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**Revisiting the Trapping of Noble Gases (He – Kr) by the Triatomic H$_3^+$ and Li$_3^+$ Species: A Density Functional Reactivity Theory Study**

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**Abstract**

Small atomic clusters with exotic stability, bonding, aromaticity and reactivity properties can be made use of for various purposes. In this work, we revisit the trapping of noble gas atoms (He – Kr) by the triatomic H$_3^+$ and Li$_3^+$ species by using some analytical tools from density functional theory, conceptual density functional theory, and the information-theoretic approach. Our results showcase that though similar in geometry, H$_3^+$ and Li$_3^+$ exhibit markedly different behaviour in bonding, aromaticity, and reactivity properties after the addition of noble gas atoms. Moreover, the exchange-correlation interaction and steric effect are key energy components in stabilizing the clusters. This study also finds that the origin of the molecular stability of these species is due to the spatial delocalization of the electron density distribution. Our work provides an additional arsenal towards better understanding of small atomic clusters capturing noble gases.

**Keywords:** Density functional theory; boron clusters; bonding; aromaticity; chemical reactivity
1. Introduction

During the past few decades, atomic clusters have been the subject of intensive research due to their indispensable roles in biomedicine, optics and synthetic materials.\[1–3\] Since Bartlett first synthesized \(\text{Xe}^+[\text{PtF}_6]^–\),\[4\] the underexplored chemistry of noble gases has witnessed rapid developments, motivating both synthetic and theoretical chemists jumping into this field.\[5\] It has found that noble gas insertion compounds play an important role because of their unique properties in geometrical structure, molecular stability, bonding, chemical reactivity, and other physicochemical properties.

In continuation with our previous work,\[6\] we intend to revisit the trapping of noble gases by \(\text{H}_3^+\) and \(\text{Li}_3^+\) species from the perspective of stability, bonding, aromaticity, and reactivity properties using the framework of conceptual density functional theory (CDFT) augmented by the information-theoretic approach (ITA). Also employed are well-established analytical tools, such as aromaticity descriptors NICS (nucleus independent chemical shift) and GIMIC (gauge-including magnetically induced currents), “spike” region for noncovalent interactions and our newly developed analytical tools in analyzing strong covalent interactions and reactivity patterns in terms of local temperatures, that are intrinsically different from their thermodynamic definitions. Combining these effective methods allows us to gain insights into these species and to obtain many unexpected properties of these small atomic clusters.

2. Methodology
In Kohn-Shan DFT, we can decompose the total energy difference ($\Delta E$) into its components as\(^7,8\)

$$\Delta E[\rho] = \Delta T_s[\rho] + \Delta E_e[\rho] + \Delta E_{xc}[\rho] \quad (1)$$

and

$$\Delta E[\rho] = \Delta E_s[\rho] + \Delta E_c[\rho] + \Delta E_q[\rho] \quad (2)$$

where $T_s$, $E_e$, and $E_{xc}$ are the noninteracting kinetic, electrostatic, and exchange–correlation energies, respectively. The electrostatic energy $E_e$ includes three independent components: the nuclear–electron attraction, $V_{ne}$; the classical interelectron Coulombic repulsion, $J$; and the nuclear–nuclear repulsion, $V_{nn}$. The last term $E_{xc}$ consists of exchange ($E_x$) and correlation ($E_c$) components. $E_s$ stands for the energetic contribution from the steric effect, and $E_q$ signifies the contribution originating from Fermionic quantum effect (due to the exchange–correlation interaction). The steric effect $E_s$ has been shown to be simply the Weizsäcker kinetic energy as will be shown later in Eq. (8). The definition of $E_q$ is by simply combining Eqs. (1), (2) and (8), which reads

$$\Delta E_q[\rho] = \Delta E_{xc}[\rho] + \Delta T_s[\rho] - \Delta E_s[\rho] \quad (3)$$

This new formulation has its own distinct physical meaning with a corresponding physical state.\(^8\) It has been applied to a number of molecular systems and phenomena, such as conformational changes,\(^8\,–\,13\) anomic effect,\(^14\,–\,16\) the cis-effect,\(^17\) , etc. The results are consistent with our chemical intuition and conventional wisdom.

