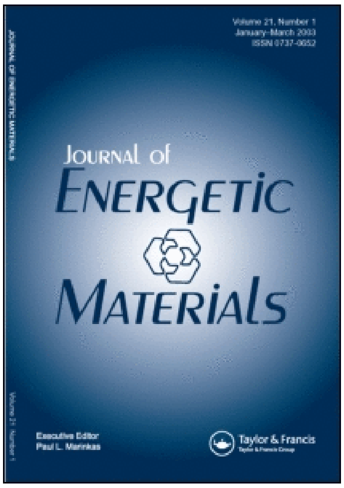

Journal of Energetic Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

A First-Order Linear Model for the Estimation of Detonation Velocity

Lem Türker[a]
[a] Department of Chemistry, Middle East Technical University, Ankara, Turkey

To cite this Article Türker, Lem(2011) 'A First-Order Linear Model for the Estimation of Detonation Velocity', Journal of Energetic Materials, 29: 1, 7 — 25

To link to this Article: DOI: 10.1080/07370652.2010.495107

URL: http://dx.doi.org/10.1080/07370652.2010.495107

Journal of Energetic Materials, 29: 7–25, 2011

ISSN: 0737-0652 print/1545-8822 online
DOI: 10.1080/07370652.2010.495107

A First-Order Linear Model for the Estimation of Detonation Velocity

LEMİ TÜRKER

Department of Chemistry, Middle East Technical University, Ankara, Turkey

A linear multivariable model has been derived for the estimation of detonation velocity. Then, its two simplified forms, first-order linear models, have been proposed as estimators of detonation velocities of a large population of explosives having different skeletal structures. Then, the models are analyzed mathematically and regression equations are obtained and discussed. The first model possesses two independent variables E/M and density, whereas the second one is based on E/M only. The total energy (E) is obtained at the level of UB3LYP/6-31G(d) and M is the molecular weight of the explosive considered.

Keywords: detonation velocity, DFT calculations, explosives, nitramines, regression analysis

Introduction

For the design of a novel explosive material having good impact and friction sensitivities, as well as high thermal stability and enhanced detonation performance, theoretical and computational approaches are indispensable to determine which structures have optimized properties. Thus, intensive research on new and

Address correspondence to Lemi Türker, Department of Chemistry, Middle East Technical University, 06531, Ankara, Turkey. E-mail: lturker@metu.edu.tr

powerful energetic materials having certain desired properties is an ongoing effort of scientists and engineers. Detonation velocity is an important performance characteristic of explosives that can be calculated by some elaborate computer codes having different levels of sophistication [1–5]. Generally, the computation of detonation parameters by those computer codes requires heat of formation ($\triangle H_f$) and the density data of an explosive as well as the equation of state of detonation products [6,7]. Moreover, for these computations some highly expensive or restricted computer programs are needed. When designing novel explosive structures, the inputs ($\triangle H_f$ and density) required for these computer programs should be previously calculated. Therefore, simple and inexpensive methods are always desirable.

The velocity of detonation at which the detonation shock wave proceeds through an explosive charge is an important detonation parameter in addition to the detonation rate [1]. Some useful equations relate detonation velocity to the other Chapman-Jouguet state parameters [1].

A shock wave propagates into a reactive gas mixture that is in a metastable thermodynamic–chemical (pseudo) equilibrium with frozen reaction. The intensity of the shock wave and the corresponding change of state are sufficiently large to start the reaction process [8]. Numerous articles exist in the literature concerning the kinetics of detonation for various explosives [9–17].

Using the thermochemical properties of an idealized detonation reaction, Kamlet and coworkers estimated detonation velocity [18–21]. The work of Rothstein and Peterson is another empirical approach to detonation velocity cited among several existing in the literature [22].

The above-mentioned empirical formulas for detonation velocity require some parameters. The detonation performance of a pure nitrated high explosive can most approximately be formulated as a function of its heat content in the condensed phase, its elemental composition, and its load 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 the ^{15}N nuclear magnetic resonance (NMR) chemical shift, δ_N, of nitrogen atoms in nitro groups of a limited number of nitramine-type explosives with rigid structures [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 [18–20] 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 is the density of a compound, N is moles of gaseous detonation products, M is average molecular weight of gaseous products, and Q is the chemical energy of detonation.

