

NEW APPROACH TO PREDICT HUGONIOT PROPERTIES OF EXPLOSIVES MATERIALS

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Abstract

To characterise explosives materials, investigations for four well experimentally characterised energetic materials, Cyclotrimethylenetrinitramine (RDX), Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), Pentaerythritol tetranitrate (PETN) and Triamino-trinitrobenzene (TATB) were conducted using quantum mechanics and analytical methods. Furthermore, using the pressure p and the ratio of specific densities, v/v_0 , p - v Hugoniot diagrams of the four explosives were obtained. Using, the Stine equation [Stine, J. Energ. Mater., 1990] and more recent least squares fitting algorithms, new constants were obtained, to determine the detonation velocity, D , which was then used to define the Raleigh line. The ratio of specific heats, γ , a value anywhere between 2 and 3 and usually approximated from experimental data, was obtained by making the explosive products Hugoniot tangent to the Rayleigh line through varying γ . The effect, sensitivity and importance of having the correct value of γ were demonstrated. The predicted parameters namely the shock, particle and detonation velocities, the CJ pressure and density, the ratio of specific heats and the Hugoniot diagrams all compared quite well with published experimental data.

1. Introduction

To better design energetic materials and predict their energy output and response it is necessary to characterise these materials in terms of their energetics. Indeed, this characterisation demands a series of experiments ranging from slow cook off of the material to high velocity flyer plate impact tests are necessary to obtain parameters such as the detonation velocity, densities, shock and particle velocities and critical pressures. These experimental parameters are required to obtain the Chapman-Jouguet parameters that define the point at which the detonation occurs. The main objective of this work is to conduct numerical experiments to examine the parameters that define detonation process and establish a

completely numerical approach by using quantum mechanics and analytical methods. To this end, four well known and experimentally characterised energetic materials were considered and the results compared with experimental values. The four materials chosen are RDX, HMX, PETN and TATB. The detonation velocity is one of the key performance characteristics of energetic materials which can be determined by some computer codes [1-4]. Also, pressure-specific volume relationship called Hugoniot curve is a valuable tool to understand the material response and evaluate their performance. A treatment of the Hugoniot curve is found in the book Explosives Engineering by Cooper [5]. Each material has a unique Hugoniot curve that is usually obtained from a series of experimental tests that could be quite expensive and time consuming. In this work, the main focus was on the characterisation of the detonation of the energetic materials (including the Hugoniot) using the numerical simulations technique. This analysis method provided a valuable way to understand the detonation process and obtain their corresponding parameters. The computation of detonation parameters by computer codes usually requires the heat of formation ΔH_f and the density of energetic materials; therefore, the knowledge of heat of formation of materials remains the key issue. In this work, the hybrid density-functional theory (DFT) [6] approach was used to predict heats of formation in the solid phase and detonation properties using quantum chemistry calculations.

2. Computational methods and details

All calculations on structural properties of compounds, were carried out in the framework of density-functional theory (DFT) [7]. In the present work, B3LYP hybrid functional [8-10] was used in conjunction with 6-311++G(3d,3p) basis sets. The geometry of molecules were optimized using gradient techniques at the HF/STO-3G, HF/6-31G, B3LYP/6-311G, and B3LYP/6-311++G(3d,3p) levels without symmetry constraints. All calculations were performed using the Gaussian 03 [11] packages. The B3LYP functional is a reliable method providing accurate results when compared to experimental data and *ab initio* methods [12].

In this study, heats of formation $\Delta_f H_{Solid}^0$ were determined using Hess' law of constant heat summation [13] given by:

$$\Delta_f H_{Solid}^0 = \Delta_f H_{Gas}^0 - \Delta H_{Sub} \quad (1)$$

where $\Delta_f H_{Gas}^0$ is the heat of formation at the gas phase predicted by using isodesmic reaction approach [4]. In this approach, the number of electron pairs and chemical bond types are assumed to be conserved in the chemical reaction.

