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含能材料感度判别理论研究——从分子、晶体到复合材料

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摘 要:近30多年来,通过量子化学计算和分子动力学模拟,国内外已提出过许多关于含能材料撞击感度的微观理论判据。本文主要介绍我们研究小组从高能分子、高能晶体到高能复合材料的热解机理和感度判别的相关工作,其中关于高能晶体和复合材料的感度判别的一些结果和判据是首次报道。

关键词:量子化学;含能材料;热解机理;感度;分子动力学
中图分类号:TJ55;O64 **文献标识码**:A **DOI**:10.3969/j.issn.1006-9941.2012.05.002

1 引 言

含能材料的感度是它在外界刺激下爆炸的难易程度,属于安全性研究,事关重大,主要应依靠实验测定[1]。各类感度的理论预测和判别均已取得一定进展,也值得加以推进和发展。本文主要介绍通过量子化学(QC)计算和分子动力学(MD)模拟,我们研究小组获得的关于高能分子、高能晶体和高能复合材料撞击感度和热感度的微观理论判别的一些结果和规律。

首先简介如图1所示的微观理论计算和模拟的方法。除Monte Carlo方法外,其余QC方法包括各种水平的第一性原理Ab initio和DFT方法以及各类半经验分子轨道方法,紧束缚(TB)晶体轨道法;X_α方法;经典MD、从头算MD和DF-TB等半经验量子MD方法,我们均有较多应用,且在已出版和即将出版的学术专著中,对撞击感度判别均有较详细的评介[1-8]。这在某种程度上反映了我国对"量子炸药化学"或"含能材料计算学"研究的历史、水平和地位。其次将依次展开关于高能分子、高能晶体和高能混合体系的感度理论判据讨论。

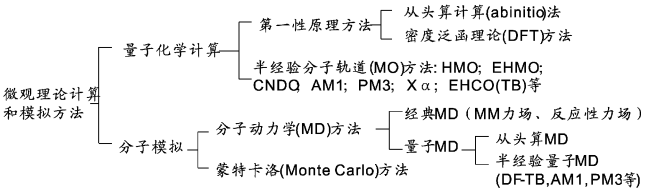

图1 微观理论计算和模拟方法

Fig.1 Methods of microcosmic theoretical computations and simulations

2 高能分子QC计算,撞击感度的热力学和动力学判据

2.1 历史回顾

分子是保持化合物性质的最小单元。对高能物质感度的理论研究,最早和最多的工作是基于对高能分子进行QC计算。从20世纪70-80年代至今,国外提出的关于(机械)撞击(impact)感度的理论判据主要有:原子或原子基团(如NO_2)上电荷[9-13]、电负性[14]、静电势[15-17]、前沿轨道能级差[18]、引发键键长[19]和键离解能[20]等。但法国人Delpuech等最早(1979年)以电子结构参数$\Delta C^0/\Delta l$判别的是冲击(shock)波感度,而不是撞击感度。

20世纪80年代初,我们曾以HMO方法计算含杂π体系(如苯胺和苯酚系列硝基衍生物)的电子结构,通过建立分子图(π原子电荷、π键级和自由价)关联体系的反应性[21];通过HMO和CNDO/2计算,从电子微观层次阐明了TATB特别稳定和钝感的缘由:分子具有高对称(属D_{3h}群)的大π结构(Π_{18}^{24});C—NO_2键级值很大表明该键不易断裂;发现其硝基

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上(—NO_2)上的电子密度(Q_{NO_2})最大,不容易发生氧化反应[2,21]。此后,我们发表了以电子结构参数判别撞击感度的最早一组文章,表明我国最早提出以引发键键级[22]、键离解能[23]和双原子作用能[24]判别热稳定性和撞击感度,并发现甲苯和苯酚类硝基衍生物的引发键并非 R—NO_2 键,而是甲基 C—H 和羟基 O—H 键[25]。

20 世纪 90 年代,通过 AM1 和 PM3 等半经验 MO 计算,本课题组发表了研究撞击感度和热解机理的另一组文章[26-30],从动态计算结果发现引发键键级与断裂该键的活化能两种判据良好地线性相关,并首次提出了以热解引发步骤的活化能作为感度理论判据。

