Quantum Chemistry Derived Criteria for Impact Sensitivity

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Abstract: Energetic materials are a special and important kind of substance. Impact sensitivity, which refers to the vulnerability to explosion under external stimuli, measures the safety and reliability of an energetic material and is a critical property. Various efforts have been made to rationalize the impact sensitivity of different types of energetic materials. Since a chemical explosion is a chemical reaction dominated phenomenon, a comprehensive understanding of such explosive processes requires detailed information of chemical bonding and molecular interaction.

Quantum chemistry provides a modern theory of chemical bonding and computational quantum chemistry is a powerful tool to investigate chemical phenomena. Even at the very beginning of computational quantum chemistry, researchers in the field of energetic materials have begun to apply quantum chemistry to explosive properties. In this paper we review the quantum chemistry studies on impact sensitivity and examine various quantum chemistry derived parameters used to rationalize the impact sensitivity ordering of various energetic materials.

Keywords: Impact sensitivity · Quantum chemistry

1 Introduction

Energetic materials are a kind of substance whose safety is utmost important. A key property related to safety is the sensitivity [1]. There are several types of sensitivity: electric spark sensitivity, electrostatic sensitivity, shock sensitivity, friction sensitivity and impact sensitivity. Of all these sensitivities, impact sensitivity is one of the most important characteristics of energetic materials and is widely studied. Experimentally impact sensitivity is usually determined using drop hammer test. For many years scientists have been working hard to understand why some materials are so sensitive to impact, whereas others are not. Robertson and Yoffe believed that impact-initiated explosions are thermal decomposition processes [2], which is substantiated by later researches [3,4]. It is generally accepted that hot spots play dominant roles in the initiation process [3–7]. From a chemical point of view, a chemical explosion (unless explicitly stated, "explosion" in the following always refers to "chemical explosion") is a series of fast chemical reactions that release great amount of energies in the form of heat, sound and light, accompanied by a rapid and great expansion of volume and release of gases. Chemical reactions always involve chemical bond formation and breaking. Thus, it is very natural and appropriate to employ chemical bonding theory to rationalize the explosive phenomenon. It is worthy to point out that most results reviewed here correspond to isolated molecules. As such the impact sensitivity against which correlations are made corresponds to intrinsic sensitivity or stability of the molecule as opposed to the measured sensitivity of condensed phase.

As far as we know, application of quantum chemistry to energetic materials can at least be traced back to 1970s [8,9]. With the advances of theoretical chemistry and application of computational chemistry, various concepts and indices or parameters derived from quantum chemistry, such as charges, bond order, electrostatic potentials, bond dissociation energy, energy barrier, band gap, are suggested to explain the impact sensitivity of energetic materials. Impact sensitivity is reasonably rationalized with these indices and several review papers or books have discussed this topic [10–21]. In this review, we summarize various parameters obtained from electronic structure calculations and used as criteria to rationalize the impact sensitivity ordering of explosives.

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2 Criteria Used to Rationalize Impact Sensitivity

2.1 Atomic Charges

Atomic charges are a well-known chemical concept used by chemists to elucidate physical and chemical properties of a compound. Charges seem to be the first quantity employed by quantum chemists to explain the ordering of impact sensitivity. As early as 1970s Schroeder had employed CNDO/2 (Complete Neglect of Differential Overlap, Second Version) approximate molecular orbital (MO) theory to calculate the charges of a series of tetrazole compounds and correlated the calculated charges with the explosive properties [8,9]. Haskins used the charges obtained with iterative extended Hückel molecular orbital (EHMO) approach as a quantitative measure of the electron withdrawing power of the substituents on tetrazole rings and found that there is a relationship between the explosive behavior of the studied compounds and the EHMO calculated charges [22]. On the basis of the calculations on trinitro aromatic molecules, Owens demonstrated that larger positive charges on the carbon atom linked to a NO_2 group correspond to a stronger C—N bond (and thus a less sensitive compound) [23].

