

# **Chapter 2**

## **The Charge Transfer Limit of a Chemical Adduct: The Role of Perturbation on External Potential**

### 2.1. Introduction:

In this chapter, full profiles of the components (positive and negative) of density functional reactivity theory (DFRT) based stabilization energy with respect to the amount of charge transfer ( $\Delta N$ ) are investigated on some Diels–Alder pairs and charge transfer complexes formed by  $\text{BH}_3\text{--NH}_3$  and their derivatives. This chapter provides a mathematical proof for Parr and Pearson equation<sup>1</sup> by introducing the new concept i.e., ‘the charge transfer limit of a chemical adduct’. Apart from this, the effect of inclusion of perturbation on the external potential of the two adduct formation species on the values of charge transfer as well as stabilization energy has been carried out.

Stabilization energy, arising out of only the charge-transfer interaction between an electron donor (B) and an electron acceptor (A), was formulated by Parr and Pearson<sup>1</sup> using chemical potential equalization principle.<sup>2-4</sup> Based on this formulation Roy and co-workers have developed a scheme, known as CDASE (Comprehensive Decomposition Analysis of Stabilization Energy), which is useful in explaining the thermodynamic and kinetic aspects of different types of chemical interactions.<sup>5-11</sup> As per this scheme, at equilibrium (i.e., when the chemical potentials of the donor and the acceptor become equal), the positive component (i.e.,  $\Delta E_{B(A)}$ ) of the stabilization energy ( $\Delta E_{SE(AB)}$ ) can be exploited to investigate the kinetic aspect (i.e., the rate) and the negative components (i.e.,  $\Delta E_{A(B)}$ ) can be used to explain thermodynamic aspect [i.e., the stability of the chemical adduct (AB) formed] of the chemical interaction. However, full profiles of these energy components as well as the net stabilization energy with respect to charge transfer ( $\Delta N$ ) remain to be investigated. Here ‘full profile’ means the range between the two ‘zero’ stabilization energy limits.

In section 2.2, a brief theoretical background along with the criteria of choosing different charge transfer values ( $\Delta N$ ) up to the two limits are given. Section 2.3 describes the computational details which includes methodology adopted as well as the representative systems chosen (e.g., Diels-Alder type of adducts as well as simple charge transfer complexes like  $\text{BH}_3\text{--NH}_3$  and its derivatives). Analysis of the generated energy components are made in section 2.4. Section 2.5 provides analytical explanation of the obtained charge transfer limits ( $\Delta N_{limit}$ ). Changes in the profiles of charge transfer versus the energy components after inclusion of first and second order perturbation on the external potential (of interacting atoms) in the energy components is elaborated in section 2.6. Finally, in the concluding section (section 2.7) overall outcome of the study is

summarized. This section also includes a critical assessment of solvent effects, dispersion interaction, methods and basis sets on the charge transfer limits.

## 2.2. Charge Transfer Limits:

The expressions of different energy components used here are those developed by Parr and Pearson<sup>1</sup> with modified notations proposed by Roy and collaborators.<sup>5</sup> When an electron acceptor (A) and an electron donor (B) start interacting the change in their energies (with respect to charge transfer) can be expressed as,

$$\Delta E_{B(A)} = \Delta N (-\mu_B^0 + \frac{1}{2}\eta_B \Delta N) \quad (2.1)$$

$$\Delta E_{A(B)} = \Delta N (\mu_A^0 + \frac{1}{2}\eta_A \Delta N) \quad (2.2)$$

Here,  $\Delta N$  represents the charge transfer and  $\mu$  and  $\eta$  represent the corresponding chemical potential and hardness, respectively. The full form of equations (2.1) and (2.2), are given by equations (1.49) and (1.50) and the net energy change (i.e., the stabilization energy) is given by equation (1.48). The corresponding charge transfer,  $\Delta N_{eqtm}$ , is given by,

$$\Delta N_{eqtm} = \left( \frac{\mu_B^0 - \mu_A^0}{\eta_A + \eta_B} \right) \quad (2.3)$$



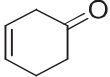
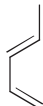

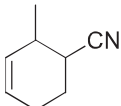
Equation (2.3) is same as equation (1.47). Here, the right subscript ‘eqtm’ is used to stress the fact that equations (1.47) - (1.50) are derived following chemical potential (of A and B) equalization principle. That is when the chemical potentials of A and B (i.e.,  $\mu_A$  and  $\mu_B$ , respectively) are equalized (an equilibrium situation) the adduct AB will be the most stable one. At the equilibrium situation, the most negative  $\Delta E_A + \Delta E_B = \Delta E$  value will be  $\Delta E_{SE(AB)}$  [equation (1.48)] and the corresponding  $\Delta N = \Delta N_{eqtm}$  [equation (2.3)]. However, on moving towards lower and higher charge transfer sides of  $\Delta N_{eqtm}$ , then  $\Delta E$  will start increasing and finally reaching to ‘zero’ values on both sides. Thus, the purpose of the present study is to generate the profiles of  $\Delta E_{B(A)}$ ,  $\Delta E_{A(B)}$  and  $\Delta E$  against  $\Delta N$  (starting from  $\Delta N_{eqtm}$ ) up to the two ‘zero’  $\Delta E$  values (one on the lower i.e., the left side and the other on the higher i.e., the right side) and verify at what  $\Delta N$  values these limits are achieved.

## 2.3. Computational Details:

The representative acceptors (A) and donors (B) chosen here are (i) Diels-Alder pairs (ii) BH<sub>3</sub>-NH<sub>3</sub> complex and some derivatives of BH<sub>3</sub>-NH<sub>3</sub> complex. The Diels-Alder pairs are acrylaldehyde

(A) – buta-1,3-diene (B) and acrylonitrile (A) – penta-1,3-diene (B). The corresponding adducts (AB) generated are the Diels-Alder products,  $\text{NH}_3\text{-BH}_3$  complex and derivatives of this complex. The donor – acceptor pairs and the adducts formed by them are depicted in Table 2.1 below.

**Table 2.1. Different Combinations of donors and acceptors and their corresponding adducts.**

Entry	Donor (B)	Acceptor (A)	Adduct (AB)
1	 buta-1,3-diene	 acrylaldehyde	 cyclohex-3-enone
2	 (E)-penta-1,3-diene	 acrylonitrile	 2-methylcyclohex-3-enecarbonitrile
3	$\text{NH}_3$ ammonia	$\text{BH}_3$ borane	$\text{NH}_3\text{-BH}_3$
4	$\text{CH}_3\text{-NH}_2$ methanamine	$\text{BH}_3$ borane	$\text{CH}_3\text{-NH}_2\text{-BH}_3$
5	$(\text{CH}_3)_2\text{NH}$ dimethylamine	$\text{BH}_2\text{F}$ fluoroborane	$(\text{CH}_3)_2\text{NH-BH}_2\text{F}$
6	$(\text{CH}_3)_3\text{N}$ trimethylamine	$\text{BH}_3$ borane	$(\text{CH}_3)_3\text{N-BH}_3$

Optimizations of the geometries followed by single point calculations are done using B3LYP functional<sup>12-14</sup> and DNP basis set, as implemented in DMOL3 program package.<sup>15,16</sup> The DNP is a double-numeric quality basis set (i.e., containing approximately two atomic orbitals for each occupied one in the free atom) augmented with polarization functions (i.e., functions having angular momentum one higher than that of the highest occupied orbital in the free atom). Earlier reports claim that DNP is much more accurate than the Gaussian 6-31G(d,p) basis sets,<sup>15-21</sup> although these two are of comparable size.

