SUPPLEMENTARY MATERIALS

3-D bond-paths of QTAIM and the Stress Tensor in Neutral Lithium Clusters, \( \text{Li}_m (m = 2-5) \), Presented on the Ehrenfest Force Molecular Graph

Alireza Azizi, Roya Momen, Steven R. Kirk* and Samantha Jenkins*

Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research and Key Laboratory of Resource National and Local Joint Engineering Laboratory for New Petro-chemical Materials and Fine Utilization of Resources, College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha, Hunan 410081, China

*email: samanthajsuman@gmail.com
*email: steven.kirk@cantab.net

1. Supplementary Materials S1. QTAIM basics and discussion surrounding the Ehrenfest Force \( F(r) \), stress tensor \( \sigma(r) \) and the bond-path framework set \( B = \{p,q,r\} \).

2. Supplementary Materials S2. Computational protocol and numerical evaluation of the Ehrenfest force \( F(r) \) partitioning.

3. Supplementary Materials S3. Poincaré-Hopf solution sets and the results for QTAIM and Ehrenfest Force \( F(r) \) partitioning schemes and plots comparing \( BCP \) and \( NNA \) properties with charged Li clusters.

4. Supplementary Materials S4. The bond-path framework sets for the QTAIM and Ehrenfest partitioning molecular graphs of the \( \text{Li}_m (m = 2-5) \) clusters.

5. Supplementary Materials S5. The variation of ellipticity \( \varepsilon \) profile with distance along Li-\( BCP-NNA-BCP \)-Li separation for the \( \text{Li}_m (m = 2-5) \) clusters.

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7. Supplementary Materials S8. The QTAIM and Ehrenfest Force \( F(r) \) partitioning measures for compressed and stretched molecular graphs of the \( \text{Li}_2 \) cluster.
1. Supplementary Materials S1.

(i) The QTAIM BCP and bond-path properties; BPL, the helicity lengths \( H, H' \) and the bond-path framework set \( B \)

QTAIM that utilizes higher derivatives of \( \rho(r_b) \) in effect, acting as a ‘magnifying lens’ on the \( \rho(r_b) \) derived properties of the wave-function to identify critical points in the total electronic charge density distribution \( \rho(r) \) by analyzing the gradient vector field \( \nabla \rho(r) \). These critical points can further be divided into four types of topologically stable critical points according to the set of ordered eigenvalues \( \lambda_1 < \lambda_2 < \lambda_3 \), with corresponding eigenvectors \( \mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3 \) of the Hessian matrix. The Hessian of the total electronic charge density \( \rho(r) \) is defined as the matrix of partial second derivatives with respect to the spatial coordinates. These critical points are labeled using the notation \((R, \omega)\) where \( R \) is the rank of the Hessian matrix, the number of distinct non-zero eigenvalues and \( \omega \) is the signature (the algebraic sum of the signs of the eigenvalues); the \((3, -3)\) [nuclear critical point (NCP), a local maximum generally corresponding to a nuclear location], \((3, -1)\) and \((3, 1)\) [saddle points, called bond critical points (BCP) and ring critical points (RCP), respectively] and \((3, 3)\) [the cage critical points (CCP)]. In the limit that the forces on the nuclei become vanishingly small, an atomic interaction line [Bader, J. Phys. Chem. A, 1998, 102, 7314–7323] becomes a bond-path, although not necessarily a chemical bond [Bader. J. Phys. Chem. A. 2009, 113, 10391-10396] with the complete set of critical points and the bond-paths of a molecule being referred to as the molecular graph.


\[
H(r_b) = G(r_b) + V(r_b),
\]

where \( G(r_b) \) and \( V(r_b) \) in equation (1) are the local kinetic and potential energy densities at a BCP, defines a degree of covalent character: A negative value for \( H(r_b) < 0 \) for the closed-shell interaction, a value of the Laplacian \( \nabla^2 \rho(r_b) > 0 \), indicates a BCP with a degree of covalent character and conversely a positive value of \( H(r_b) > 0 \) reveals a lack of covalent character for the closed-shell BCP. A shared-shell BCP always possesses both Laplacian \( \nabla^2 \rho(r_b) < 0 \) and \( H(r_b) < 0 \).