The heat of sublimation, $\Delta_f H_{Sub}$, is estimated using Politzer approach [14]. Politzer *et al.* predict heats of sublimation of a compound by considering a statistical approach where various parameters are mapped onto isodensity surfaces of the isolated molecule, and propose an empirical expression which provides the heat of sublimation of a particular compound given by:

$$\Delta H_{Sub} = \beta_1 A^2 + \beta_2 \left(v \sigma_{tot}^2 \right)^{0.5} + \beta_3 \quad (2)$$

where A is the molecular surface area. It is the collection of points where 97% of the electron density of the isolated molecule is present. The parameter v defines the balance value for the positive and the negative potential quantities on the molecular surface A . $\sigma_{tot}^2 = \sigma_+^2 + \sigma_-^2$ represents the variance of electrostatic potential values on the molecular surface and β_{1-3} represent the fit parameters computed from least-square fitting techniques. The method proposed by Stine [15] to obtain the detonation velocity, D , was used. A least squares fitting was applied to minimise the sum of the squares of the residuals formed by the difference between the calculated and the experimental values and the newer fit constants were estimated. The Rayleigh line and Hugoniot curve of gas products were obtained using the simplest theory discussed by Fickett *et al.* [16]. The model assumes that the products of reactions are instantaneously produced by the shock. The conservation of mass, momentum and energy equations were used and the gas products of reaction were assumed as an ideal gas. The four materials to be characterised are RDX, HMX, PETN and TATB and their chemical structures are illustrated in Figure 1.

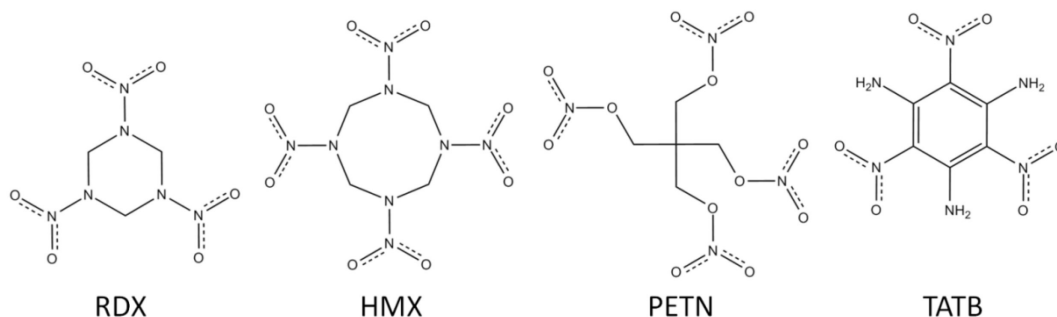
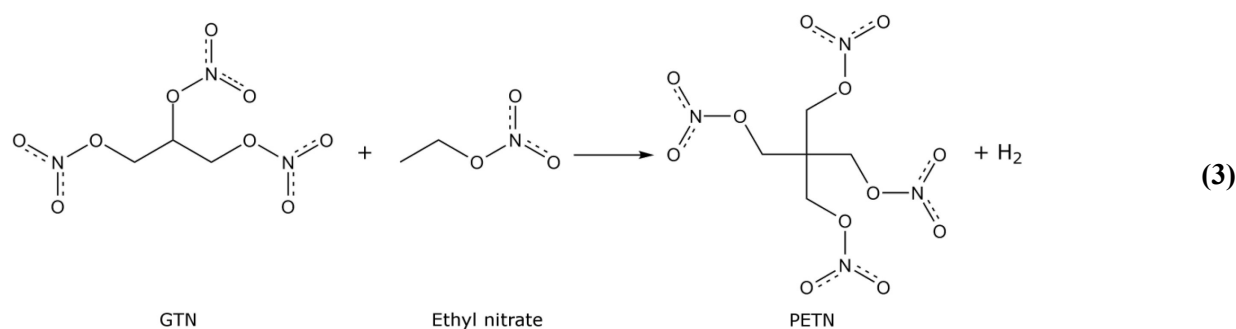


Figure 1. Chemical structure of molecules in the studied system.