Mullay examined the charges transferred to a nitro group through a trigger linkage (C—NO_2, N—NO_2 and O—NO_2. Trigger linkage, coined by Kamlet and Adolph [24], refers to a bond whose breaking initiates explosion or detonation.). He concluded that "the transferred charges can classify and correlate impact sensitivity trends of the compounds studied. Both a global quantity (related to the whole molecule) and a local quantity (related to the trigger linkage) are needed to understand impact sensitivity behavior" [25,26]. Mullay's work is significant in the sense that: (i) it shows that charges can be a good index to rationalize the sensitivity, subject to some conditions; (ii) charges of the nitro group are good indicators of relative impact sensitivity when the group is associated with the trigger linkage; (iii) knowledge of trigger linkage is a prerequisite for using nitro group charges; (iv) both global and local quantities pertinent to the trigger linkage are required to account for impact sensitivity, which implies that local quantities alone cannot explain the sensitivity well enough for a broad range of compounds. In other words, local quantities are not good indicators unless the global quantities are similar for the compounds under study. This finding may explain why indices like charges can sometimes correlate very well with the impact sensitivity when the comparison is made for analogues.

Recently, Mulliken atomic charges on nitro groups were reused to rationalize the impact sensitivity of the explosives [27]. As shown above, the correlation between the impact sensitivity and the charges on the nitro group linked to the rest part of the molecule via trigger linkage has been pointed out long before in the work of Mullay [26]. Therein, the

limitation or condition to correlate charges with impact sensitivities has also been clearly stated. We once showed that charges cannot be used to interpret the impact sensitivity even for analogous tetrazole compounds [28–30]. Charges on some specific groups like nitro group may be used to elucidate the impact sensitivity sequence if these compounds are analogous (structurally similar) and their detonation or explosion is triggered by the same initiation mechanisms (explosion is induced by breaking the similar trigger linkage, and the "aggregate effects" are similar. By "aggregate effect" we mean those that are related to the molecular packing, crystal structure, crystal defect and heat transfer, or simply speaking "condensed phase environment"). Recently, Xu et al. demonstrated that there is a linear relationship between the charges on nitro groups and the activation energies [31]. As activation energies (see below) better characterize the sensitivity, the good correlation between the charges on the nitro group and the activation energy explains why one can use the charges on the nitro group, in some cases, to discuss the impact sensitivity.

Intrinsically, however, charges on nitro groups are not, and cannot be used as ideal descriptors to describe the impact sensitivity because: (i) quantum-mechanically calculated atomic charges have no rigorous physical basis [32]. Even for nitro-group containing compounds, if the trigger linkage does not involve the NO_2 group, the charges on the nitro group cannot correlate with the impact sensitivity. For example, detonation of some compounds like nitro derivatives of phenols may be initiated by the H-transfer (O—H bond breaking) [12]. (ii) Chemically impact sensitivity is related to the feasibility of breaking of a chemical bond (trigger linkage, mostly C—NO_2 and N—NO_2 bonds), assuming the aggregate effect is similar within the compounds. Such feasibility is undoubtedly determined by the bond strength, not by charges. (iii) Inherently and theoretically there is no quantum mechanical operator corresponding to atomic charges, and all the atomic charges obtained from quantum mechanical calculations are dependent on the definition and schemes used.

The earliest scheme is the well-known Mulliken population analysis [33] that is based on partitioning the wavefunction in terms of basis functions. It suffers from five problems (i.e., more than two electrons may be assigned to an orbital, which violates Pauli principle; The off-diagonal elements may become negative; the off-diagonal contributions are always divided equally between two orbitals; the electron density may be counted as belonging to an atom even the basis functions effectively describes the wave functions far from the atom; a set of population atomic charges does not reproduce the original multipole moment.) and very unreasonable and physically nonsense results may sometimes be produced [34]. Furthermore, Wiberg and Rablen demonstrated that serious contradictions exist between atomic charges obtained with different procedures and unrealistic results are not uncommon [35]. For instance, the charges on the carbon atom in CH_3NO_2

range from -0.478 to $+0.564$, and the charges on NO_2 from -0.118 to -0.632.

