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# The charge transfer limit of a chemical adduct: the role of perturbation on external potential†

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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 three different Diels–Alder pairs and twelve different charge transfer complexes formed by $BH_3$–$NH_3$ and their derivatives. One interesting observation is that the stabilization energy is zero when the charge transfer ($\Delta N$) is either zero (lower limit, L.L.) or two times (higher limit, H.L.) the charge transfer at equilibrium (*i.e.*, when chemical potentials are equalized). However, the existence of zero stabilization energy at the zero charge transfer limit is counter-argued after the inclusion of first and second order effects (due to a perturbing external potential of the partner of a given atom-in-a-molecule) in the individual energy components as well as the overall stabilization energy expressions. It has been shown that even when $\Delta N$ is zero (the lower limit), the net energy change is negative (*i.e.*, the combined system is stabilized), highlighting the role of non-bonding interactions, rather than charge-transfer, in stabilizing the combined system at the initial stage of adduct formation. The higher limit (H.L.) of charge transfer is also shifted to a much lower value due to the inclusion of this external potential perturbation.

## 1. Introduction

Stabilization energy arising out of only the charge-transfer interaction between an electron donor (B) and an acceptor (A) was formulated by Parr and Pearson[1] using the chemical potential equalization principle.[2–4] 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.[5–11] 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 the 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, a brief theoretical background along with the criteria of choosing different charge transfer values ($\Delta N$) up to the two limits is given. Section 3 describes the computational details which include the methodology adopted as well as the representative systems chosen (*e.g.*, Diels–Alder type of adducts as well as simple charge transfer complexes like $BH_3$–$NH_3$ and their derivatives). Analysis of the generated energy components is made in Section 4. Section 5 provides an analytical explanation of the obtained charge transfer limits ($\Delta N_{limit}$). Changes in the charge transfer limits after the inclusion of first and second order perturbations on the external potential (of interacting atoms) in the energy components are elaborated in Section 6. Finally, in the concluding section (Section 7) the overall outcome of the study is summarized. This section also includes a critical assessment of effects such as solvent, dispersion interaction, methods and basis sets on the charge transfer limits.

## 2. Charge transfer limits

The expressions of different energy components used in this article are those developed by Parr and Pearson[1] with modified notations proposed by Roy and collaborators.[5] 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

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

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

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Here, $\Delta N$ represents the charge transfer and $\mu$ and $\eta$ represent the corresponding chemical potential and hardness, respectively. Writing the full form of eqn (1) and (2), when the chemical potentials of A and B are equalized, we get

$$\Delta E_{B(A)} = \frac{\mu_{B^0} - \mu_{A^0}}{\eta_A + \eta_B}\left[-\mu_{B^0} + \frac{1}{2}\eta_B\left(\frac{\mu_{B^0} - \mu_{A^0}}{\eta_A + \eta_B}\right)\right] \quad (3)$$

$$\Delta E_{A(B)} = \frac{\mu_{B^0} - \mu_{A^0}}{\eta_A + \eta_B}\left[\mu_{A^0} + \frac{1}{2}\eta_A\left(\frac{\mu_{B^0} - \mu_{A^0}}{\eta_A + \eta_B}\right)\right] \quad (4)$$

So, the net energy change (*i.e.*, the stabilization energy) is given by

$$\Delta E_{SE(AB)} = \Delta E_{B(A)} + \Delta E_{A(B)} = -\frac{(\mu_{B^0} - \mu_{A^0})^2}{2(\eta_A + \eta_B)} \quad (5)$$

and the corresponding charge transfer, $\Delta N_{eqlm}$, is given by

$$\Delta N_{eqlm} = \left(\frac{\mu_{B^0} - \mu_{A^0}}{\eta_A + \eta_B}\right) \quad (6)$$

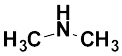
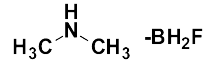
Here, the right subscript 'eqlm' is used to stress the fact that eqn (3)–(6) are derived following the chemical potential (of A and B) equalization principle. That is when chemical potentials of A and B ($\mu_A$ and $\mu_B$, respectively) are equalized (an equilibrium situation) the adduct AB will be the most stable one [*i.e.*, the most negative $\Delta E_A + \Delta E_B = \Delta E$ value will be $\Delta E_{SE(AB)}$ (eqn (5)) and the corresponding $\Delta N = \Delta N_{eqlm}$ (eqn (6))]. However, if someone moves towards lower and higher charge transfer sides 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 $\Delta N_{eqlm}$) 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.