3. Results and discussion

3.1. Gas-phase heat of formation

In this work, only PETN molecule case is provided as an example for gas-phase heat of formation calculations. The gas-phase heat of formation of PETN was estimated using isodesmic reactions given by equation 3. Using the experimental $\Delta_f H_{Gas}^0$ values of Nitroglycerin (NG) and Ethyl nitrate, $\Delta_f H_{Gas}^0$ of PETN was calculated as follows:



The heat of reaction of this equation is given by:

$$\Delta H_{rxn} = \left(\Delta_f H_{Gas, PETN}^0 + \Delta_f H_{Gas, H_2}^0 \right) - \left(\Delta_f H_{Gas, NG}^0 + \Delta_f H_{Gas, Ethyl\ nitrate}^0 \right) \quad (4)$$

Using the experimental heat of formation of the molecules making up the PETN and available in NIST website¹, the PETN heat of formation can be calculated from equation 4:

$$\Delta_f H_{Gas, PETN} = \Delta H_{rxn} + \Delta_f H_{Gas, NG} + \Delta_f H_{Gas, Ethyl\ nitrate} - \Delta_f H_{Gas, H_2} \quad (5)$$

Heats of formation of the molecules in equation 3 are listed in Table 1.

Table 1. Experimental and calculated gas-phase heats of formation of the molecules making up the PETN

Molecules	$\Delta_f H_{Gas}^0$, kcal/mol
NG	-67
Ethyl nitrate	-37
PETN	-86
H ₂	0

3.2. Heats of sublimation

¹ www.webbook.nist.gov/chemistry

For heats of sublimation, only PETN case is studied in this work. Table 2 lists some similar molecules to PETN which have been used to determine the fit parameters β_{1-3} shown in equation 2. In the framework of the Politzer approach, and the heats of sublimation ΔH_{Sub} were estimated. The experimental values of ΔH_{Sub} , of the molecules used in the fit were taken from the website www.webbook.nist.gov/chemistry. Politzer parameters shown in equation 2 are A , ν and σ_{total} and given in Table 2. Figure 2 shows the plot of predicted ΔH_{Sub} of the selected molecules similar to PETN. The curve shows a good correlation between the predicted and the measured data. The fitting procedure leads to $\beta_1 = 2 \times 10^{-4} \text{ kcal/mol.}\text{\AA}^4$, $\beta_2 = 2.104$, and $\beta_3 = 0.2374 \text{ kcal/mol}$. β_{1-3} in equation (2) leads to, $\Delta H_{Sub} = 25.0 \text{ kcal/mol}$ of PETN. Now using equation (1), the heat of formation in the solid phase of PETN is estimated to be -111 kcal/mol . The experimental value as reported in reference [17] is -128 kcal/mol , the relative error between these two values is about 15%. This deviation can be possibly reduced by using extended basis set in the hybrid functional B3LYP.

