MATEO: A software package for the molecular design of energetic materials

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ABSTRACT

To satisfy the need of energetic materials chemists for reliable and efficient predictive tools in order to select the most promising candidates for synthesis, a custom software package is developed. Making extensive use of publicly available software, it integrates a wide range of models and can be used for a variety of tasks, from the calculation of molecular properties to the prediction of the performance of heterogeneous materials, such as propellant compositions based on ammonium perchlorate/aluminium mixtures. The package is very easy to use through a graphical desktop environment. According to the material provided as input, suitable models and parameters are automatically selected. Therefore, chemists can apply advanced predictive models without having to learn how to use complex computer codes. To make the package more versatile, a command-line interface is also provided. It facilitates the assessment of various procedures by model developers.

1. Introduction

As a result of recent progress in the prediction of the performance of energetic materials from the structure of the constitutive compounds, the search for new high energy density materials (HEDMs) increasingly relies on the theoretical evaluation of their potential as components of explosives or propellants [1–4]. However, in most cases, these compounds prove very difficult to synthesize. As a result, even if a synthetic route is eventually identified, the process is likely to be very expensive, hence hampering the practical interest in the newly synthesized molecule. Therefore, it is desirable to take advantage of the expertise of organic chemists in the early stages of any search for new HEDMs. This can be done if chemists have direct access to reliable computational tools for evaluating the performance of their new synthesis targets. In practice, this is not usually the case. Indeed, a comprehensive assessment of the potential value of a new compound involves many predictive tools, including simple models to estimate crystal densities, quantum chemical methods to obtain formation enthalpies, thermochemical codes to predict detonation performance or specific impulses, and perhaps semi-empirical models to estimate chemical stabilities. The probability of mistake increases with the amount of data requested as input by the various computer codes involved. All in all, estimating the properties of a single compound may require many hours if high level quantum procedures are used to estimate enthalpies, and even much more if crystal structures

are predicted *ab initio* [5,6]. In this context, such calculations are usually not carried out by bench chemists. On the other hand, hiring specialized staff for this task is clearly a costly solution to be avoided. Finally, many chemists involved in the design of energetic compounds have to be satisfied with rough estimates of the characteristics of their target materials. In some cases, the selection of target compounds for synthesis relies only on empirical formulas and densities, despite the significance of other properties, such as performance or decomposition temperatures. Therefore, a software package has been designed in order to allow chemists to carry out an optimal screening of candidate compounds when searching for new HEDMs, especially for propellant applications. Although it relies on quantum chemistry, thermodynamics and detonics, this so-called MATEO package – named after the French acronym for Energetic and Organic Materials – can be used without detailed knowledge in these fields. In this paper, it is first compared with published or commercially available software. Then, some models presently implemented in the package are presented, with strategies for further improvement. Finally, the modular architecture of the software is outlined and illustrative applications are presented.

2. Comparison with other software

Much effort has been put into providing chemists with user-friendly computational tools. Today, many molecular modeling programs allow the user to interactively build a molecule and compute its properties on the basis of quantum chemistry or molecular mechanics, usually through a sophisticated graphical user interface [7–10]. Some of them can predict not only properties of gas phase compounds, but also some aspects of materials made from these

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compounds [10–12]. Integrated software packages allow theoretical predictions to be directly compared with values from a database [13]. Nevertheless, despite friendly interfaces, running these programs usually requires some knowledge of the underlying models from the user, in order to select suitable options (e.g. basis set, Hamiltonian, force field, and convergence criteria) depending on the system under study. As a consequence, they cannot be used by all organic chemists. Furthermore, such tools are mostly developed for pharmacological research, either by software companies or within large organizations involved in molecular sciences. Similar programs are still lacking for the design of explosives and propellants, which involves specific models not implemented in general purpose modeling software to predict properties such as density, specific impulse, and heat of explosion.

In this context, thermochemical models used to compute the performance of energetic materials on one hand, and molecular models developed to evaluate the properties of their constitutive ingredients on the other hand, are often implemented in independent programs. Moreover, the molecular models available may require different data as input, for instance 2D versus 3D molecular structure. It may be necessary to provide this data separately to the respective computer codes. This process is error-prone and requires a good knowledge of the computer programs used. Hence the interest in integrating them behind a user friendly interface. No such software has been reported yet. However, it is of interest to compare MATEO with two recent programs, LOTUSES [14–17] and EDPHT [18], also aimed at providing chemists with efficient tools to assess target molecules as potential energetic compounds.

First, LOTUSES and EDPHT rely extensively on empirical methods to predict the performance of explosives. Such techniques often yield good results for compounds similar to those considered for the parameterization. However, for unusual molecules commonly considered as promising candidates for new HEDMs, either parameters are lacking or the results are unlikely to match the reliability of more sophisticated procedures, e.g. using quantum chemical calculations to predict formation enthalpies [19,20], carrying out systematic investigations of possible crystal packing arrangements

to obtain densities [21] and sublimation enthalpies [5] or resorting to a full-blown thermochemical code to calculate the performance [22]. In contrast, MATEO attempts to preserve a better reliability by retaining such procedures to the extent that they do not hamper the possibility for the chemist to get quick answers to his questions about the expected behavior of compounds under consideration. Indeed, our selection of models is optimized for an hybrid approach to the design of explosives, taking into account the expertise of organic chemists in addition to computational predictions concerning the behavior of the material. Thus, MATEO fills the gap between the simple models implemented in LOTUSES/EDPHT and high-level theories which require calculations to be carried out by specialists [23–25].

Secondly, LOTUSES and EDPHT are standalone programs, essentially developed from scratch. In contrast, MATEO is designed as a front-end to various computer codes, providing a simplified command line interface (CLI) that may be used along with publicly available graphical tools. By developing a simplified CLI rather than focusing on a sophisticated GUI, as the one developed for LOTUSES, our initial aim was to make it easy for chemists to obtain data about candidate compounds under consideration for synthesis from files edited using their favorite molecular editors, such as ChemDraw [9] or Chemtool [26]. For most practical cases, opening such a file with the MATEO application immediately pops-up a new window showing a summary of predicted properties (Fig. 1). On the other hand, the CLI allows advanced users to easily implement custom scripts, which is especially useful for a quick assessment of new models, as it provides a simple way to carry out systematic calculations on large sets of compounds.