## 3. Computational details

The representative acceptors (A) and donors (B) chosen here are (i) three Diels–Alder pairs, (ii) $BH_3$–$NH_3$ complex and (iii) some derivatives of the $BH_3$–$NH_3$ complex. The Diels–Alder pairs are acraldehyde (A) – butadiene (B), acrylonitrile (A) – penta-1,3-diene (B) and nitroethene (A) – hexa-1,3-diene (B). The corresponding adducts (AB) generated are the Diels–Alder products, $NH_3$–$BH_3$ complex and derivatives of this complex. Out of 15 donor–acceptor pairs and the adducts formed by them, 4 are depicted in Table 1.

The other 11 pairs and the corresponding adducts are shown in Table S1 of the ESI.† Optimizations of the geometries followed by single point calculations are performed using the B3LYP functional[12–14] and DNP basis set, as implemented in the DMOL3 program package.[15,16] 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** basis sets,[15–21] although these two are of comparable size.

Table 1 Different combinations of donors and acceptors

| S. no. | Donor (B) | Acceptor (A) | Adduct (AB) |
|---|---|---|---|
| 1 |  buta-1,3-diene |  acrylaldehyde |  cyclohex-3-enone |
| 2 | $NH_3$ ammonia | $BH_3$ borane | $NH_3$–$BH_3$ |
| 3 | $CH_3$–$NH_2$ methanamine | $BH_3$ borane | $H_3C$–$NH_2$–$BH_3$ |
| 4 |  dimethylamine | $BH_2F$ fluoroborane |  -$BH_2F$ |

Here, it is important to note that the values of $\Delta E$, $E_{B(A)}$, $E_{A(B)}$, $\Delta E_{SE(AB)}$, $\Delta N$ and $\Delta N_{eqlm}$ are generated as per the CDASE scheme[5] (and so, as per the equations developed by Parr and Pearson[1]), where the reactivity parameters *e.g.*, $\mu$ and $\eta$ (and hence, IP and EA) are of isolated donors (B) and acceptors (A). Thus, geometry optimization of the adduct (AB) is not necessary. The optimized coordinates of all the chosen donors and acceptors are shown in Tables S2–S15 of the ESI.†

## 4. Results and discussion

As discussed in Section 2, it is obvious that eqn (3)–(6) represent only the values at equilibrium *i.e.*, at a single point. However, eqn (1) and (2) are used to generate the values of $\Delta E_{B(A)}$ and $\Delta E_{A(B)}$ (and hence $\Delta E$) at points other than the equilibrium one. When these values are plotted against $\Delta N$ [starting from ($\Delta N_{eqlm}$, $\Delta E_{SE(AB)}$) and moving towards the lower and higher sides] something interesting is observed. For all the chosen pairs the limiting $\Delta N$ values are obtained as 0 (zero) and $2\Delta N_{eqlm}$ (Tables 2–5, Tables S16–S26, ESI† and Fig. 1–4, Fig. S1–S11, ESI†).

Here, the 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, a physically zero $\Delta E$ value at

Table 2 Changes in $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and $\Delta E$ values with respect to charge transfer ($\Delta N$) for Diels–Alder pair acraldehyde ($CH_2$=CH–CHO, A) and buta-1,3-diene ($CH_2$=CH–CH=$CH_2$, B)

| S. no. | $\Delta N$ | $\Delta E_{B(A)}$ (kJ mol$^{-1}$) | $\Delta E_{A(B)}$ (kJ mol$^{-1}$) | $\Delta E$ (kJ mol$^{-1}$) |
|---|---|---|---|---|
| 1 | 0.0 | 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 | 18.14 | −21.422 | −3.282 |
| 5 | 0.06845 | 25.977 | −29.891 | −3.914 |
| 6[a] | 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 |

