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Mechanochemistry of Degree Two

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We simplify some proposed formulas for hydrostatic pressure on a molecule by G. Subramanian, N. Mathew and J. Leiding, J. Chem. Phys. **143**, 134109 (2015). We apply the formulas to an artificial triatom ABC whose potential energy surface is formed by a combination of Morse curves. **Keywords:** mechanochemistry, isotropic hydrostatic pressure, shock wave, barrier breakdown point, Newton trajectory

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I. INTRODUCTION

The effect of any external force on some atoms of a molecule, wether constant or spatially varying, changes the potential energy surface (PES). Mechanochemistry [1, 2] is concerned with the use of mechanical forces to modify the PES of a system. In particular, the application of pressure is a fascinating method for triggering chemical reactions [3–7]. It modifies the reaction pathways and rates [8]. Usual one studies the effective 'linear' mechanochemical potential

$$V_F(\mathbf{w}) = V(\mathbf{w}) - F \mathbf{l} \cdot \mathbf{w} \tag{1}$$

¹⁹ where V(.) is the PES or the free energy surface of a molecule [9], \mathbf{w} is the coordinate vector usually expressed 20 $_{21}$ in a Cartesian system [10–14] for an N-atomic molecule. ²² w has N x-components w_{3i+1} with i = 0, ..., N-1, it has ²³ N y-components w_{3i+2} with i = 0, ..., N - 1, and it has ²⁴ N z-components w_{3i+3} with i = 0, ..., N - 1. Vector **l** is 25 the normalized direction of an external force vector acting on the molecule, and F is the magnitude of the force. 26 $_{27}$ l · w is the scalar product. The approach (1) is the sim-²⁸ plest possible method with a linear external force. The ²⁹ solution curves for the motion of the stationary points ³⁰ are Newton trajectories (NT) [15–17]. In most studies in the literature, it is assumed for simplicity that the exter-31 nal force acting on the atoms is constant, as in Eq.(1). 32 ³³ However, this is not always the case. When pressure is ³⁴ exerted, it is usually isotropic, and a selected direction, l, cannot be prescribed. 35

Pressure-initiated structural transitions of proteins
³⁷ have been reported [4, 5] in biochemistry. A large number
³⁸ of other physicochemical effects can be realized at high
³⁹ pressures. Shock waves are ultrafast nonequilibrium pro⁴⁰ cesses [18, 19]. They can play an important role in the
⁴¹ ignition of explosives [20, 21].

Here we simplify some known formulas for an approach
of hydrostatic pressure, and apply they to an artifical triatomic molecule. In Section II we report the formulas to
mechanochemistry of degree two. The application on a
triatom ABC is given in Section III, where Section IV
gives a short report of an application on the MislowEvans rearrangement. Section V reverses the view to
shock waves for the triatomic ABC with an assumption
of an inversion of the pressure after the shock. Finally
we discuss and conclude the paper.

II. A SIMPLE FORMULA FOR HYDROSTATIC PRESSURE

This work uses a development of articles [22–24]. Here we try to simplify the proposed formulas. The general approach for an effective potential, V_F , under external for ce is [22]

$$V_F(\mathbf{w}) = V(\mathbf{w}) - V_{ex}(\mathbf{w}) .$$
⁽²⁾

⁵⁸ We use the geometric centroid of the molecule, **c**. It is a ⁵⁹ point in 3D space with the three components

$$\mathbf{c} = (c_1, c_2, c_3) = \frac{1}{N} \sum_{i=0}^{N-1} (w_{3i+1}, w_{3i+2}, w_{3i+3}) .$$
(3)

 $_{\rm 60}$ So every component is the sum of N j-components of the $_{\rm 61}$ N atoms

$$c_j = \frac{1}{N} \sum_{i=0}^{N-1} w_{3i+j}, \quad j = 1, 2, 3.$$
 (4)

⁶² Now we restrict ourselves to a harmonic external poten-⁶³ tial, the 'hydrostatic' pressure [22–26]

$$V_F(\mathbf{w}) = V(\mathbf{w}) + \frac{F}{2} \sum_{j=1}^{3} \sum_{i=0}^{N} (w_{3i+j} - c_j)^2 \qquad (5)$$

