Hardness Profile: A Critical Study

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The change in hardness and chemical potential along a reaction coordinate has been studied on the basis of the finite difference formula for hardness and chemical potential. The conditions where the hardness profile can have an extremum along the reaction coordinate are identified. Numerical demonstrations of inversion of the NH_3 molecule and CH_3 radical and isomerization of HCN to HNC are given in support of the theoretical results.

1. Introduction

In recent years, density functional theory (DFT) has been emerging as an important and computationally inexpensive quantum chemical tool for studying various chemical problems. DFT-based reactivity descriptors,[1] such as chemical potential (μ) and hardness (η), have now been extensively used for rationalization and interpretation of diverse aspects of chemical binding and reaction mechanism. The chemical potential and hardness are defined as follows:[2,3]

$$\mu = \left[\frac{\partial E}{\partial N}\right]_v \tag{1}$$

$$\eta = \frac{1}{2}\left[\frac{\partial^2 E}{\partial N^2}\right]_v = \frac{1}{2}\left[\frac{\partial \mu}{\partial N}\right]_v \tag{2}$$

where E, N, and v represent, respectively, the energy, the number of electrons, and the external potential of the system. The chemical potential characterizes the escaping tendency of electrons, and the hardness can be seen as a resistance to electron transfer.[1,4] Apart from these two global reactivity parameters, there are DFT-based local parameters, such as the Fukui function $[f(r)]$[5] and local softness $[s(r)]$. These local parameters are found to be very useful for explaining chemical reactivity[6] and especially for the interpretation of regioselectivity in various addition reactions.[7−9]

The change of chemical potential and hardness along a reaction coordinate has been found to be useful to understand various aspects of the progress of a chemical reaction.[10,11] In fact, it is always interesting to observe how a molecular property changes during the course of a chemical reaction. The concept of hardness has drawn special attention due to the discovery of the principle of maximum hardness (PMH), which states that, under constant μ and v, η should be maximum when energy has the minimum value.[12] The constraints of μ and v are impossible to satisfy during the course of a chemical reaction, and thus, the PMH may not hold well during a chemical reaction. However, it has been observed in many types of reactions, such as inversion, isomerization, exchange, and addition, that the hardness value goes through a minimum at or near the transition state (TS).[13−17] These observations were seen as a corollary of the PMH, which also show that the PMH may hold well in many cases even if the constraints of μ and v are relaxed to some extent.

Owing to the discontinuity in the E vs N curve, Parr and Pearson[3] proposed the following operational definition of the chemical potential and hardness from a finite difference approach:

$$\mu = -{}^1/_2(\mathrm{IE} + \mathrm{EA}) \tag{3}$$

$$\eta = {}^1/_2(\mathrm{IE} - \mathrm{EA}) \tag{4}$$

where IE and EA are the first vertical ionization energy and electron affinity, respectively. Following Koopmans' theorem, the chemical potential and hardness values can be approximated in terms of the energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) as

$$\mu = {}^1/_2(\epsilon_{\mathrm{LUMO}} + \epsilon_{\mathrm{HOMO}}) \tag{5}$$

$$\eta = {}^1/_2(\epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}}) \tag{6}$$

The finite difference definitions of μ and η are henceforth referred to as operational chemical potential and operational hardness, respectively. The operational chemical potential and hardness have been used in almost all the studies of hardness and chemical potential profiles for chemical reactions. Although it has been reported from numerical observations that the hardness goes through a minimum at the TS[13] and that the most stable conformer of a species has the highest hardness value,[16] no critical analysis has so far been made for understanding the reason behind such an observation. It has been routinely stated that those observations are the consequences of the PMH. In the present study, we have made a critical analysis of the hardness profile along the reaction coordinate of a chemical reaction in terms of the change in energies of the N, $N - 1$ and $N + 1$ electron systems. The effect of various constraints on the hardness profile has been analyzed, and conditions when the hardness profile passes through a minimum at the TS are discussed. In this context, it should be mentioned here that the change of operational hardness and chemical potential along a reaction coordinate was discussed before in terms of chemical binding for a diatomic process.[18,19] The conditions under which

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the PMH holds well were derived in terms of the stability of the cationic and anionic species.[18] It has also been shown that when operational definitions are used, the PMH can be identified as the principle of maximum ionization energy or minimum electron affinity under constant chemical potential.[18] Most importantly, it was pointed out that the rigorous and operational definition of hardness may not always lead to the same conclusion.[19] In the present paper, we discuss the conditions of obtaining an extremum in the hardness or chemical potential profiles in terms of variations of individual energy components for the neutral, cationic, and anionic species along the reaction coordinate. Special emphasis has been given to the variations of individual energy components at the TS, and the conditions for an extremum in the hardness profile at the TS have been identified.