稍后,在运用第一性原理 DFT 方法系统计算研究四唑化合物结构-性能的基础上[4],又发表了关于四唑及其金属盐的感度判别的另两篇论文[31-32]。发现当国内外提出的各种热力学静态判据都不能解释实验事实时,只有活化能动力学判据才有效,从而证明活化能判据具有较大普适性,建议感度理论研究应该从热力学向动力学发展[33]。

进入 21 世纪,寻求高能量密度材料(HEDM)成为全世界含能材料研究的热点和重点。我们建议了高能量密度化合物(HEDC)的能量和稳定性相结合的定量标准(即密度 $\rho\approx1.9\ g\cdot cm^{-3}$,爆速 $D\approx9.0\ km\cdot s^{-1}$,爆压 $p\approx40.0\ GPa$,引发键离解能 $BDE\approx80\sim120\ kJ\cdot mol^{-1}$)和基于量子化学加以估算的一套方法[6,34-37],通过第一性原理主要是 DFT 计算表明,热力学引发键键级判据和动力学活化能(均裂反应的键离解能亦即其活化能)判据的结合运用,在寻求 HEDC 的理论设计中,发挥了重要作用[34-45]。

在高能富氮化合物(HNEC)理论设计中,我们也依据 HEDC 的定量标准加以判别和筛选,并直接用动力学引发键均裂键离解能(BDE)亦即活化能,研究和判别了它们的热解机理、感度和稳定性[46-59]。

2.2 键级(BO)和活化能(E_a)判据

对于系列结构和热解机理相类似的爆炸物,其热解引发键的键级越小,则其撞击感度便越大;键级最小者感度最大。这就是最小键级原理(PSBO),亦即键级(BO)判据[2,3,22,60]。有趣的是,高能化合物引发键的键级往往在分子中也是数值最小的键级。PSBO 由 C—NO_2 化合物计算首次发现[22],后被广泛应用于硝酸酯[61,62]、硝胺[63-65]、叠氮[66,67]和笼状[68]等高能化合物[5]。基于 DFT 计算,将 BO、Q_{NO_2}(硝基上电荷)与 E_a 相关联的报道可见文献[34,69]。值得指出的是,当前热门研究的反应性力场的建立通常都是基于键级概念,以键级与能量的关联可构建反应性力场;足见,抓住表征化学键上电子集居数多少和键强弱的键级概念,并以引发键的键级关联热解和感度,确实抓住了本质,经得住时间和历史的检验。

对于系列结构和热解机理相类似的爆炸物,其引发热解反应所需活化能(E_a)越大,则感度便越小。这就是判别感度相对大小的活化能(E_a)判据[26-32]。因为生成两个自由基的均裂反应的键离解能(BDE),亦即该反应的活化能(E_a)。所以 BDE 即产物为自由基的化学反应的 E_a。也就是说,BDE 是 E_a 的特例,E_a 判据已包括了 BDE 判据。炸药中有许多热解引发反应为 H 转移反应,例如苯酚和甲苯硝基衍生物的热解引发反应[29,30,43,44];对此类反应,PSBO 和 E_a 判据仍然适用,而 Q_{NO_2} 与 BDE 判据便失效了。

我们之所以强调对结构和热解机理相似的系列爆炸物的感度进行理论判别,主要基于两点。一是影响感度因素很多,只有将同系物的系统误差彼此抵消或减小,才能求得实验感度与结构之间的规律性联系。二是分子和电子结构参数如原子间键级、键长、原子上电荷、前沿轨道能级差等等,只有在同系物中比较才有普遍意义。以对分子计算的结构参数去关联所有各类爆燃物的实验感度是不可能实现的。

2.3 键级(BO)和活化能(E_a)判据的应用举例

2.3.1 引发键判别

由表 1 和表 2 可见,在 NG 和 HMX 分子中,O—NO_2 和 N—NO_2 键的键级和 BDE 分别均为最小值,表明 O—NO_2 和 N—NO_2 键分别是 NG 和 HMX 的热解和起爆的引发键。