To overcome the deficiency of atomic charges, charge density is employed to discuss the impact sensitivity of nitroaromatic compounds [36–39]. Anders and Borges calculated the electron density of 17 nitroaromatic molecules and performed the distributed multipole analysis (DMA). The DMA multipole moments are insensitive to the change of Gaussian basis set. The analyses reveal that more insensitive materials possess large delocalized electron densities in the aromatic ring of the component molecule [36]. Stephen and co-workers [37–39] carried out a charge density study on 1,3,5-triamino 2,4,6-trinitrobenzene using density functional B3P86 and 6-311G** basis set and Atoms in Molecules (AIM) theory. The bond topological analysis reveals that the C—NO_2 bond charges are highly depleted whereas the ones of C—NH_2 bond are highly concentrated. According to their study, the weakest bond (trigger linkage) has the lowest value of Laplacian of electron density, and there is a relationship between the bond charge depletion and the impact sensitivity. Very recently Yau and co-workers assessed the applicability of AIM method used to correlate the stationary properties with various performance and vulnerability properties of energetic materials. They concluded that predictions of the stability of a molecule based solely on properties of low-density bond critical points generated from a single DFT calculation are unreliable [40].

2.2 Electrostatic Potentials

Physically meaningful quantities reflecting charge distribution are electrostatic potentials. Previously, it was found that the electrostatic potential at the midpoint of a bond is related to the bond strength [41]. In 1985 Owens et al. studied some polynitroaromatic compounds and showed that the measured impact and shock sensitivities correlate well with the electrostatic potential at the midpoint of the longest C—NO_2 bond, V_{mid}. V_{mid} is defined as the sum of charges on the carbon and nitrogen atoms over half of the bond length [42]. They examined the relationship between V_{mid} and impact sensitivity for a series of nitroaromatics [43]. Later, the authors defined a quantity Π [44]:

$$\Pi = 1/n \sum |V_i(r) - \bar{V}_s| \tag{1}$$

$$V(r) = \sum_A \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r')dr'}{|r' - r|} \tag{2}$$

In Equation (2), Z_A is the charge on nucleus A, located at R_A, and $p(r)$ is the electronic density function. $V(r)$ is a real physical property that can be determined experimentally by diffraction methods as well as computationally. The potentials are approximate ones estimated from atomic charges in Ref. [42]. Later the authors [44] used accurately calculated electrostatic potentials and obtained a good cor-

relation between the impact sensitivity and the calculated Π (in kcal mol^{-1}) defined above. For instance, a linear relationship shown as Equation (3) between the experimental and predicted h_{50} (in cm) of nitroaromatics was calculated with a correlation coefficient of 0.989.

$$h_{50} = \alpha[\Pi^2 V_{s,max}(\text{ring})]^{-1} + \beta\Pi^2 + \gamma \tag{3}$$

$V_{s,max}(\text{ring})$ is the maximum electrostatic potential over the benzene ring. $\alpha = 8.844 \times 10^6$, $\beta = 1.291$ and $\gamma = -981.6$ [44]. These studies indicate that a key factor in determining the impact sensitivity may be the extent to which the stabilizing effect of charge delocalization has been counteracted.

