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Potential of mean force calculations using ab initio tight-binding molecular dynamics: Application to N–NO$_2$ bond dissociation in DMNA and HMX

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ABSTRACT

We discuss implementation of the umbrella sampling technique using the weight histogram analysis method in FIREBALL, a density functional theory method based on local-orbitals and pseudopotential theory. With this implementation, we calculate free energy curves of chosen reaction pathways from quantum mechanical forces; therefore, the potential of mean force yields energetic evaluations which include the electronic rearrangements as the structure changes during molecular dynamics simulations. The free energy curve is calculated along the entire reaction pathway rather than the traditional approach of using static single-point calculations along a reaction potential surface. We present results on the N–NO$_2$ bond dissociation in gas-phase DMNA and HMX. The results obtained in our calculations are in good agreement with other methodologies, which demonstrates that the umbrella sampling model implemented in FIREBALL is able to correctly predict the free energies changing along the reaction potential surface.

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1. Introduction

Nitramines have been used as explosives in mining, artillery, and engineering over a long period of time. In the past couple decades, extensive efforts have been devoted to understanding of the chemical mechanism of nitramine decomposition and combustion processes. Thermal decomposition of these energetic materials has been observed to form very simple final product molecules such as HCN, NO, N$_2$O, NO$_2$, CO, CO$_2$, H$_2$O, H$_2$CO etc. Based on the many suggested initial steps in the thermal decomposition of high-energy nitramine materials, N–NO$_2$ bond rupture is viewed as preferential in cyclic compounds such as RDX and HMX [1]. In DMNA, which is the simplest nitramine compound, the calculated N–NO$_2$ rupture is 35 kcal/mol [2,3]. There is a strong experimental basis from which we can compare computational information about the relative molecular fragments quantities produced along the decomposition in various conditions [4,5]. Beside the leading mechanisms via N–NO$_2$ dissociation, other complementary processes can occur through the C–N ring bond breaking and formation of HONO [6].

A look at previous work shows that there are numerous intermediates in decomposition reactions for RDX and HMX [7]. All of the previous theoretical work involved isolated molecules, and the question remains regarding bulk effects on all the possible decomposition processes. A first static effect can be expected with the existence of intermolecular repulsions or possible weak bonds between hydrogens and NO$_2$ groups, and a second collective dynamic effect might influence the chemical fragmentation energetics. Molecular dynamic (MD) studies can therefore give some complementary information into the energetics of decomposition pathways. These dissociation energies would reflect the overall effects since molecular dynamics allows one to access all harmonics (cubic, quartic, etc) rather than just absolute quantities. The umbrella sampling technique makes possible the estimation of an average of the forces acting on one element of the system among its different possible molecular configurations, leading to the determination of the potential of mean force (PMF), also called Free Energy (Helmholtz) [8,9].

In dealing with bond dissociation mechanisms, an estimation of these forces with a quantum mechanical framework is most desirable, rather than empirical or semi-empirical approaches. A first-principles molecular dynamic approach must therefore be used, where the energy and the forces are determined from the solution of the Schrödinger equation, and where all atomic displacements are calculated following classical equations of motions. At the end of the simulation, a statistical analysis will give the PMF along a chosen reaction coordinate. In this study the chosen reaction coordinate is related to the dissociation of the N–NO$_2$ bond which is the most simple decomposition mechanism to study in both DMNA and HMX model HE nitramine molecules. As a first step we are interested into developing the PMF approach with the use of the umbrella sampling technique and validate it on the gas phase molecules with some comparisons to other ab initio

methods, such GAUSSIAN 03. This Letter is organized as follows. Initially, in Section 2, a few concepts on the subject of the potential of mean force are described, and the implementation of the umbrella sampling method in the ab initio density-functional theory based tight-binding method (called FIREBALL) is discussed. In Section 3, the results of N–NO$_2$ dissociation in DMNA and HMX molecules using the PMF methodology are presented. The conclusions of these methods and results are summarized in Section 4.

2. Methods

2.1. Ab initio tight-binding method (FIREBALL)

The umbrella sampling technique described in this manuscript has been implemented into a self-consistent ab initio tight-binding method based on density-functional theory (DFT), called FIREBALL. A summary of the main features of the FIREBALL method are discussed here, for a more detailed discussion, we refer the reader to Refs. [10,11,19,20] and references therein.