表 1 NG 的(U)B3LYP/6-31G* 计算键级和键离解能

Table 1 Bond orders and bond dissociation energy (BDE) of NG at the (U)B3LYP/6-31G* level

compund	Mulliken bond orders			BDE/kJ·mol^{-1}		
	C—O	C—O	O—NO_2	C—O	C—O	O—NO_2
NG	0.2886	0.1615	0.1491	311.49	286.06	136.27

表 2 HMX 的(U)B3LYP/6-31G* 计算键级和键离解能

Table 2 Bond orders and BDE of HMX at the (U)B3LYP/6-31G* level

compund	Mulliken bond orders			BDE/kJ·mol^{-1}		
	C—H	C—N	N—NO_2	C—H	C—N	N—NO_2
HMX	0.362	0.237	0.160	368.94	248.44	197.73

2.3.2 BO 和 BDE 判据的应用示例

图 2 中 12 种螺环硝胺化合物的分子结构和热解机理比较相似,比较如表 3 所示引发键的键级和/或 BDE,则判别它们稳定性和感度的相对大小。表 3 预示稳定性排序为 TNSU > TNSDo > TNSO > TNSH > NSP > TNSN > *m*-DNSP > TNSD > TNSHe > TeNSP > *o*-DNSP > TriNSP。再结合计算所得密度、爆速和爆压等能量标准,则可成功设计 HEDC 分子[6,36]。

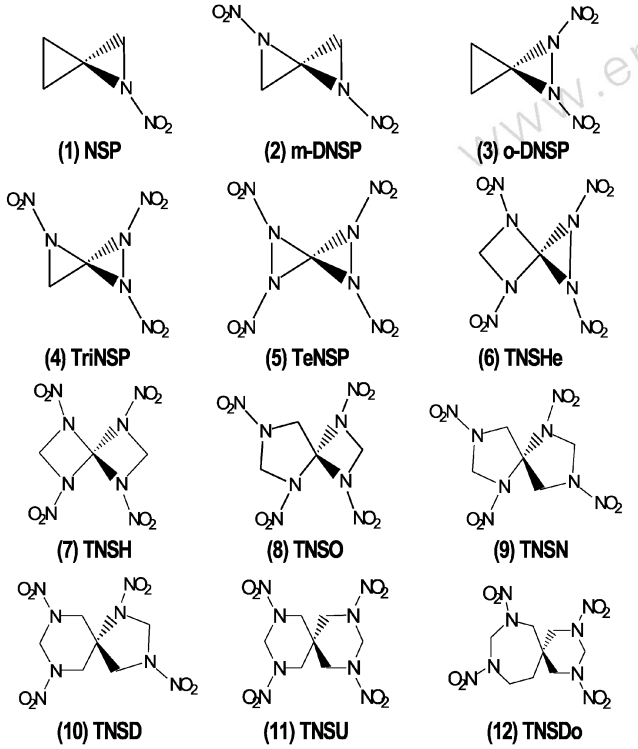


图 2 12 种螺环硝胺化合物的分子结构

Fig. 2 Molecular structures of 12 spiro nitramines

3 高能晶体 QC 计算和从头算 MD 模拟,前沿带隙判据

3.1 历史回顾

通常条件下单体炸药多以固态(晶体)存在,研究高能晶体的感度判别显然很有意义。关于高能晶体 QC 计算,早先国内外只有金属叠氮化物的 DV-X_α 和 EHCO 半经验计算。我们最早提出以前沿带隙(ΔE_g)即“最易跃迁原理”(PET)关联撞击感度[3,70],意即对于系列同系物,在外界作用下,电子最易从其最高占有晶体轨道(HOCO)跃迁到最低未占晶体轨道(LUCO)、实现其引发决定速率步骤者,则其感度便最大。此后,我们开拓 Crystal98 程序,最早实现了对高能晶体的第一性原理 DFT 计算,如首次报导了 HMX 和 TATB 晶体的结构-性能关系[71,72]。2005 年以来,我们用 DFT 方法,在系统计算研究多类高能(分子型、离子型和配位型以及缺陷)晶体的能带和电子结构的基础上[7,73-93],归纳出关于感度理论判别的第一性原理带隙(ΔE_g)判据[88,89],同时与高水平从头算 MD 模拟结果,进一步证明、支持和发展了 PET。