2. Hardness Profile

From the finite difference formula of eq 4, the operational hardness can be written as

$$\eta = {}^{1}/_{2}(E_{N-1} + E_{N+1} - 2E_N) \tag{7}$$

where E_{N-1}, E_{N+1}, and E_N are, respectively, the total energies of the $N - 1$, $N + 1$, and N electron systems at the equilibrium geometry of the N electron system. For a chemical process, the change in hardness along the reaction coordinate, q, can be expressed as

$$\frac{\partial\eta}{\partial q} = \frac{1}{2}\left[\frac{\partial E_{N-1}}{\partial q} + \frac{\partial E_{N+1}}{\partial q} - 2\frac{\partial E_N}{\partial q}\right] \tag{8}$$

Now at the TS, since E_N attains its maximum value, ($\partial E_N/\partial q)|_{\mathrm{TS}} = 0$

$$\frac{\partial\eta}{\partial q}|_{\mathrm{TS}} = \frac{1}{2}\left[\frac{\partial E_{N-1}}{\partial q}\bigg|_{\mathrm{TS}} + \frac{\partial E_{N+1}}{\partial q}\bigg|_{\mathrm{TS}}\right] \tag{9}$$

Hence, $(\partial\eta/\partial q)|_{\mathrm{TS}}$ will be equal to zero only when

$$\frac{\partial E_{N-1}}{\partial q}|_{\mathrm{TS}} = -\frac{\partial E_{N+1}}{\partial q}|_{\mathrm{TS}} \tag{10}$$

Thus, the operational hardness profile goes through an extremum at the TS when (i) the slope of the energy versus reaction coordinate curve for the $N - 1$ electron system is equal and opposite to that for the $N + 1$ electron system at the TS and (ii) both the energy derivatives in eq 10 are equal to zero. The second condition can be satisfied when energy profiles for the $N - 1$ and $N + 1$ electron systems have extrema at the TS. For a symmetrical reaction profile, the second condition is always satisfied at the symmetric point, and thus, it can logically be concluded that the operational hardness profile along the reaction coordinate has an extremum at the symmetric point. For example, the D_{3h} TS for the inversion of NH_3 must correspond to an extremum of hardness. The effect of symmetry on the hardness profile was pointed out before by others.[20,21] Pal et al.[20] studied the variation of the hardness and chemical potential in asymmetric variations of the nuclear potential about the unstable equilibrium position of a linear water. Makov[21] observed that the hardness is an extremum with respect to symmetry-breaking variations about a symmetric configuration of the nuclei. In general, the hardness profile will not show any extremum at the TS, since neither of the two conditions mentioned above is likely to be satisfied in the majority of the cases.

Numerical evidence[13,16,22] suggests that the extremum in the hardness profile at the TS region should be a minimum. That the hardness would be a minimum at the TS can be expected also from other grounds. Long ago Bader pointed out that an activated complex, which frequently corresponds to the TS, should have low-lying excited states, or a very small HOMO–LUMO gap.[23] For a minimum at the TS of a hardness profile for a reaction, in addition to the condition mentioned above, the following condition must also be satisfied:

$$\frac{\partial^2 E_{N-1}}{\partial q^2}|_{\mathrm{TS}} + \frac{\partial^2 E_{N+1}}{\partial q^2}|_{\mathrm{TS}} - 2\frac{\partial^2 E_N}{\partial q^2}|_{\mathrm{TS}} > 0 \tag{11}$$

Now at the TS, since $(\partial^2 E_N/\partial q^2)|_{\mathrm{TS}} < 0$, the third term in the above expression is always positive. The curvatures of the energy profiles for the $N - 1$ and $N + 1$ electron systems thus primarily determine whether an extremum in the hardness profile will be a maximum or minimum. Very recently, Jaque and Toro-Labbe studied the reaction profile for the double-proton-transfer processes in bimolecular complexes of formic acid and dithioformic acid.[22] They observed that a maximum in the energy profile (TS) corresponds to a minimum value of hardness and concluded the PMH holds even though the chemical and external potentials are not constant along the reaction profile. We emphasize that the minimum at the TS in the hardness profile for the double-proton-transfer reactions arises merely due to the symmetric nature of the energy profiles for the N, $N - 1$, and $N + 1$ electron systems, when each of these three energy profiles has an extremum at the TS. Thus, the right-hand side of eq 8 becomes equal to zero at the TS and the hardness profile has an extremum at the same point. The observation,[22] therefore, should not be interpreted as a consequence of the PMH.