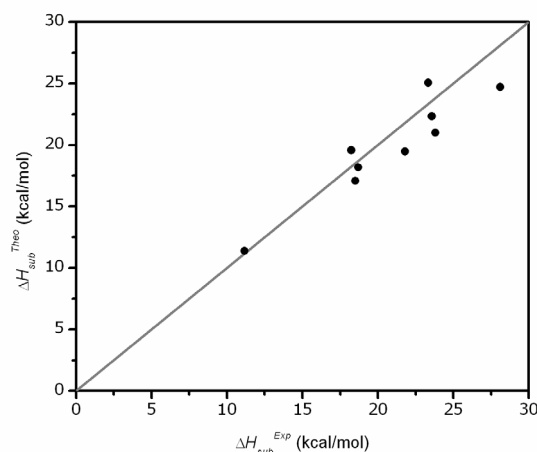
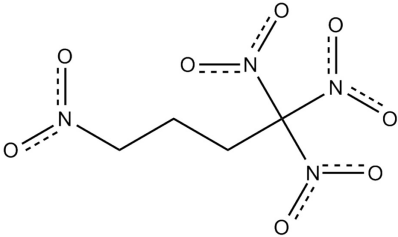
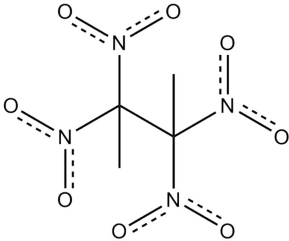
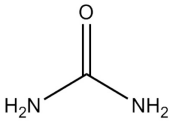
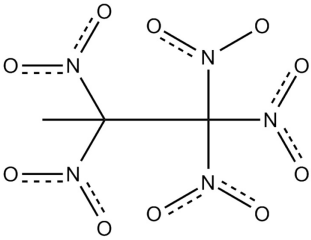
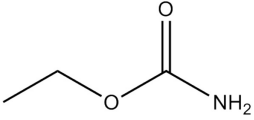
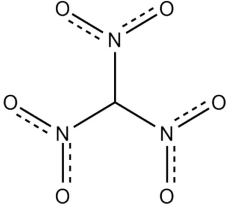
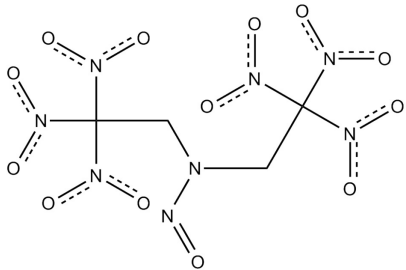
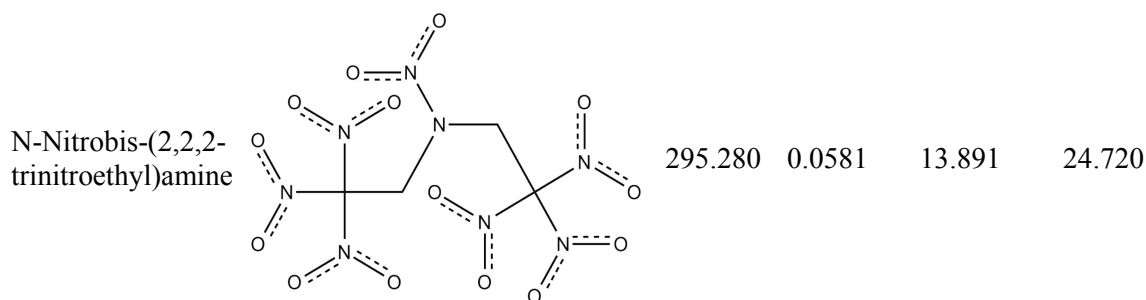


Figure 2. Predicted heats of sublimation of the selected molecules versus the experimental values

Table 2. Molecular Properties.

Names	Chemical structures	$A \text{ (\AA}^2\text{)}$	ν	$\sigma_{total} \text{ (kcal/mol)}$	$\Delta H_{sub} \text{ (kcal/mol)}$
1,1,1,3-Tetranitro-2-methylpropane		235.350	0.125	10.963	91.200

1,1,1,4-Tetranitrobutane		227.320	0.1099	14.962	99.600
2,2,3,3-Tetranitrobutane		204.470	0.1351	12.394	78.200
Urea		95.830	0.2472	19.361	98.600
1,1,1,2,2-Pentanitropropane		228.030	0.0596	12.561	77.400
Ethyl carbamate		135.060	0.2167	16.026	76.300
Trinitromethane		147.910	0.0378	16.571	46.700
N-Nitrosobis-(2,2,2-trinitroethyl)amine		284.250	0.0521	18.059	23.326



3.3. Determination of the detonation velocity

Starting with the empirical method proposed by Stine [15] to obtain the detonation velocity, D , equation (6), for a given compound:

$$D = D_0 + \rho \left[c_1 n_C + c_2 n_N + c_3 n_O + c_4 n_H + c_5 \Delta_f H_{Solid}^0 \right] / M \quad (6)$$

Where D_0 is a constant, n_i , $i = C, N, O, H$, are the specific number of atoms in the molecule, and c_i , $i = 1$ to 5, are the corresponding characteristic constants for the carbon (C), nitrogen (N), oxygen (O) and hydrogen (H) atoms in the molecule, and the heat of formation ($\Delta_f H_{Solid}^0$), respectively. ρ is the density and M is the molecular weight of the material. Equation (6) is expressed in terms of a set of known and well characterised explosives, for which experimental detonation velocities, heats of formation and densities are available. Using a least square fitting approach to equation (6), the constants D_0 and c_i could be obtained. These constants can be used to predict the detonation velocities of new compounds that have similar chemical composition.