Theory

Design of a novel explosive material requires elaborate work, which requires estimation of certain ballistic properties of the proposed structure prior to its synthesis. Therefore, the structure–activity relationships are important [30]. Detonation velocity is a vital characteristic of an explosive to be measured (for existing explosives) or estimated (for nonexistent explosives). As mentioned above, there exist several complicated methods to predict the detonation velocities of explosive materials. However, a simple, straightforward but sufficiently accurate method is always desired. The problem at this stage is how to be sure of the accuracy of the quantity/property sought if the material is yet nonexistent. One approach to the problem could be to propose a model equation for that property/quantity that gives accurate estimates for known compounds.

In the present study, initially some general mathematical models were developed and then adapted and analyzed for detonation velocity, one of which has the general form represented by Eq. (1), which is a linear estimator model with two independent variables (X_1 and X_2).

$$D = B_0 + B_1X_1 + B_2X_2 \tag{1}$$

Construction of a Multivariable Model

Let us define vectors **A** and **C** in n-dimensional Euclidian linear space [31] such that $\mathbf{A}(B_0, B_1, \ldots, B_{n-1})$ and $\mathbf{C}(1, X_1, X_2, \ldots, X_{n-1})$. Furthermore, let any B_i be a real number and components of vector **C** be certain molecular descriptors. Then, obviously Eq. (2) holds for the dot products.

$$\mathbf{A}.\mathbf{C} = B_0 + B_1X_1 + \cdots + B_{n-1}X_{n-1} \tag{2}$$

Let

$$\mathbf{D} = \mathbf{A}.\mathbf{C} \tag{3}$$

Then, the scalar product of vectors **A** and **C** is also equal to

$$D = ||A||||C|| \cos\gamma \tag{4}$$

where γ is the angle between vectors **A** and **C**. Using Eq. (2), Eq. (4) can be written as

$$D = \sqrt{\sum_{i=0}^{n-1} B_i^2}\sqrt{1 + \sum_{i=1}^{n-1} X_i^2}\cos\gamma \tag{5}$$

Note that if D is positive and real, then B_i $(i=0, 1, 2, \ldots, n-1)$ all have to be real or $\sum_{i=0}^{n-1} B_i^2$ has to be positive; otherwise D cannot be real. Modifying Eq. (5) one gets

$$D = \sqrt{\frac{n\sum_{i=0}^{n-1} B_i^2}{n}}\sqrt{1 + \sum_{i=1}^{n-1} X_i^2}\cos\gamma \tag{6}$$

On the other hand, it is known that the geometric mean for a set of numbers is less than the arithmetic mean [32]; that is,

$$\sqrt[n]{a_1^\alpha a_2^\alpha \ldots a_n^\alpha} \leq \frac{a_1^\alpha + a_2^\alpha + \cdots + a_n^\alpha}{n} \tag{7}$$

Knowing this property, Eq. (6) can be converted to inequality (8)

$$D \geq \sqrt{n\sqrt{\prod_{i=0}^{n-1} B_i^2}\sqrt{1+\sum_{i=1}^{n-1} X_i^2}\cos\gamma} \tag{8}$$

Inequality (8), which is a general multivariable model (n-dimensional), can be simplified for three-dimensional space to yield inequality (9). It contains only two variables, X_1 and X_2.

$$D \geq \sqrt{3B_0B_1B_2}\sqrt{1+X_1^2+X_2^2}\cos\gamma \tag{9}$$

Mathematical Analysis of the Model

Because D is a real nonzero quantity, any term on the right-hand side of inequality (9) has to be real and nonzero. Note that inequality (9) is strictly restrictive on the unimaginary nature of B_i, whereas the general equation, Eq. (5), is weakly restrictive. Thus, it mainly requires that cos $\gamma > 0$ $(0 \leq \gamma < 90)$ and inequality (10) holds.

$$B_0B_1B_2 \succ 0 \tag{10}$$

Inequality (10) necessitates either all of $B_i > 0$ or any two of B_0, B_1, and B_2 have to be mutually negative so that inequality (10) holds (note that in n-dimensional space $\prod_{i=0}^{n-1} B_i \succ 0$ has to hold). So, in three-dimensional space D could be represented by any of Eqs. (11)–(14). They are possible models obtained at first glance.

$$D = B_0 + B_1X_1 + B_2X_2 \tag{11}$$

$$D = -B_0 - B_1X_1 + B_2X_2 \tag{12}$$

$$D = -B_0 + B_1X_1 - B_2X_2 \tag{13}$$

$$D = B_0 - B_1X_1 - B_2X_2 \tag{14}$$

Analysis of these equations yields the following cases:

1. If $X_1 > 0$ and $X_2 > 0$, then from Eq. (11) a positive value of D exists if $B_0 + B_2X_2 \succ |B_1X_1|$.
2. If $X_1 < 0$ and $X_2 > 0$, then from Eq. (12) a positive value of D exists if $B_1X_1 + B_2X_2 \succ |-B_0|$.
3. If $X_1 < 0$ and $X_2 > 0$, then Eq. (13) yields a negative value for D, which that means the model described by Eq. (3) has to be discarded for any D having positive value E/M.
4. If $X_1 < 0$ and $X_2 > 0$, then Eq. (14) gives a positive value for D if and only if $B_0 - B_1X_1 \succ |-B_2X_2|$.