Here, it is important to note that the values of  $\Delta E$ ,  $\Delta E_{B(A)}$ ,  $\Delta E_{A(B)}$ ,  $\Delta E_{SE(AB)}$ ,  $\Delta N$  and  $\Delta N_{eqm}$  are generated as per the CDASE scheme<sup>5</sup> (and so, as per the equations developed by Parr and Pearson<sup>1</sup>), where reactivity parameters e.g.,  $\mu$  and  $\eta$  (and hence, IP and EA) are of isolated donors (B) and acceptors (A). IP and EA are obtained using equations (1.13) and (1.14), respectively. Calculation of  $\mu$  and  $\eta$  is done through equations (1.15) and (1.20a) [i.e., through  $\Delta$ SCF method]. Thus, geometry optimization of the adduct (AB) is not necessary.

#### 2.4. Results and Discussion:

As discussed in section 2.2, it is obvious that the equations developed by CDASE scheme [i.e., equations (1.47) - (1.50)] represent only the values at equilibrium i.e., at a single point. However, equations (2.1) and (2.2) are used to generate the values of  $\Delta E_{B(A)}$ ,  $\Delta E_{A(B)}$  (and hence  $\Delta E$ ) at points other than the equilibrium one. When these values are plotted against  $\Delta N$  [starting from  $(\Delta N_{eqm}, \Delta E_{SE(AB)})$  and moving towards lower and higher sides] something interesting is observed. For all the chosen pairs (Table 2.1) the limiting  $\Delta N$  values are obtained as 0 (zero) and  $2\Delta N_{eqm}$  (Tables 2.2 - 2.7 and Figures 2.1 - 2.6).

**Table 2.2. Changes in  $\Delta E_{B(A)}$ ,  $\Delta E_{A(B)}$  and  $\Delta E$  values (in kJ mol<sup>-1</sup>) with respect to charge transfer ( $\Delta N$ ) for Diels-Alder pair acrylaldehyde ( $\text{CH}_2=\text{CH}-\text{CHO}$ , A) and buta-1,3-diene ( $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ , B).**

Entry	$\Delta N$	$\Delta E_{B(A)}$	$\Delta E_{A(B)}$	$\Delta E$
1	0.00000	0.000	0.000	0.000
2	0.00845	3.077	-3.827	-0.750
3	0.02845	10.507	-12.734	-2.227
4	0.04845	18.140	-21.422	-3.282
5	0.06845	25.977	-29.891	-3.914
6*	0.08845	34.017	-38.142	-4.125
7	0.10845	42.261	-46.175	-3.914
8	0.12845	50.708	-53.989	-3.281
9	0.14845	59.359	-61.585	-2.226
10	0.16845	68.213	-68.964	-0.751
11	0.17689	72.013	-72.013	0.000

\* The  $\Delta N_{eqtm}$  value is 0.08845 (when  $\Delta E = \Delta E_{SE(AB)}$  i.e., the most negative one).

**Table 2.3. Changes in  $\Delta E_{B(A)}$ ,  $\Delta E_{A(B)}$  and  $\Delta E$  values (in kJ mol<sup>-1</sup>) with respect to charge transfer ( $\Delta N$ ) for Diels-Alder pair acrylonitrile (CH<sub>2</sub>=CH-CN, A) and penta-1,3-diene (CH<sub>2</sub>=CH-CH=CH-CH<sub>3</sub>, B).**

Entry	$\Delta N$	$\Delta E_{B(A)}$	$\Delta E_{A(B)}$	$\Delta E$
1	0.00000	0.000000	0.000000	0.000000
2	0.01929	006.478	-009.153	-002.675
3	0.03929	013.387	-018.414	-005.027
4	0.05929	020.492	-027.444	-006.952
5	0.07929	027.794	-036.243	-008.449
6	0.09929	035.293	-044.811	-009.518
7	0.11929	042.988	-053.148	-010.160
8*	0.13929	050.75	-061.12	-010.370
9	0.15929	058.969	-069.129	-010.160
10	0.17929	067.254	-076.772	-009.518
11	0.19929	075.737	-084.185	-008.448
12	0.21929	084.416	-091.367	-006.951
13	0.23929	093.291	-098.318	-005.027
14	0.25929	102.364	-105.038	-002.674
15	0.27859	111.302	-111.302	-000.000

\* The  $\Delta N_{eqtm}$  value is 0.13929 (when  $\Delta E = \Delta E_{SE(AB)}$  i.e., the most negative one).

**Table 2.4. Changes in  $\Delta E_{B(A)}$ ,  $\Delta E_{A(B)}$  and  $\Delta E$  values (in kJ mol<sup>-1</sup>) with respect to charge transfer ( $\Delta N$ ) for borane (BH<sub>3</sub>, A) and ammonia (NH<sub>3</sub>, B).**

Entry	$\Delta N$	$\Delta E_{B(A)}$	$\Delta E_{A(B)}$	$\Delta E$
1	0.00000	0.00000	0.00000	0.00000
2	0.00952	2.60656	-2.88669	-0.28012
3	0.01952	5.41984	-5.8783	-0.45846
4*	0.02952	8.30929	-8.8272	-0.5179
5	0.03952	11.2749	-11.7334	-0.45845
6	0.04952	14.31668	-14.5968	-0.28012

7	0.05904	17.28225	-17.28225	0.00000
---	---------	----------	-----------	---------

\* The  $\Delta N_{eqtm}$  value is 0.02952 (when  $\Delta E = \Delta E_{SE(AB)}$  i.e., the most negative one).

**Table 2.5. Changes in  $\Delta E_{B(A)}$ ,  $\Delta E_{A(B)}$  and  $\Delta E$  values (in kJ mol<sup>-1</sup>) with respect to charge transfer ( $\Delta N$ ) for borane (BH<sub>3</sub>, A) and methanamine (CH<sub>3</sub>-NH<sub>2</sub>, B).**

Entry	$\Delta N$	$\Delta E_{B(A)}$	$\Delta E_{A(B)}$	$\Delta E$
1	0.00000	0.00000	0.00000	0.00000
2	0.00765	1.78365	-2.32241	-0.53876
3	0.02765	6.63615	-8.2789	-1.64275
4	0.04765	11.75934	-14.06449	-2.30515
5*	0.06765	17.15323	-19.67918	-2.52595
6	0.08765	22.81782	-25.12297	-2.30515
7	0.10765	28.7531	-30.39586	-1.64275
8	0.12765	34.95908	-35.49784	-0.53876
9	0.13529	37.40139	-37.40139	0.00000

\* The  $\Delta N_{eqtm}$  value is 0.06765 (when  $\Delta E = \Delta E_{SE(AB)}$  i.e., the most negative one).