Now let us consider the change in μ along the reaction coordinate. From eq 3 one can write

$$\mu = {}^{1}/_{2}[E_{N+1} - E_{N-1}] \tag{12}$$

The change in μ along the reaction coordinate can thus be expressed as

$$\frac{\partial\mu}{\partial q} = \frac{1}{2}\left(\frac{\partial E_{N+1}}{\partial q} - \frac{\partial E_{N-1}}{\partial q}\right) \tag{13}$$

If μ remains constant along the reaction profile, then $\partial\mu/\partial q = 0$, and

$$\frac{\partial E_{N-1}}{\partial q} = \frac{\partial E_{N+1}}{\partial q} \tag{14}$$

When μ is not constant along the reaction coordinate, an extremum for μ should appear at a point in the chemical potential profile when eq 14 is satisfied. Equations 10 and 14 can be satisfied simultaneously only when both the energy derivatives are equal to zero. Noteworthy is that for a symmetrical reaction profile eqs 10 and 14 can simultaneously be satisfied at the TS and both the hardness and chemical potential have an extremum at the TS. In general, the condition of constant μ (eq 14) leads eq 8 to

$$\frac{\partial\eta}{\partial q} = \left[\frac{\partial E_{N-1}}{\partial q} - \frac{\partial E_N}{\partial q}\right] = \frac{\partial(IE)}{\partial q} \qquad (15)$$

Thus, under a condition of constant μ, the variation in hardness is the same as the variation of IE. Otherwise, the variation in hardness can be considered the opposite of the variation of EA. Similar conclusions were reached before by Pal and co-workers.[18] Assuming the Fukui function $f(r)$ as $f(r) = \rho(r)/N$ and a constant value of μ, Gazquez et al.[14] derived the following expression:

$$\Delta E_\mu \approx -(1/2)N^2\Delta\eta \qquad (16)$$

Thus, when a system evolves toward a state of greater hardness, under a condition of constant μ, its stability increases.[14] However, our above-mentioned analysis shows that the PMH may not hold in many cases even when μ remains constant, unless other conditions as mentioned above are also satisfied.

The hardness profile may have an extremum at any point along the reaction coordinate if the right-hand side of eq 8 becomes equal to zero due to cancellation of the numerical values of the energy derivatives. An extremum in the chemical potential profile can also appear at a point along the reaction coordinate where the slopes of the energy profiles of the cationic and anionic systems are equal (eq 14). There is no reason to believe that extrema in the energy profiles of the cationic and anionic systems have to always be at the TS, and thus the chemical potential profile may not exhibit any extremum at the TS. Like the hardness profile, the chemical potential profile will also go through an extremum at the TS in the case of a symmetric reaction profile.

Similarly, one can go through the whole analysis of the hardness and chemical potential profiles based on the operational definitions using HOMO and LUMO energies (eqs 5 and 6). The hardness and chemical potential will show an extremum at the TS only when the HOMO and LUMO energies have extrema at the TS, i.e.

$$\frac{\partial\epsilon_{\mathrm{HOMO}}}{\partial q}\Big|_{\mathrm{TS}} = \frac{\partial\epsilon_{\mathrm{LUMO}}}{\partial q}\Big|_{\mathrm{TS}} = 0 \qquad (17)$$

Since this condition is unlikely to be satisfied in the majority of the cases, the hardness profile cannot have any extremum at the TS even under a condition of constant μ.

3. Numerical Demonstrations

Three representative examples are taken for providing numerical demonstrations of the theoretical results obtained in the previous section. The first example is the inversion of ammonia. Incidentally, this example was also used when the hardness profile was first demonstrated in support of the PMH.[13] The inversion of ammonia like motion for methyl radical (CH_3) is taken as the second example, and isomerization of HCN to HNC is considered as the third example. In all the cases, the hardness and chemical potential values were calculated by using eqs 3 and 4. IEs and EAs were calculated by the ΔSCF procedure, i.e., by performing separate SCF calculations for N, $N - 1$, and $N + 1$ electron systems. The energy of each system was calculated at the B3LYP level with the 6-311++G(2d,p) basis set. In the case of NH_3 (CH_3), the angle between the C_3 axis and the N−H (C−H) bond was taken as the reaction coordinate. The geometrical parameters of NH_3 (CH_3) were optimized at the B3LYP/6-311++G(2d,p) level for each value of the reaction coordinate. The energies of the $N - 1$, and $N + 1$ electron systems were then determined at the same level keeping the geometries fixed as in the corresponding N electron system. The same procedure was followed for the isomerization of HCN to HNC. In this case, the NCH angle was taken as the reaction coordinate.