⁶⁴ F is the 'pseudo-hydrostatic pressure' with units of ⁶⁵ kcal mol⁻¹ Å⁻². Positive values of F correspond to com-⁶⁶ pression. The harmonic ansatz acts differently on atoms

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72 ⁷⁴ mental small molecules acts differently. For this 'gas ¹¹⁰ example the N-th atom by ⁷⁵ method' the dynamics is made of two subsystems. One is the molecule under study. The other is a fictitious 76 77 ideal gas which exerts on the given molecule the desired pressure, see [30, 31] and references therein. 78

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The stationary points of the PES move under the ac- 112 become sufficiently trivial 80 ^{\$1} tion of the force. Their displacement emerges when the $_{82}$ effective gradient is zero. For example for x-components ⁸³ of the 3D configuration space we have

$$V_F(\mathbf{x}) = V(\mathbf{x}) + \frac{F}{2} \sum_{i=0}^{N-1} \left[w_{3i+1} - \frac{1}{N} \sum_{k=0}^{N-1} (w_{3k+1}) \right]^2$$
(6)

84 thus

$$\frac{\partial}{\partial x_k} V(\mathbf{x}) + F \sum_{i=0}^{N-1} (w_{3i+1} - c_x) (\delta_k^{3i+1} - \frac{1}{N}) = 0 \quad (7)$$

s for k = 1, 4, ..., 3N-2. δ_k^j is 1 for k = j and zero for $k \neq j$. ⁸⁶ If we add up all j, then the summand with $\delta_k^{3j+1} = 1$ ⁸⁸ the singular matrix

$$\mathbf{P} = \frac{1}{N} \begin{bmatrix} (N-1) & -1 & -1 & \dots & -1 \\ -1 & (N-1) & -1 & \dots & -1 \\ \dots & & & \\ -1 & -1 & \dots & -1 & (N-1) \end{bmatrix}$$
(8)

⁸⁹ and the effective gradient is

$$\frac{\partial}{\partial \mathbf{x}} V(\mathbf{x}, \mathbf{y}, \mathbf{z}) + F \mathbf{P} \mathbf{x} .$$
(9)

 $_{90}$ P is a stress tensor for a molecule under pseudo-⁹¹ hydrostatic pressure. Analogous relations apply to the $_{92}$ y- and z components of the molecule in the type

$$\frac{\partial}{\partial \mathbf{y}} V(\mathbf{x}, \mathbf{y}, \mathbf{z}) + F \mathbf{P} \mathbf{y} = \mathbf{0} , \ \frac{\partial}{\partial \mathbf{z}} V(\mathbf{x}, \mathbf{y}, \mathbf{z}) + F \mathbf{P} \mathbf{z} = \mathbf{0} .$$
(10)

⁹³ With respect to the external force, the 3N coordinates ⁹⁴ of the 3D configuration space are separable. Therefor, ¹⁴² And again analogous relations hold for y- and z-parts of ⁹⁵ the gradient of the original PES is modified by a linear ¹⁴³ the Hessian, but mixed parts are the usual ones. ⁹⁶ coordinate part, in each line. For F = 0 we naturally 97 obtain the original stationary points. Starting from ⁹⁸ such stationary points, we can increase the parameter $_{99}$ F and obtain the movement of the stationary point for 100 the effective PES by solving the nonlinear system of 145 $_{101}$ equations (9,10). 102

To calculate the stationary points, we have to consider ⁶⁶ Fig.10 of reference [23] for a triatomic molecule, and in ¹⁰⁴ the total degrees of freedom (DoF) of the molecule. In ⁶⁹ reference [27]. The name pseudo-hydrostatic pressure is ¹⁰⁵ the 3D configuration space, these are 6 DoF, three for the coined for the ansatz with the centroid in Eq.(5) which 106 overall motion of the molecule and three for a rotation. acts differently on corresponding parts of the molecule. 107 Here we propose to fix the centroid c at the origin, and Note that approach (5) is different from the sliding ¹⁰⁸ fix three additional DoFs to suppress the overall rotation. ⁷³ shear stress [28, 29]. Also the use of a bulk of environ-¹⁰⁹ Then we can express one of the atoms by the others; for

$$(x_N, y_N, z_N) = -\sum_{i=0}^{N-2} (w_{3i+1}, w_{3i+2}, w_{3i+3}) .$$
(11)