**Table 2.6. Changes in  $\Delta E_{B(A)}$ ,  $\Delta E_{A(B)}$  and  $\Delta E$  values (in kJ mol<sup>-1</sup>) with respect to charge transfer ( $\Delta N$ ) for fluoroborane (BH<sub>2</sub>F, A) and dimethylamine [(CH<sub>3</sub>)<sub>2</sub>-NH, B].**

Entry	$\Delta N$	$\Delta E_{B(A)}$	$\Delta E_{A(B)}$	$\Delta E$
1	0.0000	0.00000	0.00000	0.00000
2	0.0061	1.21869	-3.28974	-2.07105
3	0.0461	9.79913	-24.16965	-14.37053
4	0.0861	19.39431	-43.82804	-24.43373
5	0.1261	30.00423	-62.2649	-32.26067
6	0.1661	41.6289	-79.48025	-37.85134
7	0.2061	54.26832	-95.47406	-41.20574
8*	0.2461	67.92248	-110.24636	-42.32388
9	0.2861	82.59138	-123.79712	-41.20574
10	0.3261	98.27503	-136.12637	-37.85134
11	0.3661	114.97342	-147.23409	-32.26067

12	0.4061	132.68656	-157.12029	-24.43373
13	0.4461	151.41444	-165.78497	-14.37053
14	0.4861	171.15707	-173.22812	-2.07105
15	0.4922	174.25733	-174.25733	0.00000

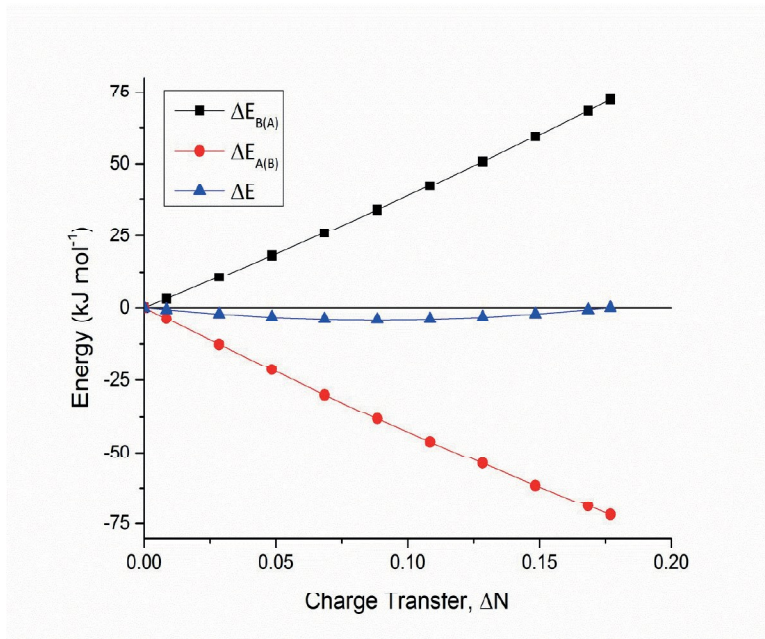
\* The  $\Delta N_{eqtm}$  value is 0.02461 (when  $\Delta E = \Delta E_{SE(AB)}$  i.e., the most negative one).

**Table 2.7. Changes in  $\Delta E_{B(A)}$ ,  $\Delta E_{A(B)}$  and  $\Delta E$  (in  $\text{kJ mol}^{-1}$ ) values with respect to charge transfer ( $\Delta N$ ) for borane ( $\text{BH}_3$ , A) and trimethylamine [ $(\text{CH}_3)_3\text{-N}$ , B].**

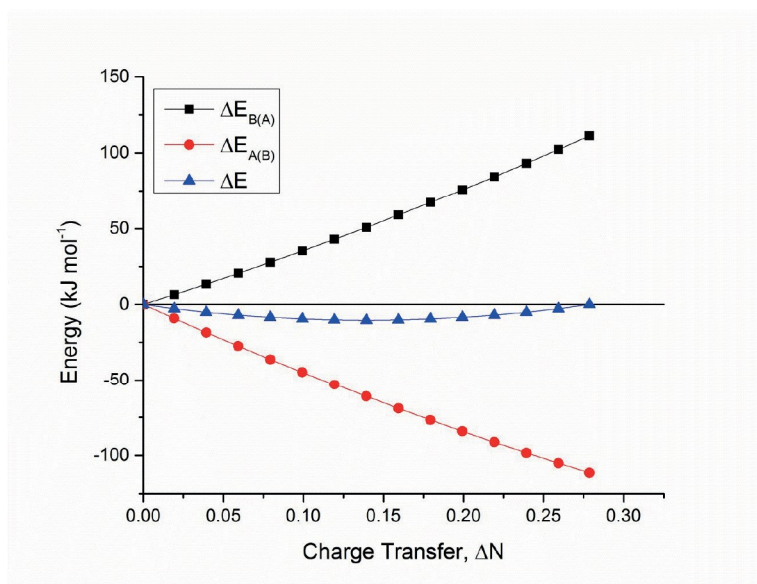
Entry	$\Delta N$	$\Delta E_{B(A)}$	$\Delta E_{A(B)}$	$\Delta E$
1	0.00000	0.0000	0.00000	0.00000
2	0.01435	2.0702	-4.33822	-2.26802
3	0.04435	6.78261	-13.12293	-6.34033
4	0.07435	12.01544	-21.52312	-9.50768
5	0.10435	17.76871	-29.53878	-11.77007
6	0.13435	24.0424	-37.16991	-13.12751
7*	0.16435	30.83653	-44.41652	-13.57999
8	0.19435	38.15109	-51.2786	-13.12751
9	0.22435	45.98608	-57.75616	-11.77007
10	0.25435	54.34151	-63.84919	-9.50768
11	0.28435	63.21736	-69.55769	-6.34033
12	0.31435	72.61365	-74.88166	-2.26802
13	0.328706	77.29466	-77.29466	0.00000

\* The  $\Delta N_{eqtm}$  value is 0.16435 (when  $\Delta E = \Delta E_{SE(AB)}$  i.e., the most negative).

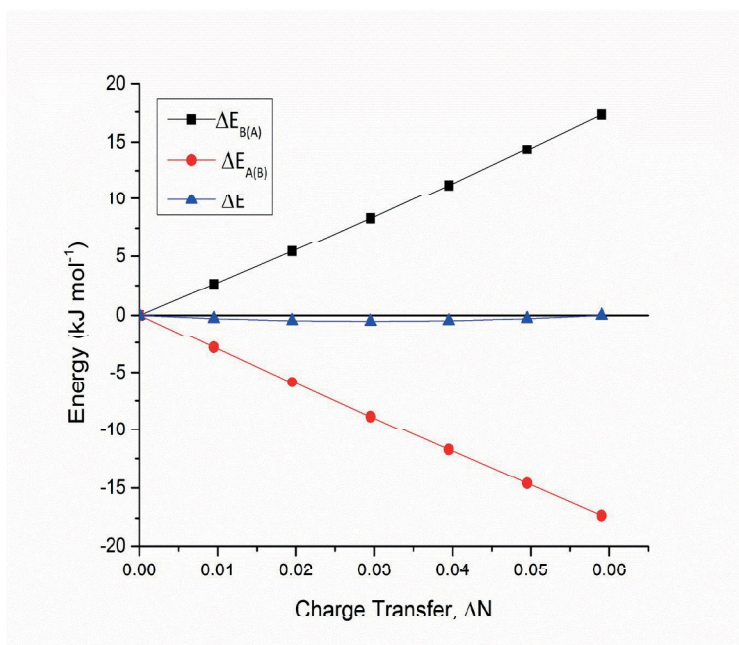




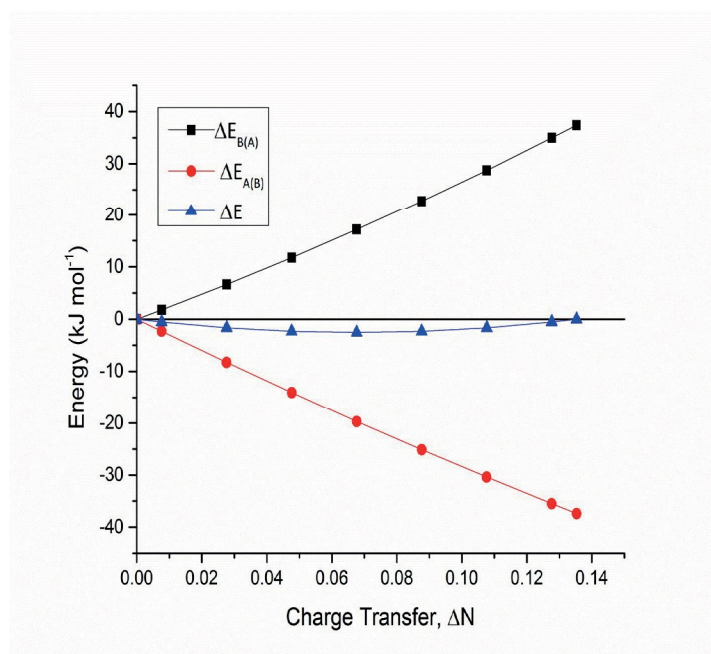
**Figure 2.1.** Plot showing the profiles of  $\Delta E_{B(A)}$ ,  $\Delta E_{A(B)}$  and  $\Delta E$  values with respect to  $\Delta N$  for adduct formation process between acrylaldehyde ( $\text{CH}_2=\text{CH}-\text{CHO}$ , A) and buta-1,3-diene ( $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ , B).