3.4. Determination of constants D_0 and c_i

The base set of explosives compounds selected to obtain the constants D_0 and c_i are exactly the same five known and well characterised explosives chosen by Stine in his original work [15]. These molecules are BTNEU, HMX, TNETB, ABH and Exp1D. Table 3 shows the equivalent chemical names along with all the necessary basic parameters such as the density, experimental detonation velocity, D_{exp} and molecular weight that are required in equation (6).

Table 3. Chemical characteristics of BTNEU, HMX, TNETB, ABH, and Exp1D.

Chemical Formula	Compound	Enthalpy of Formation (kcal/mol)	Density (g/cm ³)	Mol Weight (g/mol)	D_{exp} km/s
C ₂₄ H ₆ N ₁₄ O ₂₄	ABH	116.3	1.78	874	7.60
C ₆ H ₆ N ₆ O ₆	BTF	144.5	1.86	252	8.49
C ₅ H ₆ N ₈ O ₁₃	BTNEU	-72.9	1.86	386	9.01

$C_4H_8N_8O_8$	HMX	17.9	1.89	296	9.12
$C_6H_6N_6O_{14}$	TNETP	-118.5	1.78	386	8.46
$C_6H_6N_4O_7$	Exp1D	-94.0	1.55	246	6.85

In order to compute the detonation velocity D of RDX, HMX, PETN and TATB, parameters given in Table 3 are used in equation (6) and then a least squares fitting is applied to minimise the sum of the squares of the residuals formed by the difference between the calculated value of D and the experimental value D_{exp} , and the D_0 , c_1 , c_2 , c_3 , c_4 and c_5 constants are estimated. The constants D_0 and c_i ($i = 1$ to 5) obtained from the least squares fitting of equation (6) are given in Table 4.

Table 4. New data set of D_0 and c_i parameters to be used in equation (6).

	D_0 (km/s)	c_1	c_2	c_3	c_4	c_5
New data	2.96	-7.039	51.586	69.034	2.214	0.463
Stine	3.69	-13.85	37.74	68.11	3.95	0.6917

The least square fitting produced new data of the D_0 and c_i parameters that differ from Stine's coefficients. This deviation is simply due to the fact that in this work more optimized least square fitting algorithms have been used.

Table 5. Detonation velocities using Stine and new constants in equation (6).

Compound	D_{exp} km/s	D_{Stine} km/s	$D_{New\ data}$ km/s	% of error, Stine data ²	% of error, New data ³
ABH	7.60	7.63	7.60	0.3990	0.0007
BTF	8.49	8.50	8.49	0.1415	0.0003
BTNEU	9.01	8.95	9.01	0.6775	0.0004
HMX	9.12	9.02	9.12	1.0090	0.0001
TNETB	8.46	8.48	8.46	0.2300	0.0006
Exp1D	6.85	6.86	6.85	0.1644	0.0000

From Table 5, the calculated % error using new data is lower than this using Stine's values. For this reason the named constants new data are used for all estimations of detonation velocities. The value of each term in equation (6) has been determined, now it is possible to calculate the detonation velocities for the selected explosives for this study – PETN, RDX, HMX and TATB. The experimental heats of formation at the solid states, extracted from NIST website⁴, for RDX, HMX and TATB, have been used in equation (6) for the calculations of the detonation velocities D . Table 6 shows a comparison between the calculated

² % of error = $100 * |(D_{exp} - D_{Stine}) / D_{exp}|$

³ % of error = $100 * |(D_{exp} - D_{New\ Data}) / D_{exp}|$, in the case of the new constants

⁴ www.webbook.nist.gov/chemistry

and measured detonation velocities using equation (6) and very good agreement is obtained between experimental and calculated values of D . Note that HMX was listed as a molecule in the Stine's set.