111 If we place the centroid into the origin then Eqs.(6,7)

$$\frac{\partial}{\partial \mathbf{x}} V(\mathbf{x}, \mathbf{y}, \mathbf{z}) + F \mathbf{I} \mathbf{x} = \mathbf{0}$$
(12)

113 with the $(N-1) \times (N-1)$ unit matrix I for the remain-¹¹⁴ ing (N-1) **x** coordinates; the last line for x_N is missing. ¹¹⁵ Analogous equations apply for the **y**- and **z**-parts. The ¹¹⁶ result (12) is also obtained if we replace the last column ¹¹⁷ and the last line of \mathbf{P} with the centroid Eq.(11). Be- $_{118}$ cause the centroid **c** is localized at zero, the coordinates ¹¹⁹ (**x**,**y**,**z**) are really in direction of the force, V_{ex} , in the case ¹²⁰ of Eq.(3). Thus, Eqs.(12) for \mathbf{x} and analogous equations ¹²¹ for \mathbf{v} and \mathbf{z} depict the natural directions for the action of $_{122}$ the hydrostatic pressure. Eqs.(12), together with the y- $_{123}$ and **z**-parts, means that on the pathway of the moving ¹²⁴ stationary points on the original PES, $V(\mathbf{w})$, the gra- $_{87}$ remains. It can be written in the following form using $_{125}$ dient is equal to F w. The gradient points in direction $_{126}$ w, and its magnitude is |Fw|. In contrast, in the case $_{127}$ of a linear force, Eq.(1), the gradient must point in the 128 constant direction, l, with the magnitude F. For every $_{129}$ direction, l, there exists a separate NT, and all these ¹³⁰ NTs connect stationary points with an index difference ¹³¹ of one [32–34]. We also assume that a curve of stationary $_{132}$ points of V_F under force connects some original station-¹³³ ary points of the original PES, as shown in the example 134 below. The calculation of moving stationary points under ¹³⁵ hydrostatic pressure can be performed using the method ¹³⁶ of enforced geometry optimization (EGO), or along con-137 strained geometry optimization (CGO) [35, 36]. Here in this approach the general optimization is to replace by Eqs.(9) and (10). 139

With Eq.(12) we obtain the x-part of the Hessian of 140 ¹⁴¹ the hydrostatic pressure approach using

$$H(\mathbf{x}) = \frac{\partial^2}{\partial \mathbf{x}^2} V(\mathbf{x}, \mathbf{y}, \mathbf{z}) + F \mathbf{I} .$$
 (13)

III. EXAMPLE: A TRIATOMIC MOLECULE

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We treat a non-linear triatomic molecule ABC with ¹⁴⁶ three Morse potentials between the three atoms. The $_{147}$ atoms can be located in the (x, y) plane. With



3.8 3.6 r 3

FIG. 1. Level lines of the PES sections for the triatomic molecule. Distances r_i are in Å. The full 3D PES in 4D space is not representable. The missing dimension in each panel is fixed at the equilibrium value of the corresponding missing r_i .

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$$r_1(x_1, y_1, x_2, y_2) = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2},$$

$$r_2(x_1, y_1, x_3, y_3) = \sqrt{(x_1 - x_3)^2 + (y_1 - y_3)^2},$$

$$r_3(x_2, y_2, x_3, y_3) = \sqrt{(x_2 - x_3)^2 + (y_2 - y_3)^2}$$
(14)

149 we define

$$p_n(r_n) = D_n(1 + e^{-2\alpha_n(r_n - \sigma_n)} - 2e^{-\alpha_n(r_n - \sigma_n)})$$
. (15)