3.2 第一性原理带隙判据

3.2.1 示例 1:HMX 四种晶型的带隙[77]

由图 3 可见,四种晶型 HMX 的带隙值(ΔE_g)分别为 2.42, 3.62, 0.02, 3.38 eV。由此可判别它们的稳定性递减(感度递增)排序为 $\beta > \gamma > \alpha > \delta$-HMX,与实验事实良好相符。

表 3 螺环硝胺分子中各化学键的 Mulliken 键集居数和键离解能

Table 3 Mulliken populations of various chemical bonds and BDE of spiro nitramines

No.	compound	Mulliken populations						BDE/kJ·mol^{-1}			
		C—C	C—N	N—N	N—NO_2	N—O	C—H	C—C	C—N	N—N	N—NO_2
(1)	NSP	0.2274	0.1392		0.1854	0.3016	0.3732	191.79	147.57		134.35
(2)	*m*-DNSP	0.2474	0.1182		0.1692	0.3010	0.3684	187.57	186.56		128.83
(3)	*o*-DNSP	0.1965	0.0955	0.0035	0.1211	0.2930	0.3821	178.49	177.11	81.80	97.78
(4)	TriNSP	0.2831	0.0407	-0.0180	0.1119	0.2920	0.3696	181.96	168.11	71.76	85.60
(5)	TeNSP		0.0885	-0.0409	0.1062	0.2978			153.80	86.36	103.72
(6)	TNSHe		0.0639	-0.0346	0.0976	0.2960	0.3835		121.59	92.59	97.32
(7)	TNSH		0.1807		0.1499	0.3147	0.3838		197.65		140.71
(8)	TNSO	0.3167	0.1686		0.1523	0.2964	0.3667	256.77	195.64		142.76
(9)	TNSN	0.3176	0.1941		0.1637	0.3123	0.3714	262.80	271.29		132.59
(10)	TNSD	0.2943	0.1787		0.1734	0.2927	0.3696	240.08	242.34		92.97
(11)	TNSU	0.3113	0.2224		0.1730	0.3116	0.3701	275.18	285.31		160.67
(12)	TNSDo	0.3273	0.2069		0.1737	0.3087	0.3653	304.85	317.57		158.41

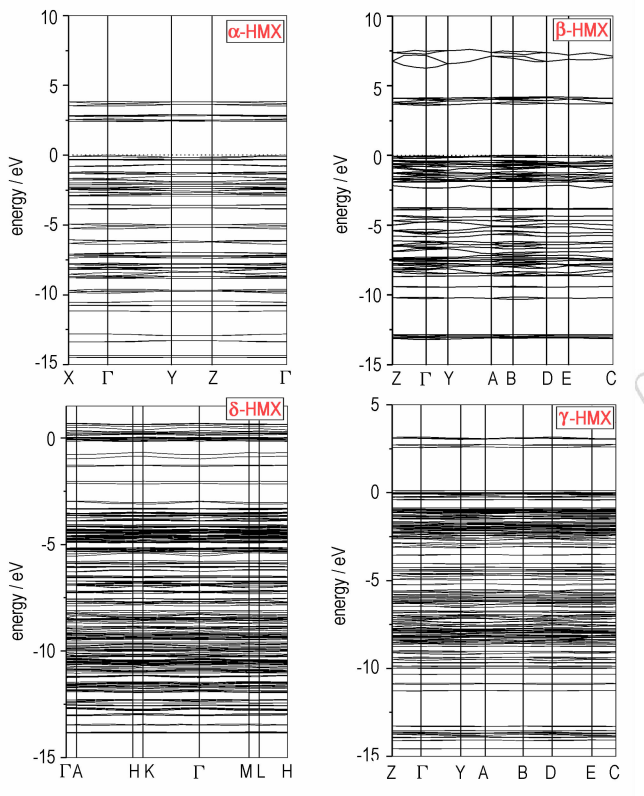


图 3 四种晶型 HMX 的能带结构

Fig. 3 Band structures of the four polymorphs of crystalline HMX

3.2.2 示例 2：不同压力下 ε-CL-20 的能带结构[94]