In CDFT,\(^18\,–\,20\) besides the well-known local descriptor Fukui function\(^21,22\),
we very recently evaluated the local temperature $T(r)$ of a molecule using the kinetic energy density (KED),

$$T(r) = \frac{2\tau(r)}{3k_B}$$

where $\tau(r)$, $\rho(r)$, and $k_B$ are the KED, electron density, and Boltzmann constant, respectively. Among various KEDs, two well-appreciated definitions are the Hamiltonian KED

$$\tau(r) = -\frac{1}{2}\sum_i \phi_i^*(r) \nabla^2 \phi_i(r)$$

with $\phi_i(r)$ as the occupied Kohn–Sham orbitals, and the Lagrangian KED

$$\tau(r) = \frac{1}{2}\sum_i \phi_i^*(r) \nabla \phi_i(r) = -\frac{1}{2}\sum_i \phi_i^*(r) \nabla^2 \phi_i(r) + \frac{1}{4} \nabla^2 \rho(r)$$

where $\nabla^2 \rho(r)$ is the Laplacian of the electron density. In addition, in the literature [24–29] there exist two famous approximate forms of KEDs: the Thomas–Fermi formula (derived for the homogeneous electron gas) and the Weizsäcker KED (exact for one-electron and two-electron Hartree-Fock systems), as defined by Eqs. (7) and (8), respectively:

$$\tau_{TF}(r) = 3/5 \left( \frac{6\pi^2}{2^3/3} \right) \rho(r)^{5/3}$$

$$\tau_{W}(r) = \frac{1}{8} \frac{\nabla \rho(r)^2}{\rho(r)}$$

Very recently, based on the early work of Ghosh and Parr[30,31] and inspired by the definition of Fukui function, we proposed to employ the local temperature to appreciate chemical reactivity. For nucleophilic attack, using the local temperature, we define

$$\theta^+(r) = \left( \frac{\partial T(r)}{\partial N} \right)_{\mu(r)}^+ = T_N(r) - T_{N+1}(r)$$

and for electrophilic attack, we define
\[
\theta^-(\mathbf{r}) = \left( \frac{\partial T(\mathbf{r})}{\partial N} \right)_{\mu(\mathbf{r})} = T_{N-1}(\mathbf{r}) - T_N(\mathbf{r}) \quad (10)
\]

where \(T_N, T_{N+1},\) and \(T_{N-1}\) are local temperatures for the system with \(N, N + 1,\) and \(N - 1\) electrons, respectively, in the \(N\) electron (fixed) geometry. Condensed-to-atom local temperatures were also defined. An in-depth discussion and applications of local temperatures can be found in our recent publication.[23] The uniqueness of the descriptor of local temperature is manifold, compared to its predecessor Fukui function. The scope of applications is greatly expanded due to its connection to the information theory. Moreover, the local temperature can be used to explore bonding (through a relevant quantum topology analysis), especially for weakly bonded systems as it is based on the KDE. Similar examples are the well-known electron localization function (ELF)[32,33], as devised to identify the localization of electron pairs, and our recently proposed SCI (strong covalent interaction) index,[34] which can be used to determine multiple bond orders (up to quintuple bond). Suffice to note that CDFT is still an active field with lots of progresses keep emerging.

Next, we will give a brief introduction to ELF and SCI. Earlier, we assumed that the areas forming multiple covalent bonds should experience strong repulsions due to the existence of the Pauli exclusion principle, and proposed the SCI index to identify multiple covalent bonds.[34] The Pauli energy \((E_p)[35]\) is defined as

\[
E_p[\rho(\mathbf{r})] \equiv \int t_p(\mathbf{r})d\mathbf{r} = T_S[\rho(\mathbf{r})] - T_W[\rho(\mathbf{r})] \equiv \int (t_s(\mathbf{r}) - t_w(\mathbf{r}))d\mathbf{r} \quad (11)
\]

\[
T_W[\rho(\mathbf{r})] \equiv \int t_w(\mathbf{r})d\mathbf{r} = \frac{1}{8} \int \frac{[\nabla \rho(\mathbf{r})]^2}{\rho(\mathbf{r})} d\mathbf{r} \quad (12)
\]