Politzer and Murray [45] examined the relationship between the bond dissociation energy of C—NO_2 and the electrostatic potential for 11 nitroalkanes. In another paper [46] emphasizing the importance of the charge imbalance as a factor on sensitivity, they correlated the impact sensitivity with the internal charge separation measured by the average deviation of the surface potential in the molecules of nitroaromatics, nitramines and nitroheterocycles. They suggested that the extent of internal charge separation is symptomatic to impact sensitivity within a class of energetic compound. The high correlation coefficient between the sensitivity and electrostatic potential derived quantities is not surprising, assuming that the aggregate effect is similar because: (i) it reflects the bond strength, and thus the energy to break the bond. (ii) The compounds that have high correlation coefficients are confined within a class of compounds that are structurally similar (this explains why correlation between impact sensitivity and Π was performed within a certain class of compounds and different types of compounds have different quantitative relations because Π may scale differently with energies needed to break the trigger linkage.). Very recently, Murray et al. studied the links between surface electrostatic potentials of nitramines, impact sensitivities and C—NO_2/N—NO_2 bond dissociation energies [47].

The relationship between the electrostatic potential and sensitivity proposed in Ref. [46] was also tested by Rice and Hare [48]. They investigated the features of electrostatic potentials for a variety of CHNO explosive molecules and found that the level of impact sensitivity relates to the degree of positive charges build-up over the covalent bonds within the inner framework of these explosives. Large positive charge accumulation localized over covalent bonding regions is calculated with the highly sensitive explosives, whereas the insensitive explosives have no such feature. In addition, they noted that the sensitivity is related to the degree and distribution of positive charge build-up localized over the aromatic ring or over the C—NO_2 bonds of the nitroaromatic and benzofuroxan compounds. This feature, i.e. positive charge accumulation over certain covalent bonding regions associated with the impact sensi-

tivity of a compound, is understandable and acceptable, if one recalls that covalent bonding is formed upon the gathering of electrons in the bonding region between two atoms, and a positive charge accumulation means that the covalent bonding is weak. In other words, the more the accumulated positive charges, the weaker the bond (and thus the more sensitive the substance).

2.3 Bond Order

The bond order (BO) characterizes bond strength and was first proposed by Pauling [49]. Generally, BOs can be divided into two categories: phenomenological bond order and theoretical one from quantum chemistry [50]. The former uses experimentally observable properties like bond lengths and symmetrical stretching frequencies. In the sense of the quantum mechanical point of view, bond order is not an observable and does not have unique definition and physical basis. Widely used bond orders in quantum chemistry are Wiberg [51] and Mulliken [52] bond orders. Recently, the bond order has been used to calculate bond energies in establishing reactive force field in molecular dynamic simulation [53].

Xiao et al. calculated the π-bond order using HMO method and the Mulliken and Wiberg bond orders using SCF-CNDO/2 method. They found that the computed bond orders of $C-NO_2$ of TATB (triaminotrinitrobenzene or 2,4,6-triamino-1,3,5-trinitrobenzene, a powerful, but extremely insensitive explosive), no matter whether they are HMO-calculated π-bond order or CNDO/2 calculated Mulliken or Wiberg bond orders, are the largest whereas the ones of 5-nitro-aminobenzene is the smallest [54]. Larger bond orders correspond to stronger chemical bonds, and thus less sensitivity to external stimulus. They further calculated the Mulliken bond orders of the $C-NO_2$ bonds for 25 nitro-derivatives of aminobenzenes and demonstrated that the BO ordering for these compounds correlates well with the pyrolysis sequence derived from the thermal decomposition rate formula. For the nitro-derivatives of toluene and of phenols, the trigger linkage is no longer the $C-NO_2$ bonds. CNDO/2 calculations reveal that the α-C$-$H and O$-$H bonds of the nitro-derivatives of toluene and of phenols respectively possess the smallest bond orders [55]. The corresponding bond orders of the α-C$-$H and O$-$H bonds also correlate well with the respective ordering of impact sensitivity. AM1 and PM3 calculated $C-NO_2$ bond orders of the TATB derivatives correlate linearly with the experimental impact sensitivity, h_{50} [56]. Density functional theory B3LYP calculated bond orders for nitro derivatives of toluene and aminobenzenes reproduce the similar impact sensitivity ordering as experimentally determined [57].