$X_2 > 0$ is considered in cases 1–4, because if D and X_2 are assumed to be the detonation velocity and density of an explosive, respectively (which are always positive), then cases 1, 2, and 4 hold.

On the other hand, taking the derivatives of D (Eq. (5)) with respect to B_i for a three-dimensional case, one obtains

$$\frac{\partial D}{\partial B_i} = \frac{B_i\sqrt{1 + X_1^2 + X_2^2}}{\sqrt{B_0^2 + B_1^2 + B_2^2}} \cos\gamma \tag{15}$$

In Eq. (15), the derivative $\frac{\partial D}{\partial B_i} = 0$ requires either $B_i = 0$ or $\cos\gamma = 0$. But, considering Eq. (4), $\cos\gamma = 0$ necessitates the detonation velocity to be zero, which is an improper state and to be rejected for explosives. If all B_i are different than zero, then $\frac{\partial D}{\partial B_i} = 0$ condition for the existence of extrema for the right-hand sides of Eq. (15) does not hold for any real values of the parameters X_1 and X_2.

These mathematical results are numerically demonstrated in the Results and Discussion section.

Method

In the present study, the initial geometry optimizations were achieved by using a molecular mechanics (MM2) method, followed by the semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [33,34] at the restricted level [35,36]. Then, STO, Restricted Hartree-Frock (RHF) and density functional theory (DFT) [37,38] type quantum chemical calculations were 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 [38,39]. The correlation term of B3LYP consists of a Vosko-Wilk-Nusair (VWN3) local correlation functional [40] and Lee-Yang-Parr (LYP) correlation functional [41].

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 determine whether any bond cleavage occurred during the geometry optimization process. The geometry optimizations and the vibrational analysis computations were performed using the Spartan 06 package program [42].

Results and Discussion

The results of the above mathematical analysis of the proposed linear first-order model with two independent variables for the detonation velocity are independent of the character of independent variable X_i in Eq. (1) and the number of data points in the pool. However, to verify the model and to make use of it for practical purposes, namely, to estimate D values or guess the affect of variables on D, one has to determine coefficients $B_0 - B_2$. The numerical values of the coefficients are obviously dictated by the values of X_1 and X_2 and the population number involved in the regression analysis. At this stage, the problem is to guess suitable descriptor variables, standing for X_1 and X_2. For that purpose, various molecular and quantum chemical properties of a series of explosive materials have been tested. It has been found that there exists a linear relation between the D values and E/M values, where E is the total energy in au corrected for zero-point energy (ZPE) obtained at the level of UB3LYP/6-31G(d) and M is the molecular weight of the explosive in grams. Also a similar linear relation is found between D and density (d; see Figs. 1 and 2 and Table 1).

Regression Analysis

Table 1 shows various data of the present computational study. The explosive compounds in the table are shown by their abbreviated names, which are provided in the Appendix. The experimental (observed) D values in Table 1 were excerpted from the literature [43,44] as were the densities [45–47]. Some of the explosive structures considered are simply aromatic nitro compounds like TNT, TNB, etc., whereas some are nitramines like EDNA (an acyclic explosive). The list also includes some mixed types like TNAZ, which possesses nitro groups, so that some of them are attached to an aliphatic carbon and one is attached to an amine group. The explosives PA and PAM contain phenolic and amine groups, respectively, attached to

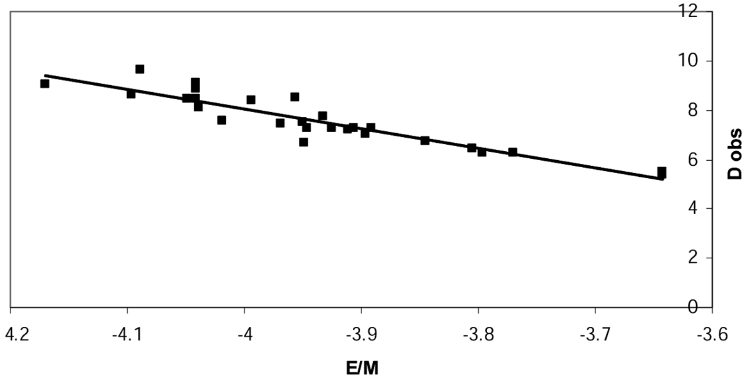

Figure 1. Plot of D_{obs} (km/s) versus E/M (au/g).