with the Weizsäcker kinetic energy \(T_W\) as defined in Eq. (12), \(T_S\) as the total noninteracting kinetic energy, and \(t_s(\mathbf{r})\) and \(t_w(\mathbf{r})\) the corresponding local energy
density. To convert the Pauli energy to a dimensionless quantity, we define a local function \( \zeta(r) \),\(^{[34]} \)

\[
\zeta(r) \equiv \frac{\epsilon_{P}(r)}{\epsilon_{TF}(r)} = \frac{\epsilon_{S}(r) - \epsilon_{W}(r)}{\epsilon_{TF}(r)} \quad (13)
\]

and then the SCI index is defined as the reciprocal of \( \zeta(r) \),\(^{[34]} \)

\[
\text{SCI} = \frac{1}{\zeta(r)} \quad (14)
\]

This index is similar to the ELF (electron localization function) index,\(^{[32,33]} \)

\[
\text{ELF} = \frac{1}{1 + \zeta^2(r)} \quad (15)
\]

We have to mention that the SCI index has its own unique features compared to that of ELF. While ELF was defined to identify localized regions, the SCI index has a clear physical meaning of the Pauli energy contribution. We have also revealed that our SCI results are consistent. For example, a double covalent bond always exhibits a dumbbell signature isosurface, and a donut or torus for a triple covalent bond.\(^{[34]} \)

For systems with complex bond types, one can predict their covalent bond multiplicity based on the signature isosurfaces. More examples about SCI index applications can be found elsewhere.\(^{[36]} \)

### 3. Computational Details

Starting from the equilateral triangle \( \text{H}_3^+ \) and \( \text{Li}_3^+ \),\(^{[37,38]} \) we gradually added one, two, and three noble gas atoms, leading to a total of 26 systems in this work. All quantum chemical calculations (structure optimization, vibrational analysis, etc.) were performed with the Gaussian 16 package\(^{[39]} \) at the B3LYP/aug-cc-pVTZ level\(^{[40–42]} \) of theory with default ultrafine integration grids and tight self-consistent field convergence criteria to rule out numerical noises. Molecular
wavefunctions were fed into the Multiwfn 3.8 program[43] to evaluate the SCI index, ITA quantities, local temperatures, and noncovalent interactions (NCI). To assess aromaticity characteristics of a planar structure, we apply NICS (nucleus independent chemical shift)[44] and GIMIC (gauge-including magnetically induced currents)[45] for this purpose. Our previous studies[46–52] have demonstrated their effectiveness and reliability for other systems. Details of their definitions and applications can be found elsewhere.[53,54] The total energy components were obtained with the keyword of iop(5/33=1).

4. Results and Discussion

We first take a look at the noncovalent interactions (NCI)[55] and strong covalent interactions (SCI)[34] of all systems with [H₃Kr₃]⁺ and [Li₃Kr₃]⁺ as an illustration (Figure 1). In Figures 1a and 1d, one can clearly observe a “spike” region somewhere in the vicinity of zero both for [H₃Kr₃]⁺ and [Li₃Kr₃]⁺, indicative of very weak, attractive van der Waals interactions. But where do they come from? One can see that for H₃Kr₃⁺ (in Figure 1b), the NCI isosurface mainly lies between the H and Kr atoms; for [Li₃Kr₃]⁺ (in Figure 1e), both interatomic Li-Kr and Li-Li interactions are noncovalent in nature. The observation is in line with our previous work of “bare” H₃⁺ and Li₃⁺. Furthermore, in Figures 1c and 1f, no signature of SCI isosurface for double or triple or other bonds is observed, indicating that there is no obvious strong covalent bond.