The theoretical basis of the FIREBALL method is the use of DFT with a non-local pseudopotential scheme. The generalized norm-conserving separable pseudopotentials of the Hamann [12] form are used, employing for their construction the scheme of Fuchs and Scheffler [13]. The pseudopotentials are transformed into the fully separable form suggested by Kleinman and Bylander [14]. At the core of the method is the replacement of the Kohn–Sham energy functional by a self-consistent functional based on the input density [10,11]

$$E_{tot}[\rho] = E^{BS}[\rho_{in}(\vec{\gamma})] + \{E_{ii} - E_{ee}[\rho_{in}(\vec{\gamma})]\} + \{E_{xc}[\rho_{in}(\vec{\gamma})]$$
$$- \int \rho_{in}(\vec{r})\mu_{xc}[\rho_{in}(\vec{r})]d^3r\} \qquad (1)$$

In Eq. (1), E^{BS} is the band structure energy ($2\sum_{i\in occ}\in_i$), where $\in_i$ are the eigenvalues of the one-electron Schrödinger equation; The second term is the 'short-range' repulsive interaction which is the ion–ion interaction E_{ii} offset by the electron-electron repulsion E_{ee}. The last term is a correction to the exchange-correlation. For the exchange-correlation energy within the pseudopotential calculation, and, respectively, for the exchange-correlation potential, various parameterizations of the local-density approximation (LDA) and of the generalized gradient approximation (GGA) are available, and in this work we use Becke exchange (B88) [15] with Lee-Yang-Parr (LYP) correlation [16] throughout.

In evaluating the total energy of the system (Eq. (1)), the density is based on a sum of confined spherical atomic-like densities, $\rho_{in}(\vec{r}) = \sum_i n_i|\phi_i(r - R_i)|^2$. The occupation numbers n_i can be written down as the sum of a neutral, n_i^0, and a non-neutral contribution, δn_i [17,18]: $n_i = n_i^0 + \delta n_i$ The orbitals $\phi_i(r - R_i)$ are the slightly excited 'fireball' pseudoatomic wavefunctions which are used as basis functions for solving the one-electron Schrödinger equation. These orbitals are computed within DFT and a norm-conserving separable pseudopotential [12] and are chosen such that they vanish at some radius $r_c(\varphi_{fireball}^{atomic}|r \geqslant r_c = 0)$. This boundary condition has the effect on the electronic energy levels and is equivalent to an 'atom in the box'. The radial cutoffs (r_c) are chosen such that these electronic eigenvalues remain negative and are mildly perturbed from the free atom.

A flexible choice of basis set of double numerical (DN) or additional polarization orbitals are permitted within the FIREBALL method. For this work, orbitals of the positively charged ion are considered for the second numerical basis set. The method for creating these orbitals is done after the manner of the orbitals used in the commercial program DMOL (distributed and maintained by Accelrys, Inc.) [21,22]. The r_c values chose in this work are

r_c = 3.8 for H, r_c = 4.0 (s), 4.5 (p) for C, r_c = 3.7 (s), 4.1 (p) for N and r_c = 3.4 (s), 3.8 (p) for O atom, respectively.

In summary, the FIREBALL method maintains a short-range nonorthogonal local orbital basis, real-space analysis, and there are no integrals involving four or more centers. All the two- and three-center integrals are tabulated beforehand and placed on interpolation grids no larger than two-dimensional. Additionally, molecular dynamics simulations are performed simply by looking up the necessary integrals from the interpolation grids. The most profoundly advantage of such a method is that the computational times are greatly reduced, which can promise us to expand the simulation steps and size [23].

2.2. Potential of mean force and umbrella sampling method

Using a Boltzman distribution law, the potential of mean force (PMF) [24] is defined as

$$PMF = -kT \ln \rho(\in)$$

where $\rho(\in)$ is the average distribution function

$$\rho(\in) = \frac{\int dR\delta(\in [R] - \in)e^{\frac{-E(R,\in)}{kT}}}{\sum_R e^{\frac{-E(R)}{kT}}}$$

where R represents a set of atomic positions, i.e., a molecular geometry, and $\in$ is the reaction coordinate. The Dirac function allows summation over all geometries where $\in$ is found, and thus gives to $\rho(\in)$ the significance of a total probability to find $\in$ among all geometries. The problem of estimating this average distribution function becomes a technical issue. If $\in$ corresponds to a situation of high energy, the chance to sample this area of the hypersurface decreases dramatically, and it would be necessary to proceed to very long molecular dynamic trajectories.