The bond-path length (BPL) is defined as the length of the path of the \( \mathbf{e}_3 \) eigenvector of \( \lambda_3 \) eigenvalue, defined at the BCP, of the Hessian of the total charge density \( \rho(r) \) that follows the maximum in \( \rho(r) \). The bond-path curvature separating two bonded nuclei is defined as the dimensionless ratio:

\[
\frac{(BPL - GBL)}{GBL},
\]
Where BPL is as the associated bond-path length and the geometric bond length GBL is the inter-nuclear separation. The BPL often exceeds the GBL particularly for weak or strained bonds and unusual bonding environments. \cite{J. Phys. Condens. Matter, 2000, 12, 10325.} Earlier, one of the current authors hypothesized that a bond-path may possess 1-D, 2-D or a 3-D topology. \cite{Chem. Phys. Lett., 2000, 317, 97–102.} Bond-paths possessing zero and non-zero values of the bond-path curvature defined by equation (11) can be considered to possess 1-D and 2-D topologies respectively. For some systems subject to an applied torsion $\theta$ however, the torsional BCP may display negligible variation in the bond-path curvature defined by equation (11). Therefore, a new measure that is more appropriate for bonds with negligible values of the curvature is required. We choose this quantity to be the length traced out in 3-D by the path swept by the tips of the scaled $e_2$ eigenvectors of the $\lambda_2$ eigenvalue, the scaling factor could be the ellipticity $\varepsilon$.

With $n$ scaled eigenvector $e_2$ tip path points $q_i = r_i + \varepsilon_i e_2$ on the path $q$ where $\varepsilon_i =$ ellipticity at the $i^{th}$ bond-path point $r_i$ on the bond-path $r$. It should be noted that the bond-path is associated with the $\lambda_3$ eigenvalues of the $e_3$ eigenvector does not take into account differences in the $\lambda_1$ and $\lambda_2$ eigenvalues of the $e_1$ and $e_2$ eigenvectors. Analogously, for the $e_1$ tip path points we have $p_i = r_i + \varepsilon_i e_1$ on the path $p$ where $\varepsilon_i =$ ellipticity at the $i^{th}$ bond-path point $r_i$ on the bond-path $r$.

We will refer to the new QTAIM interpretation of the chemical bond as the bond-path framework set that will be denoted by $B$, where $B = \{p, q, r\}$. This effectively means that in the most general case a bond is comprised of three ‘linkages’; $p$, $q$ and $r$ associated with the $e_1$, $e_2$ and $e_3$ eigenvectors, respectively.

The $p$ and $q$ parameters define helicity length $H$ and $H^*$, see Scheme S1:

$$H = \sum_{i=1}^{n-1} |q_{i+1} - q_i|$$

$$H^* = \sum_{i=1}^{n-1} |p_{i+1} - p_i|$$

The helicity length $H$ or $H^*$ refers to the fact that the tips of the scaled $e_2$ or $e_1$ eigenvectors will rotate along the extent of the bond-path, defined by the $e_3$ eigenvector, between the two bonded nuclei that the bond-path connects.

In the limit of vanishing ellipticity $\varepsilon = 0$, for all steps $i$ along the bond-path, one has $H = \text{BPL}$ and $H > \text{BPL}$ otherwise. For a pure BLA coordinate motion comprising bond-paths with negligible curvature the $\{e_1, e_2, e_3\}$ bond-path framework does not undergo a torsional distortion therefore there is no relative change of the $\lambda_1$ and
\(\lambda_2\) eigenvalues for all values of the scaling factor \(\varepsilon_i\). Additionally, because \(H\) and \(H^*\) are defined by the distances swept out by the \(e_2\) tip path points, \(q_1 = r_i + \varepsilon_i e_2\) and \(p_1 = r_i + \varepsilon_i e_4\) respectively, one has \(H = H^*\) provided that identical scaling factor \(\varepsilon_i\) is used in equations (3a) and (3b).

\[\text{(a)}\quad \text{(b)}\quad \text{(c)}\quad \text{(d)}\]

**Scheme S1.** The red line represents the helical path swept out by the tips of the scaled \(e_2\) eigenvectors that we refer to as the helicity length \(H\) that is defined by equation (3a). The two blue arrows represented \(e_2\) eigenvectors scaled by the ellipticity \(\varepsilon\) where the vertical scales are exaggerated for visualization purposes. The green sphere indicates the position of the torsional Li-NNA, NNA-NNA BCPs. The path representing the helicity length \(H^*\) is not shown for clarity, is constructed from the tips of the scaled \(e_1\) eigenvectors that are mutually perpendicular to the \(e_2\) and \(e_3\) eigenvectors, defined by equation (3b).

A bond within QTAIM is defined as being the bond-path traversed by along \(e_3\) eigenvector of the \(\lambda_3\) eigenvector from the bond-path, but, as a consequence of equation (3), this definition should be expanded. The new definition of a bond should consider the bond-path to comprise the two paths swept out by the \(e_2\) and \(e_1\) eigenvectors that form the helicity length \(H\) and \(H^*\), respectively.