Third, LOTUSES and EDPHT focus on the performance of explosives, such as detonation velocity, Chapman–Jouguet pressure, explosive power and heat of explosion. In contrast, MATEO is primarily designed for the design of green propellants. It can be used to search for an inexpensive chlorine-free energetic load, in order to design propellants less environmentally harmful than ammonium perchlorate/aluminium binary mixtures. In contrast to LOTUSES and EDPHT, it predicts properties of all constituents
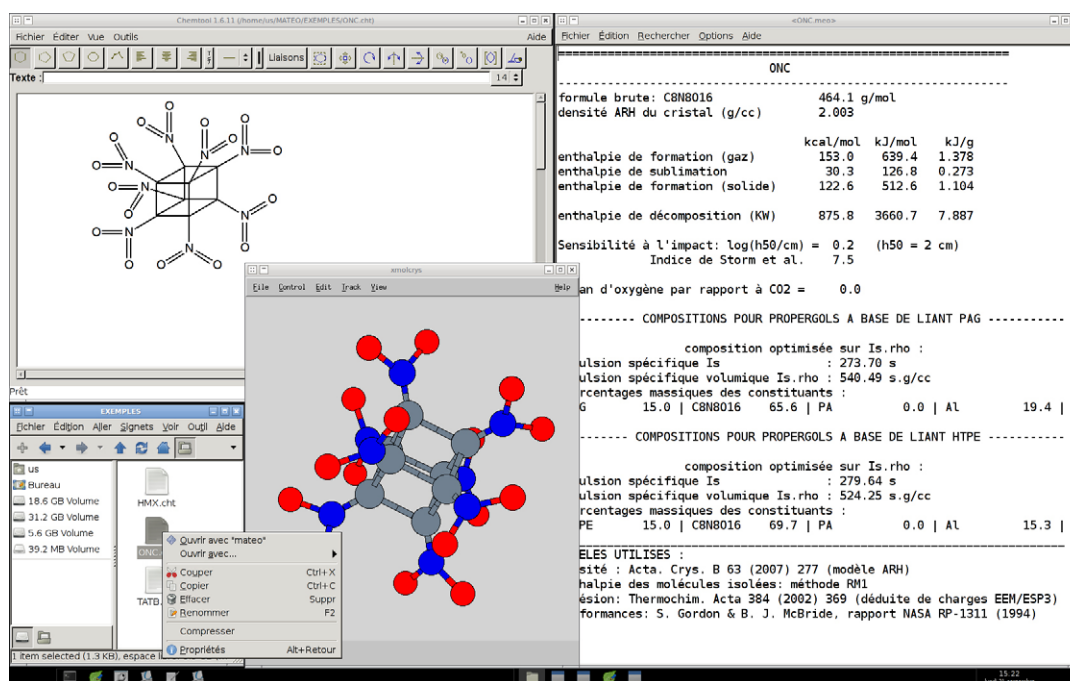

Fig. 1. Screenshot illustrating the use of MATEO to predict the properties of octanitrocubane (ONC): sketch the formula of the compound using Chemtool, save it as ONC.cht, right-click the file and select MATEO from the "open with" menu. Two new windows get opened: the first one shows the 3D geometry of the molecule, while the second one summarizes the calculated properties of ONC as a pure substance and the performance of new propellants including ONC in their formulation.

of propellants, including polymers (used as binders in propellants and explosives) and even inorganic compounds (such as inorganic salts used as oxidizers) although the prediction of their formation enthalpies requires specific models associated with a significant computational overhead (see Section 3). In fact, salts are the only materials for which MATEO cannot provide immediate estimates of the energy content.

Another difference between LOTUSES/EDPHT and MATEO is related to our concern to make the latter program widely available within our institution. While the former programs depend on proprietary software, all models and algorithms available in MATEO are either developed in our lab or freely available from internet. As a result, the package can be installed on any popular platform and made available to any user from his desktop. This is of interest since chemists tend to use Windows, while model developers are more likely to use UNIX/Linux systems. To make the distribution and maintenance of the software easier, a recipe file to build binary packages for Linux is provided in addition to the source tarball. On the other hand, MATEO, consisting mainly of Python scripts, may be easily modified as new needs arise or better models emerge.

Finally, a further distinctive feature of MATEO lies in the fact that it can predict other properties beyond performance-related data. For instance, version 3.0 of MATEO provides rough evaluations of the stability of some materials [27,28]. To help in the design of binders, it evaluates polymer densities, glass transition temperatures and cohesion energies from electrotopological indices, using well-established methods [29]. The development version of the package provides even more functionality. A recent method [30] to predict Hansen solubility parameters was recently implemented into this version, in addition to models based on these parameters to estimate the responses of gas sensors upon exposure to various pollutants. This work in progress will be reported elsewhere.

3. Available models and prospects

The primary properties implemented in MATEO are of special relevance for propellants: density, specific impulse, heat of explosion, decomposition temperature and impact sensitivity. The heat of explosion is derived from the heat of formation combined with empirical rules or thermochemical calculations to obtain the decomposition products. This section presents models implemented in the present version (3.0) of the package and used on a routine basis by bench chemists. Furthermore, it discusses possibly better alternatives still to be developed.

3.1. Densities

The use of standard additive volumes appears currently as the best approach to the prediction of crystal densities in the lack of structural data. In earlier versions of MATEO, crystal densities were estimated by a popular group contribution method [31] with specific parameters introduced for charged groups in order to handle molecular salts [32]. They are presently evaluated using the recent Atoms-Rings-Hydrogen (ARH) bonds model, an additive scheme of similar reliability [33]. The advantages of the ARH procedure over conventional group contribution methods stem from its less empirical character, providing a wider scope of applicability with fewer adjustable parameters. Such methods yield crystal densities with an average deviation from experiment close to 2%. Although the most severe deviations concern crystals that do not obey the close packing principle, there are still a significant number of close packed crystals that exhibit deviations >6–8% from experiment.