Table 6. Detonation velocities for PETN, RDX, HMX and TATB

Chemical Formula	Compound	D_{exp} , km/s ^[5]	D , km/s
$\text{C}_3\text{H}_6\text{N}_6\text{O}_6$	RDX	8.70	8.73
$\text{C}_4\text{H}_8\text{N}_8\text{O}_8$	HMX	9.12	9.12
$\text{C}_5\text{H}_8\text{N}_4\text{O}_{12}$	PETN	8.26	8.29
$\text{C}_6\text{H}_6\text{N}_6\text{O}_6$	TATB	7.76	7.91

3.5. Hugoniot curve and Rayleigh line

The Rayleigh line and Hugoniot curves of gas products are obtained using the simplest theory and are discussed in many shock physics texts such as Fickett et al. [16]. The model assumes that the products of the reaction are instantaneously produced by the shock. Using the conservation of mass, momentum and energy equations, and the equation for Rayleigh line is:

$$\rho_0^2 D^2 - \frac{(p - p_0)}{(v_0 - v)} = 0 \quad (7)$$

Which is expressed in terms of the specific volume $v = 1/\rho$, pressure and detonation velocity

For instance, an ideal gas is characterised with a constant heat capacity and a constant heat for its complete reaction $q = \Delta H_r^0$ and the Hugoniot curve that is expressed as,

$$\left(\frac{p}{p_0} + \mu^2 \right) \left(\frac{v}{v_0} - \mu^2 \right) - 1 + \mu^4 - \mu^2 \frac{2\lambda q}{p_0 v_0} = 0, \quad (8)$$

where $\mu^2 = (\gamma - 1)/(\gamma + 1)$ and $\gamma = C_p/C_v$ is the ratio of specific heats. λ is the degree of the chemical reaction, changing from 0 for no reaction to 1 for a complete reaction. In this work, it is assumed that the reaction is complete, then $\lambda=1$.

This is the equation of a rectangular hyperbola in the $p/p_0 - v/v_0$ plane, centered at the point $v/v_0 = \mu^2$ and $p/p_0 = -\mu^2$.

If the Hugoniot curve equation (8) is solved simultaneously with the Rayleigh line equation (7), the intersection of these two equations defines the CJ point at the detonation process. q represents the heat of detonation; it can be estimated using quantum mechanical method [18]. In this work, the heat of detonation q and the density ρ_0 values are extracted from references [3, 19, 20] and used in equations (7) and (8) to plot Hugoniot curves of gas products and Rayleigh lines. The line tangent at the CJ point (p_{CJ} ,

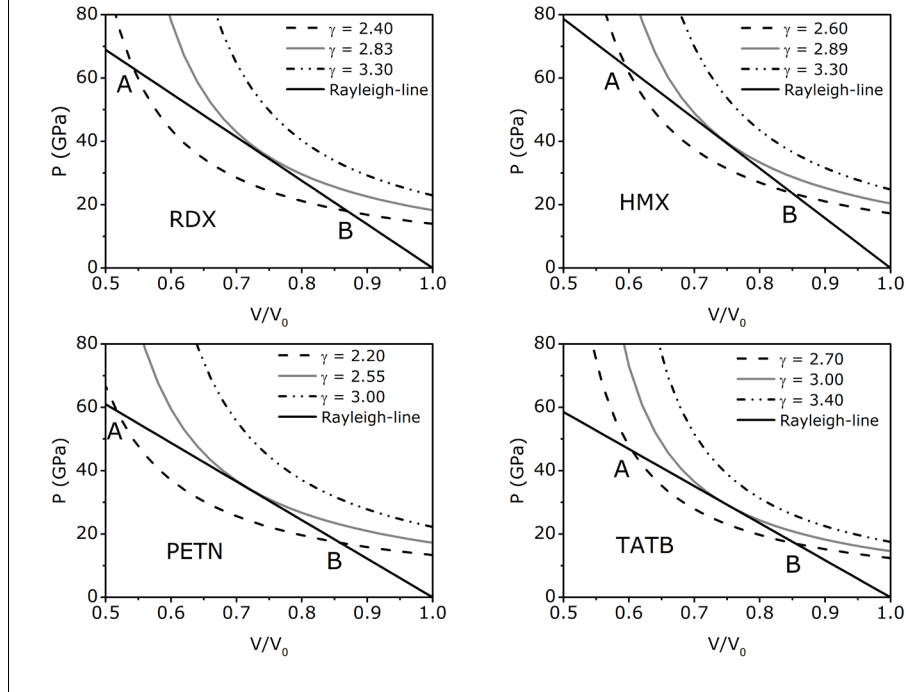
v_{CJ}) is the Rayleigh line. The slope of line tangent at the CJ point and the Rayleigh line are equal. The analytical results for the four explosives, at various corresponding values of γ , are presented in Figure 3.