Next, we will delve into the aromaticity of the H₃⁺ and Li₃⁺ clusters and the corresponding trapped noble gas clusters. It is well-documented in the literature that a negative NICS value indicates the existence of aromaticity. We clearly know that H₃⁺
and Li$_3^+$ structures are aromatic, though Li$_3^+$ is not $\sigma$-aromatic in nature.[56,57]. Does the addition of noble gases change its aromaticity? Collected in Table 1 are the NICS(0), NICS(1) and NICS(1)$_{zz}$ values, which are all negative, indicating that the each trapped cluster is still aromatic after noble gas atoms are added. One can also see that as the atomic radii of noble gases increase, the NICS values simultaneously decrease. For example, the values of NICS(0) are $-33.75, -32.86, -31.74, -22.37$ ppm for H$_3^+$, He$_3$H$_3^+$, Ne$_3$H$_3^+$, Ar$_3$H$_3^+$, and Kr$_3$H$_3^+$, respectively. The similar trend is observed for Li$_3^+$ and its trapped noble gas clusters. In addition, we employ the GIMIC diagrams as shown in Figure 2 to determine aromaticity/anti-aromaticity. It is lucidly shown that all currents run in a counterclockwise manner, which is indicative of aromaticity. It is worthwhile to note that for H$_3^+$ and its trapped noble gas clusters, sparsity of current distributions around the H$_3^+$ local motif is in line with the decreased NICS values as previously mentioned. However, this is not the case with Li$_3^+$. One possible reason is that H$_3^+$ is assembled together because of electron delocalization but for Li$_3^+$ it is weak van der Waals interactions that counts.[56] In a nutshell, addition of noble gas atoms to H$_3^+$ and Li$_3^+$ leads to different aromaticity properties.

We employ the local CDFT descriptors, the Fukui function and the local temperature, to unveil the possible electrophilic and nucleophilic sites of a molecular system. Shown in Figure 3 are the Fukui function and local temperature results for HeH$_3^+$ and HeLi$_3^+$. One can see that the overall trend for the Fukui function and the local temperature is similar. For HeHe$_3^+$ (see Figure 3A), the electrophilic ($\Theta^-/f^-$) and nucleophilic ($\Theta^+/f^+$) sites are located at the He nucleus and the H$_3$ motif, respectively.
However, the trend is reversed for electrophilic (θ+/f-) attacks of HeLi$_3^+$. Moreover, the electrophilic local temperature is more localized than the Fukui function for HeH$_3^+$ as shown in Figure 3B (upper panel). This indicates that the local temperature is a more definitive quantity in determining the reactivity sites of a molecular system. To summarize, though similar in geometry structures, HeH$_3^+$ and HeLi$_3^+$ can have very different chemical reactivity behavior.

We further dissect the molecular stability of all the noble gas trapping clusters by H$_3^+$ and Li$_3^+$. A total of 12 possible chemical reactions for each of them are proposed as shown in Table 2 by gradually adding a noble gas atom. Collected in Table 2 are the total energy difference (ΔE) and its components as well as the enthalpy difference (ΔH). One can see that ΔH is very close to ΔE and thereafter we only concentrate on ΔE. From Table 2, several points can be made accordingly. (i) The total energy difference is negative for all systems indicating that addition of noble gas atoms to the H$_3^+$ and Li$_3^+$ motifs is energetically favorable. (ii) Adding the noble gas atoms to H$_3^+$ is relatively easier than to Li$_3^+$ as evidenced by the total energy difference. (iii) In addition, we find that it becomes much more difficult to add more than one noble gas atoms to H$_3^+$, especially for Ar and Kr. For example, when one adds only one Kr atom to the H$_3^+$ motif, the ΔE is −73.1 kJ/mol. If one more Kr atom is added, the ΔE value becomes −19.8 kJ/mol. However, this is not the case for Li$_3^+$ and the corresponding two energy differences are −15.2 and −13.8 kJ/mol respectively. One possible reason for the discrepancy lies in the bonding patterns in H$_3^+$ and Li$_3^+$.[56] A more stable substrate leads to a more stable complex.
From Table 2, we find that the exchange-correlation ($\Delta E_{xc}$) part is negative, indicative of its positive role in stabilizing the complex. The negative steric hindrance ($\Delta E_s$) is largely compensated by the positive quantum effect ($\Delta E_q$). What is the origin and nature of molecular stability? In other words, is there a single energetic component that is mostly responsible for the molecular stability of these systems? Shown in Figure 4 are the strong correlations between the total energy difference and the exchange-correlation ($\Delta E_{xc}$) and the steric hindrance ($\Delta E_s$), as well as ITA quantities, Shannon entropy ($\Delta S_S$)[58] and Fisher information ($\Delta I_F$)[59], whose values are given in Table 3. In a nutshell, from the viewpoint of energetics, it is the exchange-correlation that is essentially responsible for the total energy difference, which is a good supplement to our previous publications where the electrostatic potential ($\Delta E_e$) dominated. Moreover, from the perspective of information theory, spatial delocalization of the electron density gauged by the Shannon entropy is the origin of the molecular stability of these trapping clusters. This result provides us a novel insight into this complicated phenomenon of molecular stability associated with intermolecular interactions. Similar results have been reported by us for isomeric (intramolecular) stability of fullerene buckyballs.[60]