**(ii) Ehrenfest Force \(F(r)\), see also the main text**

Consequently \(F(r)\) can be proposed in terms of the molecular Coulomb potential integral equation or in terms of the divergence of the quantum stress tensor. The latter form of \(F(r)\) allows us to map onto a surface integral \(S(r)\) using the Gauss’s theorem as an integration of the force density, over the basin of an atom \(\Omega\):

\[
F(\Omega) = -N \oint_{\Omega} dS(r, \Omega) \cdot \sigma(r)
\]  

Thus \(\sigma(r)\) can be used to determine the force exerted on each element of the atomic surface, \(S(r, \Omega)\), and its product with an element of the surface gives the force acting on this region. [Faraday Discuss, 2006, 135, 79–95.], [Chem. - Eur. J., 2012, 18, 4982–4993.] Consider a tiny cube of fluid flowing in 3-D space the stress \(\Pi(\chi, \lambda, \varepsilon)\)
y, z, t), a rank-3 tensor field, has nine components [Wyatt, R. E. Quantum Dynamics with Trajectories. *Interdiscip. Appl. Math.* xxii,405 (2006).] of these the three diagonal components $\Pi_{xx}$, $\Pi_{yy}$, and $\Pi_{zz}$ correspond to normal stress. A negative value for these normal components signifies a compression of the cube, conversely a positive value refers to pulling or tension, where more negative/positive values correspond to increased compression/tension of the cube. Diagonalization of the stress tensor, $\sigma(r)$, returns the principal electronic stresses $\Pi_{xx}$, $\Pi_{yy}$, and $\Pi_{zz}$ that are realized as the stress tensor eigenvalues $\lambda_{1\sigma}$, $\lambda_{2\sigma}$, $\lambda_{3\sigma}$, with corresponding eigenvectors $e_{1\sigma}$, $e_{2\sigma}$, $e_{3\sigma}$ are calculated within the QTAIM partitioning.

As a comparison with the examination of the gradient of the electron density in the QTAIM theory, a complementary scheme can be proposed from the investigation of the primitive amount of the Ehrenfest Force, the Ehrenfest potential, $F(r)$, using the definition:

$$F(r) = - \nabla V^F(r) \tag{2}$$

Alongside the condition that the potential energy of interaction of an electron at an infinite distance from a molecule is zero:

$$\lim_{|r|\to\infty} V^F(r) = 0 \tag{3}$$

With this definition, $V^F(r)$ is closely related to the average potential defined by Slater. [Phys. Rev., 1951, 81, 385–390.], [Int. J. Quantum Chem., 1997, 62, 47–53.] In this analogy we can follow the trajectories of $F(r)$ that terminate at points where $F(r) = 0$. One can then calculate and observe inter atomic Ehrenfest Force surfaces which satisfy the zero-flux condition $F(r) \cdot \mathbf{n}(r) = 0$. The Ehrenfest Hessian may then also be defined as $\nabla \nabla \cdot \sigma(r)$.

The BCP can be characterized similarly to the critical points (CP) of the electron density distribution in QTAIM as long as at the Ehrenfest BCPs all the force applied on an electron are balanced [J. Chem. Phys., 2009, 130, 154104.] ($F(r) = 0$), i.e. with the notation (3, -1), according to the eigenstructure (eigenvalues/eigenvectors) of the Ehrenfest Hessian.

The advantage of using the Ehrenfest partitioning is to gain physically meaning for a capping surface at a threshold value of $V^F(r)$, that it is the outer boundary of molecule. We can use, for example, the ionization potential $V_1$ to define the molecular boundary using: [Phys. Rev. A, 1991, 44, 7071–7083.]

$$V^F(r) = - V_1 \tag{4}$$

Ionization energy $E_1$, or ionization potential $V_1$, is the minimum amount of necessary energy to remove an electron from the neutral atom that can be determined from experiment. By contrast, within QTAIM the
somewhat arbitrary conventional definition of the molecular boundary uses a threshold of 0.001 a.u. for the electron density.
2. Supplementary Materials S2. Computational protocol and numerical evaluation of the Ehrenfest force $F(r)$ partitioning