More accurate predictions can be made on the basis of systematic searches for the lowest-energy crystal structures [6]. However, such time-consuming procedures are excluded if the software is to be used interactively by bench chemists. Another approach consists in introducing a larger number of empirical volumes to account for the variety of possible environments of an atom within a molecule, as done with the so-called Atom_Code procedure [34]. However, as more empirical parameters are introduced, their respective values get more likely to be statistically ill-defined. To avoid this numerical problem while providing sufficient volume data to accommodate the variety of atomic environments encountered in molecular crystals, we suggest that the atomic volumes should be directly calculated from available crystal structures rather than fitted against experimental densities. This requires a well-defined procedure to assign atomic volumes V_k for atoms k in the unit cell, whose sum must yield the total unit cell volume. For this purpose, a Voronoï analysis appears as a natural approach. In a subsequent step, atom typing can be done on the basis of the V_k values and their dependence on the atom environment. The advantage of such a procedure stems from the fact that the definition of atomic volumes can take into account their actual dependence on the atom environment, while this dependence must be postulated *a priori* when these volumes are fitted against experimental data.

For liquids, such an approach is not possible. It would require a well-defined procedure to derive atomic volumes from available liquid data. MATEO predictions of liquid densities rely on a very simple assumption concerning the dependence of the atomic molar volume on van der Waals parameters, which was found to work remarkably well [35]. Preliminary unpublished data indicate that even more reliable liquid densities will be obtained on the basis of the ARH approach [33].

3.2. Formation enthalpies

In addition to densities, solid-state formation enthalpies are required to compute the performance of energetic materials. While LOTUSES obtains the corresponding values directly from group contributions, MATEO calculates them as differences between formation enthalpies $\Delta_f H^o$ of isolated species and sublimation enthalpies $\Delta_{sub} H^o$ arising from the interactions between molecules or ions. In earlier versions, $\Delta_f H^o$ was estimated on the basis of the P2 model [19] which proved successful not only for energetic materials and related compounds [36] but also to some extent for ions [5,37]. However, this procedure relies on electronic structures computed using the DN** numerical basis set [19]. The latter is not very popular among the quantum chemistry community, in contrast to Gaussian basis functions. To our knowledge, it is available only in proprietary software, such as the Spartan program [8]. As a result, the possibility to carry out calculations was restricted by licence issues. Thus, the fact that current components of MATEO are either locally developed or implemented in open source codes is deemed significant enough to be mentioned as a distinctive feature of the package in Section 2.

The default method presently used to compute gas-phase formation enthalpies of neutral compounds is the semi-empirical RM1 Hamiltonian [38]. These calculations are carried out using the MOPAC7 program [39]. For ions, this procedure is unreliable. Therefore, density functional theory (DFT) is used instead. The formation enthalpy $\Delta_f H^o$ of an isolated ion is obtained as the difference between the experimental formation enthalpy of its constitutive atoms and the theoretical atomization enthalpy of the ion:

$$\Delta_f H^o = \sum_Z n_Z \Delta_f H^o(Z) - \left(\sum_Z n_Z H^o(Z) - H^o \right) \tag{1}$$

In this equation, n_Z is the occurrence of element Z in the empirical formula of the ion, $\Delta_f H^o(Z)$ its experimental formation enthalpy, $H^o(Z)$ its theoretical enthalpy, and H^o the theoretical enthalpy of the compound under study (theoretical enthalpies are calculated

Table 1

Data used to calculate the formation enthalpies of ions from B3LYP/6-31+G**//AM1 total energies, for elements H, C, N, O and F: formation enthalpy $\Delta_f H^o(Z)$, CBS-Q theoretical enthalpy $H^o(Z)$, and atom equivalent X_Z (kJ/mol).

Z	$\Delta_f H^o(Z)$	$H^o(Z)$	X_Z
H	218.0	−1306.1	34.1
C	716.7	−99,198.7	177.1
N	472.7	−143,136.7	189.0
O	249.2	−196,872.3	213.8
F	79.4	−261,604.4	230.9

Table 2

Bond enthalpies Δ_{i-j} derived from a fit against 352 small molecules and corresponding standard bond energies E_{i-j} [69] (kJ/mol).

Bond type	Fitted value	Standard value
C–H	406.7	414.2
N–H	561.4	389.1
O–H	382.8	464.4
C–C	363.3	347.3
C≐C	515.2	–
C=C	633.6	610.9
C≡C	841.1	836.8
C–N	325.8	305.4
C≐N	461.0	–
C=N	595.6	615.0
C≡N	875.2	891.2
C–O	339.4	357.7
C≐O	442.3	–
C=O	585.8	744.7
N–N	335.7	160.7
N=O	547.8	598.3

with respect to an hypothetical reference system with all interactions between particles turned off). MATEO resorts to values of $H^o(Z)$ calculated at the CBS-Q *ab initio* level [40] using the Gaussian program [41]. The standard enthalpy H^o is simply obtained as

$$H^o = E_o + \sum_Z n_Z X_Z \tag{2}$$

where E_o is the total electronic energy calculated using the B3LYP functional and the 6-31+G** basis set, and X_K is an atom equivalent accounting for the zero-point and thermal contributions to H^o, the pressure–volume product, and systematic deficiencies of the B3LYP/6-31+G** procedure for evaluating E_o. The parameters involved in this procedure are listed in Table 1.