由图 4 可见，ε-CL-20 的带隙（ΔE_g）随压强增加而逐渐减小；在 0，5，10，50，100，200，400 GPa 压力下 ΔE_g 依次为 3.492，3.450，3.323，2.742，2.102，1.401，0.085 eV，可预示随压力增大，ε-CL-20 晶体的稳定性下降、感度增大；高压下显示金属性。

3.3 从头算 MD 模拟高能晶体的热分解机理

从头算 MD 是 Car 和 Parrinello 首先提出的理论方法，故又称（CP-MD）[95]。这是量子化学 DFT 与分子动力学（MD）相结合的第一性原理方法。因既能获得原子运动轨迹，又能提供电子结构、计算化学反应，故而是当前最先进准确很有发展前途的分子模拟方法。由于它能直观有效地预测高能化合物的热解起爆机理，关联多类感度特性，故我们率先用于高能晶体的热和冲击感度的理论研究[84,85]。当然，CP-MD 耗计算资源很多，仅适用于相对较小的体系。

3.3.1 示例 1：叠氮化银晶体的热分解机理[91]

对于如图 5 所示 AgN_3 超晶胞（2 × 2 × 2），完成了 5 个温度的从头算 MD 模拟：298 K、473 K、498 K、523 K（熔点）、548 K 和 573 K。图 6 和图 7 分别给出了其晶格结构和态密度随温度的变化。由图 6 明显可见，在 523 K 时，N 晶格开始发生扩散；到 573 K 时，晶格则遭完全破坏，呈液态状。由图 7 可见，温度低于 548 K 体系电子结构无显著变化。573 K 时电子的离域增大，带隙关闭，体系中出现金属态。在 573 K 时，发现 N—N 键断裂、N_2 形成、N 自由基富集和 Ag 原子簇形成等奇妙图像。为此，我们提出 AgN_3 的分解机理如图 8 所示。