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

Table 3 Changes in $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and $\Delta E$ values with respect to charge transfer ($\Delta N$) for borane ($BH_3$, A) and ammonia ($NH_3$, B)

| S. no. | $\Delta N$ | $\Delta E_{B(A)}$ (kJ mol$^{-1}$) | $\Delta E_{A(B)}$ (kJ mol$^{-1}$) | $\Delta E$ (kJ mol$^{-1}$) |
|---|---|---|---|---|
| 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[a] | 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 |

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

Table 4 Changes in $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and $\Delta E$ values with respect to charge transfer ($\Delta N$) for borane ($BH_3$, A) and methanamine ($CH_3$–$NH_2$, B)

| S. no. | $\Delta N$ | $\Delta E_{B(A)}$ (kJ mol$^{-1}$) | $\Delta E_{A(B)}$ (kJ mol$^{-1}$) | $\Delta E$ (kJ mol$^{-1}$) |
|---|---|---|---|---|
| 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[a] | 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 |

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

Table 5 Changes in $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and $\Delta E$ values with respect to charge transfer ($\Delta N$) for fluoroborane ($BH_2F$, A) and dimethylamine [$(CH_3)_2$–NH, B]

| S. no. | $\Delta N$ | $\Delta E_{B(A)}$ (kJ mol$^{-1}$) | $\Delta E_{A(B)}$ (kJ mol$^{-1}$) | $\Delta E$ (kJ mol$^{-1}$) |
|---|---|---|---|---|
| 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[a] | 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 |

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

$2\Delta N_{eqlm}$ apparently points to the situation that when the donor (B) is forced to donate more electrons than $\Delta N_{eqlm}$ the adduct (AB) starts destabilizing again and at $2\Delta N_{eqlm}$ the stabilization energy becomes 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.* $\Delta N$) experimentally is something which seems to be 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, this 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.

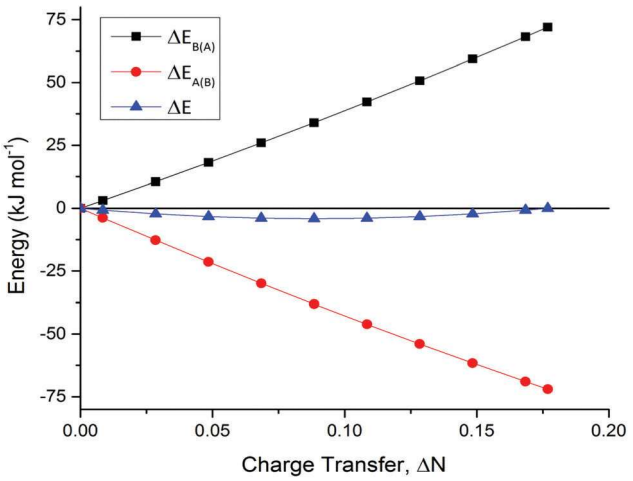



Fig. 1 Plot showing the profiles of $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and $\Delta E$ values with respect to $\Delta N$ for acrylaldehyde ($CH_2$=CH–CHO, A) and buta-1,3-diene ($CH_2$=CH–CH=$CH_2$, B).

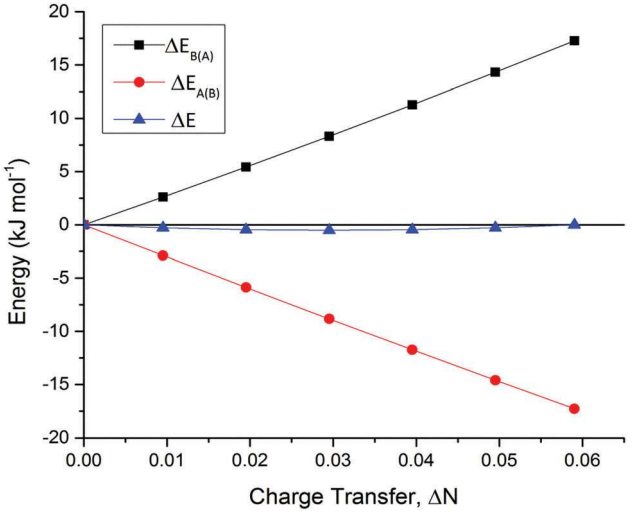



Fig. 2 Plot showing the profiles of $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and $\Delta E$ values with respect to $\Delta N$ for borane ($BH_3$, A) and ammonia ($NH_3$, B).