As mentioned in Section 2, many hours are often required to carry out such calculations on a desktop computer. In addition, numerical problems, such as convergence failures, are likely to arise. Therefore, simpler procedures are desirable. Taking advantage of the relatively good quality of RM1 data for neutral species, one possibility is to consider that ions are obtained through a local transformation of a neutral molecule. For instance, the charged group $=NH_2^+$ can be considered as the product of the $C \rightarrow N$ transformation applied to the neutral group $=CH_2$. In principle, the enthalpy change $\Delta H (C \rightarrow N)$ associated with this transformation depends primarily on the local environment, although a long-range contribution is expected from the Coulombic interactions. According to such a procedure, the formation enthalpy the $R=NH_2^+$ ion could be calculated as

$$\Delta_f H^o(R=NH_2^+) = \Delta_f H^o(R=NH_2) + \Delta H(C \rightarrow N) \tag{3}$$

where $\Delta_f H^o(R=NH_2)$ is calculated at the RM1 level, while the enthalpy change is the sum of a short range contribution ΔH_{SR} and a Coulombic contribution ΔE_Q:

$$\Delta H(C \rightarrow N) = \Delta H_{SR}(C \rightarrow N) + \Delta E_Q(C \rightarrow N) \tag{4}$$

Because of its short-range character, the first term depends only on the atoms closest to the $=NH_2^+$ group in the R radical. It can thus be assumed constant for a number of compounds and fitted accordingly. This step is made possible by the recent possibility to derive reliable theoretical $\Delta_f H^o$ values for sufficiently small ions through the use of composite *ab initio* methods [42,43]. As for the Coulombic term, it might in principle be obtained from atomic charges derived from the electronegativity equalization principle [44]. The success of this approach depends on the possibility to obtain a realistic description of intramolecular Coulombic energies from such charges. The success of molecular mechanics force fields – which also rely on simple atomic charge schemes – suggests that this strategy might prove successful.

Notwithstanding salts, polymers are other materials for which specific models are needed. Indeed, although the RM1 method is suitable to calculate $\Delta_f H^o$ values for isolated chains, it must be applied to oligomers of sufficient size to minimize the influence of end groups, which may lead to lengthy calculations and convergence failures. A simpler procedure, preferably less empirical than group contribution methods, is therefore needed. For the time being, when provided a polymer as input, MATEO simply estimates

$\Delta_f H^o$ of the isolated chain by substracting bond enthalpies Δ_{i-j} from the sum of $\Delta_f H^o(Z)$ values for the free atoms. A dataset of bond enthalpies has been fitted against $\Delta_f H^o$ values of 352 small molecules. The values thus obtained are listed in Table 2 and compared to standard bond energies from the literature.

To be applicable to strained polymer chains, some strain corrections C_k are clearly needed. In other words, starting from Eq. (1), the atomization enthalpy of the molecule should be expressed as

$$\Delta_f H^o = \sum_Z n_Z \Delta_f H^o(Z) - \sum_{i-j} \Delta_{i-j} + \sum_k C_k \tag{5}$$

where $i - j$ runs over the chemical bonds in the compound and k over the strained groups. The derivation of the strain increments C_k is planned for future work. As it stands, on the basis of the 16 empirical Δ_{i-j} values listed in Table 2, this simple approach yields reasonable results for unstrained polymers, as illustrated in Section 5.

3.3. Sublimation enthalpies

In the lack of crystal structure data, sublimation enthalpies must be expressed in term of molecular descriptors characterizing intermolecular interactions. The first approach implemented in MATEO is suitable for neutral molecules. On the basis of semi-empirical considerations [45], a three parameters equation with explicit terms for van der Waals, Coulombic and hydrogen-bonded interactions is used [36]. Two parameter sets are available, depending on the model employed for the charge distribution. Both of them yield very similar results. The absolute deviation from experimental values is about 100 J/g on average, but some deviations as high as 700 J/g are noted, especially for hydrogen-bonded systems [46].

The second approach was developed for molecular salts. The sublimation enthalpies of many of these compounds cannot be measured as the transition often occurs above the decomposition temperature of the ions. This hampers the development of a predictive model for this property of organic salts. In this context, two strategies have been employed, both assuming that the cohesion stems essentially from Coulombic interactions. The first one relies on volume-based thermodynamics, an approach originally developed for inorganic salts [47–49]. The second one takes advantage of a database of theoretical cohesion energies calculated for known crystal structures of molecular salts. This database is employed to fit a semi-empirical relationship between cohesion energies and atomic charges on the ions [37]. This latter approach is

the only one presently implemented in the MATEO package. It was found to be fairly successful for nitrate salts, with estimated values within 500 J/g from theoretical ones [37]. However, according to recent work, specific parameterizations of the volume-based thermodynamics approach focused on nitrogen- and carbon-containing cations [25] can yield even better results [24]. Thus, taking into account the detailed charge distribution on each ion is not sufficient to improve simple volume-based schemes. The most obvious factor that might influence the cohesion energy is the shape of the ions. To date, only very preliminary work has been done to take shape influence explicitly into account [50].

3.4. Performance criteria

Various criteria have been defined to characterize the performance of energetic materials either as explosives or propellants. For instance, the explosive power is useful to estimate the performance of a material considered as an explosive. Its value is equal to the product of the heat of explosion Q reported on a per mass basis by the volume V of gases liberated. Using MATEO, Q is obtained as $Q = \Delta_{ex}H^o/M_W$ where M_W is the molecular weight of the compounds, and the explosion enthalpy $\Delta_{ex}H^o$ is given by the difference between the formation enthalpy of the compound in the solid state and corresponding values $\Delta_f H^o(k)$ for the decomposition products k in gas phase:

$$\Delta_{ex}H^o = (\Delta_f H^o - \Delta_{sub}H^o) - \left(\sum_k n_k \Delta_f H^o(k) \right) \qquad (6)$$

In practice, $\Delta_f H^o$ and $\Delta_{sub}H^o$ are evaluated as described in Sections 3.2 and 3.3. Since the products are mostly made of small stable molecules such as H_2O, N_2, CO_2 or CO, experimental values of $\Delta_f H^o(k)$ are available. The only difficulty is thus the determination of the relative amounts n_k of each product. For this purpose, empirical rules are available in MATEO, namely the original and modified versions of the Kistiakowsky–Wilson (K–W) rules, and the Kamlet rules [51]. By default, MATEO resorts to the original K–W rules but introduces an empirical scaling factor, as discussed in Section 5. Since this approach to estimate Q implies the determination of the composition of the explosion products, their volume V under standard conditions can be readily calculated, and the explosive power QV follows.

