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Velocity of Detonation-A Mathematical Model

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Abstract

Based on the principles of conservation of energy and momentum, a mathematical formula has been derived for the squares of detonation velocities of a large set of explosives. The equation is a function of the total energy and molecular weight of an explosive compound considered. A regressed equation has been obtained for a pool of explosives of various types including nitramines, aliphatic and aromatic nitro compounds. Also another regressed equation for nitramines only is given. For the regression, the total energies are obtained using DFT (UB3LYP/6-31G(d)). The regression statistics are given and discussed.

Keywords: Detonation velocity, explosives, DFT calculations, regression analysis, nitramines.

1. Introduction

The research for new energetic materials having certain desired properties is an ongoing effort of scientists and engineers. Nowadays, the theoretical and computational approaches are indispensable for the design of novel explosive materials by helping systematically the improvement of scientific formulations having good thermal stability, impact and friction sensitivities and enhanced detonation performance. Detonation velocity is one of the important performance characteristics of explosives which can be calculated by some computer codes having different level of sophistication[1–5]. The computation of detonation parameters by computer codes usually requires the heat of formation (ΔH_f) and the density of explosive as well as the equation of state of detonation products[6,7]. In addition to that for these computations it is necessary to possess some highly expensive or restricted computer programs. While designing novel explosive structures, the inputs (ΔH_f and density) required for these computer programs are to be previously calculated. Therefore, the need for some simple, and cheap methods are always desirable.

A shock wave propagates into a reactive gas mixture which is in a metastable thermodynamic-chemical (pseudo) equilibrium with frozen reaction. The intensity of the shock wave and the corresponding change of state is sufficiently large to start the reaction process[8]. There exist numerous articles in the literature concerning the kinetics of detonation of various explosives[9–17]. Some of these publications are on certain novel concepts rather than straightforward experimental measurements[10]. For instance, Bernard using Eyring's activated complex theory, found that the detonation rate was determined by the rate at which activated complex molecules transversed the potential energy barrier along the reaction path[14].

Besides the detonation rate, the velocity of detonation at which the detonation shock wave proceeds through an explosive charge is an important detonation parameter[1]. Some useful equations relate the detonation velocity to the other Chapman-Jouguet state parameters[1]. Kamlet and coworkers invoke the thermo chemical properties of an idealized detonation reaction and make use of these for the estimation of detonation velocity[18–21]. Some empirical approaches to the detonation velocity exist in the literature such as the work of Rothstein and Peterson[16,22].

While using these empirical formulas for the detonation velocity, the detonation performance of a pure nitrated high explosive can most approximately be formulated as a function of its heat content in condensed phase, its elemental composition and loading density[16,18,21,22].

Usually, assumed decomposition products are to be used for calculation of detonation performance.

An empirical relation is also found between the detonation velocities and ^{15}N NMR chemical shift, δ_N, of nitrogen atoms in nitro groups of a limited number of nitramine type explosives with rigid structure[23,24].

Quantum chemical calculations at different levels were reported for the determination of detonation velocities mainly based on the method of Kamlet and Jacobs approach and using Kistiakowsky-Wilson's equation of state[25–29]. In that method, the detonation velocity (D) is given by

$$D = 1.01\ (NM^{1/2}\ Q^{1/2})^{1/2}\ (1 + 130\rho)$$

Where ρ: density of a compound, N: moles of gaseous detonation products, M: average molecular weight of gaseous products, Q: chemical energy of detonation.

2. Theory

2. 1. The Physical Model

The physical model developed presently is based on the following main assumptions.

i) The explosive material is oxygen sufficient and the material balance exists between the explosive and its explosion products.
ii) The energy and momentum are conserved. Thus, the quantity of an explosive material having mass M which is equal to its molecular weight (in grams) explodes and pushes a shell of mass M. Meanwhile the energy and momentum of the explosion products are transferred to the shell which, then acquires an initial velocity of V_0.
iii) The product gases have mass (m_i) and velocity (ν_i). Then, in the light of above assumptions the conservation of momentum implies,

$$\sum_{i=1}^{n} m_i v_i = MV_0 \tag{1}$$

where "i" stands for individual gaseous product "i". Since the explosive is assumed to be oxygen sufficient (that is the oxygen balance is zero) then the material balance requires

$$M = \sum_{i=1}^{n} m_i \tag{2}$$

It is known that the detonation velocity (D) and the velocity of matter (W) are expressed as,[30]

$$D = \gamma_0 \sqrt{\frac{p_1 - p_0}{\gamma_0 - \gamma_1}} \tag{3}$$

$$W = \sqrt{(p_1 - p_0)(\gamma_0 - \gamma_1)} \tag{4}$$

Where p_0 and p_1 are the pressures for undisturbed and shock disturbed media, respectively. Whereas γ_0 and γ_1 are the specific volumes ($\gamma = 1/\rho$, ρ: density) for the undisturbed and disturbed states. Note that formulas 3 and 4 are valid irrespective of the state of aggregation[30].