The inherent difficulties of the computation of the Ehrenfest force $F(r)$ were examined during a previous investigation by some of the current authors, [Phys. Chem. Chem. Phys., 2013, 15, 17823–17836.] attributing the spurious artifacts to the diffuse GTOs used in basis sets. Research has been undertaken in accurately computing quantum stress tensor properties using Gaussian basis sets. In the work by Tachibana et al., [J. Mol. Struct. THEOCHEM, 2010, 951, 49–59.] they studied the effect of the basis sets expansion on the electronic stress tensor calculations, compared with the exact wave function for the ion H+ 2, showing that the calculations for cc-pV5Z and cc-pV6Z basis sets are in close agreement with the spindle form of the exact wave function. In addition, other authors[J. Chem. Phys., 2012, 137, 134101.] showed the effect of the basis sets on the stress tensor, calculating the profiles of the magnitude of the attractive $F(r)$ for the H and H$_2$ ground states. In this case, the expanded basis set aug-cc-pV5Z provided the best agreement with the exact computation of $F(r)$. It was suggested in 2007 by Hernández-Trujillo and co-workers that spurious artifacts are pushed into the bonding regions upon close-approach of the nuclei [Faraday Discuss., 2007, 135, 79–95.] in the $F(r)$ calculations if GTOs with s and p functions with exponents of order of $10^5$ and $10^3$ were used. This can be contrasted with conventional basis sets such as pV6Z which have exponent values of order $10^3$ and $10^1$ respectively. Following that suggestion we decided to use the extended relativistic Atomic Natural Orbital (ANO-RCC) GTO basis sets developed by Ross and collaborators. [Theor. Chim. Acta, 1990, 77, 291–306.], [Theor. Chem. Acc., 2004, 111, 345–351.], [J. Phys. Chem. A, 2005, 109, 6575–6579.] These basis sets were constructed by averaging over several atomic states, positive and negative ions and atoms in an external electric field, with the key feature that they are highly focused at the nuclei.

(i) Computational protocol

Previously, as a starting point, some of the current authors, decided that the standard cc-pV5Z and cc-pV6Z basis sets cannot be modified by removing the same number of exponents in each GTO. [Phys. Chem. Chem. Phys., 2013, 15, 17823–17836.] This was because in these basis sets the same kind of Gaussian functions have different numbers of exponents, thus an uneven modification of the standard basis sets causes a loss of the functional nature of the basis set. The ANO-RCC basis sets, however, have the same number of exponents in each GTO, allowing us to remove the same number of exponents from each function in the GTO. For each atom the basis sets were rewritten into the form of the standard basis sets (cc-pVXZ(X = D,T,Q)), then only exponents in a specific range for each function were kept and the others removed. This yielded a new kind of
modified ANO RCC basis set where the highly focused functions prevail over diffuse functions. Thus each atom has an *engineered* ANO-RCC basis set: values for the preserved exponents in each basis set can be found in our previous contribution. [*Phys. Chem. Chem. Phys.*, 2013, 15, 17823–17836.] These values were determined by calculation of the $\mathbf{F}(\mathbf{r})$ trajectories for each modified basis set with different ranges of exponents until a well-behaved set of $\mathbf{F}(\mathbf{r})$ (free of spurious features) was obtained.

(ii) Numerical evaluation of the Ehrenfest force $F(r)$ Partitioning Scheme

A convenient start point is the simple system, $\text{H}_2$, which is a highly symmetrical molecule, with an Ehrenfest $\text{BCP}$ halfway between the two hydrogen nuclei. Fig. 1 shows the Ehrenfest force trajectory calculation for the $\text{H}_2$ molecule. In Fig. 1(a) and (b) the aug-$\text{cc}$-pVQZ basis set and the non-modified ANO-RCC basis sets were respectively used. These basis sets contain diffuse functions and despite the fact that in the ANO-RCC the functions are more localized at the nuclei than in the aug-$\text{cc}$-pVQZ, the appearance of spurious features evidenced a strong dependence of the computation of the $\mathbf{F}(\mathbf{r})$ on the presence of diffuse functions in the basis sets. The $\text{cc}$-pVQZ basis set contains 10 GTOs (4s,3p,2d,1f) while ANO-RCC contains 16 GTOs (8s,4p,3d,1f) and although the shape of the $\mathbf{F}(\mathbf{r})$ trajectories is mostly the same, the location of the spurious features changes by 1 a.u., further away from the nuclei. The original aug-$\text{cc}$-pVQZ was not modified and therefore not shown (for details refer to subsection (i)), Fig. 1(c) shows the modified ANO-RCC basis (for the values in the preserved exponents [*Phys. Chem. Chem. Phys.*, 2013, 15, 17823–17836.]). The plot does not contain any spurious surfaces and a monotonic behaviour of the $\mathbf{F}(\mathbf{r})$ is apparent. Considering that higher order derivatives used in the computation of the $\mathbf{F}(\mathbf{r})$ may act to magnify errors in the $\mathbf{F}(\mathbf{r})$ calculation, to ensure a correct calculation, the researcher should be particularly careful with the critical point properties calculated from the optimized geometries.
3. Supplementary Materials S3. Poincaré-Hopf solution sets of the QTAIM and Ehrenfest Force $F(r)$ partitioning schemes and plots comparing $BCP$ and $NNA$ properties with charged Li clusters.