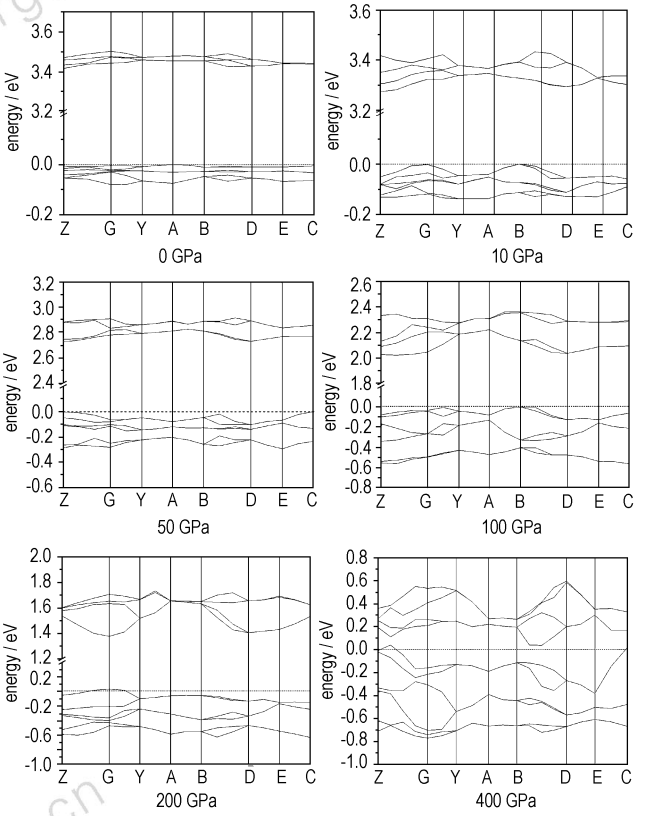


图 4 不同压力下 ε-CL-20 能带结构

Fig. 4 Band structures of crystalline ε-CL-20 at different pressures

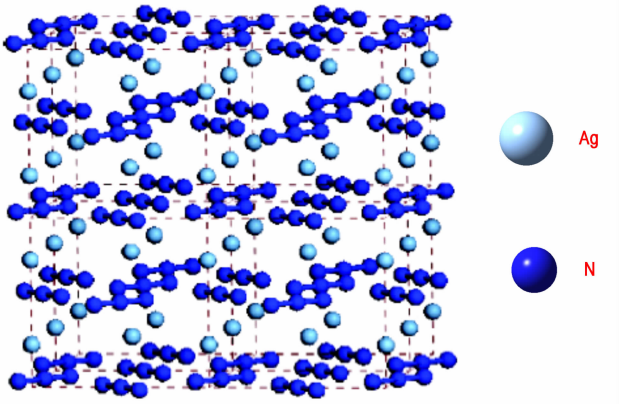


图 5 AgN_3 超晶胞（2x2x2）结构

Fig. 5 （2x2x2） supercell of silver azide crystal

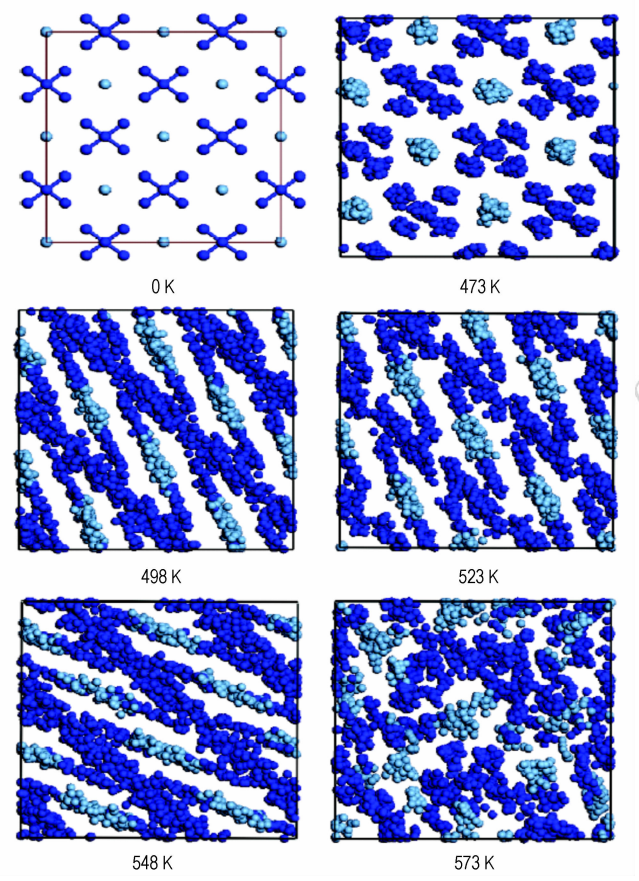


图 6 不同温度下 AgN_3(001)面的变化

Fig. 6 Projection of Ag and N atoms onto AgN_3(001) for the postequilibration period

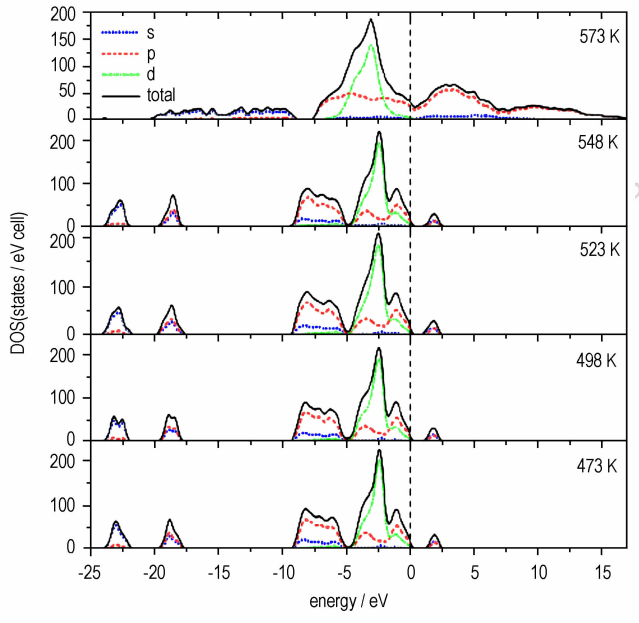


图 7 AgN_3 的态密度随温度的变化

Fig. 7 Electronic density of states (DOS) of silver azide at 473, 498, 523, 548, 573 K