Combining eqs. 3 and 4 and assuming that the initial velocity (V_0) of the shell is equal to *W* at the end of explosion. Then, one gets

$$D = \frac{\gamma_0 W}{(\gamma_0 - \gamma_1)} \tag{5}$$

In compact form, eq.5 is

$$D = RW \tag{6}$$

where $R = \frac{\gamma_0}{(\gamma_0 - \gamma_1)}$. Solving for V_0 (assuming $V_0 = W$) from eq. 1 and inserting into eq. 6,

$$D = \frac{R\sum_{i=1}^{n} m_i v_i}{M} \tag{7}$$

On the other hand, ineq. 8 holds for $\alpha \geq 1$ that is an arithmetic mean cannot exceed the root-mean-power[31].

$$\frac{1}{n}\sum_{i=1}^{n} a_i \leq \left(\frac{1}{n}\sum_{i=1}^{n} a_i^{\alpha} \right)^{\frac{1}{\alpha}} \tag{8}$$

Let $a_i = m_i v_i$. Then, by using ineq. 8 and $\alpha = 2$ one obtains ineq. 9.

$$\frac{\sum_{i=1}^{n} m_i v_i}{n} \leq \sqrt{\frac{\sum_{i=1}^{n} m_i^2 v_i^2}{n}} \tag{9}$$

The right hand side of ineq. 9 can be rearranged to produce ineq. 10

$$\frac{\sum_{i=1}^{n} m_i v_i}{n} \leq \sqrt{\frac{2}{n}\sum_{i=1}^{n} m_i E_i} \tag{10}$$

Where, $E_i = \frac{1}{2} m_i v_i^2$ is the kinetic energy of particle i. By a simple mathematical manipulation ineq. 10 can be converted to

$$\frac{\sum_{i=1}^{n} m_i v_i}{n} \leq \sqrt{\frac{2}{n}\sqrt{\left(\sum_{i=1}^{n} m_i E_i\right)^2}} \tag{11}$$

On the other hand, the Cauchy-Bunyakovsky[32,33] inequality 12,

$$\left(\sum_{i=1}^{n} x_i y_i\right)^2 \leq \left(\sum_{i=1}^{n} x_i^2\right)\left(\sum_{i=1}^{n} y_i^2\right) \tag{12}$$

can be applied for the $(\sum_{i=1}^{n} m_i E_i)^2$ term of ineq. 11 that is,

$$\left(\sum_{i=1}^{n} m_i E_i\right)^2 \leq \left(\sum_{i=1}^{n} m_i^2\right)\left(\sum_{i=1}^{n} E_i^2\right) \tag{13}$$

Inserting the right hand side of ineq. 13 into ineq. 11

for $\left(\sum_{i=1}^{n} m_i E_i\right)^2$ term, one obtains ineq. 14.

$$\sum_{i=1}^{n}\frac{m_i v_i}{n} \le \sqrt{\frac{2}{n}\sqrt{\left(\sum_{i=1}^{n} m_i^2\right)\left(\sum_{i}^{n} E_i^2\right)}} \tag{14}$$

On the other hand, by multiplying and dividing the numerator of eq. 7 by n, one obtains

$$D = \frac{Rn\sum_{i=1}^{n}\frac{m_i v_i}{n}}{M} \tag{15}$$

Inserting the right hand side of ineq. 14 into eq. 15 for $\sum_{i=1}^{n}\frac{m_i v_i}{n}$ one gets ineq. 16.

$$D \le \frac{Rn}{M}\sqrt{\frac{2}{n}\sqrt{\left(\sum_{i=1}^{n} m_i^2\right)\left(\sum_{i=1}^{n} E_i^2\right)}} \tag{16}$$

Ineq. 16 shows that there should be an intricate functional relationship between D^2 and kinetic energies of product molecules.