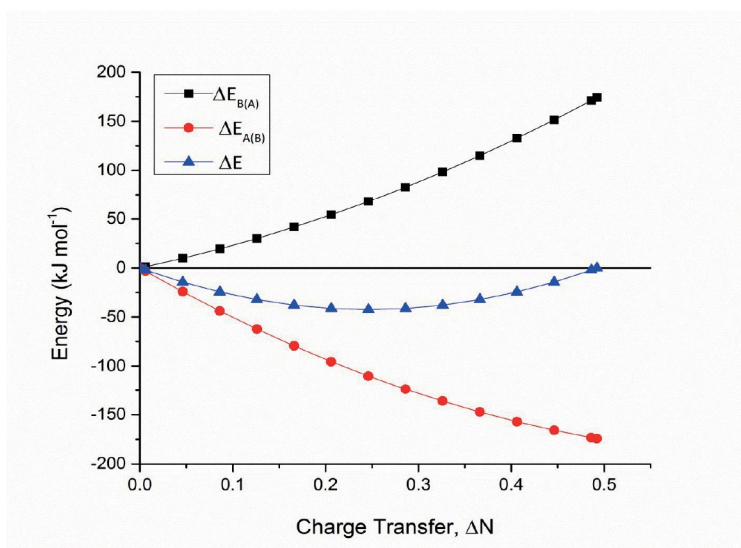
**Figure 2.2.** Plot showing the profiles of  $\Delta E_{B(A)}$ ,  $\Delta E_{A(B)}$  and  $\Delta E$  values with respect to  $\Delta N$  for adduct formation process between acrylonitrile ( $\text{CH}_2=\text{CH}-\text{CN}$ , A) and penta-1,3-diene ( $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$ , B).



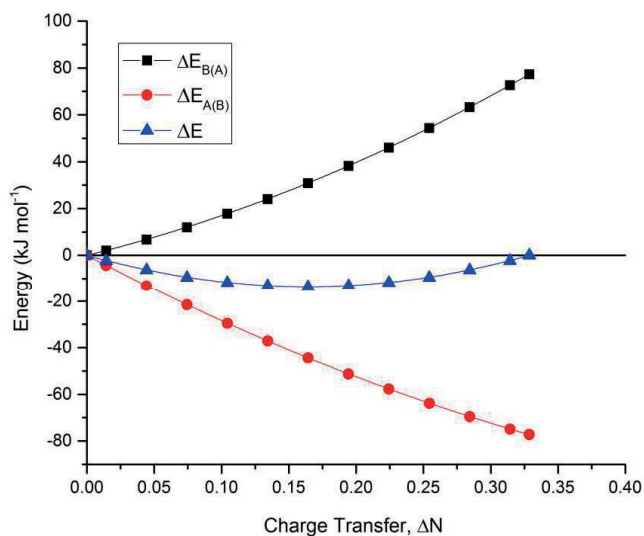
**Figure 2.3.** Plot showing the profiles of  $\Delta E_{B(A)}$ ,  $\Delta E_{A(B)}$  and  $\Delta E$  values with respect to  $\Delta N$  for adduct formation process between borane ( $\text{BH}_3$ , A) and ammonia ( $\text{NH}_3$ , B).



**Figure 2.4.** Plot showing the profiles of  $\Delta E_{B(A)}$ ,  $\Delta E_{A(B)}$  and  $\Delta E$  values with respect to  $\Delta N$  for adduct formation process between borane ( $\text{BH}_3$ , A) and methanamine ( $\text{CH}_3\text{-NH}_2$ , B).



**Figure 2.5.** Plot showing the profiles of  $\Delta E_{B(A)}$ ,  $\Delta E_{A(B)}$  and  $\Delta E$  values with respect to  $\Delta N$  for adduct formation process between fluoroborane ( $\text{BH}_2\text{F}$ , A) and dimethylamine [ $(\text{CH}_3)_2\text{-NH}$ , B].



**Figure 2.6.** Plot showing the profiles of  $\Delta E_{B(A)}$ ,  $\Delta E_{A(B)}$  and  $\Delta E$  values with respect to  $\Delta N$  for adduct formation process between borane ( $\text{BH}_3$ , A) and trimethylamine [ $(\text{CH}_3)_3\text{-N}$ , B].

Here, zero  $\Delta E$  value at  $\Delta N = 0$  represents the situation that the adduct formation has not started yet (as this is an energy lowering process). However, physically zero  $\Delta E$  value at  $2\Delta N_{eqtm}$  apparently points to the situation that when the donor (B) is forced to donate more electrons than  $\Delta N_{eqtm}$  the adduct (AB) starts destabilizing again and at  $2\Delta N_{eqtm}$  stabilization energy become

zero. However, in reality this does not happen as the adduct has to pass through the stabilization energy minimum.

It should be noted that generating  $\Delta E$  values at different  $\Delta N$  (and hence plotting  $\Delta E$  vs.  $\Delta N$ ) seems experimentally a formidable task. This is because when an electron donor and an electron acceptor start interacting, electron transfer cannot be controlled step by step (by fractional amount, in particular). However, that neither deters one to plot theoretically generated  $\Delta E$  values against  $\Delta N$  nor questions the validity or correctness of the plot as all these parameters are evaluated from the basic electronic properties (like  $\mu$  and  $\eta$  and hence indirectly IP and EA) of the interacting chemical systems.

Although, zero value of  $\Delta E$  at  $\Delta N = 0$  is understandable (as the expression of stabilization energy is derived here only on the basis of charge transfer i.e.,  $\Delta N$ ), the other solution i.e.,  $\Delta N_{limit} = 2 \Delta N_{eqtm}$  is quite intriguing. Nevertheless, this observation can be explained from the analysis in the following section.

### 2.5. Theoretical Derivation of Charge Transfer Limits:

The energy of the acceptor (A) during the charge transfer process can be written (after truncating third and higher order terms)<sup>1</sup> as,

$$E_A = E_{A^0} + \frac{1}{1!} \left( \frac{\partial E_{A^0}}{\partial N} \right)_v (N_A - N_{A^0}) + \frac{1}{2!} \left( \frac{\partial^2 E_{A^0}}{\partial N^2} \right)_v (N_A - N_{A^0})^2 \quad (2.4)$$

Similarly, for the donor (B),

$$E_B = E_{B^0} + \frac{1}{1!} \left( \frac{\partial E_{B^0}}{\partial N} \right)_v (N_B - N_{B^0}) + \frac{1}{2!} \left( \frac{\partial^2 E_{B^0}}{\partial N^2} \right)_v (N_B - N_{B^0})^2 \quad (2.5)$$

Substituting  $\Delta N = N_A - N_{A^0} = N_{B^0} - N_B$  (as A accepts electrons and B donates electrons,  $\Delta N$  is a positive quantity), equations (2.4) and (2.5) can be written as,

$$E_A = E_{A^0} + \mu_{A^0} \Delta N + \frac{1}{2} \eta_A \Delta N^2 \quad (2.6)$$

$$E_B = E_{B^0} - \mu_{B^0} \Delta N + \frac{1}{2} \eta_B \Delta N^2 \quad (2.7)$$

It should be noted here, that in the original paper by Parr and Pearson,<sup>1</sup> hardness ( $\eta$ ) was expressed as  $\frac{1}{2!} \left( \frac{\partial^2 E}{\partial N^2} \right)_v$ , however later on it is a common practice to express  $\eta$  as  $\left( \frac{\partial^2 E}{\partial N^2} \right)_v$ .