Although the 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.*, $\Delta N_{limit} = 2\Delta N_{eqlm}$ is quite intriguing. Nevertheless, this observation can be explained from the analysis in the following section.

## 5. Theoretical derivation of charge transfer limits

The energy of the acceptor (A) during the charge transfer process can be written (after truncating the third and higher

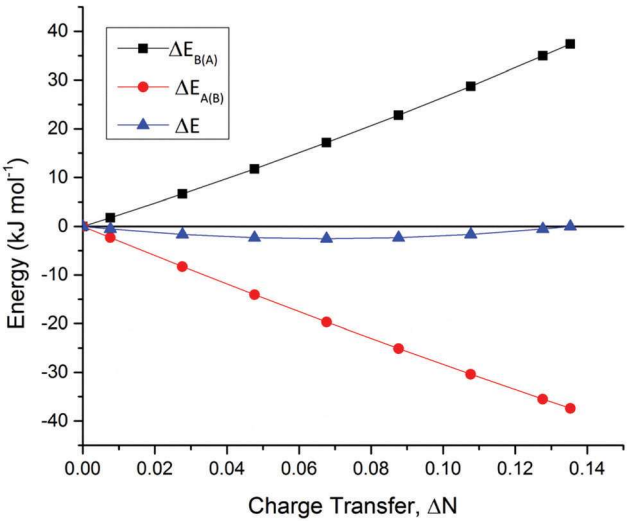



Fig. 3 Plot showing the profiles of $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and $\Delta E$ values with respect to $N$ for borane ($BH_3$, A) and methanamine ($CH_3$–$NH_2$, B).

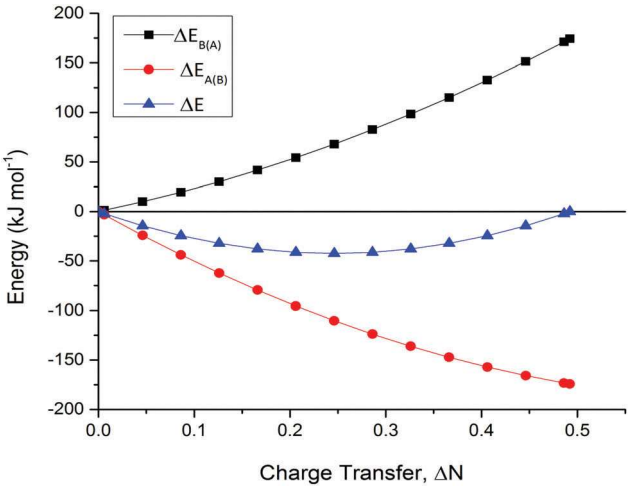



Fig. 4 Plot showing the profiles of $\Delta E_{B(A)}$, $\Delta E_{A(B)}$ and $\Delta E$ values with respect to $\Delta N$ for fluoroborane ($BH_2F$, A) and dimethylamine [$(CH_3)_2$–NH, B].

order terms)[1] as

$$E_A = E_{A^0} + \frac{1}{1!}\left(\frac{\partial E_{A^0}}{\partial N}\right)_v (N_A - N_{A^0}) + \frac{1}{2!}\left(\frac{\partial^2 E_{A^0}}{\partial N^2}\right)_v (N_A - N_{A^0})^2 \quad (7)$$

Similarly, for the donor (B),

$$E_B = E_{B^0} + \frac{1}{1!}\left(\frac{\partial E_{B^0}}{\partial N}\right)_v (N_B - N_{B^0}) + \frac{1}{2!}\left(\frac{\partial^2 E_{B^0}}{\partial N^2}\right)_v (N_B - N_{B^0})^2 \quad (8)$$

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), eqn (7) and (8) can be written as

$$E_A = E_{A^0} + \mu_{A^0}\Delta N + \frac{1}{2}\eta_A \Delta N^2 \quad (9)$$

$$E_B = E_{B^0} - \mu_{B^0}\Delta N + \frac{1}{2}\eta_B \Delta N^2 \quad (10)$$

[It should be noted here, that in the original paper by Parr and Pearson,[1] 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 $\left(\frac{\partial^2 E}{\partial N^2}\right)_v$].