3.6. The Gamma, γ , effect

The detonation process of an explosive the reaction occurs immediately and this implies that once the unreacted material passes through the detonation wave. It is assumed that it is instantaneously converted to a new material and as discussed previously the final state is determined by the intersection of equation (8) and the Raleigh line equation (7). The correct value of γ which is the ratio of the specific heat at constant pressure to that at constant volume (C_p/C_v) is important because it influences significantly the tangent of the Hugoniot energy and as a result will influence the CJ point. As pointed out by Cooper [5], an explicit value of γ is not available but experiments have shown that it ranges between 2 and 3. Many texts provide approximate values for γ . However, in this work the idea was also to explore the influence of γ on equation (8). For given values of p and v , γ was varied between 2 and 3 for the four explosives. Figure 3 shows the effect of γ on equation (8) and its relation to intersecting the Raleigh line, for the four molecules. In the case of PETN, when γ is equal to 2.2, the equation (8) intersects the Raleigh line at two points A and B and as γ is gradually increased (around 2.55) at some point it is tangent to the Raleigh line and if further increased (3.0) it stays above the Raleigh line. Similar analysis is observed for HMX, RDX and TATB. In this way the CJ point for the four explosives were obtained and these are given in Table 7 and the results reported in Figure 3. The values of γ compare very well with published experimental data.

Table 7. Experimental and calculated properties of explosives.

	ρ_0 (kg/m ³)	γ		p_{CJ} (GPa)	
		Theo	Exp ^[3]	Theo	Exp ^[3]
RDX	1800	2.83	2.98	36.45	34.70
HMX	1900	2.89	3.00	40.60	39.30
PETN	1770	2.55	2.64	34.50	33.50
TATB	1895	3.00	2.72	29.23	31.50

Figure 3. Hugoniot curves to demonstrate the γ effect relative to the Raleigh lines for the four explosives.

4. Conclusions

Through the investigation conducted in this for four well experimentally characterised energetic materials, RDX, HMX, PETN and TATB using quantum mechanics calculations coupled with analytical methods, it is now possible to estimate some parameters such as the detonation velocity and the Chapman-Jouguet pressure and density that define the detonation of a CHNO based explosives. The detonation velocities of explosives were obtained using Stine's equation. However, new and seemingly more accurate constants were obtained for this equation using instead a more optimized algorithm for a least squares fitting. With these new accurate constants leading to precise predicted detonation velocities when they were compared to experimental values. The specific heat ratio, a parameter found in the Hugoniot energy equation for the products, and the Chapman-Jouguet pressures and specific densities were obtained for the studied

explosives using the point where the Raleigh line tangents to this Hugoniot diagram. The values obtained for Chapman-Jouguet parameters and the specific heat ratios compared very well with published experimental values for all four explosives. A sensitivity analysis of the specific heat ratio was examined and it was shown that the tangent that energy Hugoniot makes with the Raleigh line is quite sensitive and care needs to be taken in its determination since the Chapman-Jouguet parameters are determined using this tangent point. To conclude, the potential use of the molecular modelling approach together with the analytical methods shows that now a CHNO based explosives can be numerically characterised and parameters such as CJ , specific heat ratio, γ , p_{CJ} and detonation velocities can be obtained quite accurately prior to experiments. This approach should be also as supporting information to suggest a minimum number of or just confirmation experiments if necessary.

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