**Table S3(i).** The solution sets of the Poincaré-Hopf relation for the topology results from the QTAIM partitioning scheme using the ANO-RCC basis set, for each value of $m$ the Li$_m$ neutral. The topological complexity $\Sigma_{abrc}$ represents the sum the $BCPs (b)$, $RCPs (r)$ and $CCPs (c)$ and quantum topology is denoted by $D_{QT}$.

<table>
<thead>
<tr>
<th>Li$_m$ ($m = 2$-5)</th>
<th>Multiplicity</th>
<th>$a$</th>
<th>$b$</th>
<th>$r$</th>
<th>$c$</th>
<th>$\Sigma_{abrc}$</th>
<th>$D_{QT}$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Li$_3$</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>Li$_4$ (1)</td>
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<td>2</td>
<td>7</td>
<td>2</td>
<td>0</td>
<td>11</td>
<td>2</td>
</tr>
<tr>
<td>Li$_4$ (2)</td>
<td>1</td>
<td>2</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>7</td>
<td>1</td>
</tr>
<tr>
<td>Li$_5$ (1)</td>
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<td>0</td>
<td>3</td>
<td>0</td>
<td>16</td>
<td>2</td>
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<td>2</td>
<td>8</td>
<td>2</td>
<td>0</td>
<td>12</td>
<td>2</td>
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</table>

**Table S3(ii).** The Poincaré-Hopf topologies from Ehrenfest Force $F(r)$ partitioning scheme, see the caption of **Table S3(i)** for further details.

<table>
<thead>
<tr>
<th>Li$_m$ ($m = 2$-5)</th>
<th>$m$</th>
<th>$a$</th>
<th>$b$</th>
<th>$r$</th>
<th>$c$</th>
<th>$\Sigma_{abrc}$</th>
<th>$D_{QT}$</th>
</tr>
</thead>
<tbody>
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<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Li$_3$</td>
<td>3</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Li$_4$ (1)</td>
<td>4</td>
<td>0</td>
<td>5</td>
<td>2</td>
<td>0</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
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<td>0</td>
<td>4</td>
<td>1</td>
<td>0</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>Li$_5$ (1)$^a$</td>
<td>5</td>
<td>0</td>
<td>7</td>
<td>3</td>
<td>0</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>Li$_5$ (2)</td>
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<td>0</td>
<td>6</td>
<td>2</td>
<td>0</td>
<td>8</td>
<td>2</td>
</tr>
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</table>

$^a$ modified ANO-RCC basis set.
Table S3(iii). The QTAIM partitioning scheme BCP and NNA measures where the subscripts ‘\(b\)’ and ‘\(a\)’ refer to the BCP and NNA respectively, for the molecular graphs of the Li\(_m\) (\(m = 2-5\)) clusters. The Li-NNA BCP, NNA-NNA BCP and NNA-BCP distance refer to separations, Laplacian \(\nabla^2 \rho(r_a)\) and \(\rho(r_a)\) of the NNA, the Li-NNA BCP, Laplacian \(\nabla^2 \rho(r_b)\), \(\rho(r_b)\), total local energy density \(H(r_b)\), metallicity \(\xi(r_b)\), ellipticity \(\varepsilon\) are presented, atomic units are used, refer to the left panels of Figures 1 for the corresponding molecular graphs.