Eqn (9) and (10) can be rearranged to

$$\Delta E_A = E_A - E_{A^0} = \mu_{A^0}\Delta N + \frac{1}{2}\eta_A \Delta N^2 \quad (11)$$

$$\Delta E_B = E_B - E_{B^0} = -\mu_{B^0}\Delta N + \frac{1}{2}\eta_B \Delta N^2 \quad (12)$$

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

$$\Delta E = \Delta E_A + \Delta E_B = -(\mu_{B^0} - \mu_{A^0})\Delta N + \frac{1}{2}(\eta_A + \eta_B)\Delta N^2 \quad (13)$$

From eqn (13) it is obvious that $\Delta E = 0$ (*i.e.*, no net change in energy due to charge transfer) leads to two different solutions of $\Delta N$, the lower one (named as 'Lower Limit', L.L.) is

$$\Delta N_{L.L.} = 0 \quad (14)$$

(*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

$$\Delta N_{H.L.} = \frac{2(\mu_{B^0} - \mu_{A^0})}{\eta_A + \eta_B} \quad (15)$$

Comparing eqn (14) and (15) 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 $\Delta N_{H.L.} = \frac{2(\mu_{B^0} - \mu_{B^0})}{\eta_A + \eta_B} = 2\Delta N_{eqlm}$.

## 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 the 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.*, $\Delta N_{H.L.} = 2\Delta N_{eqlm}$) 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 $\Delta N = \Delta N_{eqlm}$ (as mentioned in Section 4).

However, as the following derivation shows, the inclusion of the first and second order contributions to the energy expressions of the donors and acceptors, due to the 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 $N_{H.L.}$ appears to be an expected one (from our knowledge of the conventional potential energy curve). The energy of an atom-in-a-molecule

can be expanded up to a full second order as[22–24]

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

or

$$E_A(N_A, Z_A) = E_{A^0} + \left(\mu_{A^0}\Delta N_A + v_A^0 \Delta Z_A\right) + \frac{1}{2}\left[\eta_A(\Delta N_A)^2 + 2\alpha_A \Delta N_A \Delta Z_A + \beta_A(\Delta Z_A)^2\right] \quad (16)$$

Similarly for donor B,

$$E_B(N_B, Z_B) = E_{B^0} + \left(\mu_{B^0}\Delta N_B + v_B^0 \Delta Z_B\right) + \frac{1}{2}\left[\eta_B(\Delta N_B)^2 + 2\alpha_B \Delta N_B \Delta Z_B + \beta_B(\Delta Z_B)^2\right] \quad (17)$$

In eqn (16) and (17) $v = \left(\frac{\partial E}{\partial Z}\right)_N = \frac{V_{ne}}{Z} < 0$ 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 $\beta = \left(\frac{\partial v}{\partial Z}\right)_N < 0$.[24] It should 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 eqn (16) and (17) we get

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

or

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

or

$$\Delta E = \frac{1}{2}(\eta_A + \eta_B)\Delta N^2 - [(\mu_{B^0} - \mu_{A^0}) - (\alpha_A \Delta Z_A - \alpha_B \Delta Z_B)]\Delta N + \left(v_A^0 \Delta Z_A + v_B^0 \Delta Z_B + \frac{1}{2}\beta_A {\Delta Z_A}^2 + \frac{1}{2}\beta_B {\Delta Z_B}^2\right) \quad (18)$$

as $\Delta N = \Delta N_A = -\Delta N_B$.