Equations (2.6) and (2.7) can be rearranged to,

$$\Delta E_A = E_A - E_{A^0} = \mu_{A^0} \Delta N + \frac{1}{2} \eta_A \Delta N^2 \quad (2.8)$$

$$\Delta E_B = E_B - E_{B^0} = -\mu_{B^0}\Delta N + \frac{1}{2}\eta_B\Delta N^2 \quad (2.9)$$

Hence, the total energy change  $\Delta E$  during the charge transfer process is,

$$\Delta E = \Delta E_A + \Delta E_B = -(\mu_{B^0} - \mu_{A^0})\Delta N + \frac{1}{2}(\eta_A + \eta_B)\Delta N^2 \quad (2.10)$$

From equation (2.10) it is obvious that  $\Delta E = 0$  (i.e., no net change in energy due to charge transfer) lead to two different solutions of  $\Delta N$ , the lower one (named as ‘Lower Limit’, L.L.) is,

$$\Delta N_{L.L.} = 0 \quad (2.11)$$

(i.e., when there is no charge transfer and is the situation when the two interacting species are yet to start electron exchange) and the second one (named as ‘Higher Limit’, H.L.) is,

$$\Delta N_{H.L.} = \frac{2(\mu_{B^0} - \mu_{A^0})}{\eta_A + \eta_B} \quad (2.12)$$

Comparing equations (2.11) and (2.12) we see why the  $\Delta E$  versus  $\Delta N$  plot touches the x-axis (i.e., the  $\Delta N$  axis) at  $\Delta N_{L.L.} = 0$  and at  $\Delta N_{H.L.} = \frac{2(\mu_{B^0} - \mu_{A^0})}{\eta_A + \eta_B} = 2 \Delta N_{eqtm}$ .

## 2.6. Inclusion of the Effect of External Potential Perturbation in the Energy Expression:

Now, the question is how much acceptable are the two solutions of  $\Delta N$  for which stabilization energy is zero (as  $\Delta E$  is zero, no net stability due to interaction)? Although, apparently the first solution (i.e.,  $\Delta N_{L.L.} = 0$ ) is acceptable, the second solution (i.e.,  $\Delta N_{H.L.} = 2 \Delta N_{eqtm}$ ) looks to be too appealing to believe. This is because this seems not to be an achievable charge transfer as the adduct has to pass through the most stable structure when,  $\Delta N = \Delta N_{eqtm}$  (as mentioned in Section 2.4).

However, as the following derivation shows, inclusion of the first and second order contributions to the energy expressions of the donors and acceptors due to perturbing external potential of the partner of the given atom in a molecule, provides more accurate expressions. This reveals some interesting observation at  $\Delta N_{L.L.}$  and also  $\Delta N_{H.L.}$  appears to be an expected one (from our knowledge of conventional potential energy curve). The energy of an atom-in-a-molecule can be expanded up to full second order as,<sup>22-24</sup>

$$E_A(N_A, Z_A) = E_{A^0} + \left( \frac{\partial E_A}{\partial N_A} \Delta N_A + \frac{\partial E_A}{\partial Z_A} \Delta Z_A \right) + \frac{1}{2} \left[ \frac{\partial^2 E_A}{\partial N_A^2} (\Delta N_A)^2 + 2 \frac{\partial^2 E_A}{\partial N_A \partial Z_A} \Delta N_A \Delta Z_A + \frac{\partial^2 E_A}{\partial Z_A^2} (\Delta Z_A)^2 \right]$$



$$\begin{aligned} \text{or, } E_A(N_A, Z_A) &= E_{A^0} + (\mu_{A^0}\Delta N_A + v_A^0\Delta Z_A) \\ &+ \frac{1}{2}[\eta_A(\Delta N_A)^2 + 2\alpha_A\Delta N_A\Delta Z_A + \beta_A(\Delta Z_A)^2] \end{aligned} \quad (2.13)$$

Similarly, for donor B,

$$\begin{aligned} E_B(N_B, Z_B) &= E_{B^0} + (\mu_{B^0}\Delta N_B + v_B^0\Delta Z_B) \\ &+ \frac{1}{2}[\eta_B(\Delta N_B)^2 + 2\alpha_B\Delta N_B\Delta Z_B + \beta_B(\Delta Z_B)^2] \end{aligned} \quad (2.14)$$

In equations (2.13) and (2.14)  $v = \left(\frac{\partial E}{\partial Z}\right)_N = \frac{v_{ne}}{Z} < 0$  represents the electron-nuclear attraction per unit nuclear charge,  $\alpha = \left(\frac{\partial \mu}{\partial Z}\right)_N = \left(\frac{\partial v}{\partial N}\right)_Z < 0$ , and  $\beta = \left(\frac{\partial v}{\partial Z}\right)_N < 0$ .<sup>24</sup> It needs to be noted that  $E_{A^0}$  and  $E_{B^0}$  are the zeroth order contribution to the corresponding energies (i.e., energies of the unperturbed systems). Also,  $\Delta N_A = N_A - N_{A^0}$  and  $\Delta N_B = N_B - N_{B^0}$ .

Rearranging and adding equations (2.13) and (2.14) we get,

$$\begin{aligned} [E_A(N_A, Z_A) - E_{A^0}] + [E_B(N_B, Z_B) - E_{B^0}] &= -(\mu_{B^0} - \mu_{A^0})\Delta N + (v_A^0\Delta Z_A + v_B^0\Delta Z_B) \\ &+ \frac{1}{2}[(\eta_A + \eta_B)\Delta N^2] + \frac{1}{2}[2(\alpha_A\Delta Z_A - \alpha_B\Delta Z_B)\Delta N + (\beta_A\Delta Z_A^2 + \beta_B\Delta Z_B^2)] \end{aligned}$$

[ $\Delta N = \Delta N_A = -\Delta N_B$ ]

$$\begin{aligned} \text{or, } \Delta E = \Delta E_A + \Delta E_B &= \frac{1}{2}(\eta_A + \eta_B)\Delta N^2 + (\mu_{A^0} - \mu_{B^0} + \alpha_A\Delta Z_A - \alpha_B\Delta Z_B)\Delta N \\ &+ \left(v_A^0\Delta Z_A + v_B^0\Delta Z_B + \frac{1}{2}\beta_A\Delta Z_A^2 + \frac{1}{2}\beta_B\Delta Z_B^2\right) \end{aligned}$$

$$\begin{aligned} \text{or, } \Delta E &= \frac{1}{2}(\eta_A + \eta_B)\Delta N^2 - [(\mu_{B^0} - \mu_{A^0}) - (\alpha_A\Delta Z_A - \alpha_B\Delta Z_B)]\Delta N \\ &+ \left(v_A^0\Delta Z_A + v_B^0\Delta Z_B + \frac{1}{2}\beta_A\Delta Z_A^2 + \frac{1}{2}\beta_B\Delta Z_B^2\right) \end{aligned} \quad (2.15)$$