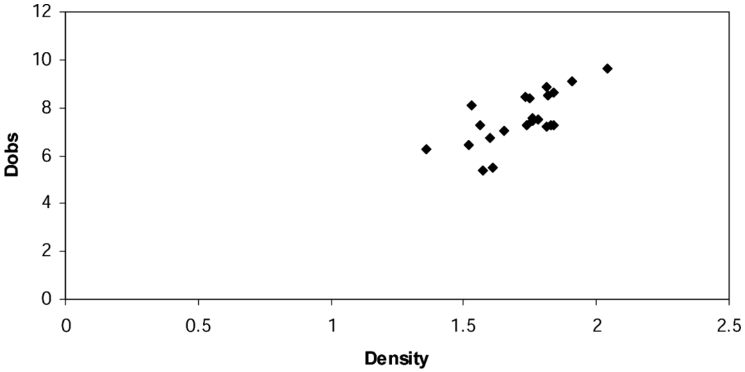

Figure 2. Plot of D_{obs} (km/s) versus density (g/cm^3).

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 (n: 22) 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 UB3LYP/6-31 G(d) type and corrected for zero-point vibrational energy (in Hartree unit). For the sake of simplification, symbol E will be used for the total energy.

The regression analysis yields Eq. (16).

$$D = -7.157115\left(\frac{E}{M}\right) + 1.262652d - 22.739270 \qquad (16)$$

where units of E, M, and d are in au (Hartree unit), gm, and gm/cm^3, respectively. Note that E (total energy) is a negative quantity (see Table 1 for E/M values) and structures having more negative E values are more stable. Explosives are inherently less stable than nonexplosive compounds. Thus, the coefficient of E/M ratio in Eq. (16) has a negative value. The numerical values of coefficients of Eq. (16) show that inequality (10), $B_0B_1B_2 \succ 0$, is valid and Eq. (16) is actually Eq. (12) with numerical coefficients. Moreover, constraint $B_1X_1 + B_2X_2 \succ |-B_0|$ given in case 2 is fulfilled.

Table 1

E/M ratios, calculated and observed detonation velocities, and percentage errors for the explosives considered

NAME	E/M (au/g)[a]	Density (g/cm^3)	D_{cal} (km/s) Eq. (16)	D_{cal} (km/s) Eq. (17)	D_{obs} (km/s)	% err Eq. (16)	% err Eq. (17)
DMNA	−3.76946	1.36	5.96	6.25	6.29	−5.30	−0.63
EDNA	−3.99331	1.75	8.05	8.08	8.42	−4.38	−4.06
OCPX	−3.89138	1.56	7.08	7.25	7.28	−2.72	−0.47
DMEDNA	−3.80547	1.52	6.42	6.54	6.42	−0.05	1.93
TNB	−3.96813	1.76	7.88	7.87	7.42	6.24	6.09
1,8-DNN	−3.64269	1.57	5.31	5.22	5.38	−1.22	−3.06
1,5-DNN	−3.64273	1.61	5.36	5.22	5.52	−2.80	−5.51
TENN	−3.90599	1.84	7.53	7.36	7.30	3.28	0.88
TNT	−3.89601	1.65	7.23	7.28	7.02	2.96	3.75
PAM	−3.94959	1.78	7.78	7.72	7.50	3.68	2.94
PA	−4.01929	1.76	8.25	8.29	7.57	8.98	9.50
DPM	−3.94626	1.83	7.82	7.69	7.29	7.20	5.53
DPE	−3.91073	1.81	7.54	7.40	7.20	4.66	2.82
DIGEN	−4.03928	1.53	8.10	8.45	8.12	−0.21	4.09
HNS	−3.92557	1.74	7.55	7.52	7.27	3.90	3.50
Tetrogen	−4.04152	1.73	8.37	8.47	8.46	−1.05	0.13
TNAZ	−4.09688	1.84	8.90	8.92	8.62	3.32	3.51
DNDC	−3.84520	1.60	6.80	6.86	6.75	0.76	1.75
RDX	−4.04173	1.81	8.47	8.47	8.89	−4.68	−4.69
HNIW	−4.08895	2.04	9.10	8.86	9.62	−5.39	−7.91
HMX	−4.04174	1.91	8.60	8.47	9.13	−5.81	−7.19
TNAD	−3.95566	1.82	7.87	7.77	8.52	−7.63	−8.80

[a] E values used are corrected for ZPE.