Finally, we also tabulate some ITA quantities (GBP entropy $S_{GBP}$[30] and information gain $\Delta I_G$[61,62]) in Table 3 and the correlation coefficient ($R$) between the total energy and its components with ITA quantities as shown in Table 4. It is known that ITA and energetic quantities can be strongly intercorrelated.[63–65] These different but strongly correlated relationships provide effective measurements...
about the electron density distribution of the systems; thus, they attribute useful and novel insights into the nature and origin of various physicochemical phenomena, including isomeric stability of fullerenes and trapping noble gas clusters as in this work.

5. Conclusions

To summarize, in this work, we present the results of bonding, aromaticity and reactivity properties for the trapping of noble gas atoms (He–Kr) by the triatomic H$_3^+$ and Li$_3^+$ species from certain theoretical and analytical tools. Though similar in geometrical structure, the trapping noble gas clusters of H$_3^+$ and Li$_3^+$ differ much in bonding, aromaticity, and reactivity properties. The core reason lies in the structural motifs of H$_3^+$ and Li$_3^+$. We further analyzed the origin and nature of the molecular stability in terms of energetics and information theory. We have shown that it is the exchange-correlation interaction and steric effect that are responsible for the total molecular stability. Shannon entropy results corroborate that electron delocalization is the origin of the molecular stability. We mention in passing that more future studies along this direction will help us better appreciate atomic clusters with many unconventional properties and unveil many novel and potential applications.

Declarations

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Code availability: No new code is generated from this work.

Authors’ contributions: P.K.C., C.Y.R., and D.B.Z. conceived and designed the overall project. X.H., C.N.G., M.L., S.J.Z., and X.J.W. carried out the computational studies. X.H., P.K.C., and D.B.Z. analyzed the data and wrote the manuscript with the input of all authors. All authors edited and approved the manuscript.

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Figure 1. Noncovalent interactions (NCI) and strong covalent interactions (SCI) for upper panel \([\text{H}_3\text{Kr}]^+\) and lower panel \([\text{Li}_3\text{Kr}]^+\).
Figure 2. GIMIC distributions of upper panel $H_3^+$ and corresponding trapped noble gas clusters; lower panel $Li_3^+$ and corresponding trapped noble gas clusters from three different views.
Figure 3. Electrophilic ($\Theta^-/f^-$) and nucleophilic ($\Theta^+/f^+$) local temperature and Fukui functions for upper panel (A) HeH$_3^+$ and lower panel (B) HeLi$_3^+$, mapped onto the surface of molecular density with an isovalue of 0.004 au.
Figure 4. Strong correlations between the total energy difference ($\Delta E$) and (a) the exchange-correlation potential ($\Delta E_{xc}$), (b) steric hindrance ($\Delta E_s$), (c) Shannon entropy ($\Delta S_S$), and (d) Fisher information ($\Delta I_F$).
Table 1. NICS(0), NICS(1) and NICS(1)_{zz} values of H$_3^+$ and Li$_3^+$ and corresponding trapped noble gas clusters. Units are in ppm.

