/_2\, N_{e\mathrm{AB}}^2 \eta_{\mathrm{AB}} - N_{e\mathrm{A}}\, \mu_{\mathrm{A}} + {}^1\!/_2\, N_{e\mathrm{A}}^2 \eta_{\mathrm{A}} - N_{e\mathrm{B}}\, \mu_{\mathrm{B}} + {}^1\!/_2\, N_{e\mathrm{B}}^2\, \eta_{\mathrm{B}} + E_{\mathrm{core}}[\rho_{\mathrm{AB}}] - E_{\mathrm{core}}[\rho_{\mathrm{A}}] - E_{\mathrm{core}}[\rho_{\mathrm{B}}] + E_{\mathrm{AB}}^{\mathrm{NN}} \tag{14}$$

where the quantities μ_{AB} and η_{AB} are the equilibrium chemical potential and the hardness of the system AB, while the quantities μ_{A}, η_{A}, μ_{B}, and η_{B} are the chemical potentials and hardnesses of the isolated species.

In order to simplify the term $(E_{\mathrm{core}}[\rho_{\mathrm{AB}}] - E_{\mathrm{core}}[\rho_{\mathrm{A}}] - E_{\mathrm{core}}[\rho_{\mathrm{B}}])$, first one may assume that the core densities of A and B remain unchanged at any distance during the interaction $\rho_{c_{\mathrm{AB}}}(\mathbf{r}) \approx \rho_{c_{\mathrm{A}}}(\mathbf{r}, R_{\mathrm{eq}}) + \rho_{c_{\mathrm{B}}}(\mathbf{r}, R_{\mathrm{eq}})$ (where R_{eq} means that the sum of the core densities is taken at the equilibrium distance between A and B) and that there is practically no overlap between the core densities of A and B at the equilibrium distance. Under these circumstances, one can show that if $(N_e/N) \ll 1$, then the sum of the terms in $(E_{\mathrm{core}}[\rho_{\mathrm{AB}}] - E_{\mathrm{core}}[\rho_{\mathrm{A}}] - E_{\mathrm{core}}[\rho_{\mathrm{B}}])$, associated with the first two terms in the right-hand side of eq 13 is approximately equal to $-N_{\mathrm{A}}N_{\mathrm{B}}/R_{\mathrm{eq}}$. If it is further assumed that the core terms related with the second functional derivatives of the kinetic and the exchange-correlation energies cancel each other, then one can see that if A and B have zero net charge, the term $(E_{\mathrm{core}}[\rho_{\mathrm{AB}}] - E_{\mathrm{core}}[\rho_{\mathrm{A}}] - E_{\mathrm{core}}[\rho_{\mathrm{B}}])$ is approximately equal to the negative of the average nuclear−nuclear repulsion energy.

Now, since μ_{AB} has been defined as the chemical potential of AB at equilibrium, it is composed of two contributions. The first one comes from the charge transfer, while the second one comes from the change in the external potential. If the latter is neglected, then[7,18]

$$\mu_{\mathrm{AB}} \approx (\mu_{\mathrm{A}}\, S_{\mathrm{A}} + \mu_{\mathrm{B}} S_{\mathrm{B}})/(S_{\mathrm{A}} + S_{\mathrm{B}}) \tag{15}$$

where $S_{\mathrm{A}} = 1/\eta_{\mathrm{A}}$ and $S_{\mathrm{B}} = 1/\eta_{\mathrm{B}}$.

In the case of η_{AB} one can make use of the approximate additivity of the softnesses of the constitutive parts[25,26] to evaluate the softness of the system AB. In general,

$$\eta_{\mathrm{AB}} = 1/S_{\mathrm{AB}} \approx k/(S_{\mathrm{A}} + S_{\mathrm{B}}) \tag{16}$$

where k is a proportionality constant. If $k = 2$, eq 16 becomes the arithmetic average, which has been found to give a fairly good estimate of the global softness of a system in its equilibrium state, in terms of the global softnesses of the constitutive parts[26], while $k = 1$ corresponds to the assumption of an harmonic mean approximation for the hardness.[27]