From equation (2.15) it is obvious that when perturbation corrections in the external potential are not considered, both  $\Delta Z_A$  and  $\Delta Z_B$  values are zero and hence at the two zero interaction energy limits we get two  $\Delta N$  values which are the two unperturbed solutions (i.e.,  $\Delta N_{L.L.} = 0$  and  $\Delta N_{H.L.} = 2\Delta N_{eqtm}$ ) When the stabilization energy is zero (i.e.,  $\Delta E = \Delta E_A + \Delta E_B = 0$ ) the right hand side of equation (2.15) turns out to be a quadratic equation with respect to  $\Delta N$  as a variable. The corresponding charge transfer values at this zero stabilization energy are,

$$\begin{aligned} \Delta N_{limit} &= \frac{[\mu_{B^0} - \mu_{A^0} - (\alpha_A\Delta Z_A - \alpha_B\Delta Z_B)] \pm \sqrt{[\mu_{B^0} - \mu_{A^0} - (\alpha_A\Delta Z_A - \alpha_B\Delta Z_B)]^2 - 2(\eta_A + \eta_B)\left(v_A^0\Delta Z_A + v_B^0\Delta Z_B + \frac{1}{2}\beta_A\Delta Z_A^2 + \frac{1}{2}\beta_B\Delta Z_B^2\right)}}{(\eta_A + \eta_B)} \end{aligned} \quad (2.16)$$

Again, when the chemical potentials are equalized (leading to the formation of the most stable adduct) from equations (2.13) and (2.14) we can write,

$$\mu_{A^0} + \eta_A \Delta N_A + \alpha_A \Delta Z_A = \mu_{B^0} + \eta_B \Delta N_B + \alpha_B \Delta Z_B$$

or,

$$(\eta_A + \eta_B) \Delta N_{eqtm} = (\mu_{B^0} - \mu_{A^0}) + (\alpha_B \Delta Z_B - \alpha_A \Delta Z_A)$$

$$(\Delta N_A = -\Delta N_B = \Delta N_{eqtm})$$

or,

$$\Delta N_{eqtm} = \left( \frac{\mu_{B^0} - \mu_{A^0}}{\eta_A + \eta_B} \right) - \left( \frac{\alpha_A \Delta Z_A - \alpha_B \Delta Z_B}{\eta_A + \eta_B} \right) = \frac{\mu_{B^0} - \mu_{A^0} - (\alpha_A \Delta Z_A - \alpha_B \Delta Z_B)}{\eta_A + \eta_B} \quad (2.17)$$

From equations (2.16) and (2.17) we can write,

$$\Delta N_{limit} = \Delta N_{eqtm} \pm \frac{\sqrt{[\mu_{B^0} - \mu_{A^0} - (\alpha_A \Delta Z_A - \alpha_B \Delta Z_B)]^2 - 2(\eta_A + \eta_B)(v_A^0 \Delta Z_A + v_B^0 \Delta Z_B + \beta_A \Delta Z_A^2 + \beta_B \Delta Z_B^2)}}{(\eta_A + \eta_B)} \quad (2.18)$$

Now, substituting  $\Delta N_{eqtm}$  from equation (2.17) in equation (2.15) we get,

$$\begin{aligned} \Delta E_{eqtm} = & \frac{1}{2}(\eta_A + \eta_B) \frac{((\mu_{B^0} - \mu_{A^0}) - (\alpha_A \Delta Z_A - \alpha_B \Delta Z_B))^2}{(\eta_A + \eta_B)^2} \\ & - [(\mu_{B^0} - \mu_{A^0}) - (\alpha_A \Delta Z_A - \alpha_B \Delta Z_B)] \frac{((\mu_{B^0} - \mu_{A^0}) - (\alpha_A \Delta Z_A - \alpha_B \Delta Z_B))}{(\eta_A + \eta_B)} \\ & + \left( v_A^0 \Delta Z_A + v_B^0 \Delta Z_B + \frac{1}{2} \beta_A \Delta Z_A^2 + \frac{1}{2} \beta_B \Delta Z_B^2 \right) \end{aligned}$$

or,

$$\Delta E_{eqtm} = - \frac{((\mu_{B^0} - \mu_{A^0}) - (\alpha_A \Delta Z_A - \alpha_B \Delta Z_B))^2}{2(\eta_A + \eta_B)} + \left( v_A^0 \Delta Z_A + v_B^0 \Delta Z_B + \frac{1}{2} \beta_A \Delta Z_A^2 + \frac{1}{2} \beta_B \Delta Z_B^2 \right) \quad (2.19)$$

A systematic analysis of equations (2.15) – (2.19) will help to understand the full profile of  $\Delta E$  as well as the locations of  $\Delta N_{L,L}$ ,  $\Delta N_{H,L}$ ,  $\Delta N_{eqtm}$  and  $\Delta E_{eqtm}$ . From equation (2.15) it is obvious that when charge transfer ( $\Delta N$ ) is zero (just before the charge transfer starts) contribution from the first two terms will be zero. As, both of  $v^0$  and  $\beta$  are  $< 0$  and  $\Delta Z > 0$  (because in the adduct AB, outer electrons of an atom core face the influence of both the atomic cores)<sup>23,24</sup> the third term will be negative. This means that stabilization has started before the onset of charge transfer. The phenomena which are causing this stabilization are intermolecular interactions (e.g., dipole-dipole, charge-induced dipole and dispersion, collectively known as ‘van der Waals interaction’). Although this interaction is weak (and so the numerical value of the third term is small) definitely it will be there. Also, negative  $\Delta N_{L,L}$  is not acceptable as, by definition,  $\Delta N$  should

be positive [see arguments just before equation (2.6)]. However,  $\Delta N_{H.L.}$  will not be equal to  $2\Delta N_{eqm}$ , as was the case when perturbation to the external potential was not considered (to be discussed later).

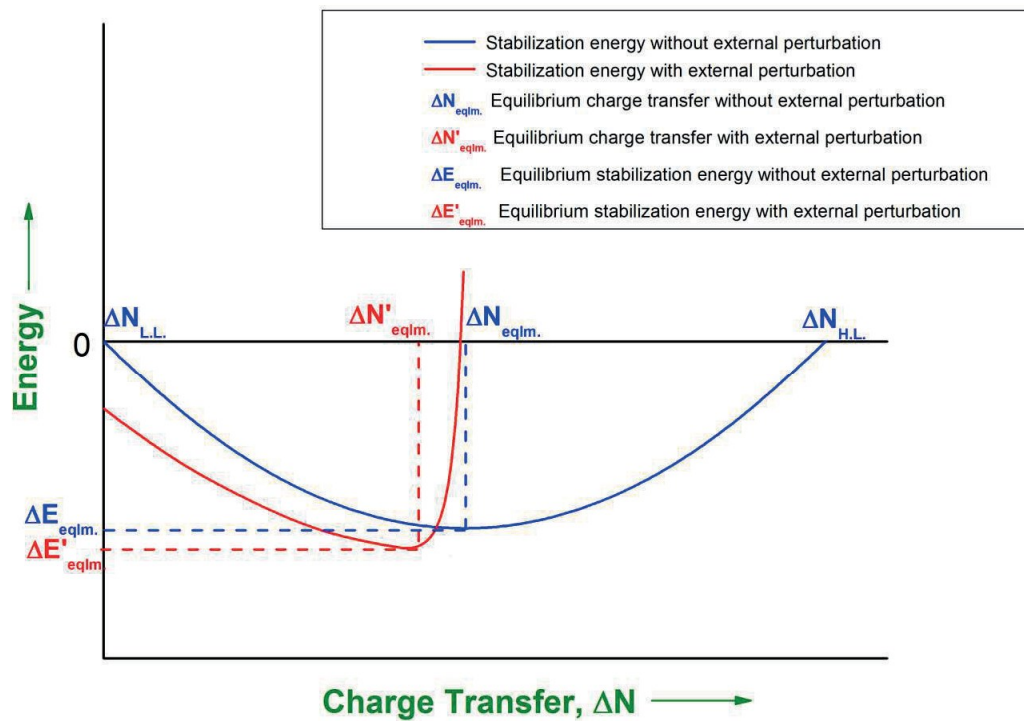
Once the charge transfer starts all the terms in equation (2.15) will contribute to the stabilization in the adduct formation process. Contribution from  $\alpha_A \Delta Z_A - \alpha_B \Delta Z_B$  will be small due to cancellation of contributions from A and B.<sup>24</sup> However, third term will again be negative. Thus, for a particular  $\Delta N$  the  $\Delta E$  value is expected to be more negative than the situation when perturbation to the external potential is not considered [equation (2.10)].