| Molecule  | NICS(0) | NICS(1) | NICS(1)$_{zz}$ | Molecule  | NICS(0) | NICS(1) | NICS(1)$_{zz}$ |
|-----------|---------|---------|----------------|-----------|---------|---------|----------------|
| H$_3^+$   | –33.75  | –2.16   | –7.94          | Li$_3^+$  | –11.06  | –6.73   | –7.26          |
| HeH$_3^+$ | –33.34  | –2.09   | –7.56          | HeLi$_3^+$| –10.97  | –6.69   | –7.07          |
| He$_2$H$_3^+$ | –33.05 | –2.04   | –7.26          | He$_2$Li$_3^+$ | –10.89 | –6.65   | –6.88          |
| He$_3$H$_3^+$ | –32.86 | –2.00   | –7.00          | He$_3$Li$_3^+$ | –10.82 | –6.63   | –6.68          |
| NeH$_3^+$ | –32.64  | –2.01   | –7.01          | NeLi$_3^+$ | –11.05  | –6.73   | –7.06          |
| Ne$_2$H$_3^+$ | –32.08 | –1.92   | –6.29          | Ne$_2$Li$_3^+$ | –11.07 | –6.75   | –6.86          |
| Ne$_3$H$_3^+$ | –31.74 | –1.85   | –5.67          | Ne$_3$Li$_3^+$ | –11.08 | –6.77   | –6.65          |
| ArH$_3^+$ | –26.16  | –1.35   | –4.26          | ArLi$_3^+$ | –11.01  | –6.72   | –6.80          |
| Ar$_2$H$_3^+$ | –25.95 | –1.11   | –2.66          | Ar$_2$Li$_3^+$ | –10.97 | –6.72   | –6.34          |
| Ar$_3$H$_3^+$ | –25.75 | –0.98   | –1.41          | Ar$_3$Li$_3^+$ | –10.93 | –6.73   | –5.84          |
| KrH$_3^+$ | –21.47  | –1.01   | –2.70          | KrLi$_3^+$ | –10.98  | –6.71   | –6.63          |
| Kr$_2$H$_3^+$ | –22.31 | –0.60   | –0.43          | Kr$_2$Li$_3^+$ | –10.92 | –6.71   | –6.01          |
| Kr$_3$H$_3^+$ | –22.37 | –0.45   | 1.18           | Kr$_3$Li$_3^+$ | –10.87 | –6.70   | –5.34          |
Table 2. Total energy decomposition analysis for reactions as outlined below. Some plausible reactions that could occur due to the attack of noble gas atoms onto the equilateral triangle H$_3^+$/Li$_3^+$ moiety. Units are in kJ/mol.