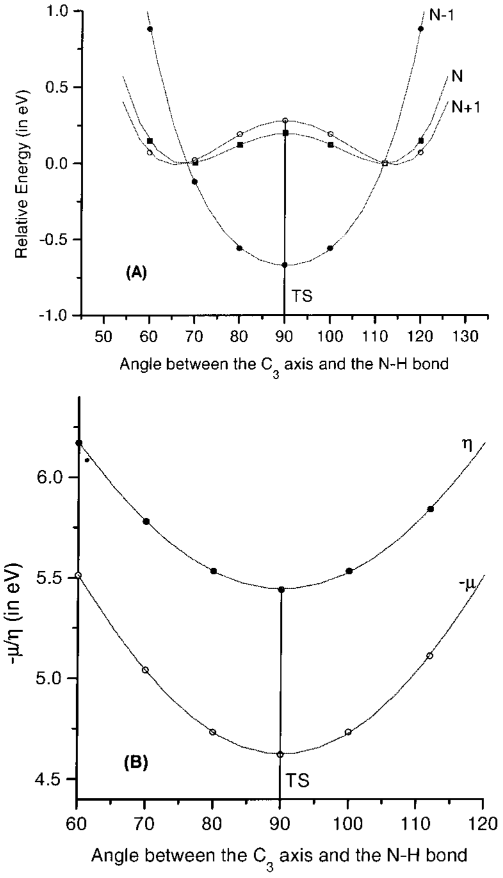

Figure 1. (A) Change in energies at the B3LYP/6-311++G(2d,p) level for the neutral (N), cationic ($N - 1$), and anionic ($N + 1$) systems along the reaction coordinate (the angle between the C_3 axis and the N−H bond in degrees) for inversion of NH_3. (B) Change in the hardness and negative of the chemical potential along the reaction coordinate for inversion of NH_3.

Figure 1A shows the variation of the energies of NH_3 and the corresponding cationic and anionic systems with the change in reaction coordinate for inversion. The energy of the neutral system shows a maximum when the geometry of NH_3 becomes planar (at the value of 90° for the reaction coordinate), which corresponds to the TS for inversion of NH_3. The energy profiles for the cationic and anionic species also have, respectively, a minimum and a maximum at the TS. Thus, eqs 10 and 14 can be satisfied at the TS, and both the operational hardness and chemical potential profiles should have extrema at the TS. The magnitudes of the curvatures of the energy profiles for the N, $N - 1$, and $N + 1$ electron systems determine (see eq 11) whether the extrema in the hardness and chemical potential profiles will be a maximum or minimum. In the case of inversion of NH_3, Figure 1A shows that $(\partial^2E_{N-1}/\partial q^2)|_{\mathrm{TS}} > 0$ and $(\partial^2E_{N+1}/\partial q^2)|_{\mathrm{TS}} < 0$. Since $(\partial^2E_N/\partial q^2)|_{\mathrm{TS}}$ is always negative and the magnitudes of $(\partial^2E_{N+1}/\partial q^2)|_{\mathrm{TS}}$ and $(\partial^2E_N/\partial q^2)|_{\mathrm{TS}}$ are quite close for the inversion of NH_3, the hardness profile should go through a minimum at the TS, whereas the chemical potential profile should have a maximum at the TS. Figure 1B presents the variation of the hardness and chemical potential values of NH_3 along the reaction coordinate. As expected, the hardness goes through a minimum and the chemical potential passes through a maximum at the TS. From the variations of energies of N, N