¹⁵⁰ Parameters for the three different bonds are

¹⁵¹ $D_1 = 4, \ \alpha_1 = 7.5, \sigma_1 = 2,$ ¹⁵² $D_2 = 6$, $\alpha_2 = 4.5, \sigma_2 = 3$, and 153 $D_3 = 4, \ \alpha_3 = 1.5, \sigma_3 = 2.5.$

¹⁵⁴ D_n is the dissociation energy of the bond in kcal mol⁻¹, 155 α_n is the inverse width of the potential in 1/A, and σ_n is ¹⁵⁶ the equilibrium distance of the corresponding bond in Å. 157 The potentials are defined so that three different bond ¹⁵⁸ strength are obtained, as well as different dissociation 159 hights. To summarize, we set

$$V(x_1, y_1, x_2, y_2, x_3, y_3) = p_1(r_1(x_1, y_1, x_2, y_2)) + p_2(r_2(x_1, y_1, x_3, y_3)) + p_3(r_3(x_2, y_2, x_3, y_3)) . (16)$$

¹⁶⁰ Three 2D sections of the PES are shown in Fig.1. It can ¹⁶¹ be seen that the bond r_3 is the weekest, but the bond r_2 ¹⁶² is the strongest. The ground state is the triatomic state 163 with A=(-1.48.0), B=(0.18,-1.12), C=(1.3,1.12), com-¹⁶⁴ pare the blue triangle in Fig.2 with the correct distances 165 $r_1 = 2, r_2 = 3, r_3 = 2.5$. Note that we have set $y_1 = 0$ 192 and $(c_x, c_y) = (0, 0)$ to exclude the overall DoF.

The three remaining gradient components of interest

$$g_1(\mathbf{x}, \mathbf{y}) = \frac{\partial}{\partial x_1} V(\mathbf{x}, \mathbf{y}) , \ g_3(\mathbf{x}, \mathbf{y}) = \frac{\partial}{\partial x_2} V(\mathbf{x}, \mathbf{y}) ,$$
$$g_4(\mathbf{x}, \mathbf{y}) = \frac{\partial}{\partial y_2} V(\mathbf{x}, \mathbf{y}) .$$
(17)

¹⁶⁹ With centroid **c=0** and atom A on the x-axis, it is $y_1 = 0$ 170 and $(x_3, y_3) = -(x_1, 0) - (x_2, y_2)$. The matrix **P** reduces to a 2×2 unit matrix for the **x** coordinates, but it is an $_{172}$ 1×1-'matrix' with the value 1 for the single remaining y_2 ¹⁷³ coordinate. For the remaining 3 coordinates we need to $_{174}$ solve 3 non-linear equations corresponding to Eqs.(9,10). 175 Note that the other coordinates are to replace in the gra-176 dient formulas.

$$g_1(x_1, 0, x_2, y_2, -x_1 - x_2, -y_2) + F x_1 = 0$$

$$g_3(x_1, 0, x_2, y_2, -x_1 - x_2, -y_2) + F x_2 = 0$$

$$g_4(x_1, 0, x_2, y_2, -x_1 - x_2, -y_2) + F y_2 = 0$$
 (18)

177 The partial derivatives of the gradients have to refer to 178 the variables in the definition (16), and the substitution ¹⁷⁹ of (x_3, y_3) is performed after the derivation. In Fig.2 we 180 report the effect of pressures F = 10 and F = 50 kcal $_{181}$ mol⁻¹ Å⁻². The blue triatom is the ground state, but ¹⁸² orange is the slightly suppresed form. The green triatom 183 is under F = 50 kcal mol⁻¹ Å⁻² pressure. The weekest 184 bond between atoms B and C is the most strongly short-185 ened. Note that the pressure of the additional paraboloid $_{186}$ in Eq.(3) pushes all atoms together which means that 187 the steep side of the Morse potentials is involved when 188 Eqs.(18) are solved. So all three bonds become shorter, 189 but one needs strong forces for an action. So to say, ¹⁹⁰ the pressure-volume curve of the molecule goes in the ¹⁹¹ expected direction [37, 38].