The regression analysis produces Eq. (16) having the coefficient of determination $R^2 = 0.8876$ and simple correlation coefficients, $r_{YX1} = -09326525$, $r_{YX2} = 0.7096844$, and $r_{X1X2} = 0.6523887$. The partial regression coefficients are $r_{YX1 \cdot X2} = -0.8796089$ and $r_{YX2 \cdot X1} = 0.3702363$. Note that the r_{X1X2} value indicates a fair colinearity between variables X_1 and X_2. Its importance will be mentioned below. When using Eq. (16), one has to retain the coefficients and E/M values in full digits to get the best calculated value of D and then round the result.

Note that the E/M ratio is a negative quantity due to the total energy value.

The presently calculated $F_{2,19}$ value for the regression is 75.08143, whereas the tabulated [48,49] $F_{2,19}$ values are 3.52 and 5.93 at the 5 and 1% levels of significance, respectively ($F_{2,19}$ stands for $F_{k\text{-}1,n\text{-}k}$, where k is the number of parameters estimated and n is the population number. Presently, $k = 3$ and $n = 22$). Thus, the regressed equation (Eq. (16)) is acceptable. All these regression statistics indicate that the present model is quite a good estimator for the detonation velocities of the explosives in a wide range of structural variations. It has a simple form as well.

The model described by Eq. (16) shows that as the E/M ratio increases in absolute value, D increases because E/M is a negative quantity. D also increases with increasing density, which is a well-known fact in the practice of explosives. The simple and partial regression coefficients reveal that D is more dependent on the E/M ratio than the density. Table 1 shows D values predicted by Eqs. (16) and (17), which are in the range of 10% error. This is expected because in the theoretical part Eq. (6) is approximated by means of inequality (8). Then the main usage of Eq. (16) is not to reproduce experimental D values precisely but to guide scientists when designing novel explosives. The experimental detonation velocity is dependent on the charging density of the explosive considered, whereas Eq. (16) in the present form cannot be used for varying charging densities of one particular explosive. For that purpose Eq. (12) has to be regressed for varying densities of that explosive. Densities in Eq. (16) are excerpted from the literature and some may not be very exact. Some errors may also be present in D_{obs} values.

For the purpose of designing novel explosive materials, the E/M ratio is important and worth contemplation. The quantum chemical variable E of E/M ratio is implicitly related to molecular geometry and thus is related to volume. Hence, the E/M ratio is inherently related to density. This fact is also reflected by the fairly high value of r_{X1X2}. However, volume and thus the density of a single molecule (as considered presently) cannot be equal to crystal density. Consequently, some deviations are expected between the presently calculated and observed detonation velocities (see Fig. 3).

Inspection of Fig. 1 reveals that a fairly good correlation exists between the E/M values (in au/gm) of the explosives and the observed detonation velocities in km/s. The correlation is especially good for E/M values algebraically greater than -3.95 au/g or D_{obs} values less than 8 km/s. Those values generally stand for explosives having either/both peculiar structures, like HNIW, TEX, etc., or more than two nitro groups, like HMX, TNAD, etc.

In light of the fact that the E/M ratio is implicitly related to density because of the reasons mentioned above ($r_{X1X2} = 0.65$), Eq. (16) can be modified to Eq. (17), which is a simple one-variable linear model. The regression analysis produces Eq. (17) having the coefficient of determination $R^2 = 0.8698$ and correlation coefficient $r_{YX} = -0.932652$. When using Eq. (17), one has to retain the coefficients and E/M values in full digits to get the best calculated value of D and then round the result. Note once again that the E/M ratio is a negative quantity due to the total energy value.

$$D = -24.52194 - 8.16353\left(\frac{E}{M}\right) \tag{17}$$

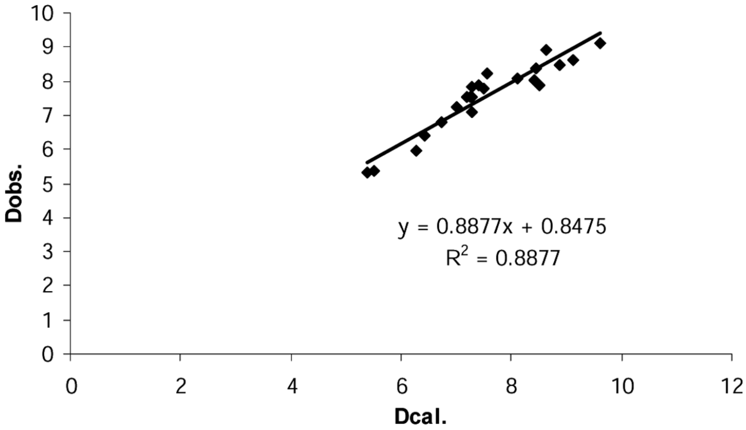

Figure 3. Plot of D_{obs} versus D_{cal} (Eq. (16)) (both in km/s).