| Reactions                              | $\Delta H$ | $\Delta E$ | $\Delta E_e$ | $\Delta E_s$ | $\Delta E_R$ | $\Delta E_{SC}$ | $\Delta T_s$ |
|----------------------------------------|------------|------------|---------------|---------------|---------------|-----------------|--------------|
|                                          |            |            |               |               |               |                 |              |
| H$_3^+$                                 |            |            |               |               |               |                 |              |
| 1 H$_3^+$ + He $\rightarrow$ HeH$_3^+$  | −4.9       | −7.5       | −17.6         | −193.8        | 203.9         | −6.2            | 16.3         |
| 2 HeH$_3^+$ + He $\rightarrow$ He$_2$H$_3^+$ | −4.4       | −6.6       | −11.6         | −169.5        | 174.6         | −4.1            | 9.2          |
| 3 He$_2$H$_3^+$ + He $\rightarrow$ He$_3$H$_3^+$ | −3.9       | −5.9       | −10.8         | −151.3        | 156.1         | −3.8            | 8.7          |
| 4 H$_3^+$ + Ne $\rightarrow$ NeH$_3^+$  | −11.4      | −13.9      | −20.0         | −238.3        | 244.4         | −4.6            | 10.7         |
| 5 NeH$_3^+$ + Ne $\rightarrow$ Ne$_2$H$_3^+$ | −9.2       | −11.4      | −10.6         | −208.0        | 207.2         | −3.6            | 2.9          |
| 6 Ne$_2$H$_3^+$ + Ne $\rightarrow$ Ne$_3$H$_3^+$ | −7.9       | −9.9       | −7.4          | −186.8        | 184.3         | −3.7            | 1.2          |
| 7 H$_3^+$ + Ar $\rightarrow$ ArH$_3^+$  | −48.7      | −48.2      | −39.0         | −349.4        | 340.3         | −16.8           | 7.7          |
| 8 ArH$_3^+$ + Ar $\rightarrow$ Ar$_2$H$_3^+$ | −20.1      | −23.4      | −9.7          | −243.4        | 229.8         | −11.3           | −2.3         |
| 9 Ar$_2$H$_3^+$ + Ar $\rightarrow$ Ar$_3$H$_3^+$ | −16.0      | −18.3      | −3.9          | −199.4        | 185.0         | −9.3            | −5.1         |
| 10 H$_3^+$ + Kr $\rightarrow$ KrH$_3^+$ | −73.1      | −68.6      | 155.3         | −408.6        | 184.8         | −25.1           | −198.7       |
| 11 KrH$_3^+$ + Kr $\rightarrow$ Kr$_2$H$_3^+$ | −19.8      | −24.7      | 132.7         | −309.2        | 151.9         | −10.7           | −146.7       |
| 12 Kr$_2$H$_3^+$ + Kr $\rightarrow$ Kr$_3$H$_3^+$ | −17.2      | −20.1      | 146.6         | −239.3        | 72.6          | −9.2            | −157.5       |
| Li$_3^+$                                |            |            |               |               |               |                 |              |
|                                          |            |            |               |               |               |                 |              |
| 1 Li$_3^+$ + He $\rightarrow$ HeLi$_3^+$ | −1.4       | −2.9       | −12.6         | −101.9        | 111.6         | −4.7            | 14.4         |
| 2 HeLi$_3^+$ + He $\rightarrow$ He$_2$Li$_3^+$ | −1.2       | −2.6       | −11.9         | −98.8         | 108.1         | −4.8            | 14.1         |
| 3 He$_2$Li$_3^+$ + He $\rightarrow$ He$_3$Li$_3^+$ | −1.1       | −2.5       | −12.1         | −93.2         | 102.8         | −4.9            | 14.5         |
| 4 Li$_3^+$ + Ne $\rightarrow$ NeLi$_3^+$  | −5.1       | −6.5       | −9.8          | −161.0        | 164.3         | −4.8            | 8.1          |
| 5 NeLi$_3^+$ + Ne $\rightarrow$ Ne$_2$Li$_3^+$ | −4.7       | −6.1       | −4.2          | −159.4        | 157.5         | −4.7            | 2.8          |
| 6 Ne$_2$Li$_3^+$ + Ne $\rightarrow$ Ne$_3$Li$_3^+$ | −4.5       | −5.9       | −2.7          | −159.0        | 155.8         | −4.8            | 1.7          |
| 7 Li$_3^+$ + Ar $\rightarrow$ ArLi$_3^+$  | −12.1      | −13.5      | −3.1          | −182.8        | 172.4         | −7.7            | −2.8         |
| 8 ArLi$_3^+$ + Ar $\rightarrow$ Ar$_2$Li$_3^+$ | −11.2      | −12.6      | 0.0           | −177.8        | 165.2         | −7.9            | −4.8         |
| 9 Ar$_2$Li$_3^+$ + Ar $\rightarrow$ Ar$_3$Li$_3^+$ | −10.2      | −11.7      | 1.5           | −173.2        | 160.0         | −8.3            | −4.9         |
| 10 Li$_3^+$ + Kr $\rightarrow$ KrLi$_3^+$ | −15.2      | −16.6      | 153.5         | −223.3        | 53.2          | −6.9            | −163.3       |
| 11 KrLi$_3^+$ + Kr $\rightarrow$ Kr$_2$Li$_3^+$ | −13.8      | −15.2      | 177.6         | −228.5        | 35.7          | −6.9            | −185.9       |
| 12 Kr$_2$Li$_3^+$ + Kr $\rightarrow$ Kr$_3$Li$_3^+$ | −12.4      | −13.8      | 184.4         | −224.6        | 26.4          | −7.3            | −191.0       |
Table 3. ITA quantities for chemical reactions in table 2. Atomic unit.