Alternative performance criteria for propellants are the specific impulse I_s, or the product $I_s\rho$ where ρ is the density of the propellant. Although simple correlations can be used to estimate I_s from molecular structures [52], they are restricted to purely organic substances. In practice, I_s values for formulated propellants, including aluminium and ammonium perchlorate, are more relevant to efficiently guide chemists toward promising synthesis targets. Therefore, MATEO relies on a standard procedure involving calculations of the chemical equilibrium between the decomposition products [22] in order to predict the composition of the exhaust gases and the corresponding performance of considered propellants. This can be done using free software [53]. In contrast to high level *ab initio* procedures or the generation of systematic crystal packings, such thermochemical calculations may be retained in MATEO as they can be done almost instantaneously using modern desktop computers.

3.5. Stability

Some preliminary models are implemented in MATEO to estimate both mechanical and thermal stabilities. Mechanical stability is most often characterized by the impact sensitivity h_{50} [46]. Early work correlated h_{50} with the elemental composition of the material [54,55]. Such correlations have been extended and applied to a large database of impact sensitivities [27]. Despite many attempts to develop more reliable models [56–59], they presently remain among the most successful approaches [60]. MATEO presently relies on such relationships [27] to estimate h_{50}.

According to the hot spot theory, impact initiation occurs when temperature gets sufficiently high locally to initiate the chemical decomposition of the material. Therefore, h_{50} may be expected to correlate with the decomposition temperature T_{dec} of the material, as obtained for instance from DSC measurements [4]. Preliminary results confirm to some extent such a correlation for neutral compounds with reasonable stability ($h_{50} > 50$ cm, $T_{dec} > 250\,^\circ$C) but point to some exceptions (namely for some salts) [46]. The decomposition temperature itself is clearly a property of interest for practical applications. Nonetheless, only two estimation schemes are reported in the literature to predict T_{dec} for molecular compounds [61,36]. This reflects the fact that this property is very difficult to correlate with the structure of individual molecules. Indeed, T_{dec} does not primarily depend on the features of the compound before it decomposes, but rather on the energy barriers along the decomposition pathway. To circumvent the need for a full characterization of the potential energy surface, two complementary approaches are used.

The first one reduces the problem to thermodynamics considerations. On the basis of the Hammond postulate [62], one may assume that the apparent activation energy for decomposition decreases as more energy is released in the process. This allows one to consider only the compound of interest and its decomposition products, rather than the whole reaction pathway [61].

The second approach, in contrast to the first one, emphasizes kinetic aspects. It relies on the notion of trigger bonds. More specifically, it is assumed that the rate-determining step in the decomposition reaction is associated with the initial cleavage of X-NO_2 linkages (the so-called explosophore bonds). This is a common hypothesis in the energetic materials community. In this situation, it is reasonable to expect a correlation between the activation energy for the X-NO_2 bond dissociation and molecular descriptors (primarily the X-NO_2 bond strength). This approach available in MATEO [28] is supported by the fact that T_{dec} correlates to some extent with the lowest X-NO_2 bond dissociation energies in the molecule [46]. However, it only applies to nitramines, nitroalkanes and nitric esters, since the assumption of explosophores X-NO_2 bonds proves unreliable for nitroaromatic compounds [63].

The natural route toward better models consists in combining both approaches. By taking advantage of calculated heats of explosion to include thermodynamic considerations into our present scheme [28], as done by Saraf et al. [61], it will be possible to take into account the role of autocatalytic aspects.

4. Overview of the MATEO package

MATEO is mostly implemented as a set of Python scripts, with only few components in C language for better performance. Standard computational approaches as well as graphical tools rely on existing software. Therefore, only the new models developed in our group to satisfy the specific needs associated with the design of new HEDMs require software development. This allows for an easy maintenance of the package.

As indicated in Section 2, predicting the main properties of interest for new materials is a matter of a few clicks if MATEO is used within a graphical desktop environment. By default, the following properties of the input compound are calculated: empirical formula, density, formation and sublimation enthalpies, oxygen balance, Storm sensitivity index and corresponding impact sensitivity. In addition to these intrinsic properties of the material, the maximal impulse that can be obtained from loading propellants based on the ammonium perchlorate—aluminium mixture with

the compound studied is calculated. This result is provided for all binders of interest, assuming a minimal amount of each binder to ensure satisfactory mechanical properties.

Finally, all results are stored in an output text file with `meo` suffix. An example of such an output file is displayed on the screenshot in Fig. 1. Of course, if a compound lies outside the scope of the standard MATEO models, no attempt is made to compute the corresponding property.

Using the program from the command-line provides the user with further control on the amount of data provided as input, the properties calculated and the models employed. The general syntax is:

```
# mateo <options> <compounds specification>
```

The compound studied may be input either as a filename, a SMILES string or an empirical formula. In the latter case, its density and formation enthalpy must be provided as input as they cannot be calculated from the structural formula. This is made possible using the `-d` and `-e` options:

```
# mateo -d 1.654 -e -63.2 C6N6H6O6
```

yields an output file `C6N6H6O6.meo` in which only properties that can be computed without knowledge of the structural formula of the compound are reported. This includes calculated data concerning the optimal propellant compositions loaded with the input substance. However, the program is most often used to compute the properties of new compounds for which densities and enthalpies have to be predicted. In that case, their molecular structures have to be provided either as 2D or 3D data. In the former case, MATEO relies on the BALLOON program [64] to generate a 3D model.