The presently calculated $F_{1,20}$ value for the regression is 133.6577, whereas the tabulated [48,49] $F_{1,20}$ values are 4.35 and 8.10 at the 5 and 1% levels of significance, respectively. Thus, the regressed equation (Eq. (17)) is acceptable. All these regression statistics indicate that the present model (Eq. (17)) is as good estimator for the detonation velocities of the explosives in a wide range of structural variations as the previous model (Eq. (16)). It has a simple form as well. Table 1 shows the percentage errors, which are less than 10% in absolute value and mostly less than 5%.

Another point to be considered is cosγ values for the sets of calculated and observed detonation velocities. Using the regression coefficients of Eq. (17) with the calculated and observed D values, the averages of cosγ values are found to be close to zero for all the explosives considered; thus γ (the angle between vectors **A** and **C**; see Theory section) is about 90°.

Another point to be mentioned is that the involvement of the total energy in the independent variable (X_1 in Eqs. (16) and (17) enables one to obtain distinguished D_{calc} values for isomeric compounds, because E values inherently contain topological properties of the molecules. Thus, the topological 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 [18–21, 25–29] (see Introduction section). In the method of Kamlet and Jacobs, to estimate the D value of a nonexistent explosive material (often the case when designing new explosive materials), various required but unknown parameters are to be calculated (such as density), so that in practice the solution of such a dilemma necessitates carrying out many time-consuming repeated quantum chemical calculations in order to approximate the required parameters. Equation (17) does not require density and hence is more practical than Eq. (16) and the methods given in the literature; for example, Kamlet-Jacobs. Although the precision of Eqs. (16) and (17) is not perfect, they can be employed for quick screening purposes.

On the other hand, the mathematical interpretation of regression Eq. (16) reveals that positive D values (physically meaningful ones) require

$$d \geq 5.668\left(\frac{E}{M}\right) + 18.0091 \tag{18}$$

and for meaningful d values, E/M has to be less than $-3.17\,\text{au/g}$. Note that these values are the lowest upper bounds for E/M ratios. A similar analysis for Eq. (17) shows that E/M has to be less than $-3.00\,\text{au/g}$. From these results one gets an important structural constraint for the design of novel explosives; that is, their atoms in kind and their structural geometries and bonding have to be arranged in such a way that the E/M ratio should be less than $-3.17\,\text{au/g}$ within the restrictions of the present level of calculations (UB3LYP/6-31G(d)). Note that the above-mentioned constraint has been obtained based on regression Eq. (16). Thus, it is an upper bound for E/M (algebraically) having some approximate character within the precision of the regression Eq. (16). However, the well-known explosives listed in Table 1 have E/M lower than this upper bound.

Conclusion

In the present study, the mathematical analysis of the proposed linear, bivariable, and one-variable models have been supported by numerical treatment by means of regression analysis. The regressed equations (Eqs. (16) and (17)) enable one to obtain a fairly accurate idea about D values of explosives by certain straightforward quantum chemical calculations. Equation (17) is an alternative to Eq. (16) if one does not know the maximum theoretical density of explosive considered. The models used could be improved to obtain more precise D values, but then it would not be as simple as the present one. For instance, one should obtain better results if the bivariable model is replaced with a three- or four-variable one with suitable molecular descriptors. Also, basis set dependence of the D_{calc} values could be investigated for a certain collection of compounds as a future study.

References

[1] Mader, C. L. 1998. *Numerical Modeling of Explosives and Propellants*, 2nd ed. New York: CRC Press.

[2] Cowperthwaite, M. and W. H. Zwisler. 1973. *TIGER Computer Program Documentation*. Stanford Research Institute. Austin, TX: SRI Pub. No. 2106.

[3] Fried, L. E., W. M. Howard, and P. C. Souers. 1998. *CHEETAH 2.0 User's Manual*. Livermore, CA: Lawrence Livermore National Laboratory.

[4] Levine, H. B. and R. E. Sharples. 1962. *Operator's Manual for RUBY*. Livermore, CA: Lawrence Livermore Laboratory Report UCRL-6815.