From eqn (18) 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 $\Delta N_{H.L.} = 2\Delta N_{eqlm}$). When the stabilization energy is zero (*i.e.*, $\Delta E = \Delta E_A + \Delta E_B = 0$) the right hand side of eqn (18) 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

$$\Delta N_{limit} = \frac{[\mu_{B^0} - \mu_{A^0} - (\alpha_A \Delta Z_A - \alpha_B \Delta Z_B)] \pm \sqrt{[\mu_{B^0} - \mu_{A^0} - (\alpha_A \Delta Z_A - \alpha_B \Delta Z_B)]^2 - 2(\eta_A + \eta_B)\left(v_A^0 \Delta Z_A + v_B^0 \Delta Z_B + \frac{1}{2}\beta_A \Delta Z_A^2 + \frac{1}{2}\beta_B \Delta Z_B^2\right)}}{(\eta_A + \eta_B)} \quad (19)$$

Again, when the chemical potentials are equalized (leading to the formation of the most stable adduct) from eqn (16) and (17) 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

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

or

$$\Delta N_{eqlm} = \left(\frac{\mu_{B^0} - \mu_{A^0}}{\eta_A + \eta_B}\right) - \left(\frac{\alpha_A \Delta Z_A - \alpha_B \Delta Z_B}{\eta_A + \eta_B}\right) = \frac{\mu_{B^0} - \mu_{A^0} - (\alpha_A \Delta Z_A - \alpha_B \Delta Z_B)}{\eta_A + \eta_B} \quad (20)$$

From eqn (19) and (20) we can write

$$\Delta N_{limit} = \Delta N_{eqlm} \pm \frac{\sqrt{[\mu_{B^0} - \mu_{A^0} - (\alpha_A \Delta Z_A - \alpha_B \Delta Z_B)]^2 - 2(\eta_A + \eta_B)\left(v_A{}^0 \Delta Z_A + v_B^0 \Delta Z_B + \beta_A {\Delta Z_A}^2 + \beta_B {\Delta Z_B}^2\right)}}{(\eta_A + \eta_B)} \quad (21)$$

Now, substituting $\Delta N_{\mathrm{eqlm}}$ from eqn (20) in eqn (18) we get

$$\begin{aligned}\Delta E_{\mathrm{eqlm}} &= \frac{1}{2}(\eta_{\mathrm{A}}+\eta_{\mathrm{B}})\frac{((\mu_{\mathrm{B}^0}-\mu_{\mathrm{A}^0})-(\alpha_{\mathrm{A}}\Delta Z_{\mathrm{A}}-\alpha_{\mathrm{B}}\Delta Z_{\mathrm{B}}))^2}{(\eta_{\mathrm{A}}+\eta_{\mathrm{B}})^2}\\ &\quad-[(\mu_{\mathrm{B}^0}-\mu_{\mathrm{A}^0})-(\alpha_{\mathrm{A}}\Delta Z_{\mathrm{A}}-\alpha_{\mathrm{B}}\Delta Z_{\mathrm{B}})]\\ &\quad\times\frac{((\mu_{\mathrm{B}^0}-\mu_{\mathrm{A}^0})-(\alpha_{\mathrm{A}}\Delta Z_{\mathrm{A}}-\alpha_{\mathrm{B}}\Delta Z_{\mathrm{B}}))}{(\eta_{\mathrm{A}}+\eta_{\mathrm{B}})}\\ &\quad+\left(v_{\mathrm{A}}^0\Delta Z_{\mathrm{A}}+v_{\mathrm{B}}^0\Delta Z_{\mathrm{B}}+\frac{1}{2}\beta_{\mathrm{A}}\Delta Z_{\mathrm{A}}{}^2+\frac{1}{2}\beta_{\mathrm{B}}\Delta Z_{\mathrm{B}}{}^2\right)\end{aligned}$$

or

$$\begin{aligned}\Delta E_{\mathrm{eqlm}} &= -\frac{((\mu_{\mathrm{B}^0}-\mu_{\mathrm{A}^0})-(\alpha_{\mathrm{A}}\Delta Z_{\mathrm{A}}-\alpha_{\mathrm{B}}\Delta Z_{\mathrm{B}}))^2}{2(\eta_{\mathrm{A}}+\eta_{\mathrm{B}})}\\ &\quad+\left(v_{\mathrm{A}}^0\Delta Z_{\mathrm{A}}+v_{\mathrm{B}}^0\Delta Z_{\mathrm{B}}+\frac{1}{2}\beta_{\mathrm{A}}\Delta Z_{\mathrm{A}}{}^2+\frac{1}{2}\beta_{\mathrm{B}}\Delta Z_{\mathrm{B}}{}^2\right)\end{aligned} \quad (22)$$