2. 2. The Regression Model

The complexity of functional relationship governing D reflected by ineq.16, necessitates to use some approximations to relate D to certain measurable/calculable independent variables. The regression model is based on

i) The potential energy (E_p) of an explosive is converted to kinetic energy of the explosion products ($E_p = \sum_{i=1}^{n} E_i$).

ii) The potential energy is a certain fraction of the calculated total energy (E_T) of the explosive molecules considered that is

$$E_p = kE_T \tag{17}$$

Thus, assuming the conservation of energy, E_p of the explosive material considered is distributed as the kinetic energy E_i of the product molecules. Note that for most of the explosives the products are the same but the number of molecules produced are different. On the other hand, M which is equal to molecular weight of the explosive (see the 2nd assumption in the “physical model“ part above) considered is an easily accessible quantity.

Squaring both sides of ineq. 16,

$$D^2 \le \frac{2R^2 n}{M^2}\sqrt{\left(\sum_{i=1}^{n} m_i^2\right)\left(\sum_{i=1}^{n} E_i^2\right)} \tag{18}$$

Multiplying and dividing the right side of ineq. 18 by E_p and then transferring M into the square-root sign in the form of M^2, one gets ineq. 19.

$$D^2 \le \frac{2R^2 nE_p}{M}\sqrt{\left(\sum_{i=1}^{n}\frac{m_i^2}{M^2}\right)\left(\sum_{i=1}^{n}\frac{E_i^2}{E_p^2}\right)} \tag{19}$$

Inserting eq. 17 into ineq. 19 for E_p produces,

$$D^2 \le \frac{2R^2 nkE_T}{M} - \sqrt{\left(\sum_{i=1}^{n}\frac{m_i^2}{M^2}\right)\left(\sum_{i=1}^{n}\frac{E_i^2}{k^2E_T^2}\right)} \tag{20}$$

Since $E_T \ge E_i$, $M \ge m_i$, then obviously $\sum_{i=1}^{n}\frac{E_i^2}{E_T^2} \le n$ and $\sum_{i=1}^{n}\frac{m_i^2}{M^2} \le n$. So, ineq. 20 can be written as

$$D^2 \le 2R^2 n^2\left(\frac{E_T}{M}\right) \tag{21}$$

To equate the both sides of ineq. 21, a proportionality factor, L, is imposed that is

$$D^2 = L\left(\frac{E_T}{M}\right) \tag{22}$$

Furthermore, to consider the effect of number of NO_2 groups on $D^2 = f(E_T/M)$ functional relation, it is assumed that

$$L = aN + b \tag{23}$$

Where, N is the number of NO_2 groups and a and b are certain constants. Combining eqs. 23 and 22 and using new coefficients, the following regression model is obtained and used for numerical testing.

$$D^2 = B_0 + B_1\left(\frac{NE_T}{M}\right) + B_2\left(\frac{E_T}{M}\right) \tag{24}$$

3. Method

3.1. Geometry Optimizations and Energies

In the present study, the initial geometry optimizations have been achieved by using MM2 method (molecular mechanics), followed by the semi-empirical PM3 (parametric method-3) self-consistent fields molecular orbital (SCF MO) method[34,35] at the restricted level[36,37]. Then, the STO (Slater-type orbitals), RHF (restricted Hartree-Fock) and Density Functional Theory (DFT)[38,39] type quantum chemical calculations have been consecutively performed for the geometry optimizations (finally at the level of UB3LYP/6-31G(d)) to obtain energetically the most favorable structures of the species presently considered. The exchange term of B3LYP consists of hybrid Hartree-Fock and local spin density (LSD) exchange functions with Becke’s gradient correlation to LSD exchange[39,40]. The correlation term of B3LYP consists of Vosko, Wilk, Nusair (VWN3) local correlation functional[41] and Lee,Yang, Parr (LYP) correlation functional[42].