[5] Mader, C. L. 1963. *Detonation Properties of Condensed Explosives Computed Using Becker-Kistiakowsky-Wilson Equation of State*. Los Alamos, NM: Los Alamos Scientific Laboratory. Report LA-29000.

[6] Keshavarz, M. H. 2007. A simple theoretical prediction of detonation velocities of non-ideal explosives only from elemental composition. In P.B. Warey (ed.), *New Research on Hazardous Materials*, New York: Nova.

[7] Türker, L., S. Gümüş, T. Atalar, and Y. Çamur. 2007. Theoretical treatment of some novel nitropyrimidines. In P.B. Warey (ed.), *New Research on Hazardous Materials*, New York: Nova.

[8] Gruschka, H. D. and F. Wecken. 1971. *Gasdynamic Theory of Detonation*. New York: Gordon and Breach Science Publishers.

[9] Lepier, G. A. and J. Cooper. 1997. The kinetics of detonation of nitroguanidine. *Propellants, Explosives, Pyrotechnics*, 22(6): 347–350.

[10] Walker, F. E. 1994. A new kinetics and the simplicity of detonation. *Propellants, Explosives, Pyrotechnics*, 19(6): 315–326.

[11] Paillard, G., G. Dupre, and S. Al Aitch. 1989. Influence of chemical kinetics on detonation structure: The case of chlorine dioxide. *Annales de Physique*, 14(6): 641–648.

[12] Kondrikov, B. N. and G. I. Mendeleev. 1983. Chemical kinetics of detonation in some organic liquids. *Progress in Astronautics and Aeronautics: Shock Waves, Explosions, Detonations*, 87: 426–441.

[13] Bdzil, J. B., R. Engelke, and D. A. Christenson. 1981. Kinetics study of a condensed detonating explosives. *Journal of Chemical Physics*, 74(10): 5694–5699.

[14] Bernard, M. L. 1973. Prediction of detonation regime of explosives condensed by chemical kinetics. *Comptes Rendus des Séances de l'Academie des Sciences, Series C*, 277(15): 613–614.

[15] Bernard, M. L., P. Autard, G. Thomas, P. Le Gall, and J. T. Serve. 1973. Kinetic theory of condensed explosive detonation. *Comptes Rendus des Séances de l'Academie des Sciences, Series Comptes Rendus des Seances de l'Academie des Sciences, Series B*, 277(16): 671–673.

[16] Ye, S., K. Tonokura, and M. Koshi. 2003. Energy transfer rates and impact sensitivities of crystalline explosives. *Combustion and Flame*, 132: 240–246.

[17] Brill, T. B. and R. J. Karpowicz. 1982. Solid phase transition kinetics. The role of intermolecular forces in the condensed-phase decomposition of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine. *Journal of Physical Chemistry*, 86: 4260–4265.

[18] Kamlet, M. J. and S. J. Jacobs. 1968. Chemistry of detonation: Simple method of calculation properties of CHNO explosives. *Journal of Chemical Physics*, 48: 23–35.

[19] Kamlet, M. J. and J. E. Ablard. 1968. Chemistry of detonations II. Buffered equilibrium. *Journal of Chemical Physics*, 48: 36–42.

[20] Kamlet, M. J. and C. Dikinson. 1968. Chemistry of detonations III. Evaluation of simplified calculational method for Chapman-Jouguet detonation pressures on the basis of available experimental information. *Journal of Chemical Physics*, 48: 43–50.

[21] Kamlet, M. J. and H. Hurwitz. 1968. Chemistry of detonations IV. Evaluation of a simple predictorial method for detonation velocities of CHNO explosives. *Journal of Chemical Physics*, 48: 3685–3692.

[22] Rothstein, L. R. and R. Petersen. 1979. Prediction of high explosive detonation velocities from their composition and structure. *Propellants, Explosives, Pyrotechnics*, 4: 56–60.

[23] Zeman, S. 1992. Relationship between the Arrhenius parameters of the low temperature thermolysis and ^{13}C and ^{15}N chemical shifts of nitramines. *Thermochimica Acta*, 202: 191–200.

[24] Zeman, S., R. Huczala, and Z. Friedl. 2002. The study of chemical micromechanism governing detonation initiation of some m-dinitrobenzenopolyazaarenes. *Journal of Energetic Materials*, 20(1): 53–69.

[25] Klapoetke, T. M., F. X. Steemann, and M. Suceska. 2008. Computed thermodynamic and explosive parameters of

1-azido-2-nitro-2-azapropane (ANAP). *Propellants, Explosives, Pyrotechnics*, 33(3): 213–218.