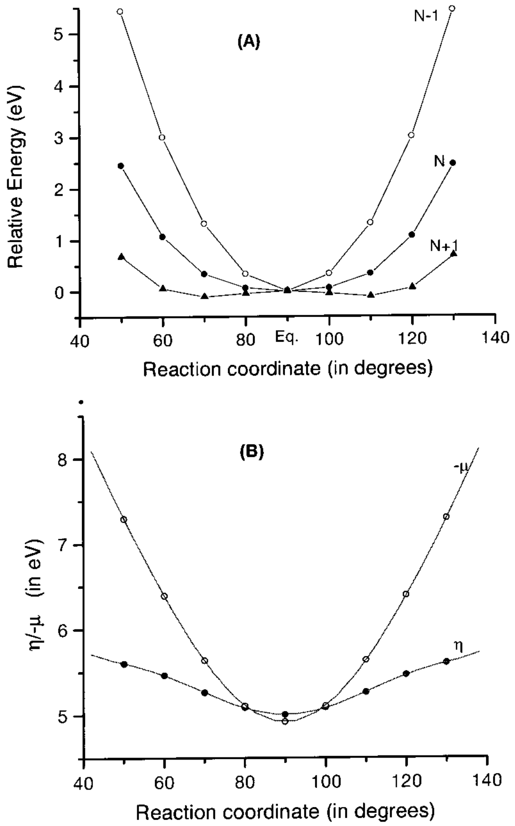

Figure 2. (A) Change in energies at the B3LYP/6-311++G(2d,p) level for the neutral (N), cationic ($N - 1$), and anionic ($N + 1$) systems along the reaction coordinate (the angle between the C_3 axis and the C−H bond in degrees) for inversion of NH_3 like motion of the CH_3 radical. (B) Change in the hardness and negative of the chemical potential along the reaction coordinate for CH_3.

$- 1$, and $N + 1$ electron systems (Figure 1A), it can be expected that there will not be any other extrema along the hardness profile except that at the TS. The same observation can be made from the variation of η in Figure 1B. It should be emphasized here that the symmetry of the reaction profile is responsible for the existence of extrema at the TS for the three energy profiles (E_N, E_{N-1}, and E_{N+1}), and as a consequence both the hardness and chemical potential profile also have extrema at the TS. It is also clear that the PMH can hold well even when neither μ nor v remains constant if the energy profiles for the $N - 1$ and $N + 1$ electron systems satisfy certain conditions. The HOMO and LUMO energies of NH_3 are also found to attain their maximum values at the TS for inversion.[24] Thus, it can be said from eq 17 that the operational hardness calculated from the HOMO and LUMO energies (eq 6) will go through an extremum at the TS.

In the case of the CH_3 radical, the variation of η and μ along the reaction coordinate corresponding to inversion of an ammonia molecule is found to be quite interesting. At equilibrium, the CH_3 radical has a planar configuration. Figure 2A displays the variation of energies for the CH_3 radical and its cationic and anionic forms along the reaction coordinate (the angle between the C_3 axis and the C−H bond). Due to the symmetric nature of the reaction coordinate, all three energy profiles go through an extremum at the equilibrium configuration of the CH_3 radical (90°). Consequently, the hardness and chemical potential profiles also have extrema (see Figure 2B) at the equilibrium configuration of the CH_3 radical. Now the interesting point is that the hardness attains its minimum value when the energy of the CH_3 radical reaches its minimum value.

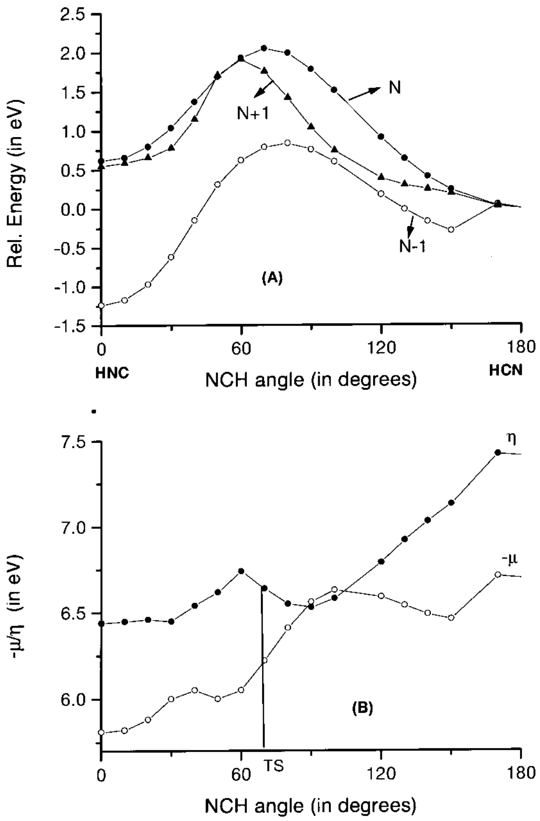

Figure 3. (A) Change in energies at the B3LYP/6-311++G(2d,p) level for the neutral (N), cationic ($N - 1$), and anionic ($N + 1$) systems along the reaction coordinate (the N−C−H angle in degrees) for isomerization of HCN to HNC. (B) Change in the hardness and negative of the chemical potential along the reaction coordinate for isomerization of HCN to HNC.

