Electronic excitation energies in crystals of PETN, RDX and HMX

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Abstract. The key role in the model of detonation based on metallization of an explosive plays a fundamental band gap of a molecular crystal. For determining it in a shocked crystal prerequisite calculation for perfect PETN, RDX, and HMX is performed at 0K. Densities of states for these explosives are obtained and fundamental gaps are determined. Calculations are done within the framework of the Density Functional Theory and its planewave and pseudopotential implementation in the ABINIT package.

1. Introduction
About 15 years ago Grebenkin [1] proposed that the reaction propagation in solid explosives is supported by the electronic thermal conductivity. He obtained the relation between a detonation velocity $D$ and a fundamental band gap of an explosive molecular crystal $\varepsilon_g$ which is related to conductivity in a non-conducting material. In final form this relation looks like

$$D = D_0 \exp\left(-\varepsilon_g / 4RT\right),$$

here $D_0$ - constant, $R$ - molar gas constant, $T$ - temperature in kelvins.

It can be seen that velocity is bigger for explosives with a small band gap. But at ambient conditions most of explosives have a quite noticeable gap value that leads to very poor electronic thermal conductance. Grebenkin suggested that in a shock wave a gap is narrower as well (some time narrowing is referred as metallization). To study detonation properties on the framework of the detonation model developed in [1] it is necessary to calculate a fundamental band gap for a crystal of explosive and its dependence on external pressure. PETN, RDX, and HMX are heavily used explosives. These explosives are molecular crystals with following chemical formulas of molecule: $C_5H_8N_4O_12$, $C_3H_6N_6O_6$, and $C_4H_8N_8O_8$, respectively. For determination of a gap program packages which are based on an implementation of the Kohn-Sham (KS) Density Functional Theory (DFT) are used. The milestones for these packages are the pseudopotential method and the planewave basis set. We explored the convergence of the total energy and pressure with respect to some parameters of a calculation: number of planewaves and number of k-points in an irreducible Brillouin zone. Type of pseudopotential and an approximation for an exchange-correlation energy of the non-homogeneous electron gas are important as well. In this work only norm-conserving pseudopotentials and the Local Density Approximation (LDA) are used. All calculations were performed with the ABINIT package.
[2]. The article is divided in the three sections: convergence study, 0K isotherm and behavior of a gap under compression of a crystal.

2. Convergence study

The convergence of the band gap with respect to the planewave energy cut-off at a fixed number of k-points was studied. Nuclear positions and unit cell volumes were taken from X-ray crystallography investigations [3-6]. The dependences of a fundamental gap on an energy cut-off for ideal crystal structure of \(\alpha\)-PETN, RDX and \(\beta\)-HMX are presented on figure 1.

![Dependence of fundamental gap on planewave energy cut-off](image)

**Figure 1.** Dependences of a fundamental band gap for of \(\alpha\)-PETN, \(\beta\)-HMX and RDX on planewave energy cut-off.

It can be seen that the convergence for a gap value occurs when energy cut-off chosen is equal about 30 hartree or 800 eV for all three crystals. The same behavior with respect to the energy cut-off due to the same set of norm-conserved pseudopotentials used should be expected. Such a large value of the cut-off is attributed to the hydrogen pseudopotential because it requires a rather large expansion over the planewaves to represent a distribution of electrons of molecular hydrogen atoms. In the case of convergence with respect to a number of k-points there is an opposite situation. The dependence of a gap on a number of k-points is shown on figure 2. Although only a few k-points (about 3) are enough to obtain a convergence for the gap of RDX crystal (as for \(\beta\)-HMX, data for which are similar to RDX’s one and aren’t shown on figure 2) a quite dense grid of k-points (over 20 k-points in an irreducible Brillouin zone) is necessary to obtain a rather poor convergence for \(\alpha\)-PETN. More k-points are required to converge the gap for PETN since it has two rather small lattice parameters in comparison with RDX.
For nuclear positions taken from experimental data LDA DFT predicts non-zero pressure. The reason is that experimental nuclear positions and volume don’t match those defined by the minimum of a total energy for a system “electrons-nuclei” in LDA DFT, i.e. equilibrium positions and volume. This effect is largely due to absence of the Van der Waals contribution to forces in the DFT and in particular in the LDA.

To estimate a value of the non-zero pressure a convergence with respect to a number of planewaves was investigated. The dependence of a pressure value on a planewave energy cut-off is presented on figure 3.

**Figure 2.** Dependences of a fundamental band gap for α-PETN and RDX on a number of k-points in an irreducible Brillouin zone.