<table>
<thead>
<tr>
<th>(\text{Li}_m)</th>
<th>(\text{BCP})</th>
<th>(\text{Li}-\text{NNA, NNA-NNA})</th>
<th>(\text{NNA-BCP})</th>
<th>(\nabla^2 \rho(r_a))</th>
<th>(\rho(r_a))</th>
<th>(\nabla^2 \rho(r_b))</th>
<th>(H(r_b))</th>
<th>(\xi(r_b))</th>
<th>(\varepsilon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(_2)</td>
<td>Li1-NNA(_4)</td>
<td>2.5518</td>
<td>0.7273</td>
<td>0.0142</td>
<td>-0.0134</td>
<td>0.0135</td>
<td>0.0039</td>
<td>-0.0024</td>
<td>3.4523</td>
</tr>
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<td>Li(_2)</td>
<td>Li2-NNA(_3)</td>
<td>2.5518</td>
<td>0.7273</td>
<td>0.0142</td>
<td>-0.0134</td>
<td>0.0135</td>
<td>0.0039</td>
<td>-0.0024</td>
<td>3.4523</td>
</tr>
<tr>
<td>Li(_3)</td>
<td>Li1-NNA(_4)</td>
<td>2.6233</td>
<td>0.7554</td>
<td>0.0134</td>
<td>-0.0080</td>
<td>0.0123</td>
<td>0.0058</td>
<td>-0.0018</td>
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</tr>
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<td>Li2-NNA(_4)</td>
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<td>1.7056</td>
<td>0.0134</td>
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<td>0.0058</td>
<td>-0.0018</td>
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<tr>
<td>Li(_3)</td>
<td>Li3-NNA(_4)</td>
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<td>0.0123</td>
<td>0.0058</td>
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<td>Li1-NNA(_5)</td>
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<td>0.8841</td>
<td>0.0143</td>
<td>-0.0099</td>
<td>0.0135</td>
<td>0.0058</td>
<td>-0.0019</td>
<td>2.3284</td>
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<tr>
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<td>Li2-NNA(_5)</td>
<td>3.4458</td>
<td>1.5870</td>
<td>0.0143</td>
<td>-0.0099</td>
<td>0.0123</td>
<td>0.0064</td>
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<td>-0.0019</td>
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<td>Li1-NNA(_6)</td>
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<td>0.0111</td>
<td>0.0065</td>
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<td>Li2-NNA(_6)</td>
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<td>-0.0095</td>
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<td>0.0065</td>
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<td>Li(_5)(2)</td>
<td>Li1-NNA(_6)</td>
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<td>Li2-NNA(_6)</td>
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<td>0.9577</td>
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<td>-0.0017</td>
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10
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Table S3(iv). The results for Ehrenfest Force $F(r)$ partitioning molecular graph of the Li$_m$ ($m = 2$-5) clusters, where the bonded Li NCP- Li NCP separations, $\nabla^2 \rho(r_{Fb})$, $\rho(r_{Fb})$, $H(r_{Fb})$, $\xi(r_{Fb})$, two choices of the Ehrenfest Force $F(r)$ ellipticity $\varepsilon_{F} = (|\lambda_{1F}|/|\lambda_{2F}|) - 1$ and Ehrenfest ellipticity $\varepsilon_{Fb} = (|\lambda_{2F}|/|\lambda_{1F}|) - 1$ are presented, refer to the main text and the right panels of Figures 1 for the corresponding molecular graphs. The QTAIM ellipticity $\varepsilon = (|\lambda_{1}|/|\lambda_{2}|) - 1$, stress tensor ellipticities $\varepsilon_{\sigma} = (|\lambda_{2\sigma}|/|\lambda_{1\sigma}|) - 1$ and $\varepsilon_{\sigma H} = (|\lambda_{1\sigma}|/|\lambda_{2\sigma}|) - 1$ are calculated on the Ehrenfest Force $F(r)$ molecular graph, where the subscript “$H$” refers to the ordering of the eigenvalues that corresponds to the Hessian.

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<th>Li-Li</th>
<th>$\rho(r_{Fb})$</th>
<th>$\nabla^2 \rho(r_{Fb})$</th>
<th>$H(r_{Fb})$</th>
<th>$\xi(r_{Fb})$</th>
<th>$\varepsilon$</th>
<th>$\varepsilon_{\sigma}$</th>
<th>$\varepsilon_{\sigma H}$</th>
<th>$\varepsilon_{FA}$</th>
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$^a$ modified ANO-RCC basis set.
Table S3(v). The eigenvector following path lengths \((H, H'),\) \((H_{01}, H_{01}'),\) \((H_{01}H_{01}'\), \((H_{FA}, H_{FA}'),\) \((H_{FB}, H_{FB}'),\) obtained by projecting eigenvectors onto the Ehrenfest Force \(F(r)\) molecular graph. Note, \(\varepsilon_{FA} = (|\lambda_{1F}|/|\lambda_{2F}|) - 1\) and \(\varepsilon_{FB} = (|\lambda_{2F}|/|\lambda_{1F}|) - 1.\)