A solution to this problem is to use the umbrella sampling technique which with the aid of a restraint potential, $\in$ is confined to oscillate around one particular value. Therefore one trajectory is realized in each defined window. Once the distributions obtained are modified through the introduction of the umbrella potential, it is necessary to later unbias them. The distribution $\rho^b(\in)$ ($\rho^u(\in)$ for the unbiased one) is redefined as

$$\rho^b(\in) = \frac{\int dR\delta(\in [R] - \in)e^{\frac{-E(R,\in)}{kT}}e^{\frac{-V(\in)}{kT}}}{\sum_R e^{\frac{-E(R)}{kT}}e^{\frac{-V(\in)}{kT}}}$$

starting with this literal expression there is no simple way to make a direct relation between $\rho^b(\in)$ and $\rho^u(\in)$.. In each window i, the distribution functions may also be expressed as $\rho_i^u(\in) = \frac{N_i^u(\in)}{n_i}$ and $\rho_i^b(\in) = \frac{N_i^b(\in)}{n_i}$ with n_i being the number of points in the sampling of window i, and N_i^u and N_i^b being the number of counts where the reaction coordinate equals $\in$ for the unbiased and biased cases. We can say that N_i^u and N_i^b are proportional; $N_i^u = CN_i^b$ and then rewrite the unbiased PMF expression as

$$PMF_u = -kT \ln \frac{N_i^u(\in)}{n_i} = -kT \ln \frac{N_i^b(\in)}{n_i} - kT \ln C.$$

Considering that the constant of proportionality depends on the umbrella potential;

$$C = \alpha_i e^{\frac{V_i(\in)}{kT}}$$

the PMF becomes

$$PMF_u = PMF_b - V_i(\in) + F_i$$

with $F_i = -kT \ln \alpha_i$. After the simulation, we know $\rho^b(\in)$ and $V_i(\in)$. Different techniques have been developed to find the various F_i and connect the windows. We choose the weight histogram analysis

method (WHAM) [25] where the unbiased distribution function is averaged over all the different N_w windows, and in order to determine the F_i, we apply the formulation of Ref. [24], where the F_i are calculated in a self-consistent way.

2.3. Computational details

The harmonic umbrella potential $V(i)$ for each window i is chosen as,

$$V(i) = \frac{1}{2}K(\in - \in_0(i))^2,$$

where $\in_0(i)$ is the ith fixed value of the reaction coordinate $\in$, and K is the force constant. As we study the DMNA and HMX N–NO$_2$ dissociation, $\in$ is chosen as the internuclear N–N distance. There is no precise rule for the choice of the force constant, K, other than to attempt to get a balance between the number of points inside the window and the number of points outside the window. If the number of points inside is too small, then the sampling is not characteristic of the window itself, and K is too small. If all the points are in the window, then there is no overlap between the windows, and in such case, the different windows cannot be connected in order to find a general final PMF, and K is too large. We have checked that the number of points in each sampling i is not too small, (up to 30 percent), and on the opposite, that the samplings on neighbor windows overlap in order to perform the WHAM analysis.

All MD trajectories are realized at the constant temperature T = 300 K using the Gear corrector- predictor algorithm. In our initial simulations, we use DMNA as a model to determine the force constant K in each window, repeating the trajectories with new K in order to center the distribution of points in the window. In a second time we determine the distributions for HMX. The samplings differ between the molecules. In DMNA case the different samplings are calculated with 5 ps trajectories in windows of 0.05 Å, using a time step of 0.2 fs. After an equilibration time of 1 ps, we obtain a distribution over 20000 points for each window of the reaction coordinate $\in$ .. If for a small K the distribution of points for one sampling is narrow and doesn't overlap with neighbor windows, we add a new window and so divide the length of the previous one.

For HMX, we use the same time step but a larger value (0.1 Å) to define the windows. Aditionally, we also make only 0.8 ps trajectories with a 0.08 ps equilibration time, which leads to a distribution of 3500 points. The times necessary to obtain the distribution function for one window (20000 points for DMNA and 3500 points for HMX) are approximately the same for both samples. As we are interested in the next step to estimate the PMF in HMX condensed phase, it is important to save some CPU time and therefore to know qualitatively how a smaller number of points might influence the final results. A comparison of the energetical curves obtained is made with some energetic profiles calculated with GAUSSIAN 03 [26] using the BLYP and B3LYP method with 6-311 G** basis set. Both the energy curves include a quasi-harmonic free energy correction from frequencies of the stable points computed following a previous geometry optimization at the same method.