FIG. 2. Mechanical pressure on a triatomic molecule. Atom A is fixed on the x-axis. Blue is the force-free minimum, orange is under $F = 10 \text{ kcal mol}^{-1} \text{ Å}^{-2}$, but green under F = 50kcal mol⁻¹ Å⁻². Coordinates are given in Å. The centroid, **c**, is allways at the origin.

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Under the Morse potential (16) with an external dis-194 turbance (5) there are no transition states (TS) in a finite 195 ¹⁹⁶ region. This is because Morse potentials have artifical TS for infinite distances, and the harmonic potential only has 197 ¹⁹⁸ a minimum at c. The sum of the both parts in Eq.(3) in-¹⁹⁹ duces an overall increasing PES for increasing distances $_{200}$ from c. In this case, increasing the hydrostatic pressure does not increase a possible reaction rate. 201

CHEMICAL EXAMPLE IV.

In experiments with large molecules, a part of the 203 ²⁰⁴ molecule must be a punch, another an anvil [18, 25, 39– 44]. There have to be heterogeneous components, a com-205 pressible mechanophore and an incompressible ligand. 206 Over the anvil, isotropic stress leads to relative motion of 207 the rigid ligand which anisotropically deforms the com-208 ²⁰⁹ pressible mechanophore. The anvil acts as a counterpart 211 ²¹² can deform the bonds anisotropically. A small example ²³⁹ pressures (20-40 GPa) and temperatures (3000-5000 K) 213 is the Mislow-Evans rearrangement [43] where the step to 240 that are difficult to study experimentally and theoreti-²¹⁴ the TS is shown in Fig.3. Used are pressures of 100-150 ₂₄₁ cally [57]. $_{215}$ GPa (1GPa =10⁴ bar). A carbon atom numbered by C ²¹⁶ forms the anvil for the oxygen atom to built the five-ring 217 of the TS.



FIG. 3. Mislow-Evans rearrangement to SP by mechanical pressure [43]. 218

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Quite another physical example is the phase tran- 242 220 formation under pressure from body-centered cubic to 221 hexagonal close-packed structure in iron [44]. 222

TRIATOMIC MOLECULE – DISSOCIATION 223

224 225 molecule ABC we artificially turn around the direction 251 the force. A bond breaking point (BBP) [58, 59] emerges of the pressure. One can compare the 'virtual negative' 226 227 228 229 230 231 232 mation of cavitations [48–50], compare Fig. 4. 233

234 235



FIG. 4. Scheme of the pressure of a blast wave in time, with peak overpressure p_{max} which happens at time of arrival of the blast. First acts a positive phase impulse I+ at phase duration t_+ , but then acts a negative phase impulse I- at phase duration t_{-} , compare an explanation in Ref. [48].

²³⁶ [51], or pulsed ultrasonification [52–54]. Quite more comto the real bond changes under pressure. Thus isotropic 237 plicated are weak detonation waves which can be nontension leads to the relative motion of rigid ligands, which 238 linearly stable [55, 56]. They create environments in



FIG. 5. PES sections showing the global minimum of the triatom at F = 0. Left is fixed $y_2 = -1.116$ but in the right panel it is $x_2 = 0.178$ fixed. Coordinates are in Å.

243 We apply 'virtual negative' pressure difference to the 245 global minimum of the triatom. Two PES sections are ²⁴⁶ shown in Fig.5. We obtain the effect of 'pulling' again $_{247}$ on the weakest bond, r_3 , well represented by coordinate $_{248}$ y_2 of the right panel. The action continues in the right 249 panel of Fig.5 along the valley to the bottom right cor-To check the hydrostatic pressure formulas for TSs of $_{250}$ ner. y_2 is stretched up to F = -5.35 kcal mol⁻¹ Å⁻² of $_{252}$ for the bond r_3 . The former minimum for varible y_2 pressure difference with an application in the original 253 in the right panel of Fig.5 opens to a shoulder in Fig.6. Eq.(5) by using a negative F, thus turning around the $_{254}$ The term BBP describes the disappearence of the barparaboloid in the negative direction. We can understand 255 rier; of course, a chemical reaction will take place before such a 'negative pressure difference' as the situation af- 256 at a given temperature. After the BBP, the system of ter a shock wave has passed the molecule [18–20, 45–47]. $_{257}$ Eqs.(18) does not converge if the force parameter F is Then a certain hypotension may happen because of for- 258 further increased, or the search for a stationary point ²⁵⁹ jumps to another region of the PES. This is an indica-Another sort of experiment with possible 'negative 260 tion of the opening of the PES. It happens in analogy pressure difference' is high-intensity focused ultrasound $_{261}$ to the case of NTs, for a linear approach as in Eq.(1).