**Figure 3.** Dependence of a pressure value on a planewave energy cut-off for α-PETN.
It can be seen that the value of a planewave energy cut-off needed to obtain convergence for pressure is larger on about 10% than the value of cut-off to converge gap. 

After convergence study fundamental band gaps for \( \alpha \)- and \( \beta \)-PETN, RDX and \( \beta \)-HMX were determined and are summarized in table 1.

**Table 1.** Values of a fundamental gap for perfect crystals of \( \alpha \)-, \( \beta \)-PETN, RDX and \( \beta \)-HMX.

| Crystal   | Fundamental band gap (theory), eV | Fundamental band gap (experiment), eV |
|-----------|-----------------------------------|--------------------------------------|
| RDX       | 3.58                              | \( \geq 6.53, 5.09 \) [7]*            |
| \( \beta \)-HMX | 3.43                            | 6.39, 5.32 [7]*                      |
| \( \alpha \)-PETN | 4.31                            | 6.42 [7], 3.76 [8]                    |
| \( \beta \)-PETN | 3.72                            | -                                    |

*In crystals of RDX and \( \beta \)-HMX there are two absorption bands determined experimentally, so two values of gap are presented.

It can be seen that the LDA DFT underestimates the value for a gap with respect to experimental one.

3. 0K isotherm

0K isotherm for a dependence of pressure on a crystal volume under hydrostatic compression for \( \alpha \)-PETN was investigated. The result obtained in this work, data from other works, and available experimental data are presented on figure 4. Works [9], [10] and [11], and [12] on figure 4 correspond all-electron Hartree-Fock (HF) method, Generalized Gradient Approximation (GGA) KS DFT and GGA KS DFT with Van der Waals (VdW) corrections, respectively.

![Figure 4](image)

**Figure 4.** Comparison of 0K isotherm for \( \alpha \)-PETN with other works. Every point on figure 4 corresponds to relaxed nuclear positions at a fixed compressed volume. This is done to account for change in geometry of molecules that comprise the unit cell of crystal under compression of a crystal lattice. The initial volume of a crystal on figure 4 corresponds to the experimental one. It can be seen that in a molecular crystal such as \( \alpha \)-PETN LDA predicts pressure which is lesser than HF and GGA with VdW corrections predicted for the same volume. All the methods predict the right behavior for an isotherm, but the closest one to the experimental is the VdW corrected GGA [10] (although it seems the HF method is close to experimental data too).

4. Band gap
For the same conditions under which 0K isotherm was calculated for α-PETN a dependence of a fundamental gap value on pressure was determined. It is shown on figure 5.

![Figure 5](image)

**Figure 5.** Dependence of a fundamental gap value on pressure for α-PETN.

It is seen that the compression of α-PETN from the experimental density to a density twice the experimental density leads to a narrowing of the gap (in the LDA case) from 3.80 to 3.15 eV. On the figure 5 there is also shown the only previous result (to our best knowledge) of calculation of the same dependence but for the GGA level of DFT [11]. Because there is no systematic way to control the accuracy of DFT level of theory we suppose there is no preference for LDA to GGA result and vice versa. Nevertheless it can be seen that the GGA predicts the same behaviour as the LDA but for different values of a gap. That can be attributed rather to the different charge distributions via different equilibrium internal coordinates and volumes. And different charge distributions generate distinct sets of eigenvalues via the Hohenberg-Kohn theorem. It leads to different values of a gap.

5. Conclusions

It is obtained that for the pseudopotentials used a value of pressure has a stronger dependence on a number of planewaves than a value of a fundamental gap. Consequently, for a reliable prediction of a dependence of a gap on pressure it is necessary to carry out calculations with such a number of planewaves at which pressure can be calculated with a given accuracy. It is showed that under compression of α-PETN up to 26 GPa the fundamental gap is narrowed (in the LDA case) from 3.80 to 3.15 eV. We suppose if we were use the right model for calculation of pressure (VdW corrections) and a more sophisticated model for electronic excitations like the “GW” Approximation (GWA) or the Time-Dependent DFT we couldn’t expect noticeable narrowing of a fundamental gap of α-PETN crystal caused by a deformation of molecules under strong compression like in a detonation wave. This point of view is based on the value of pressure in Chapman-Jouget point for PETN which is ca. 30 GPa and the fact that level of the DFT chosen underestimates pressure as can be seen from figure 4. It is also well known that the LDA DFT underestimates the band gap value with respect to an experimental one and to a GWA value [13]. In this case a value of the residual gap would be quite noticeable and lead to essential reduction of a detonation velocity according to the equation (1). To compare the gap value calculated in this work with that predicted by the equation (1) it is necessary to determine $D_0$. It hasn’t been done yet and we hope it will be done in a future work.
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