3. Application: N–NO$_2$ dissociation in DMNA and HMX

These two molecules (see Fig. 1) constitute model systems for the study of explosives [1–3], [27–30] and we take the geometric structures from our previous work [29]. The two structures have been fully optimized in our calculations first. Then based on these two structures, we are interested in the N–NO$_2$ bond dissociation since it is considered as one of the most important steps of the whole reaction processes [28]. Most experimental and theoretical studies indicate that the N–NO$_2$ bond fission has the lowest-energy
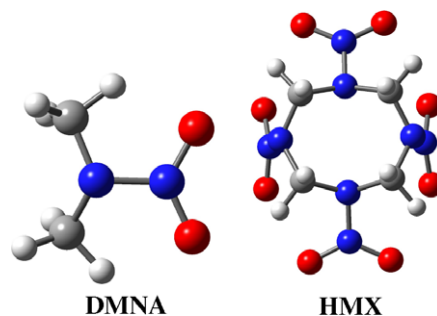

Fig. 1. The molecule structures of DMNA and HMX. (The blue balls represent N atoms, the red balls are O atom while small while balls and grey balls are H and C atoms, correspondingly.) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

barrier, however there is still some dispersion about this initial step going through at various conditions and associated kinetic parameters. In our calculation, however, we emphasis our effort on the free energy changing of N–NO$_2$ bond dissociation which will enable us to understand the reaction processes from the initial rate limiting step.

The DMNA PMF after WHAM analysis is shown in Fig. 2. A comparison with the DFT calculations obtained with GAUSSIAN 03 shows that the PMF and the GAUSSIAN 03 energy curves are in agreement which validates the implementation and utilization of the WHAM analysis in FIREBALL. As shown in Fig. 2, the free energy barrier obtained in our calculation is 37.97 kcal/mol, which is very close to the BLYP and B3LYP GAUSSIAN calculations (38.92 kcal/mol on BLYP/6-311G** method). In the Fig. 3, we show the initial optimized DMNA structure with the N–NO$_2$ bond length as 1.403 Å, which is in consistent with the previous theoretical calculations [30,31]. And when the bond length goes to 2.41 Å, it is supposed that the N–NO$_2$ is broken, as shown in Fig. 3. It should be noted that the basis set used for the calculations in FIREBALL is much simpler than the 6-311G** one used in GAUSSIAN 03.

The HMX PMF long range behavior reaches a maximum around 2.5–2.7 Å which is slightly longer from the DMNA PMF. In the HMX PMF, it reflects that the free energy barrier is 45.53 kcal/mol which is very close to the experimental value of 43 kcal/mol. Our result is
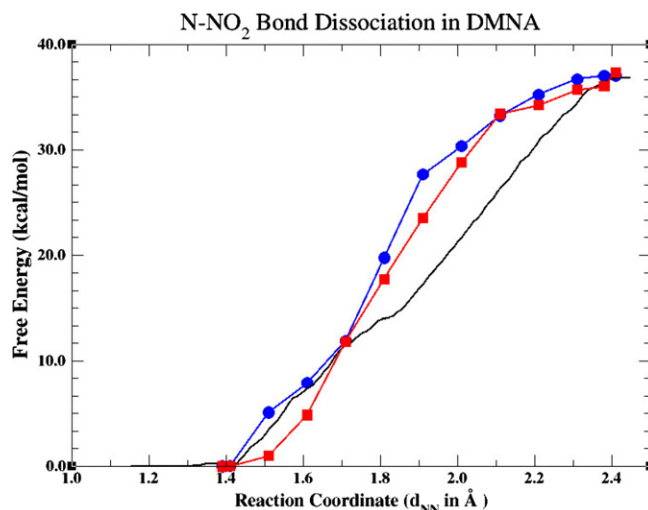

Fig. 2. DMNA PMFs, comparison to GAUSSIAN 03 calculations using BLYP or B3LYP with 6-311 G** basis sets. (The black line is our PMF of DMNA. The red line and blue line are BLYP and B3LYP free energy curves, respectively.) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
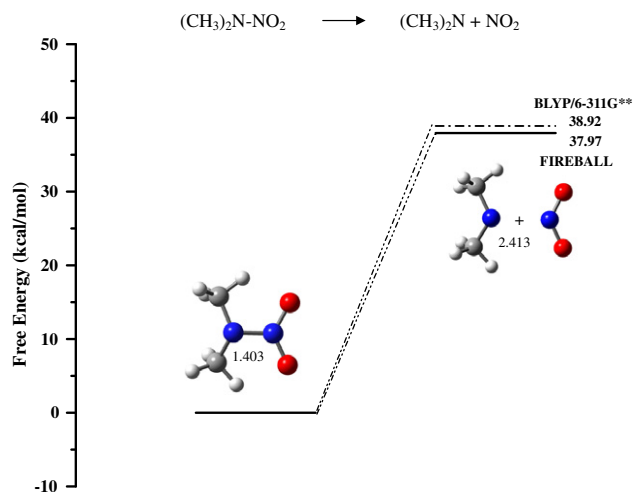
$$(CH_3)_2N\text{-}NO_2 \longrightarrow (CH_3)_2N + NO_2$$