262 At the BBP the effective PES has a shoulder point. The 290 isotropic force in Eq.(5) does not point in the direction of ²⁶³ former minimum and the former TS of the bond coalesce. ²⁹¹ a special valley. The small points of this path are slightly 264 265 266 mains nearly unchanged on this pathway. The next bond 294 One could guess that a quasi-isotropic path exists from $_{267}$ r_2 breaks for $F \approx -5.95$ kcal mol⁻¹ Å⁻² which is shown $_{295}$ the minimum to uniformly expanded bonds, however, we 268 in the left-hand scheme of the second line of Fig, 6. Sub- 296 could not find such a path. On the contrary, sometimes $_{269}$ sequently, the atom C is completely dissociated. Then $_{297}$ the determined points for changing F values jump out of $_{270}$ the remaining diatom AB will break when its TS energy $_{298}$ the r_3 -valley. ²⁷¹ is exceeded. This happens with the additional increase in $_{272}$ force by 4 units to 9.95 kcal mol⁻¹ Å⁻². The right-hand 273 panel in the second row of Fig.6 explains the situation: $_{274} x_1$ here represents the bond r_1 . The former minimum 275 flattens out at a shoulder. At the same time, a maxi-276 mum on the PES also flattens out in a shoulder. At all 277 we find the molecule exploding, however in consecutive 278 steps.



FIG. 6. Upper row: PES sections under 'virtual negative' pressure for F = -5.35 where the BBP emerges. Left $y_2 =$ -1.33 is fixed but in the right panel $x_2 = 0.09$. Second row: F = -5.95 and $x_1 = -1.43$ fixed, right for F = -9.95 and $y_2 = -1.33$ fixed, see text. Coordinates are in Å.

UPPER REGIONS OF THE PES OF ABC VI. 279

280 ²⁸¹ gions of the former saddle points of the original PES. ³¹³ other words, a BBP of a higher index. It is depicted 283 284 ²⁸⁵ BBP in Fig. 7 show this pathway to the saddle (SP) of ³¹⁷ situation is different in comparison to the case of NTs $_{286}$ bond r_3 . The SP of index one is virtually a pure exten- $_{318}$ [15, 16, 62–64]. At a VRI of a PES, a singular NT with $_{287}$ sion of r_3 near 4.15 Å, but r_1 and r_2 are nearly unchanged $_{319}$ four branches crosses. Two branches usually connect a 288 at their equilibrium values. In contrast, the calculation 320 minimum and an SP₂, while the other two branches con- $_{209}$ in the r_3 -valley is not very stable. This is because the $_{321}$ nect two SP₁. The singular NT for the VRI point on a

The BBP emerges in the right upper panel of Fig.4, while $_{292}$ shifted to the 'right' slope of the r_3 -valley by $\approx 0.01 \text{\AA}$, the left panel shows that diatom AB with distance r_1 re- $_{293}$ but they are not completely on the ground of the valley.



FIG. 7. Calculated pathways from $F = -5.3 \text{ kcal mol}^{-1} \text{ Å}^{-2}$ back to zero by 0.125 steps, after the BBP. Shown is a PES section of r_2 and r_3 like in Fig.1. Small dots are the former way to BBP and up to the TS for r_3 , but thick dots are two pathways after the BBP besides the valley of r_3 . Distances are in Å.