For each set of calculations, vibrational analyses were done (using the same basis set employed in the corresponding geometry optimizations). Note that the normal mode analysis for each structure yielded no imaginary frequencies for the $3N$-6 vibrational degrees of freedom, where N for the vibrational analysis is the number of atoms in the system. This indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. Furthermore, all the bond lengths were thoroughly searched in order to find out whether any bond cleavage occurred during the geometry optimization process. The geometry optimizations and the vibrational analysis computations were performed by using the Spartan 06 package program.[43]

4. Results and Discussion

Table 1 tabulates various data of the present computational study. The explosive compounds in the table are shown by their abbreviated names (see the list of abbreviations). The experimental (observed) D values in Table 1 were excerpted from the literature[44,45]. Some of the explosive structures considered are simply aromatic nitro compounds like TNT, TNB etc., whereas some are nitramines like CPX (a cyclic molecule) and EDNA (an acyclic explosive). The list also includes some mixed types like TNAZ which possesses nitro groups, so that some of them attached to an aliphatic carbon and one attached to an amine group. The explosives PA and PAM contain phenolic and amine groups, respectively which are attached to an aromatic nitro core structure. Note that some of the explosives included in the table are relatively huge molecules like HNS, DPE, DPM and DPA. Therefore, the population number (PN:27) of the explosive compounds considered for the present computational study span over variety of structural possibilities.

The total energies employed for the study are all obtained at the level of UB3LYP/6-31 G(d) and corrected for zero point vibrational energy (in Hartree unit). For the sake of simplification purpose, instead of E_T used in the theoretical part, just symbol E will be used below for the total energy.

The theoretical equation (eq. 22) indicates that D^2 should be a function of E/M and presently E/M ratio of

Table 1. Some data for the explosives considered.

No	Name	Oxygen Balance	Corrected Total energy [a] (E)	M	E/M	N [b]	NE/M	D^0 km/s	D_{calc} km/s	% Err
1	DMNA	–88.81	–339.560787	90	–3.76946	1	–3.76946	6.29	6.10	–2.96
2	EDNA	–31.98	–599.372314	150	–3.99331	2	–7.98663	8.42	7.99	–5.12
3	MNA	–42.07	–300.277329	76	–3.94816	1	–3.94816	6.70	7.59	13.36
4	OCPX	–58.49	–638.657318	164	–3.89138	2	–7.78276	7.28	7.22	–0.81
5	DMEDNA	–80.83	–677.937503	178	–3.80547	2	–7.61095	6.42	6.50	1.31
6	TNB	–56.31	–845.628002	213	–3.96813	3	–11.90438	7.42	7.87	6.04
7	1,8–DNN	–139.34	–794.718450	218	–3.64269	2	–7.28538	5.38	4.86	–9.59
8	1,5–DNN	–139.34	–794.726606	218	–3.64273	2	–7.28546	5.52	4.86	–11.88
9	TENN	–72.69	–1203.677160	308	–3.90599	4	–15.62395	7.30	7.46	2.27
10	TNT	–73.96	–884.909411	227	–3.89601	3	–11.68804	7.02	7.32	4.32
11	PAM	–56.11	–900.980629	228	–3.94959	3	–11.84887	7.50	7.73	3.09
12	TNN	–100.32	–999.203061	263	–3.79687	3	–11.39060	6.27	6.50	3.67
13	PA	–45.39	–920.834307	229	–4.01929	3	–12.05785	7.57	8.23	8.76
14	DPM	–62.07	–1729.335860	438	–3.94626	6	–23.67765	7.29	7.89	8.28
15	DPE	–70.76	–1768.619560	452	–3.91073	6	–23.46437	7.20	7.62	5.96
16	DIGEN	–21.61	–299.064216	74	–4.03928	1	–4.03928	8.12	8.25	1.63
17	HNS	–67.52	–1767.419410	450	–3.92557	6	–23.55344	7.27	7.74	6.47
18	Tetrogen	–21.62	–598.145000	148	–4.04152	2	–8.08304	8.46	8.38	–1.56
19	TNAZ	–16.66	–786.600000	192	–4.09688	3	–12.29062	8.62	8.76	1.59
20	CPX	–49.35	–637.463991	162	–3.93241	2	–7.86483	7.76	7.54	–2.84
21	DNDC	–72.73	–676.756000	176	–3.84520	2	–7.69041	6.75	6.85	1.41
22	RDX	–21.62	–897.265000	222	–4.04173	3	–12.12520	8.89	8.39	–5.64
23	TEX	–55.38	–1052.595000	260	–4.04844	2	–8.09688	8.47	8.38	–1.12
24	HNIW	–10.96	–1790.961000	438	–4.08895	6	–24.53371	9.62	8.88	–7.72
25	HMX	–21.62	–1196.354000	296	–4.04174	4	–16.16694	9.13	8.45	–7.48
26	TNAD	–19.87	–1273.722000	322	–3.95566	4	–15.82263	8.52	7.84	–7.99
27	MDN	6.61	–504.729920	121	–4.16953	2	–8.33906	9.05	9.17	1.28

[a] UB3LYP energies (in Hartree unit) corrected for ZPE, [b] Number of NO_2 groups, [c] From refs. 44 and 45. M: MW in grams.