On the basis of the studies on a series of compounds, Xiao proposed the *principle of smallest bond order* (PSBO) to predict the sequence of impact sensitivity [10]: among structurally analogous explosive compounds that follow the same detonation mechanism, the smaller the bond order of the trigger linkage, the larger the impact sensitivity. PSBO has been substantiated by the consistency between the predicted impact sensitivity ordering and experimental one for several classes of compounds including nitro compounds, nitramines and nitrate esters [10, 12].

2.4 Band Gap

Lead azide is a well-known detonator. Covalent metal azides and ionic metal azides follow different thermal decomposition mechanisms. Thermal decomposition of the former begins with the N_1-N_2 (the atomic numbering is M$-$N$_1$$-N_2$$-N_3$) bond breaking while the latter starts from the heterolysis of the M$-$N$_1$ bond. DV-X_α and EHMO calculations show that for ionic metal azides, the HOMO$-$LUMO energy gap can be used to elucidate the ordering of impact sensitivity [19,52,58–60]. On the basis of the analyses of the calculated results, Xiao et al. [58–60] proposed the "*Principle of Easiest Transition*": the narrower the band gap, the easier the electron transition, the more sensitive the compound. Xiao and his co-workers investigated the electronic structure and vibrational properties of the four polymorphs of crystalline octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) [61]. The calculated band gap decreases in the order of $\beta > \gamma > \alpha > \delta$, compared with the experimental impact sensitivity sequence of $\beta < \gamma \approx \alpha < \delta$. Zhang et al. also found that the impact sensitivity of some nitro aromatic explosives is related closely to the band gaps [62].

Although quantitatively the value of band gap may vary due to different theoretical methods, for example, GGA-PW91 calculated band gap of β-HMX is approx. 0.2 eV larger than the LDA computed one, the qualitative trends seem unchanged [63]. Recently the impact sensitivities and band gaps for several classes of crystals including inorganic and organic crystals were examined (see Refs. [21–36] in Ref. [19]). It is demonstrated that the band gap could be used to correlate the impact sensitivities for both molecular crystals and ionic crystals. The influence of doping on impact sensitivity was studied by computing the band gaps for a series of potassium doped cuprous azide. The calculations show that with the increase of the content of doped potassium, the band gaps increase [64,65], consistent with the observed decrease of impact sensitivity of these crystals.

2.5 Activation Energy

Here activation energy means the barrier height (that is the energy difference between the calculated total energies of the reactant(s) and transition state). Xiao et al. [66] computed the C-NO$_2$ bond dissociation energy barriers of hexanitrobenzene, 1,2,3,4-tetranitrobenzene, o-dinitrobenzene, s-trinitrobenzene, p-dinitrobenzene, m-dinitrobenzene and nitrobenzene using semi-empirical UHF-AM1 method. They not only demonstrated that the bond orders of the weakest

C-NO$_2$ bond correlate linearly with the energy barriers very well, but also revealed that energy barriers (and bond orders, of course) are able to predict the same impact sensitivity sequence as experimentally determined. Similar conclusion is reached from the studies on other systems [67–69]. Owens [70] compared the bond rupture energy barriers for each bond in hexahydro-1,3,5-trinitro-1,3,5-s-triazine, diazodinitrophenol, 3-nitro-1,2,4-triazole, nitroguanidine, ethylenedinitroamine and dinitroimidizole at semi-empirical MINDO/3 level. These molecules represent nitroamines, nitroaromatics, nitrotriazoles and nitroimidizoles which comprise different chemical families of energetic materials. The calculated barriers indicate that the weakest bond in the molecules is the bond between an NO$_2$ and the remainder of the molecule. That study also revealed a correlation between the magnitude of the energy barrier and the susceptibility to detonation. Unlike other criteria of impact sensitivity, these studies show that the barrier-sensitivity correlations are independent of chemical families, indicating a broad predictive power of energy barrier for rationalizing impact sensitivity.