<table>
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<th>(Li_m)</th>
<th>(BCP)</th>
<th>((H, H'))</th>
<th>((H_{01}, H_{01}'))</th>
<th>((H_{01}H_{01}')</th>
<th>((H_{FA}, H_{FA}'))</th>
<th>((H_{FB}, H_{FB}'),)</th>
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<td>Li1-Li2</td>
<td>(5603, 5597) (5601, 5598) (9.922, 10.02) (9.978, 10.01) (10.25, 10.14) (10.26, 10.21) (10.28, 10.40) (10.30, 10.37) (9.983, 9.925) (9.969, 9.939)</td>
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<tr>
<td>(Li_4) (1)</td>
<td>Li1-Li2</td>
<td>(10.93, 10.93) (10.98, 10.89) (11.27, 11.89) (12.08, 12.14) (15.32, 14.41) (15.40, 15.32) (10.87, 10.99) (10.94, 10.92) (10.86, 10.77) (10.81, 10.83)</td>
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<td>(Li_5) (1)</td>
<td>Li1-Li2</td>
<td>(10.67, 10.67) (10.65, 10.68) (11.48, 11.38) (11.95, 11.98) (14.50, 14.64) (15.08, 15.04) (10.62, 10.62) (10.62, 10.62) (10.61, 10.62) (10.61, 10.62)</td>
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<td>(Li_5) (2)</td>
<td>Li1-Li2</td>
<td>(10.21, 10.21) (10.23, 10.19) (10.96, 10.95) (11.50, 11.47) (14.73, 14.75) (15.19, 15.24) (10.54, 10.83) (10.66, 10.70) (10.36, 10.21) (10.29, 10.28)</td>
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**Li2**

- \( Li_1 - Li_2 \)
- \( Li_3 - Li_2 \)
- \( Li_4 - Li_3 \)
- \( Li_5 - Li_4 \)

**Li3**

- \( Li_1 - Li_3 \)
- \( Li_2 - Li_3 \)
- \( Li_3 - Li_4 \)

**Li4 (1)**

- \( Li_1 - Li_2 \)
- \( Li_2 - Li_2 \)
- \( Li_3 - Li_3 \)

**Li4 (2)**

- \( Li_1 - Li_3 \)
- \( Li_2 - Li_3 \)
- \( Li_3 - Li_4 \)

**Li5 (1)**

- \( Li_1 - Li_2 \)
- \( Li_2 - Li_2 \)
- \( Li_3 - Li_3 \)

**Li5 (2)**

- \( Li_1 - Li_3 \)
- \( Li_2 - Li_3 \)
- \( Li_3 - Li_3 \)
Table S3(vi). The QTAIM partitioning scheme BCP and NNA measures where the subscripts ‘b’ and ‘a’ refer to the BCP and NNA respectively, for the molecular graphs of the Li$_m$ (m = 2-5, q = ±1) clusters. The Li-NNA BCP, NNA-NNA BCP and NNA-BCP distance refer to separations, the Laplacian $\nabla^2 \rho(r)$ and $\rho(r)$ of the NNA, the Li-NNA BCP Laplacian $\nabla^2 \rho(r)$, $\rho(r)$, total local energy density $H(r)$, metallicity $\xi(r)$, ellipticity $\varepsilon$ are presented, atomic units are used.

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<th>Li-NNA, NNA-NNA NNA-BCP</th>
<th>$\rho(r)$</th>
<th>$\nabla^2 \rho(r)$</th>
<th>$\rho(r)$</th>
<th>$\nabla^2 \rho(r)$</th>
<th>$H(r)$</th>
<th>$\xi(r)$</th>
<th>$\varepsilon$</th>
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The linear fit between the Li-NNA BCP separation and NNA-BCP distance, with slope = 0.964, intercept = 1.901 a.u., and correlation = 0.968 is presented in sub-figure (a). The variation of the total electronic charge density difference $\rho(r_a) - \rho(r_b)$ of an NNA and neighboring bonded BCP and NNA-BCP distance for the Li$_m^q$ ($m = 2-5$, $q = 0, \pm 1$) clusters is presented in sub-figure (b), all units correspond to a.u., refer to Table S3(iv) of the main text.