Table 2. Some statistics of the present data.

	D_{obs}	D_{cal}	E/M	NE/M	D^2
Skewness	–0.119	–1.18682	0.712603	–0.96312	0.179192
Standard deviation	1.093816	1.065725	0.127444	6.123362	16.47262
Reliability at 0.1 level	0.34625	0.337358	0.040343	1.938364	5.214445
Covariance of D_{obs} with Z[a]		1.025995	–1.82652	–28.5029	
Correlation of D_{obs} with Z[a]		0.914	–0.90351	–0.29345	

[a] Z: Group of data indicated by the respective column heading.

the compounds considered fluctuates in between ca. –3.64 and –4.16 (in units of Hartree/g). Various statistical properties of the E/M ratio are shown in Table 2.

Figures 1 and 2 show the various correlative relations among the quantities E/M, NE/M and $(D_{obs})^2$. As seen there, $(D_{obs})^2$ series shows a better accord with the tendencies of NE/M series rather than E/M series.

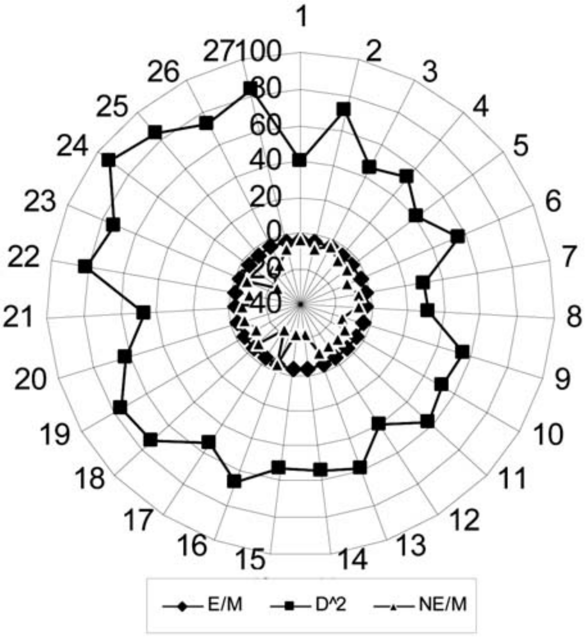

Figure 1. Correlation between independent variables considered and $(D_{obs})^2$ values. The peripheral numbers stand for the compound numbers in Table 1.

The general regression eq.24 is a linear multiple regression equation of $Y = B_0 + B_1X_1 + B_2X_2$ type having two independent variables X_1 and X_2 (NE/M and E/M) and a dependent variable Y (D^2)[46,47]. The regressed equation for the data displayed in Table 1 is

$$D^2 = -393.6877 - 0.2454(NE/M) - 114.0793(E/M) \qquad (25)$$

Note that for the calculated values of D^2 given by eqs. 25 and 26, one has to use the regression coefficients in full digits as given and then round off the results to the nearest one comparable to the observed value. In this way more accurate results are obtained.

Figure 3 displays the correlative relationship between the calculated (by means of eq. 25) and observed D values. Only in the case of MNA, D_{obs} does not follow D_{calc}. MNA is a small nitramine type compound (CH_3NHNO_2). Statistically displayed characteristics of calc. and obs. D values are shown in Table 2.

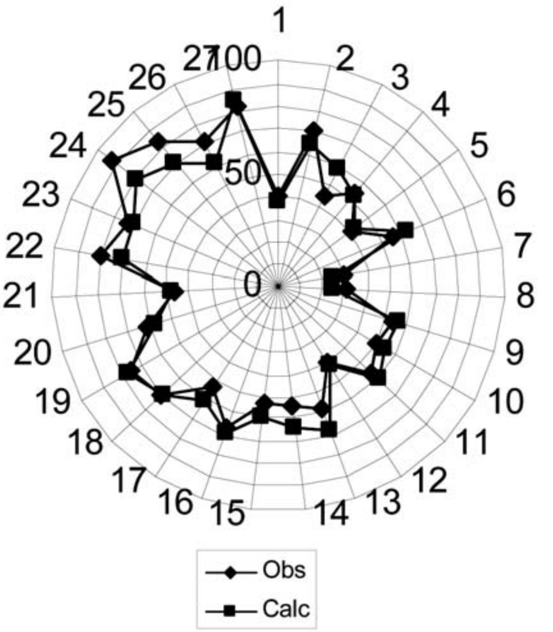

Figure 2. Correlation between the calculated and observed D^2 values. The peripheral numbers stand for the compound numbers in Table 1.