Fig. 2 outlines the data flow between the different components of MATEO. The 3D structures, either automatically generated using BALLOON or manually prepared from a molecular builder, are systematically refined using MOPAC7. From the sum of the atomic numbers associated with each atom, MATEO determines whether the compound provided as input is actually a neutral molecule. In that case, a new charge distribution is computed by the program EEMEO and subsequently used to derive the sublimation enthalpy [36], to be substracted from the RM1 gas phase enthalpy to obtain solid-state formation enthalpies. Otherwise, the compound
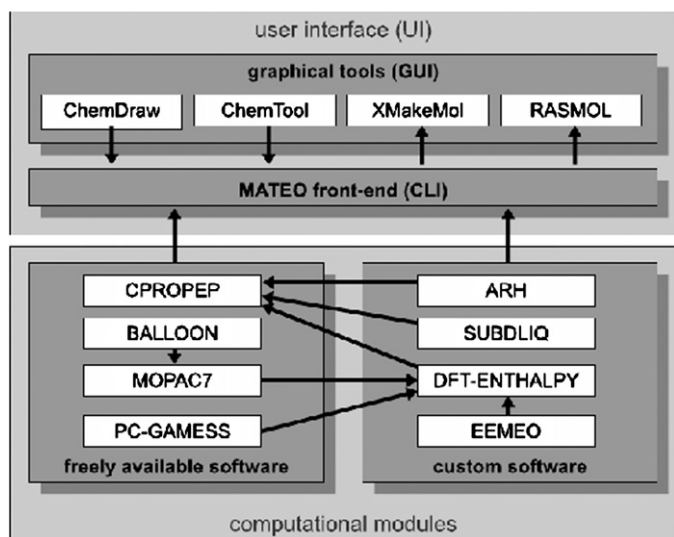
is assumed to be a cation, and the sublimation enthalpy of the corresponding nitrate salt is then directly evaluated by the DFT-ENTHALPY module [37]. In this latter case, instead of using the RM1 values for $\Delta_f H^o$, values derived according to the DFT procedure outlined in Section 3.2 are used. The energies required are computed with the PC-GAMESS/Firefly package [65], which is partially based on the GAMESS(US) [66] source code.

5. Sample calculations

The performance of the models implemented in MATEO are relatively well documented in the literature with regard to densities [33,35], formation enthalpies of molecular crystals [36] and salts [37], decomposition temperatures [28] and other properties for which published models are used [27,29]. Thus, the present section focuses on less documented aspects: formation enthalpies of polymers, heats of explosion, and optimization of composite propellants.

5.1. Formation enthalpies of polymers

A minimal amount about 15 wt% of binder is typically required in propellants to obtain satisfactory mechanical properties. This binder – in practice a polymer – affects the performance of the propellant, hence the current interest in energetic binders. Whenever new binders are considered, MATEO may be used to calculate their properties. Most of them depend only on intermolecular interactions and can be estimated on the basis of electrotopological models [29]. However, the formation enthalpies of the chains depend also on intramolecular interactions. To estimate their values simply, a preliminary model based on bond enthalpies is available in MATEO, as mentioned in Section 3.2. This model has been applied to 14 polymers for which experimental formation enthalpies are provided in the ICT database [67]. Cohesive energies derived from the van Krevelen group contribution method [68] were then substracted from the gas phase $\Delta_f H^o$ values thus obtained, in order to derive the solid state formation enthalpies $\Delta_f H^o_{sol}$.

In decreasing order of calculated $\Delta_f H^o_{sol}$, these materials are: polyacrylonitrile, polystyrene, polyisoprene, polybutadiene, polyisobutylene, polypropylene, polyethylene, polyvinylnitrate, nylon-6-6, polymethylmethacrylate, polyvinylacetate, polymethylacrylate, polyformal and polyvinylalcohol. The results are summarized in Fig. 3. The model proves to be fully consistent with experiment. In polymeric systems, cohesive energies are affected
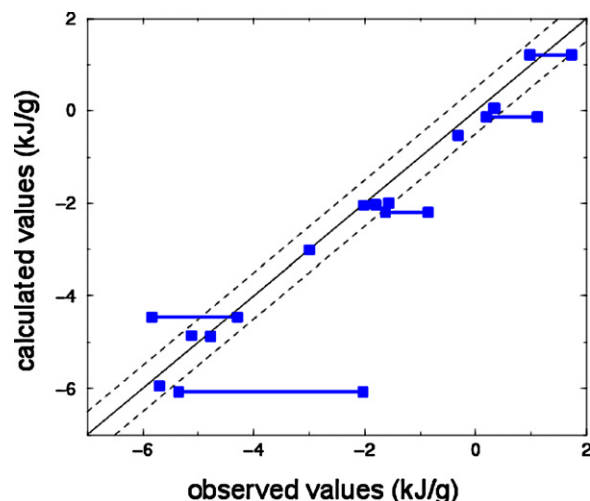
Fig. 2. Relationships between the components of the MATEO package. Publicly available computational engines are used to compute 3D molecular geometries (BALLOON [64]), gas phase formation enthalpies of neutral molecules (MOPAC7 [39]), total energies of ions (PC-GAMESS [65,66]), and propellant performance (CPROPEP [53]). Custom components include EEMEO for molecular charge distributions [36], DFT-ENTHALPY for sublimation enthalpies and solid-state formation enthalpies (Section 3.2), ARH [33] and SUBDLIQ [35] for densities, respectively in the crystal and liquid states.

Fig. 3. Calculated versus observed solid-state formation enthalpies of polymers. For each material, the minimum and maximum observed values are reported.

Table 3
Heats of explosion Q (J/g) of twenty explosives: experimental values Q_{exp} [70], and data derived from the K–W rules, using different values for formation enthalpies: experimental data from Ref. [70] if available, or Ref. [67] otherwise (Q_{KW}), group contribution values calculated using LOTUSES [70] (Q_{LOT}) and values calculated using MATEO as detailed in the text (Q_{calc}). $Q_{scaled} = Q_{calc} \times 1.15$ is the best estimate of Q_{exp} provided by MATEO, the 1.15 coefficient taking into account the systematic error associated with the use of the K–W rules. (L) indicates compounds which are liquids in ambient conditions. Values in parentheses are the relative deviations (in %) with respect to experiment, and the last row reports average absolute deviation from experiment for each procedure.