Figure S4(i). The QTAIM bond-path framework sets $B = \{q, q', r\}$, $B_\sigma = \{q_\sigma, q_\sigma', r\}$ and $B_{\sigma \mathrm{H}} = \{q_{\sigma \mathrm{H}}, q_{\sigma \mathrm{H}}', r\}$ paths for the Li$_m$ ($m = 2-5$) are presented in the left, middle and right panels in sub-figures (a-f) respectively. See caption of Figure 1 for further details.
Figure S4(ii). The QTAIM bond-path framework sets $B = \{p, p', r\}$, $B_\sigma = \{p_\sigma, p_\sigma', r\}$ and $B_{\sigma \text{alt}} = \{p_{\sigma \text{alt}}, p_{\sigma \text{alt}}', r\}$ paths for the Li$_m$ ($m = 2-5$) are presented in the left, middle and right panels in sub-figures (a-f) respectively. See caption of Figure 1 for further details.
Figure S4(iii). The QTAIM bond-path framework sets $B = \{p,q,r\}$, $B_\sigma = \{p_\sigma,q_\sigma,r_\sigma\}$ and $B_{\sigma\textit{H}} = \{p_{\sigma\textit{H}},q_{\sigma\textit{H}},r_{\sigma\textit{H}}\}$ paths for the $\text{Li}_m$ ($m = 2-5$) are presented in the left, middle and right panels in sub-figures (a-f) respectively. See caption of Figure 1 for further details.
Figure S4(iv). The Ehrenfest bond-path framework sets $B = \{p, p', r\}$, $B_\sigma = \{p_\sigma, p_\sigma', r\}$, $B_{\sigma\text{H}} = \{p_{\sigma\text{H}}, p_{\sigma\text{H}}', r\}$, $B_{Fa} = \{p_{Fa}, p_{Fa}', r\}$ and $B_{Fb} = \{p_{Fb}, p_{Fb}', r\}$ paths for the Li$_m$ ($m = 2$-5) are presented from left to right panels in sub-figures (a-f) respectively. The filter path with range 0.6 is applied to $B_{Fa}$ and $B_{Fb}$. See the caption of Figure 1 of the main text for further details.
Figure S4(v). The Ehrenfest bond-path framework sets $B = \{p,q,r\}$, $B_\sigma = \{p_\sigma,q_\sigma,r_\sigma\}$, $B_{\sigma H} = \{p_{\sigma H},q_{\sigma H},r_{\sigma H}\}$, $B_{Fa} = \{p_{Fa},q_{Fa},r\}$ and $B_{Fb} = \{p_{Fb},q_{Fb},r\}$ paths for the $\text{Li}_m \ (m = 2-5)$ are presented from left to right panels in sub-figures (a-f) respectively. Filter path range 0.6 is applied on $B_{Fa}$ and $B_{Fb}$ See caption of Figure 1 for further details.
5. Supplementary Materials S5.

Figure S5(i). The variation of ellipticity $\varepsilon$ profile with distance along the Li-BCP-NNA-BCP-Li separation in a.u. for Li$_m$ ($m = 3-5$) clusters are presented on the QTAIM molecular graphs in sub-figures (a-e) respectively, see the caption of Figure 2 of the main text for further information.
Figure S5(ii). The variation of the stress tensor ellipticity $\varepsilon_{\text{eff}}$ profile with distance along the Li-BCP-NNA-BCP-Li separation in a.u. Li$_m$ ($m = 2-5$) clusters are presented on the QTAIM molecular graphs in sub-figures (a-f) respectively, see caption of Figure 2 of the main text for further information.
Figure S6(i). The variation of ellipticity \( \varepsilon = (|\lambda_1|/|\lambda_2|) - 1 \) with distance along the Li-Li separation in a.u. for \( \text{Li}_m (m = 3-5) \) are presented on the Ehrenfest Force \( \mathbf{F}(\mathbf{r}) \) molecular graphs in sub-figures (a-e) respectively. BCP is located at a distance = 0.0 a.u.
Figure S6(ii). The variation of stress tensor ellipticity $\varepsilon_\sigma = (|\lambda_2|/|\lambda_1|) - 1$ with distance along the Li-Li separation in a.u. for $Li_m$ ($m = 2-5$) are presented on the Ehrenfest Force $\mathbf{F}(\mathbf{r})$ molecular graphs in sub-figures (a-f) respectively. See caption of Figure S6(i) for further details.
Figure S6(iii). The variation of stress tensor hessian ellipticity $\varepsilon_{\text{st}} = (|\lambda_1|/|\lambda_2|) - 1$ with distance along the Li-Li separation in a.u. for Li$_m$ ($m = 2$-5) are presented on the Ehrenfest Force $F(r)$ molecular graphs in sub-figures (a-f) respectively. See caption of Figure S6(i) for further details.
Figure S6(iv). The variation of ellipticity $\varepsilon_{FB} = (|\lambda_2|/|\lambda_1|) - 1$ with distance along the Li-Li separation in a.u. for $\text{Li}_m$ ($m = 3-5$) are presented on the Ehrenfest Force $F(r)$ molecular graphs in sub-figures (a-e) respectively. See caption of Figure S6(i) for further details.
7. Supplementary Materials S7.
Figure S7(i). The QTAIM trajectory maps are superimposed onto the corresponding molecular graphs for Li₂. The purple spheres represent the lithium nuclear critical points (NCPs), the brown and green represent QTAIM non–nuclear attractors (NNAs) and bond critical points (BCPs) respectively. Figures (a-l) are corresponding to Table 1.
Figure S7(ii). The Ehrenfest Force $\mathbf{F}(r)$ trajectory maps are superimposed onto the corresponding molecular graphs for Li$_2$. The purple and green spheres represent the lithium nuclear critical points (NCPs) and bond critical points (BCPs) respectively. Figures (a-l) are corresponding to Table 2.