The predictive power of activation energy is well exemplified in the study of tetrazole compounds. Tetrazole derivatives and their metal salts have been studied as detonator to replace lead azide [11,71]. Investigations show that 5-substituted tetrazoles are more stable than 1- and 2-substituted isomers [11] and the impact sensitivity of 5-substituted tetrazole derivatives follows the ordering in term of the substituent: $CH_3 \approx Ph < NH_2 < H < NHNO_2 < Tetrazole$ (= Tz) $< Cl < NO_2 < N_3 < N_2^+$ [72,73]. The sensitivity sequence of some metal salts of tetrazole derivatives is: Mercuric nitro Tz > Mercurous nitro Tz > Mercuric nitoamino Tz > Lead nitroamino Tz > Thallous azoTz > Potassium nitro Tz [73]. The sensitivity ordering mentioned above has been correlated with the electron-withdrawing ability of the substituent [72], EHMO calculated charges of the substituent [72], and the content of the 2H-isomers [11]. Studies demonstrated that the electron-withdrawing ability of and the charges on the substituent and the concentration of 2H-isomers cannot elucidate the experimentally determined impact sensitivity ordering of tetrazole compounds [11,29,30]. The trigger linkage was identified by systematically examining the thermal decomposition of tetrazole compounds, as the initiation process is thermal in origin [3,7,74]. It is found that the rate-limiting step of the thermal decomposition of tetrazole derivatives is the opening of the tetrazole ring [28]. Based on this finding, the energy barriers of the ring opening were computed for a series of tetrazole derivatives and metal salts at both semi-empirical PM3 [30] and density functional B3LYP [29] levels. These calculations show that there exists a nice correlation between the activation energy and the impact sensitivity. The successful rationalization of the impact sensitivity of the tetrazole compounds and some metal salts clearly demonstrates the performance of activation energy as the impact sensitivity criterion. It is worthy to point out that semi-em-

pirical quantum chemistry methods, like AM1 and PM3, though quite approximate and quantitatively less accurate in general, can produce the same or very similar rankings of sensitivity as *ab initio* or density functional methods [29,30,57].

Bond dissociation energy (BDE) defined as the energy difference between that of a reactant and the produced fragments is a kind of activation energy when the products are radicals. Xiao and Wang once used bond dissociation energies estimated from π-bond orders to rationalize impact sensitivity [75]. Correlations between impact sensitivity and the dissociation energy of the weakest bond have also been proposed [76]. Recently many researchers correlate the bond dissociation energy with impact sensitivity [77–82], indicating that energetics plays an important role in rationalizing sensitivity, because explosion in nature is fast chemical reactions, and a complete and comprehensive understanding of this phenomenon could not be done without the knowledge of kinetics.

2.6 Other Indices

Apart from the above five indices proposed to understand the impact sensitivity of explosive compounds, other quantities have also been suggested. The oxygen balance criterion proposed by Kamlet and Adolph [24,83], is worthy mentioning, even though it is not quantum chemistry derived index. This criterion has been widely used by experimentalists to explain or predict the impact sensitivity of explosives. Thus it is worthy to unravel the relationship between the oxygen content and the energy barriers to break the trigger linkage. Xiao et al. found that the diatomic interaction energies calculated with CNDO/2 can rationalize the impact sensitivity of nitroanilines[84]. Mullay [25,26] reported a correlation between impact sensitivity and molecular electronegativities of energetic materials. Politzer and co-workers correlate the impact sensitivity of seven nitramine and five nitroaliphatic explosives with the molecular mass and the reciprocals of the C–NO$_2$ and N–NO$_2$ bond lengths [85]. Apparently, the reciprocals of bond length measure the bond strength. Su et al. established a relationship between the nucleus-independent chemical shift with the impact sensitivity for organic nitro compounds [86]. The correlation coefficient is as high as 0.982. As early as 2000, Zeman [87] found there is a very nice correlation between the ^{15}N NMR shift of amine nitrogen atoms in the nitramino group and the drop energy. Kohno et al. found a good correlation between the impact sensitivity of the HMX polymorphs and the variation (which reflects the crystal effect) between partially optimized N–N bond length and that in the crystal [88].