$$Ag^+ + N_3^- \longrightarrow Ag-N-N-N \longrightarrow Ag-N-N+N$$

$$Ag^+ + N_3^- \longrightarrow Ag-N-N-N \longrightarrow Ag-N+N_2$$

$$Ag_n + Ag^+ + e \longrightarrow Ag_{n+1} \quad (n>2)$$

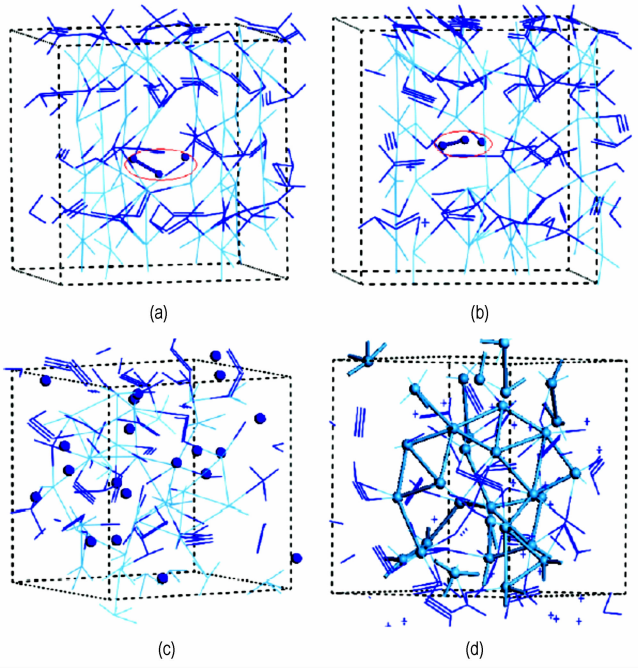


图 8 AgN_3 的分解示意

Fig. 8 Snapshots of (a) N—N rupture, (b) N_2 formation, (c) N radical formation, and (d) Ag cluster formation at 573 K during the thermal equilibration phase

从 AgN_3 带隙随温度的变化(图 9)可见,体系带隙随温度升高而呈下降趋势,与随温度升高体系感度增加的实验事实相一致,符合"第一性原理带隙判据"[88,89]。

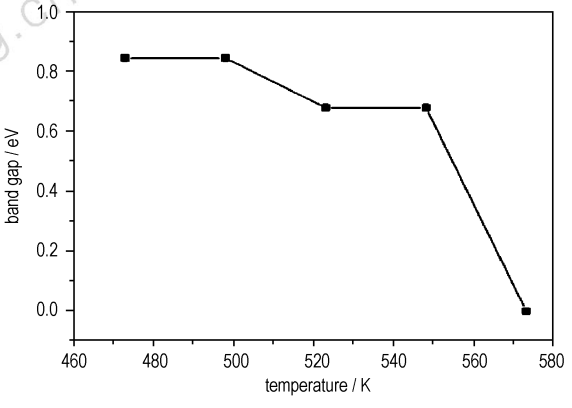


图 9 AgN_3 带隙随温度的变化示意

Fig. 9 Band gaps of silver azide as a function of temperature

3.3.2 示例 2:ε-CL-20 晶体的温度行为和感度判别[7]

对于 ε-CL-20 晶胞,完成了 5 个温度的从头算 MD 模拟:298 K、393 K、418 K、443 K 和 468 K(熔点)。

图 10 给出不同温度下 ε-CL-20 晶体的能带结构。由图 10 可见,它们的能带曲线很平坦、缺少起伏,表明晶体内分子间相互作用较弱。与温度对应为 298, 393, 418, 443, 468 K, 它们价带和导带间的带隙值分别为 3.52, 2.94, 2.91, 2.77, 2.56 eV;如图 11 所示,其前沿带隙(ΔE_g)随温度升高而减小。根据第一性原理带隙判据,可预测随温度升高其撞击感度变大,符合实验事实。