A systematic analysis of eqn (18)–(22) will help to understand the full profile of $\Delta E$ as well as the locations of $\Delta N_{\mathrm{L.L.}}$, $\Delta N_{\mathrm{H.L.}}$ $\Delta N_{\mathrm{eqlm}}$ and $\Delta E_{\mathrm{eqlm}}$. From eqn (18) it is obvious that when charge transfer ($\Delta N$) is zero (just before the charge transfer starts) the contribution from the first two terms will be zero. As both $v^0$ and $\beta$ are $<0$ and $\Delta Z > 0$ (because in the adduct AB, the outer electrons of an atomic core face the influence of both the atomic cores)[23,24] 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 $\Delta N_{\mathrm{L.L.}}$ is not acceptable as, by definition, $\Delta N$ should be positive (see arguments just before eqn (9)). However, $\Delta N_{\mathrm{H.L.}}$ will not be equal to $2\Delta N_{\mathrm{eqlm}}$, as was the case when perturbation to the external potential was not considered (to be discussed later).

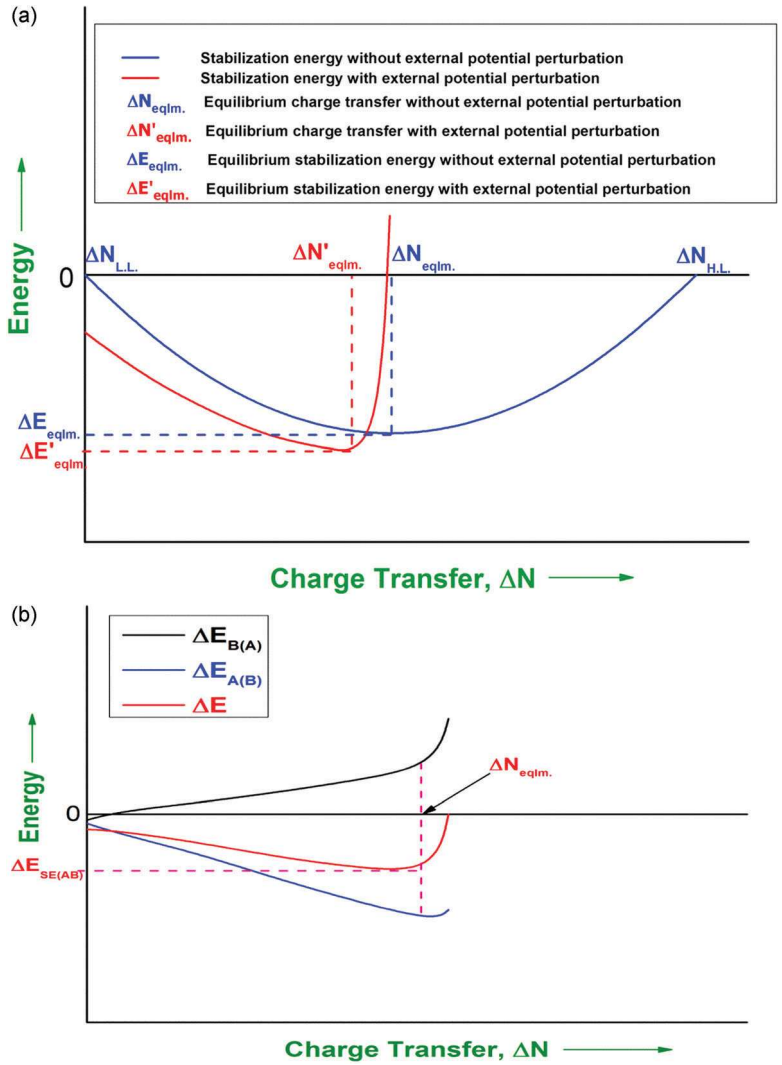



Fig. 5 (a) Profiles of stabilization energy with and without external potential perturbation. (b) Plot showing the profiles of $\Delta E_{\mathrm{B(A)}}$, $\Delta E_{\mathrm{A(B)}}$ and $\Delta E$ values with respect to $\Delta N$ after including external potential perturbation.