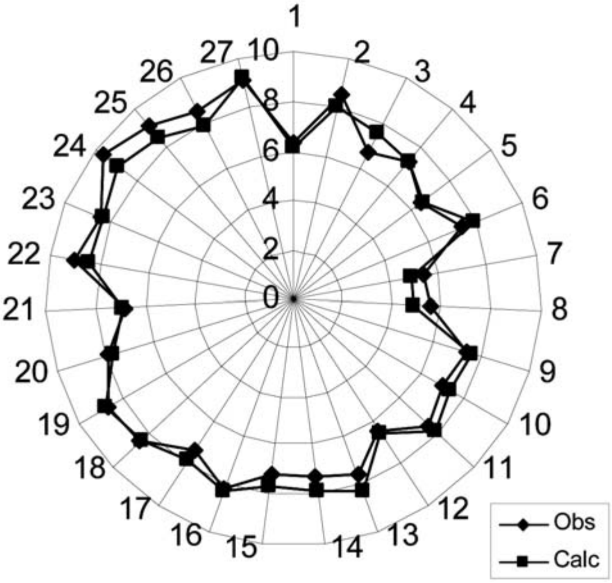

Figure 3. Correlation between the observed and calculated detonation velocities. The peripheral numbers stand for the compound numbers in Table 1.

The regression statistics of eq. 25 are given in Table 3. The R^2 of (coefficient of multiple determination[46,47]) the regression is quite good for a population of such a diverse collection of structures. The dependence of D^2 on X_1 and X_2 (NE/M and E/M, respectively) are expressed as simple and partial regression coefficients (see Table 3). The contribution of E/M term to D^2 is much greater than NE/M term, which means that D^2 is less sensitive to variations of the number of NO_2 groups. The effect of NO_2 groups should be implicitly included in the energies (E). Moreover, the value of r_{X1X2} term clearly indicates that X_1 and X_2 possess a low colinearity although they are related to each other by multiplier N. The underlying reason for it is that the variation of N (the number of NO_2 groups present) exhibits an uneven scattering in between numbers 1 and 6.

The calculated F-test value is 56.26 and the tabulated $F_{2,24}$ ($F_{k-1,n-k}$ where k : 3 and n : 27 presently. The sub indices k-1 and n, appearing as subscripts in the notation, are the number of independent variables and the population number (PN) of the regression, respectively) values are 3.40 and 5.61 for 5% and 1% significance levels, respectively[46,47]. The calculated $F_{2,24}$ value (56.26) far exceeds the tabulated values for 5% and 1% levels, thus the regressed equation is statistically significant.

Inspection of Table 1 indicates that in all the cases, with the exception of entries 3 and 8 (MNA and 1,5-DNN, respectively), the percent error ($[D_{calc} - D_{obs}] \times 100/D_{obs}$) in the detonation velocities in absolute value are all less than 10% from the observed ones. The cause of deviations for the observed and calculated D values might be various. First of all, there exist some assumptions and simplifications in the derivations of the equations (see the theory part). For instance, at the very beginning of the derivation, it has been assumed that the explosive considered is oxygen sufficient so that the material balance in between the produced gases ($\sum m_i$) and mass of the shell (M, it is assumed to be equal to the molecular weight of the explosive considered) is maintained. However, of the explosives shown in Table 1, none is oxygen sufficient except the oxygen superfluous MDN. Hence, the narrow range for variations of percent errors in D reveals that it is almost irrelevant to the oxygen balance. Secondly, the DFT calculations, including geometry optimizations, basis set adopted, etc. might be the source of the problem. Probably, if the optimized geometries for the structures, each standing for the global minimum (rather than local minimum) are obtained and some advance basis sets are employed then much better regression statistics could be obtained. Even some errors might come from the experimental D values which have been excerpted from the literature. In addition to efforts to alleviate these, the groups for the compounds could be constituted systematically (for instance for only nitramines or only for monocyclic aromatic nitro compounds) to get much better regressions. Hence, the approach has a floating character in that sense. Indeed, for 14 nitramines present in Table 1 the regressed equation

$$D^2 = -372.4122 - 1.3198(NE/M) - 106.8382(E/M) \qquad (26)$$

yields a much better coefficient of multiple determination,[46,47] R^2, value of 0.94. For the regression statistics of eq. 26, a similar discussion and conclusions can be said as done for eq. 25. For instance, the calculated F-test value is 91.80 for $F_{2,11}$ whereas the tabulated values are 3.98 and 7.20 for 5% and 1% reliability, respectively. The regression statistics of eq. 26 are given in Table 4. Note that in the pool of nitramines considered for eq.26, the members also dis-