In Fig. 7 two such pathways are shown by thick blue 200 $_{300}$ dots. The breakout goes both in the r_2 -direction, as well $_{301}$ as in the r_1 direction (which is not shown – the picture is analogous for an r_1, r_3 -section). It results in two SPs 302 on the original PES of the triatom, one in the combined 303 r_2 and r_1 valleys, an SP with index two, and one on the 304 $_{305}$ top for both distances and r_3 , a flat SP of index 3, at top ³⁰⁶ right of Fig. 7. It is at $r_1=2.65$, $r_2=3.96$, and $r_3=4.29$. ³⁰⁷ The SP_2 concerns an r_3 at equilibrium 2.5Å, but both r_1 $_{308}$ and r_2 are extended to their SP value. This means the $_{309}$ diatom BC is fixed and atom A leaves the core. In SP_3 $_{310}$ the r_3 , r_1 and r_2 are all stretched.

The two pathways emerge which a bifurcation at a 311 After the BBP we find ourselves in the 'influence' re- 312 point where the index changes from two to three: In Of theoretical interest here is that we can use the force 314 in Fig. 7 by 'BBP23'. It could be assumed that it is loparameter F to go back with to smaller values down to $_{315}$ cated near a valley-ridge inflection point (VRI) [60, 61] F = -0.125 close to zero. The small blue dots over the 316 between the valleys of interest in Fig.1. However, the



FIG. 8. PES sections of V_F showing the region around the bifurcation point of Fig. 7 of the triatom at F = -3.034 kcal $mol^{-1} Å^{-2}$. The energy increases from bottom to top. The shoulder concerns a ridge structure. Coordinates are in Å.

 $_{322}$ given PES usually requires a special direction, l, of the external force. Under the hydrostatic force, however, we $_{324}$ only have the one isotropic direction, see Eq.(5). It is 325 not to expect that the hydrostatic solutions hit the VRI ³²⁶ points. (In the 2D image of Fig.7, the VRI point is at (3.15, 2.96).) Here, at the bifurcation, the former SP of 327 $_{328}$ index two has a ridge-shoulder transition up to the SP₃, $_{329}$ see Fig. 8. The corresponding PES section r_1/r_2 still has 330 a maximum there (not shown). As with a BBP under $_{331}$ NTs, the parameter F also increases here from the side $_{332}$ SP₂ up to the bifurcation, but then decreases on the way to SP_3 . 333

The beginning of the curves of thick dots in Fig.7 at its 334 335 left point is connected with an analogous shoulder point $_{336}$ on the r_1/r_2 part of the effective PES (not shown by a 337 figure).

³³⁸ Note that a linear structure of the ABC molecule is not ³³⁹ stable under the potential (16). We do not discuss this case. 340

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VII. DISCUSSION

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 $_{345}$ isotropic use of pressure as in the approach of Eq.(5) also 346 has no connection to the normal modes of the molecule ³⁴⁷ of interest [65, 66]. We also do not discuss the influence 348 of pressure on the electronic structure of the molecules [67].349

VIII. CONCLUSION

We simplify the mechanochemical ansatz with an 351 ³⁵² external hydrostatic pressure. We apply the formula to 353 a non-linear triatomic ABC. We find that compressive ³⁵⁴ hydrostatic pressure does not lower the energy barrier 355 for a change in a non-linear triatom. In contrast, 356 a shock wave, represented by a 'negative' pressure ³⁵⁷ difference, could do this. A dissociation reaction of a ³⁵⁸ single atom from the triatom can be enforced, as well as 359 an 'explosion' of the molecule.

361 Conflict of Interest

³⁶² The authors declare that they have no affiliations with ³⁶³ or involvement in any organization or entity with any 364 financial interest in the subject matter or materials 365 discussed in this manuscript.

Author Contributions 367

368 WQ and JMB contributed to the design and implemen-³⁶⁹ tation of the research, to the analysis of the results and 370 to the writing of the manuscript.

372 Methods

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³⁷³ We used Mathematica 13.3.1.0 for Linux x86(64-bit) in 374 the calculations and in the representation of the figures.

376 Data Access Statement

³⁷⁷ Data can be obtained by WQ.

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