Compound	Q_{exp}	Q_{KW}	Q_{LOT}	Q_{calc}	Q_{scaled}	Q_{exp}/Q_{KW}
BTENA	4857	4475(−8)	5321(+10)	5377(+11)	6183(+27)	1.09
TNM (L)	2259	2195(−3)	2206(−2)	2111(−7)	2428(+7)	1.03
BTNEU	6542	6141(−6)	6382(−2)	6159(−6)	7083(+8)	1.07
MHN	6380	5936(−7)	5937(−7)	5957(−7)	6851(+7)	1.07
EGDN (L)	7390	6753(−9)	6881(−7)	6698(−9)	7703(+4)	1.09
PETN	6404	5810(−9)	6130(−4)	5962(−7)	6856(+7)	1.10
Methyl nitrate (L)	6869	5958(−13)	6562(−4)	5914(−14)	6801(−1)	1.15
Butanetriol trinitrate (L)	6153	5417(−12)	5737(−7)	5505(−11)	6331(+3)	1.14
RDX	5723	5077(−11)	5087(−11)	5325(−7)	6124(+7)	1.13
Dinitronaphthalene	2635	2309(−12)	2506(−5)	2153(−18)	2476(−6)	1.14
Nitrourea	3865	3175(−18)	3645(−6)	3031(−22)	3486(−10)	1.22
PETRIN	5301	4506(−15)	4704(−11)	4244(−20)	4881(−8)	1.18
DIPEHN	5208	4472(−14)	4814(−8)	4613(−11)	5305(+2)	1.16
DINA	5384	4556(−15)	5021(−7)	4880(−9)	5612(+4)	1.18
Erythritol trinitrate	4110	3376(−18)	3725(−9)	3513(−15)	4040(−2)	1.22
EDNA	5343	4022(−25)	5179(−3)	4332(−19)	4982(−7)	1.33
Metriol trinitrate (L)	4992	4193(−16)	4532(−9)	4291(−14)	4935(−1)	1.19
NIBTN (L)	7755	7247(−7)	7244(−7)	6717(−13)	7725(0)	1.07
Nitromethane (L)	4763	3921(−18)	4718(−1)	4329(−9)	4978(+4)	1.21
Tetryl	4773	3679(−23)	4527(−5)	3750(−21)	4312(−10)	1.30
Average abs. dev.		674	339	644	320	

by large uncertainties associated with the highly complex and not completely reproductible entanglements of the chains. In this context, it does not necessarily make sense to compute very accurate values of $\Delta_f H^o$ for individual chains, as this high accuracy is likely to be spoilt by the uncertainties associated with the interchain contribution. On the other hand, since the binder represents only 15 wt% of a propellant, a relatively significant lack of accuracy for its properties is tolerable as long as the properties of the crystalline components are satisfactorily estimated.

5.2. Heats of explosion

Beyond formation enthalpies of polymers, an examination of the ability of MATEO to predict heats of explosion is of special interest. Indeed, remarkably accurate values of Q have been recently obtained for a set of twenty explosives using the LOTUSES software [17], with calculated values Q_{LOT} within about 600 J/g (10%) from experiment Q_{exp} for various solid and liquid explosives. This result is unexpected in view of the approximations involved, namely the K–W rules and the decomposition of the formation enthalpies of liquid and solid explosives into additive group contributions [51].

The 20 compounds considered are listed in Table 3 (see Ref. [17] for the meaning of the acronyms). To get further insight into the relative reliability of various procedures to predict the heat of explosion, this property was calculated on the basis of the K–W rules combined with three sets of values for heats of formation: (1) experimental values; (2) LOTUSES values; and (3) values obtained as the differences between RM1 gas phase enthalpies and sublimation enthalpies derived from atomic charges based on electronegativity equalization [36], according to the default RM1-EEM model used by MATEO for neutral compounds and outlined in Section 3.2. In fact, some of the compounds considered are liquids under ambient conditions (Table 3). To calculate their formation enthalpies in the liquid state, standard vaporisation (rather than sublimation) enthalpies $\Delta_{vap} H^o$ must be substracted from the RM1 gas phase contribution. Because no model is presently available in MATEO to estimate $\Delta_{vap} H^o$, the latter is simply neglected. For solids, $\Delta_{sub} H^o$ is derived from atomic charges calculated on the basis of an electronegativity equalization method [36], as outlined in Section 3.2.

The results concerning heats of explosion calculated using the K–W rules are summarized in Table 3. Since these rules favor CO over CO_2, calculated values are systematically lower than experimental values Q_{exp}. For instance, using experimental formation enthalpies leads to calculated heats of explosion Q_{KW} which exhibit an average absolute deviation (aad) from experiment as high as 674 J/g. It is gratifying to note that formation enthalpies calculated using MATEO default models yields theoretical values Q_{calc} close to Q_{KW} values. In contrast, values Q_{LOT} calculated using LOTUSES are quite different, as a result of the more approximate procedure employed to derive formation enthalpies. Actually, the fact that $Q_{LOT} > Q_{KW}$ (except for BTENA and NIBTN) clearly indicates that LOTUSES overestimates the formation enthalpies of the present compounds. This overestimation makes up for the systematic error associated with the K–W rules, namely the overestimation of the formation enthalpies of the products due to CO being systematically privileged over CO_2.

Therefore, the excellent results obtained using LOTUSES for this test set (with aad = 339 J/g) are somewhat misleading. Indeed, the systematic overestimation of the formation enthalpies obtained with this program does not reflect any systematic bias associated with neglected physical aspects, since they are calculated using a group contribution method parameterized against experiment. In other words, one may expect about 50% of the formation enthalpies calculated with LOTUSES to be underestimated. In such cases, the error associated with the K–W approximation will be enhanced and lead to poor predictions.