Thus, substituting eqs 15 and 16 in eq 14 and taking into account the cancellation between the nuclear−nuclear repulsion energy and the core contribution, one obtains an approximate expression for the interaction energy between two chemical systems A and B, in terms of the chemical potentials and the softnesses of the isolated species

$$\Delta E_{\mathrm{AB}} = N_{e\mathrm{AB}} \frac{\mu_{\mathrm{A}} S_{\mathrm{A}} + \mu_{\mathrm{B}} S_{\mathrm{B}}}{S_{\mathrm{A}} + S_{\mathrm{B}}} - {}^1\!/_2\, N_{e\mathrm{AB}}^2 \frac{k}{(S_{\mathrm{A}} + S_{\mathrm{B}})} - N_{e\mathrm{A}}\, \mu_{\mathrm{A}} + {}^1\!/_2\, N_{e\mathrm{A}}^2 \frac{1}{S_{\mathrm{A}}} - N_{e\mathrm{B}}\, \mu_{\mathrm{B}} + {}^1\!/_2\, N_{e\mathrm{B}}^2 \frac{1}{S_{\mathrm{B}}} \tag{17}$$

In order to find out if there is an optimum value of the softness of system B for a given softness of system A, one may take the derivative of the interaction energy with respect to S_B, keeping constant all the other variables. Using eq 17, this procedure allows one to establish that the interaction energy becomes a minimum when

$$S_B = S_A(1 + \sqrt{y})/(y - 1) \tag{18}$$

where $y = kN_{eAB}^2/N_{eB}^2 + 2(\mu_B - \mu_A)S_A N_{eAB}/N_{eB}^2$. This situation implies that for a given chemical potential difference and a given value of S_A there is a value of S_B that would lead to the greatest possible stabilization energy. Other values of S_B may also lead to a favorable interaction between A and B, but the one given by eq 18 is the most favorable one. Note that if $y = 4$, then $S_A = S_B$, the HSAB principle. However, eq 18 establishes that the optimum value of S_B is not necessarily equal to S_A, because the position of the minimum depends also on the chemical potential difference between the two interacting species.

It is interesting to note that if $y = 4$, then the proportionality constant k may be estimated from the expression

$$k = 4N_{eB}^2/N_{eAB}^2 - 2(\mu_B - \mu_A)\, S_A/N_{eAB} \tag{19}$$

Since in general chemical potential differences are rather small, one could expect that the value of the proportionality constant would be dominated by the first term in the right-hand side of eq 19. Under this approximation, $k = 1$, the harmonic approximation, implies that $N_{eB}^2/N_{eAB}^2 = 1/4$, a value that may be obtained if one assumes that $N_{eA} \approx 1$, $N_{eB} \approx 1$, and $N_{eAB} \approx N_{eA} + N_{eB} \approx 2$. On the other hand, under the same approximation, $k = 2$, the arithmetic average, implies that $N_{eB}^2/N_{eAB}^2 = 1/2$, a value that may be obtained if one assumes that $N_{eB} \approx 1$, and $N_{eB} = \sqrt{2}$. Thus one can see that eq 19, which corresponds to the case in which $y = 4$, may lead, under very reasonable assumptions, to values of the proportionality constant k that lie very close to the values of k obtained from experimental data. Therefore, one may conclude that $y \approx 4$ and that the optimum value of S_B lies very close to S_A, as stated in the HSAB principle.

It is important to note that if one assumes that $E_{AB} \approx E_A + E_B$ and one determines the energy changes in A and in B, taking into account the charge transfer between A and B, to produce a common chemical potential, and neglecting the contribution that comes from the changes in the external potential, then, using eq 12, one can show that the interaction energy will be given by

$$\Delta E_{AB} \approx -\frac{1}{2}\frac{(\mu_A - \mu_B)^2}{\eta_A + \eta_B} \tag{20}$$

where it has also been assumed that the hardnesses of A and B remain unchanged after the charge transfer process. Equation 20 was the starting point of Chattaraj, Lee, and Parr[16] to prove the HSAB principle. Thus, in their first proof, which is based on a minimization energy argument like the one described in this work, they had to introduce through qualitative arguments the contribution to the energy change due to the change in the hardness of the system as a whole with respect to the hardnesses of the separated species, because this contribution is not present in eq 20. In the present approach this is not necessary, because this contribution is already present in eq 14. However, in their second proof, the assumptions that led to eq 20 allowed them to determine the changes in the grand potential of the two species and to recognize that the assumption of equal changes in the grand potential leads to the HSAB principle. In the present approach it is not possible to establish this result without additional assumptions, because the separation of eq 14 in two terms, one for ΔE_A and one for ΔE_B, is not unique.

This analysis seems to indicate that eq 14, together with eqs 15 and 16, includes, approximately, the contributions that arise from the charge transfer process and the contributions that arise from the change in the external potential, even if the equilibrium chemical potential is approximated by the expression corresponding to the case in which one only takes into account the changes in the energy due to the charge transfer process, neglecting the changes in the energy due to the changes in the external potential.

In conclusion, the proof presented here complements the work of Chattaraj, Lee, and Parr and allows one to get a better understanding of the HSAB principle.

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