[26] Fan, X. W. and X. H. Ju. 2008. Theoretical studies on four-membered ring compounds with NF_2, ONO_2, N_3 and NO_2 groups. *Journal of Computational Chemistry*, 29(4): 505–513.

[27] Gejji, S. P., M. B. Talawar, T. Mukundan, and E. M. Kurian. 2006. Quantum chemical, ballistic and explosivity calculations on 2,4,6,8-tetranitro-1,3,5,7-tetraazacyclooctatetraene: A high energy molecule. *Journal of Hazardous Materials*, 134(1–3): 36–40.

[28] Denffer, M. V., T. M. Klapoetke, G. Kramer, G. Spiess, J. M. Welch, and G. Heeb. 2005. Improved synthesis and X-ray structure of 5-aminotetrazolium nitrate. *Propellants, Explosives, Pyrotechnics*, 30(3): 191–195.

[29] Engelke, R. and J. R. Stine. 1990. Is N8 cubane stable? *Journal of Physical Chemistry*, 94(15): 5689–5694.

[30] Türker, L. 2009. Structure-impact sensitivity relation of certain explosive compounds. *Journal of Energetic Materials*, 27: 94–109.

[31] Efimov, N. V. and E. R. Rozendron. 1975. *Linear Algebra and Multidimensional Geometry*. Moscow: Mir Publishers.

[32] Korovkin, P. P. 1975. *Inequalities*. Moscow: Mir Publishers.

[33] Stewart, J. J. P. 1989. Optimization of parameters for semi empirical methods I. Method. *Journal of Computational Chemistry*, 10: 209–220.

[34] Stewart, J. J. P. 1989. Optimization of parameters for semi empirical methods II. Applications. *Journal of Computational Chemistry*, 10: 221–264.

[35] Leach, A. R. 1997. *Molecular Modeling*. Essex: Longman.

[36] Fletcher, P. 1990. *Practical Methods of Optimization*. New York: Wiley.

[37] Kohn, W. and L. J. Sham. 1965. Quantum density oscillations in an inhomogeneous electron gas. *Physical Review*, 140: A1133–A1138.

[38] Parr, R. G. and W. Yang. 1989. *Density Functional Theory of Atoms and Molecules*. London: Oxford University Press.

[39] Becke, A. D. 1988. Density-functional exchange—Energy approximation with correct asymptotic behavior. *Physical Review A*, 38: 3098–3100.

[40] Vosko, S. H., L. Vilk, and M. Nusair. 1980. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: A critical analysis. *Canadian Journal of Physics*, 58: 1200–1211.

[41] Lee, C., W. Yang, and R. G. Parr. 1988. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Physical Review B*, 37: 785–789.

[42] Spartan 06 Program. Irvine, CA: Wavefunction Inc.

[43] Zeman, S. 1999. Relationship between the detonation characteristics and ^{15}N chemical shifts of nitramines. *Journal of Energetic Materials*, 17: 305–330.

[44] Zeman, V., J. Koci, and S. Zeman. 1999. Electric spark sensitivity of polynitro compounds: Part II. A correlation with detonation velocities of some polynitro arenes. *Energetic Materials*, 7: 127–132.

[45] Wang, G., H. Xiao, X. Ju, and X. Gong. 2006. Calculation of detonation velocity, pressure and electric spark sensitivity of nitro arenes based on quantum chemistry. *Propellants, Explosives, Pyrotechnics*, 31: 191–195.

[46] Qui, L., H. Xiao, X. Gong, X. Ju, and W. Zhu. 2007. Crystal density predictions for nitramines based on quantum chemistry. *Journal of Hazardous Materials*, 141: 280–288.

[47] Wang, G.-X., H.-M. Xiao, X.-J. Xu, and X.-H. Ju. 2006. Detonation velocity and pressure and their relationships with electric spark sensitivities for nitramines. *Propellants, Explosives, Pyrotechnics*, 31: 102–109.

[48] Draper, N. and H. Smith. 1966. *Applied Regression Analysis*. New York: Wiley.

[49] Salvatore, D. 1982. *Statistics and Econometrics*. New York: McGraw-Hill.

Appendix—List of Abbreviations for the Explosives Considered

Abbreviation	Name
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
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
TNAD	*trans*-1,4,5,8-Tetranitrodecahydro-pyrazino[2,3-*b*] pyrazine
TNAZ	1,3,3-Trinitroazetidine
TNB	1,3,5-Trinitrobenzene
TNT	2,4,6-Trinitrotoluene