At equilibrium (i.e., when the chemical potentials of A and B are equalized) the stabilization energy ( $\Delta E_{eqm}$ ) is expressed by equation (2.19). From the arguments given in previous paragraphs here also it is expected that  $\Delta E_{eqm}$  will be more negative than when external potential perturbation is not considered [equation (1.48)]. Location of the  $\Delta N_{eqm}$  [equation (2.17)], with respect to the location of  $\Delta N_{eqm}$  without perturbation [equation (2.3)], will depend on the relative hard and soft nature of the donor and the acceptor.<sup>24</sup>

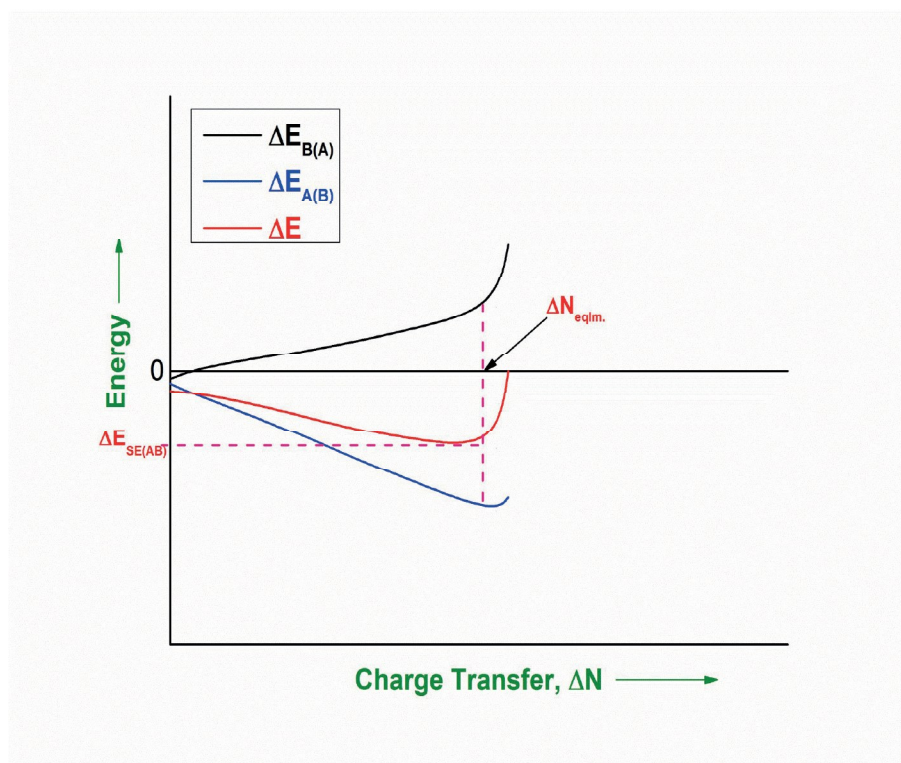
After the equilibrium point is crossed something interesting happened. The argument that  $\Delta Z > 0$  remains no longer valid. Rather, for  $\Delta N > \Delta N_{eqm}$ , the argument should be  $\Delta Z < 0$ . This is because chemical potentials of the donor and the acceptor are equalized when the chemical bonds are formed (i.e., the minimum is reached in the conventional potential energy curve). So,  $\Delta N > \Delta N_{eqm}$  indicates a situation when the distances between the two nuclei are closer than the equilibrium bond distance (i.e., left side of the minimum in the potential energy curve). In such a situation, electrons outside atomic cores of the donor and the acceptor, instead of facing the attraction of both the atomic cores will face repulsion. This is conventionally taken care by showing (in the potential energy curve) nuclear-nuclear repulsion to be much higher than the attraction due to overlapping electron cloud. However, in the present treatment such a situation can be accommodated by arguing that changes in the charge of the atomic core will be negative rather than positive (i.e.,  $\Delta Z < 0$  rather than  $\Delta Z > 0$ ). This could be a reflection of a negative Fukui function over the core region. Obviously, this is a highly unfavorable phenomenon leading to sharp decrease in stabilization of the adduct. Explanation can be given from equation (2.15), where we see that contribution of  $v_A^0 \Delta Z_A + v_B^0 \Delta Z_B$  is positive now (instead of negative) and much higher (as this is the first order contribution) than the negative contribution of the terms  $\frac{1}{2} \beta_A \Delta Z_A^2 +$



$\frac{1}{2}\beta_B\Delta Z_B^2$  (as this is the second order contribution). The analogy can be drawn to the conventional potential energy curve, in which the potential energy increases sharply in the left of the minimum. Thus,  $\Delta N_{H.L.}$  will be very close to  $\Delta N_{eqm}$  and not equal to  $2\Delta N_{eqm}$  [as was the case when perturbation to the external potential was not considered, equation (2.12)]. Finally, a tentative plot of  $\Delta E$  vs  $\Delta N$  with perturbation vis-à-vis a plot without perturbation will be looking as shown below [Figure 2.7(a)]. The plots of  $\Delta E_A$  vs.  $\Delta N$ ,  $\Delta E_B$  vs.  $\Delta N$  and  $\Delta E$  vs.  $\Delta N$  after considering perturbation is depicted in Figure 2.7(b).



(a)



(b)

**Figure 2.7.** (a) Profiles of stabilization energy with and without external potential perturbation. (b) Plot showing the profiles of  $\Delta E_{B(A)}$ ,  $\Delta E_{A(B)}$  and  $\Delta E$  values with respect to  $\Delta N$  after including external potential perturbation.

### 2.7. Conclusions:

It should be noted in this context that Klopman was the first one to explain hard-hard soft-soft interaction using polyelectronic perturbation theory.<sup>25,26</sup> According to this proposition net stabilization was attributed to three types of interactions. These are (i) electrostatic interaction between the reactants (ii) interaction between the reactants and the solvent and (iii) interaction between overlapping molecular orbitals of the reactants (i.e., the donor and the acceptor). When overlapping interaction (i.e., interaction due to formation of co-valent bond) is small or negligible the stabilization is dominantly contributed by the first two effects, which are charge-controlled or hard-hard interaction. In case of a strong frontier orbital overlap of the donor and the acceptor the interaction is mainly soft-soft or orbital-controlled. From equation (2.15) and Figure 2.7 it is obvious that even when there is no charge transfer ( $\Delta N = 0$ ), energy change ( $\Delta E$ ) is negative (i.e., there is net stabilization). Apparently, this is surprising because in the present treatment no solvent

was considered. So, there should not be any stabilization due to interaction of either the donor (B) or the acceptor (A) with the solvent. Also, both the donor and the acceptor were taken to be uncharged initially. Thus, there should not be any stabilization due to electrostatic interaction when charge transfer ( $\Delta N$ ) is zero. Thus, the only explanation of stabilization at the zero-charge transfer limit is weak non-bonding interactions (which include dipole-dipole, charge-induced dipole and London dispersion interactions) between the donor and the acceptor. However, with increasing solvent polarity (or dielectric constant,  $\epsilon$ ) charges on the donor and the acceptor will be reduced (due to solvation), decreasing the extent of mutual external potential perturbation (i.e., reducing the absolute values of  $\Delta Z_A$  and  $\Delta Z_B$ , which are positive quantities). Thus, from equation (2.19) we can argue that  $\Delta E_{eqm}$  of the adduct will be less negative (i.e., the adduct is less stable) in presence of a strong solvent. The treatment by Klopman also agrees that with increasing solvent polarity individual donor and acceptor will be solvated more reducing the chance of adduct formation.