Fig. 3. The structural and bond length change of DMNA N–NO$_2$ dissociation.

method compensates the defaults through an exploration of the energy hypersurface: the absolute error being incorporated on all neighbor points, the relative probabilities should remain qualitatively the same. It is the same idea as to say that the minimums on the potential energy surface at 0 K will be shifted in energy at 100 K, approximately in a way where their relative positions remain. Of course an amelioration of the determination of the energy will influence the forces, but probably more in absolute intensity than in relative order of importance, i.e. the force along the N–NO$_2$ will change on magnitude but still remain one of the most important at intermediate bond dissociation. In our on-going work, the PMFs will be calculated under varied temperatures using the umbrella sampling and WHAM analysis model, which can help us understand the chemical reaction constant of N–NO$_2$ dissociation.

4. Conclusion

Implementation of the umbrella sampling technique and weight histogram analysis method is validated with calculation of the DMNA and HMX gas phase potential of mean force. Results are in excellent agreement with other DFT calculations, and might be refined in a second step with further theoretical developments. With this implementation, we calculate free energy curves of chosen reaction pathways from quantum mechanical forces; therefore, the potential of mean force will yield energetic evaluations which include the electronic rearrangements as the structure changes during molecular dynamics simulations. The free energy curve is calculated along the entire reaction pathway rather than the traditional approach of using static single-point calculations along reaction potential surface. We present results on N–NO$_2$ bond dissociation in gas-phase DMNA and HMX. The results obtained in our calculations are in agreement with the other calculations, illustrating that the umbrella sampling model implemented in FIREBALL is able to correctly predict the free energies changing along the reaction potential surface. Moreover, these first tests show that a method is now available to access energetic quantitative informations in condensed phase using a local-orbital, DFT code (FIREBALL) through first principles molecular dynamic studies.

also in good agreement with the GAUSSIAN single point free energy calculations showing in Fig. 4. Both DMNA and HMX PMFs are very similar to other theoretical calculations leading to the conclusion that the umbrella sampling implemented in FIREBALL is able to predict the right result as other calculation program. Moreover, it also should be noted that a smaller number of points during the MD trajectories will still give a correct tendency. This last point is important for saving computational time when larger condensed phase reaction events are calculated. However, even if the absolute bond energy is still not perfect, its determination through calculation of the PMFs allows comparison between different chemical processes using a relative scale of energy. At last, chemical reactivity involved in the bulk of condensed phase, due to the compactness of the systems should be more sensible at first approximation to short range behavior, and therefore to profile of the energy slopes before complete dissociation.

Despite the absence of polarization orbitals and the refinements just evocated, the results are coherent and relatively close to the experimental value. This tendency shows that the approach is correct, but in a way also, shows how the statistical nature of the
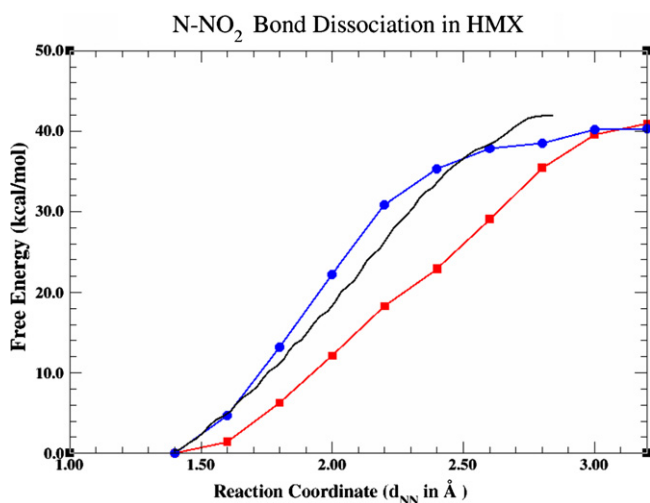
Fig. 4. HMX PMFs, comparison to GAUSSIAN 03 calculations using BLYP or B3LYP with 6-311 G** basis set. (The black line is our PMF of HMX. The red line and blue line are BLYP and B3LYP free energy curves, respectively.) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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