This is primarily due to the fact that in this case $(\partial^2 E_{N-1}/\partial q^2)|_{eq} > 0$, which overwhelms the slightly negative values arising from $- (\partial^2 E_N/\partial q^2)|_{eq}$ and $(\partial^2 E_{N+1}/\partial q^2)|_{eq}$, and the left-hand side of eq 11 becomes a positive quantity.

The situation is found to be more complex in the case of isomerization of HCN to HNC. Figure 3A displays the variation of the total energies of the neutral (N), cationic ($N - 1$), and anionic ($N + 1$) systems along the reaction coordinate (NCH angle) for the isomerization of HCN to HNC. It is clear from Figure 3A that the extrema in the energy profiles for the $N - 1$ and $N + 1$ electron systems do not appear at the TS (70°). For the $N - 1$ electron system the energy maximum occurs at 80°, and in the case of the $N + 1$ electron system the maximum appears at 60°. Consequently, eq 10 can be satisfied at the TS if the slopes of the energy profiles for the $N - 1$ and $N + 1$ electron systems are equal to and opposite each other at the TS. However, Figure 3A demonstrates that these two slopes are not equal to each other at the TS, and thus the hardness profile should have no minimum at the TS. This is precisely the case, as evidenced from the hardness profile shown in Figure 2B. Since eq 14 also cannot be satisfied at the TS, there will not be any extremum at the TS in the chemical potential pofile as well. The hardness profile for the isomerization of HCN to HNC has a few local extrema which appear when the numerical values of the slopes of the energy curves for N, $N - 1$, and $N + 1$ electron systems cancel each other and the right-hand side of eq 8 becomes equal to zero. For example, the maximum in the hardness profile at 60° occurs from the rapid increase in the energy of the $N + 1$ electron system, whereas the minimum at 90° arises from the rapid decrease in the energy of the $N +$

1 electron system. Meanwhile, the maximum and minimum of the chemical potential appear around 50° and 100°, respectively, which also results from the above-mentioned rapid change in the energy of the $N + 1$ electron system. Noteworthy is that the positions of extrema for the chemical potential are not the same as in the hardness profile. This is obviously due to the unsymmetrical nature of the reaction coordinate for isomerization of HCN to HNC, along which eqs 8 and 13 cannot be equal to zero at the same position.

4. Summary and Conclusions

The changes in the operational hardness and the chemical potential along the reaction coordinates were analyzed. The operational hardness profile passes through an extremum at the point where the first energy derivatives of $N - 1$ and $N + 1$ electron systems cancel that of the N electron system

$(\partial E_{N-1}/\partial q + \partial E_{N+1}/\partial q = 2(\partial E_N/\partial q))$.

Meanwhile, an extremum of the operational chemical potential is found at the point where these two derivatives are equal to each other

$(\partial E_{N-1}/\partial q = \partial E_{N+1}/\partial q)$.

For a symmetric reaction coordinate, such as the inversion of NH_3 and CH_3 discussed here and the double-proton-transfer processes in formic acid and dithioformic acid dimers studied by Jaque and Toro-Labbe,[22] the energy derivative of not only the N electron system but also the $N - 1$ and $N + 1$ electron systems are equal to zero at the symmetric point, which corresponds to either the minimum energy structure or the TS structure. Considering the above, it can be said that the operational chemical potential and hardness both pass through an extremum at the symmetric point for a symmetrical reaction coordinate.

Many precedent papers have reported that the operational hardness passes through a minimum in the transition-state region.[13,15,22] In most of the cases, variation of the chemical potential and hardness was examined for a symmetric reaction coordinate, and finally the observations of minimum hardness in the TS region were seen as a corollary of the PMH.[13,22,25] However, our analysis of the operational hardness profile for an unsymmetrical reaction coordinate, such as isomerization of HCN to HNC, showed that the point of lowest operational hardness did not necessarily correspond to the TS. For the CH_3 radical, the equilibrium D_{3h} structure was found to have the minimum hardness value along the reaction coordinate of inversion. These findings suggest that the change in hardness along the reaction coordinate cannot be considered in light of the PMH. Thus, the observations made from a symmetric reaction profile cannot be considered as tests of the PMH as suggested before.[13,25] This is a natural conclusion, since the prerequisites of the PMH, constant chemical and external potentials, cannot be satisfied all along the reaction coordinate of a chemical process.

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