Once the charge transfer starts all the terms in eqn (18) will contribute to the stabilization in the adduct formation process. The contribution from $\alpha_A\Delta Z_A - \alpha_B\Delta Z_B$ will be small due to cancellation of contributions from A and B.[24] However, the third term will again be negative. Thus for a particular $\Delta N$ the $\Delta E$ value is expected to be more negative than when perturbation to the external potential is not considered (eqn (13)).

At equilibrium (*i.e.*, when the chemical potentials of A and B are equalized) the stabilization energy ($\Delta E_{eqlm}$) is expressed by eqn (22). From the arguments given in the previous paragraphs here also it is expected that $\Delta E_{eqlm}$ will be more negative than when external potential perturbation is not considered (eqn (5)). The location of $\Delta N_{eqlm}$ (eqn (20)), with respect to the location of $\Delta N_{eqlm}$ without perturbation (eqn (6)), will depend on the relative hard and soft nature of the donor and the acceptor.[24]

After the equilibrium point is crossed something interesting happened. The argument that $\Delta Z > 0$ remains no longer valid. Rather, for $\Delta N > \Delta N_{eqlm}$, 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, $\Delta N > \Delta N_{eqlm}$ indicates a situation when the distances between the two nuclei are closer than the equilibrium bond distance (*i.e.*, the 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 of by showing (in the potential energy curve) that the nuclear–nuclear repulsion is much higher than the attraction due to an 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 unfavourable phenomenon leading to a sharp decrease in stabilization of the adduct. An explanation can be given from eqn (18), where we see that the 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 to the left of the minimum. Thus, $\Delta N_{H.L.}$ will be very close to $\Delta N_{eqlm}$ and not equal to $2\Delta N_{eqlm}$ (as was the case when perturbation to the external potential was not considered, eqn (15)). Finally, a tentative plot of $\Delta E$ *vs.* $\Delta N$ with perturbation *vis-à-vis* a plot without perturbation will be seen as shown below (Fig. 5a). The plots of $\Delta E_A$ *vs.* $\Delta N$, $\Delta E_B$ *vs.* $\Delta N$ and $\Delta E$ *vs.* $\Delta N$ after considering perturbation are depicted in Fig. 5b.

## 7. Conclusion

It should be noted in this context that Klopman was the first one to explain hard–hard soft–soft interaction using polyelectronic perturbation theory.[25,26] 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 the overlapping interaction (*i.e.*, interaction due to formation of a 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 the case of a strong frontier orbital overlap of the donor and the acceptor the interaction is mainly soft–soft or orbital-controlled. From eqn (18) and Fig. 5 it is obvious that even when there is no charge transfer ($\Delta N = 0$), the 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 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, $\varepsilon$) 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 eqn (22) we can argue that $\Delta E_{eqlm}$ will be less negative in the presence of a strong solvent. The treatment by Klopman also agrees that with increasing solvent polarity the individual donor and acceptor will be solvated more reducing the chance of adduct formation.

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

Ayers has proposed an equation of $\Delta N_{eqlm}$ after inclusion of the electrostatic effect, which can be further used to calculate $\Delta E_{SE(AB)}$.[28] However, reliability of the generated $\Delta N_{eqlm}$ and $\Delta E_{SE(AB)}$ values from these approximated expressions needs to be tested as these are based on (i) the '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 the local hard–soft acid–base concept.[29,30] Subsequent development of the formalism by Geerlings and co-workers[31,32] as well as by Pal and co-workers[33–35] 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, eqn (21) and (22) support the argument that the qualitative nature of the $\Delta E$ *vs.* $\Delta N$ plot will remain the 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 added to the one generated from charge transfer.[28] However, the present treatment takes care of all these effects through the first and second order perturbation of the external potentials of the donor and the acceptor. It is needless to say that the final outcome of both the approaches is the same.

Finally, eqn (21) and (22) 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 provide an alternative and unambiguous proof of the long range effect of these interactions. Although there is no straightforward way to calculate the higher limit of the charge transfer values ($\Delta N_{\text{H.L.}}$, because of the fact that it requires the evaluation of $\nu$, $\alpha$, $\beta$ 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 eqn (21) and (22) seem to be quite clear and convincing.

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