In another interesting study, Li and Evans used orbital independent energy perturbation method within the framework of DFT and expanded stabilization energy in a Taylor series up to second order in terms of  $\Delta N$  and  $\Delta v(r)$  (i.e., external potential). Through term-by-term analysis they showed that hard-hard interaction is preferred in the site of minimal Fukui function (i.e., negligible charge transfer between the frontier orbitals of the donor and the acceptor), whereas site of maximal Fukui function (i.e., large charge transfer between the frontier orbitals of the donor and the acceptor) is preferred for soft-soft interaction.<sup>27</sup> The range of charge transfer ( $\Delta N$ ) considered in this study is  $\geq 0$ .

Ayers have proposed an equation of  $\Delta N_{eqm}$  after inclusion of electrostatic effect, which can be used further to calculate  $\Delta E_{SE(AB)}$ .<sup>28</sup> However, reliability of the generated  $\Delta N_{eqm}$  and  $\Delta E_{SE(AB)}$  values from these approximated expressions need to be tested as these are based on (i) 'reactive site' model of interaction between acids and bases and (ii) reactive atoms are assumed to be 'hard spheres'. In this context it should also be mentioned that there are also prescriptions on calculating  $\Delta E_{SE(AB)}$  using local hard-soft acid-base concept.<sup>29,30</sup> Subsequent development of the formalism by Geerlings and co-workers<sup>31,32</sup> as well as by Pal and co-workers<sup>33-35</sup> extended the scope of calculating  $\Delta E_{SE(AB)}$  for strong as well as weak intermolecular interactions.

It is worth mentioning here that although the methodology adopted in the present study is B3LYP/DNP, equations (2.18) and (2.19) supports the argument that the qualitative nature of  $\Delta E$

vs  $\Delta N$  plot will remain same and only quantitative values will change when different methods and basis sets are used (as the developed formalism is independent of any method or basis set).

It should also be noted that in some DFRT (density functional reactivity theory) based treatment of stabilization energy the terms taking care of electrostatic, dispersion and charge-induced dipole interactions are simply added to the one generated from charge transfer.<sup>28</sup> However, the present treatment takes care of all these effect through the first and second order perturbation of the external potentials of the donor and the acceptor. It is needless to say that final outcome of both the approaches is same.

Finally, equations (2.18) and (2.19) not only stress the importance of electrostatic and other non-bonding interactions in evaluating the charge transfer and stabilization energy values in the process of adduct formation but also provides an alternative and unambiguous proof of the long-range effect of these interactions. Although, there is no straightforward way to calculate higher limit of the charge transfer values ( $\Delta N_{H,L}$ , because of the fact that it requires the evaluation of  $v$ ,  $\alpha$ ,  $\beta$  and  $\Delta Z$  of atoms-in-a-molecule when the adduct formation takes place between two polyatomic systems), from the viewpoint of theoretical and conceptual understanding equations (2.18) and (2.19) seems to be quite clear and convincing.

**References:**

1. R. G. Parr, R. G. Pearson, *J. Am. Chem. Soc.* **1983**, *105*, 7512.
2. R. T. Sanderson, *Science*. **1951**, *114*, 670.
3. R. T. Sanderson, *Science*. **1952**, *116*, 41.
4. R. G. Parr, R. A. Donnelly, M. Levy, W. E. Palke, *J. Chem. Phys.* **1978**, *68*, 3801.
5. P. Bagaria, S. Saha, S. Murru, V. Kavala, B. Patel, R. K. Roy, *Phys. Chem. Chem. Phys.* **2009**, *11*, 8306.
6. S. Saha, R. K. Roy, S. Pal, *Phys. Chem. Chem. Phys.* **2010**, *12*, 9328.
7. A. Sarmah, S. Saha, P. Bagaria, R. K. Roy, *Chem. Phys.* **2012**, *394*, 29.
8. A. Sarmah, R. K. Roy, *RSC Adv.* **2013**, *3*, 2822.
9. A. Sarmah, R. K. Roy, *J. Phys. Chem. C* **2013**, *117*, 21539.
10. A. Sarmah, R. K. Roy, *J. Phys. Chem. C* **2015**, *119*, 17940.
11. A. Sarmah, R. K. Roy, *Chem. Phys.* **2016**, *472*, 218.
12. A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098.
13. A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
14. C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
15. B. Delley, *J. Chem. Phys.* **1990**, *92*, 508.
16. B. Delley, *J. Chem. Phys.* **2000**, *113*, 7756.
17. R. K. Roy, S. Pal, K. Hirao, *J. Chem. Phys.* **1999**, *110*, 8236.
18. R. K. Roy, K. Hirao, S. Pal, *J. Chem. Phys.* **2000**, *113*, 1372.
19. R. K. Roy, N. Tajima, K. Hirao, *J. Phys. Chem.* **2001**, *105*, 2117.
20. R. K. Roy, *J. Phys. Chem. A* **2003**, *107*, 10428.
21. S. Saha, R. K. Roy, P. W. Ayers, *Int. J. Quantum Chem.* **2009**, *109*, 1790.
22. R. F. Nalewajski, R. G. Parr, *J. Chem. Phys.* **1982**, *77*, 399.
23. R. F. Nalewajski, *J. Chem. Phys.* **1983**, *78*, 6112.
24. R. F. Nalewajski, *J. Am. Chem. Soc.* **1984**, *106*, 944.
25. G. Klopman, *J. Am. Chem. Soc.* **1964**, *86*, 4550.
26. G. Klopman, *J. Am. Chem. Soc.* **1968**, *90*, 223.
27. Y. Li, J. N. S. Evans, *J. Am. Chem. Soc.* **1995**, *117*, 7756.
28. P. W. Ayers, *Faraday Discuss.* **2007**, *135*, 161.
29. J. L. Gazquez, F. Mendez, *J. Phys. Chem.* **1994**, *98*, 4591.

30. J. L. Gazquez, F. Mendez, *J. Am. Chem. Soc.* **1994**, *116*, 9298.
31. F. Mendez, J. Tamariz, P. Geerlings, *J. Phys. Chem. A.* **1998**, *102*, 6292.
32. S. Damoun, G. Van de Woude, K. Choho, P. Geerlings, *J. Phys. Chem. A.* **1999**, *103*, 7861.
33. S. Pal, K. R. S. Chandrakumar, *J. Am. Chem. Soc.* **2000**, *122*, 4145.
34. K. R. S. Chandrakumar, S. Pal, *J. Phys. Chem. A.* **2002**, *106*, 5737.
35. S. Das, S. Shedge, S. Pal, *J. Phys. Chem. A.* **2013**, *117*, 10933.



This document was created with the Win2PDF "print to PDF" printer available at <http://www.win2pdf.com>

This version of Win2PDF 10 is for evaluation and non-commercial use only.

This page will not be added after purchasing Win2PDF.

<http://www.win2pdf.com/purchase/>