3 Conclusions and Prospect

In this review various indices or criteria used to rationalize the impact sensitivity of energetic materials are summar-

ized. Experimental determination of impact sensitivity inherently confronts safety problems, especially with novel compounds and is harmful to operators. From this point of view, computational prediction of impact sensitivity, or sensitivity in general, is an ideal approach.

As far as the chemistry of an explosive is concerned, the bonding strength of the trigger linkage plays the important role in determining the sensitivity. Good descriptors, like activation energy, bond dissociation energy, bond order and electrostatic potential, always reflect the bond strength. The fact that these criteria work and satisfying correlations exist if the comparison is made within a class of compounds indicates two implications: (i) the descriptors capture one of the key factors dominating sensitivity, (ii) The roles of other factors (which are not considered in the descriptors) on the sensitivity are similar with in these compounds. In fact, factors such as molecular structure, physical state of an explosive, the direction in the crystal and defects do affect sensitivity [89,90]. Because of the multifactor features, reproducibility of measuring sensitivity and theoretical prediction of sensitivity is difficult.

One thing should be kept in mind that even the correlation is nice, it may simply be symptomatic [47,91], due to the complexity of explosion that involves the processes and reactions in condensed phase. Fried et al. pointed out that descriptors characterizing bond strength alone are not enough to capture high explosive sensitivity [92]. The work by Kuklja et al. demonstrated the importance of surface/interface on sensitivity [93–96]. Compared with the calculated activation barriers in the gas phase, the barriers in bulk crystals are higher while the ones on the surface or at a vacancy are lower, showing the effect of surface and vacancy on explosion and sensitivity. According to Dlott [97], sensitivity depends simultaneously on three complicated factors: the stimulus, the chemical composition and the physical or mechanical state. Among the factors other than chemical composition, the aggregate effects, which are beyond the scope of the present review, are extremely important. With the advances of high-efficient computational softwares and high-performance computers, it is high time to investigate the aggregate effects on sensitivity.

A very recent interesting work shows that bond strengths and energy content are the two primary factors determining mechanical sensitivities [98]. In addition, we notice that Zeman [99] found that there is a nice relationship between the fusion heat and the impact sensitivity of polynitro arenes. In another paper Zeman and his co-workers examined the relationships between the BDE values and logarithms of impact sensitivity of the 14 cyclic nitramines [100]. The authors found that the relationship is not unambiguous and believed that the reason of ambiguity of the relationships mainly lies in real conformation of the respective molecules and intermolecular force affects in real molecular crystals, which are not included in the calculations. These studies clearly show that to obtain comprehensive and complete understanding of impact sensitivity, ag-

gregate effect must be taken into account. This calls for investigations to be extended from gas phase to condensed phase using quantum chemical methods. It is worth mentioning that molecular dynamics (an important theoretical chemistry branch) simulations of solid energetic materials grow rapidly [21,101–103].

Furthermore, approaches to other sensitivity like electrostatic sensitivity, should also be carried out. In fact, shock sensitivity has been addressed long before by Delpuech and Cherville using charges and bond length [104,105]. Recently, there are some theoretical studies on electric spark sensitivities for nitramines and shock sensitivities [80,106]. Compared with studies on impact sensitivity, correlation of quantum chemistry derived quantities to other measures of sensitivity is quite rare and more devotions to them are expected. Whether quantum mechanic calculations could correlate well to other kinds of sensitivity depends on the initiation mechanism. For example, electric spark sensitivity might involve electronic excitation. Thus, excited state calculations might shed lights on it. Nevertheless, we can surely envision that with more and more researchers applying quantum chemistry to energetic materials, the complex explosive phenomena will be understood more deeply.

Acknowledgments

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