Table 3. Some regression statistics of eq.25 ($Y = B_0 + B_1X_1 + B_2X_2$; X_1: NE/M, X_2: E/M).

Regression coefficients			**Simple correlation coefficients**			**Partial correlation coefficients**	
B_0	B_1	B_2	r_{YX1}	r_{YX2}	r_{YX1X2}	$r_{YX1\cdot X2}$	$r_{YX2\cdot X1}$
–393.6877	–0.2453806	–114.0793	–0.29344	–0.90350	–0.22913	–0.20717	–0.89869

R^2 : 0.8242051, Unexplained standard deviation: 7.188641, Unbiased estimation of the variance of regression coefficients Sb_{X1} and Sb_{X2} are 0.236577 and 11.36444, respectively.

Table 4. Some regression statistics of eq. 26 ($Y = B_0 + B_1X_1 + B_2X_2$; X_1: NE/M, X_2: E/M).

Regression coefficients			**Simple correlation coefficients**			**Partial correlation coefficients**	
B_0	B_1	B_2	r_{YX1}	r_{YX2}	r_{YX1X2}	$r_{YX1\cdot X2}$	$r_{YX2\cdot X1}$
–372.4122	–1.31983	–106.8382	–0.75342	–0.89833	0.47736	–0.84089	–0.93235

R^2 : 0.9434789, Unexplained standard deviation: 4.488443, Unbiased estimation of the variance of regression coefficients Sb_{X1} and Sb_{X2} are 0.2561234 and 12.49209, respectively.

play some structural diversity within the family. For example, OCPX and DMEDNA are N-alkyldinitramines but MDN is a geminal dinitramine, etc. Hence, being more strict on the structures of the compounds in the family one can probably get much better regression equations.

Some improvement in the regression statistics could also be achieved by modifying the regression model as well. Presently, the factor L of eq. 23 has been assumed to be linear function of N (the number of NO_2 groups) for regression purpose (see eq. 24). However, according to eqs. 22 and 23, L should be a function of the specific volumes γ_0 and γ_1 and as well as n. Note that n which is inherently included in eq. 22, originates from eq. 1 and it stands for the number of molecules of product gases in the explosion process. First of all, the specific volumes of the structures considered cannot be related to the number of nitro groups only. Secondly, n (the number of gas molecules produced) has to be different for different explosive molecules. In spite of all these drawbacks of the model, its success might be due to the involvement of M (molecular weight) and the total energy values in the independent variables X_1 and X_2 which probably alleviate the crudeness of assumptions involved in the assumed linear dependence of L on N. Obviously, any amelioration in the mathematical form of L term should improve the regression statistics.

As mentioned in the introduction part, there exist many methods for calculation of detonation velocity. Roothstein and Peterson's method[22] makes use of $D = (F–0.26)/0.55$, where F value is obtained from molecular composition and physical state of the molecule. Therefore, Roothstein and Peterson's method is not suitable if the state of the explosive is unknown which occurs in the case of molecular design of explosives. Aizenshtadt's treatment[48] is inferior both to Kamlet's and Roothstein and Peterson's methods, besides which all other methods require measured, estimated or calculated thermo chemical and physical data. For instance, Keshavar's formula[49] requires density and approximate detonation temperature, T_{app} which necessitates approximate heat of detonation per molecule and heat capacities of the detonation products. Another method suggested by Keshavar[50] is for aromatic energetic compounds and it is a modification of Kamlet-Jacobs equation in form and requires calculated thermo chemical data. Table 5 tabulates D values of some energetic materials obtained by different methods.

The present method has some physical and mathematical bases and it is not purely empirical. Probably, better results can be obtained by using much better quantum chemical methods and basis sets in calculation of total energy values. Another point to be mentioned is that the involvement of the total energy in the independent variables (X_1 and X_2) enables one to get distinguished D_{calc} values for isomeric compounds, because E values inherently contain topological properties of the molecules. Thus, the to-

Table 5. Experimental (D^o) and calculated detonation velocities (km/s).