| No. | \( \Delta S \) | \( \Delta I \) | \( \Delta S_{\text{GBP}} \) | \( \Delta I_{\text{G}} \) | No. | \( \Delta S \) | \( \Delta I \) | \( \Delta S_{\text{GBP}} \) | \( \Delta I_{\text{G}} \) |
|-----|----------------|-------------|----------------|-------------|-----|----------------|-------------|----------------|-------------|
| 1   | –0.13          | –0.59       | 0.90           | –0.06       | 1   | –0.10          | –0.31       | 0.92           | –0.06       |
| 2   | –0.10          | –0.52       | 0.90           | –0.05       | 2   | –0.10          | –0.30       | 0.91           | –0.06       |
| 3   | –0.09          | –0.46       | 0.91           | –0.05       | 3   | –0.10          | –0.28       | 0.91           | –0.05       |
| 4   | –0.16          | –0.73       | 3.76           | –0.09       | 4   | –0.11          | –0.49       | 3.80           | –0.09       |
| 5   | –0.13          | –0.63       | 3.75           | –0.07       | 5   | –0.11          | –0.49       | 3.79           | –0.09       |
| 6   | –0.12          | –0.57       | 3.76           | –0.06       | 6   | –0.12          | –0.48       | 3.78           | –0.08       |
| 7   | –0.36          | –1.06       | 5.49           | –0.19       | 7   | –0.17          | –0.56       | 5.45           | –0.13       |
| 8   | –0.22          | –0.74       | 5.37           | –0.07       | 8   | –0.18          | –0.54       | 5.44           | –0.12       |
| 9   | –0.19          | –0.61       | 5.40           | –0.06       | 9   | –0.19          | –0.53       | 5.43           | –0.11       |
| 10  | –0.45          | –1.24       | 9.99           | –0.23       | 10  | –0.19          | –0.68       | 9.89           | –0.15       |
| 11  | –0.25          | –0.94       | 9.77           | –0.06       | 11  | –0.20          | –0.70       | 9.87           | –0.13       |
| 12  | –0.21          | –0.73       | 9.82           | –0.05       | 12  | –0.21          | –0.68       | 9.86           | –0.11       |
Table 4. Correlation matrix (R) between the total energy, its components and the ITA quantities.

|      | $\Delta E$ | $\Delta T_s$ | $\Delta E_e$ | $\Delta E_{xc}$ | $\Delta E_s$ | $\Delta E_q$ | $\Delta S_s$ | $\Delta S_{GBP}$ | $\Delta I_F$ | $\Delta I_G$ | $\Delta H$ |
|------|-------------|---------------|--------------|-----------------|--------------|--------------|--------------|-----------------|--------------|--------------|-----------|
| $\Delta E$ | 1.000       |               |              |                 |              |              |              |                 |              |              |           |
| $\Delta T_s$ | 0.484       | 1.000         |              |                 |              |              |              |                 |              |              |           |
| $\Delta E_e$ | -0.377      | -0.993        | 1.000        |                 |              |              |              |                 |              |              |           |
| $\Delta E_{xc}$ | 0.966       | 0.463         | -0.363       | 1.000           |              |              |              |                 |              |              |           |
| $\Delta E_s$ | 0.925       | 0.575         | -0.480       | 0.842           | 1.000        |              |              |                 |              |              |           |
| $\Delta E_q$ | -0.359      | 0.571         | -0.657       | -0.292          | -0.342       | 1.000        |              |                 |              |              |           |
| $\Delta S_s$ | 0.973       | 0.579         | -0.482       | 0.960           | 0.926        | -0.252       | 1.000        |                 |              |              |           |
| $\Delta S_{GBP}$ | -0.577      | -0.892        | 0.866        | -0.546          | -0.690       | -0.331       | -0.693       | 1.000           |              |              |           |
| $\Delta I_F$ | 0.925       | 0.575         | -0.480       | 0.842           | 1.000        | -0.342       | 0.926        | -0.690          | 1.000        |              |           |
| $\Delta I_G$ | 0.759       | 0.438         | -0.361       | 0.736           | 0.661        | -0.147       | 0.783        | -0.534          | 0.661        | 1.000        |           |
| $\Delta H$ | 0.997       | 0.474         | -0.366       | 0.966           | 0.902        | -0.346       | 0.965        | -0.553          | 0.902        | 0.790        | 1.000     |