While it is desirable not to rely on such a compensation of errors, one may wish to get rid of the systematic error associated with the K–W rules. The simplest approach consists in an empirical scaling of K–W based heats of explosion, applying a coefficient given by the average value c of the ratio Q_{exp}/Q_{KW}. Data in Table 3 yield $c = 1.15$. This simple procedure applied to Q_{KW} decreases the aad from 674 to 272 J/g. Applied to raw theoretical values Q_{calc} computed by MATEO, it decreases the aad from 644 to 320 J/g, a value close to that of 339 J/g associated with LOTUSES predictions (Table 3). This is quite satisfactory as the value of the $c = 1.15$ coefficient is not specifically optimized to correct MATEO predictions. This procedure appears as an efficient way to estimate heats of explosion, as illustrated in Fig. 4. One obvious drawback stems from the fact that
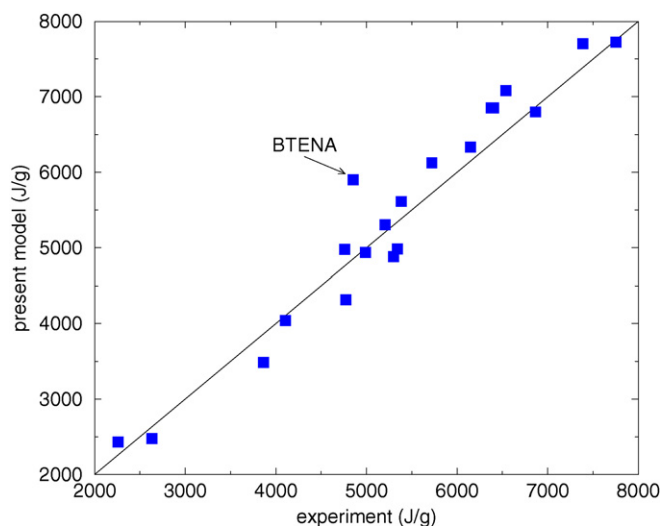
Fig. 4. Heats of explosion for the explosives listed in Table 3: values calculated using MATEO versus experimental values.

Table 4
Performances of propellants including 15 wt% of a binder based on HTPE and GAP polymers. Asterisk indicates values that have been maximized by adjusting the composition of the material.

Binder	wt% (HMX)	wt% (AP)	I_s (s)	$I_s \cdot \rho$ (s g cm^{-3})
HTPE	0	56	264	504
HTPE	85	0	250	436
HTPE	50	18	274*	502
HTPE	21	40	270	507*
GAP	0	53	255	513
GAP	85	0	261	472
GAP	69	0	276*	524
GAP	45	17	272	528*

c is purely empirical and does not correct the composition of the explosion products. A more satisfactory alternative to be explored would consist in introducing the fraction of carbon atoms that are converted to CO when applying the K–W rules. In principle, introducing a couple of additional adjustable parameters, it might be possible to correlate this fraction with the empirical formula of the compound.

A comparison of K–W data obtained using calculated formation enthalpies with corresponding data Q_{KW} derived from experimental enthalpies is useful to assess the influence of the procedure employed to predict $\Delta_f H^o$. The magnitude of the aad between Q_{calc} and Q_{KW} (210 J/g) is similar to the aad between Q_{KW} and Q_{exp} (272 J/g). This indicates that the computational procedure employed to evaluate $\Delta_f H^o$ on one hand, and the K–W rules on the other hand, yield similar contributions to the deviations between observed and predicted heats of explosion.

Finally, as alternatives to the original K–W rules, either modified K–W rules or Kamlet rules [51] may be used. Since Kamlet rules emphasizes CO_2 rather than CO formation, they tend to overestimate Q in many cases. However, for the compounds listed in 3, the deviations observed using the original K–W rules prove to be the most systematic. As a result, they provide the most reliable heats of explosion after applying the *ad hoc* 15% correction mentioned above.

5.3. Optimization of composite propellants

This section illustrates the use of MATEO to search for new compounds suitable as components of composite propellants. Starting from the ammonium perchlorate (AP)/aluminium (Al) mixture, the introduction of a third oxygen rich energetic component should in principle minimize the amount of AP required in the material to provide a given impulse I_s. The relative value of various compounds for this purpose can only be assessed from calculations on the formulated propellant, including also a binder.

To illustrate the capabilities of MATEO, we consider 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane, a powerful and costly explosive known as HMX, although it is unlikely to replace AP in solid propellants for practical applications. Table 4 summarizes the performance criteria I_s and $I_s.\rho$ calculated using MATEO for propellants including 15 wt% of binder, along with the corresponding compositions. Only two materials are considered as binders, hereafter referred to as HTPE and GAP as they are based respectively on

hydroxy-terminated polyether and glycidyl azide polymer. Results are reported for discrete compositions including only AP/Al or HMX in addition to the binder, and for HMX/AP/Al compositions optimized in order to maximize either I_s or $I_s \cdot \rho$, the amount of binder being constrained to 15 wt%.

The reference propellant AP/Al exhibits a higher value of I_s when associated with the HTPE binder, while the value of $I_s \cdot \rho$ is higher with the GAP binder. Therefore, the choice between the HTPE and the GAP binder depends on the specific application considered. Substituting completely AP/Al with HMX decreases the performance of this reference material. Indeed, although I_s increases for GAP-containing propellants, it remains lower than the value obtained for HTPE systems. In contrast, improved performance is obtained for the HMX/AP/Al composite propellants. Indeed, values of $I_s > 270$ s are obtained with no significant change of the $I_s \cdot \rho$ product. It may be noted that propellants optimized against I_s and $I_s \cdot \rho$ exhibit very different compositions, although their performance is similar. The first one is of more interest as a green substitute for standard AP/Al mixtures, since it contains only 18 wt% AP, to be compared with the 40 wt% content of the composition that maximizes $I_s \cdot \rho$. Finally, HMX/AP/Al compositions with the GAP binder appear even more interesting since they yield increased values of both I_s (>272 s) and $I_s \cdot \rho$ (>524 s). Again, the composition optimized in order to maximize I_s proves more interesting from the viewpoint of green chemistry. In this case, its AP content is reduced to zero.

6. Conclusions

Using MATEO, chemists involved in the synthesis of new energetic compounds can get immediate estimates for the relevant properties of a new molecule whose synthesis appears feasible at reasonable cost. Furthermore, the values thus obtained are quite reliable considering the models used. As such, this integrated application is ideally suited for identifying the most promising candidates among a number of compounds that might be synthesized.

Nevertheless, there is still much room for improvement. In particular, the models used to evaluate densities and enthalpies of salts need further testing. For these materials, a more efficient procedure to compute $\Delta_f H^o$ values for ions is still needed. On the other hand, models for stability aspects are still in their infancy, despite much work on the prediction of h_{50} in the last decades. Some progress in this area might come from effort to rationalize decomposition temperatures, or other data related to thermal decomposition.

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