Name	**D^o**	**K–J [51]**	**R–P [22]**	**A[48]**	**K–P [49]**	**K[50]**	**D from eq.25**
EDNA	8.42		8.31	8.64			7.99
TNB	7.42	7.68	7.27	6.91			7.87
1,8–DNN	5.38	5.67					4.86
1,5–DNN	5.52	5.64					4.86
TENN	7.30	7.56					7.46
TNT	7.02	7.02	6.97	7.23	6.98	7.17	7.32
PAM	7.50	7.67					7.73
TNN	6.27	6.70	5.69				6.50
PA	7.57	7.85	7.36	7.58			8.23
DPM	7.29	7.74					7.89
DPE	7.20	7.55					7.62
HNS	7.27	7.59	6.84		6.87		7.74
RDX	8.89		8.95	8.95		8.80	8.39
HMX	9.13		9.05	9.23			8.45

K-J: Kamlet-Jacobs, R-P: Rothstein-Petersen, K-P: Keshavarz-.Pouretdal, K: Keshavarz pological variations between the isomers are conveyed into the regression equation eventually. Hence, the present approach has some additional advantages over the literature cited empirical methods which are based on the empirical formula and M (molecular weight) only. Another advantage of the present approach is over the method of Kamlet and Jacobs[25–29] (see the introduction part). In the method of Kamlet and Jacobs, to estimate the D value of a nonexistent explosive material (often the case while designing new explosive materials) various required but unknown parameters are to be calculated (such as the density), so that in practice the solution of such a dilemma necessitates very many time consuming repeated quantum chemical calculations to be carried out in order to approximate the required parameters.

6. Conclusion

In the present study, starting from the principles of conservation of energy and momentum, a mathematical expression, relating D^2 value of an explosive with its total energy and molecular weight has been derived (eq. 22). The regressed equation (eq. 25) enables one to get some fairly accurate idea about D values of explosives by means of certain straightforward quantum chemical calculations. The model used could be improved to get more precise D values. In that sense, basis set dependence of the D_{calc} values could be investigated for certain collection of compounds as a future study.

List of abbreviations for the explosives considered

Abbreviation	Name
CPX	1,3-Dinitroimidazolidine
DMNA	2-Nitro-2-azapropane
1,5-DNN	1,5-dinitronaphthalene
1,8-DNN	1,8-dinitronaphthalene
DIGEN	1-nitro-1-azaethylene
DMEDNA	2,5-Dinitro-2,5-diazahexane
DNDC	1,4-dinitropiperazine
DPE	1,3,5-trinitro-2-[2-(2,4,6-trinitrophenyl) ethyl]benzene
DPM	1,3,5-trinitro-2-(2,4,6-trinitrobenzyl) benzene
EDNA	1,4-Dinitro-1,4-diazabutane
HMX	1,3,5,7-Tetranitro-1,3,5,7-tetrazocane (octogen)
HNIW	2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane
HNS	1,3,5-trinitro-2-[(*E*)-2-(2,4,6-trinitrophenyl)vinyl]benzene
MDN	1,1-dinitro-1-azaethane
MNA	1-Nitro-1-azaethane
OCPX	2,4-Dinitro-2,4-diazapentane
PA	2,4,6-trinitrophenol
PAM	2,4,6-trinitroaniline
RDX	1,3,5-Trinitro-1,3,5-triazinane (Hexogen)
TENN	1,4,5,8-tetranitronaphthalene
TETROGEN	1,3-Dinitro-1,3-diazetidine
TEX	4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane
TNAD	*trans*-1,4,5,8-Tetranitrodecahydro-pyrazino[2,3-*b*] pyrazine
TNAZ	1,3,3-Trinitroazetidine
TNB	1,3,5-Trinitrobenzene
TNN	1,4,5-trinitronaphthalene
TNT	2,4,6-trinitrotoluene

7. References

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Povzetek

Z matematičnim modelom, osnovanim na principu o ohranitvi energije in gibalne količine smo proučevali kvadrat hitrosti detonacije različnih eksplozivov (nitramini, alifatske in aromatske nitro spojine). Pri tem smo upoštevali celokupno energijo, dobljeno z DFT (UB3LYP/6-31G(d) metodo ter molsko maso spojin v posameznih eksplozivih. Podana je regresijska enačba za nitramine skupaj s statistično obravnavo.