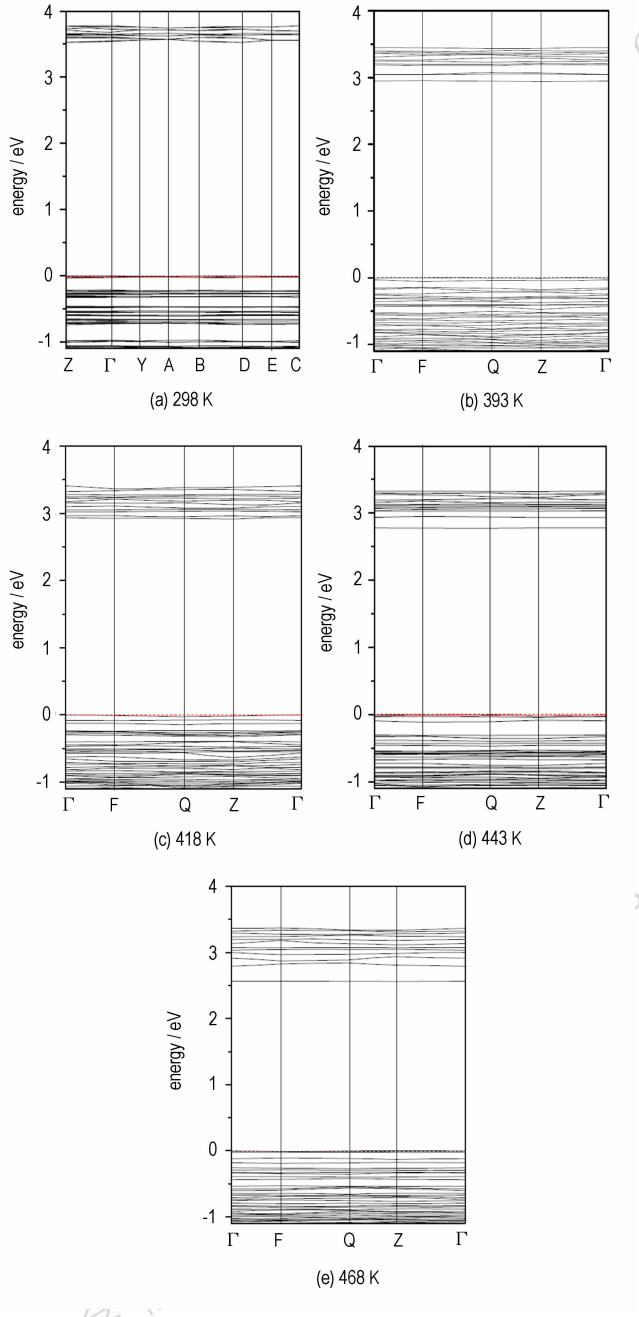


图 10 不同温度下 ε-CL-20 晶体的能带结构

Fig. 10 Band structures of crystalline ε-CL-20 at different temperatures

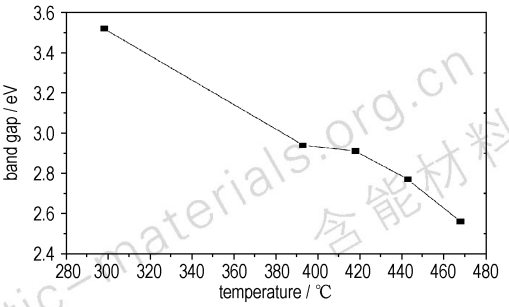


图 11 不同温度下 ε-CL-20 晶体的带隙

Fig.11 Band gaps of crystalline ε-CL-20 as a function of temperature

不同温度下 ε-CL-20 晶体的态密度(DOS)如图 12 所示。由图 12 可发现如下共有特点:首先,在价带顶部,费米能级附近均有一个尖峰,这与它们能带结构价带顶部平坦是一致的。其次,除了一些细微的差异,它们总的态密度大体上相似,这与它们能带结构具有相似性是一致的;相对较低的温度对 ε-CL-20 晶体的结构产生了一些微小的变化。再次,随温度升高,在价带顶部的态几乎连成一片,表明体系中电子的离域性增加。最后,在能量范围 −10 ~0 eV 之间,它们的态主要来自 p 态的贡献。

4 高能混合体系的 MD 模拟,感度与结构、能量和力学性能的关系

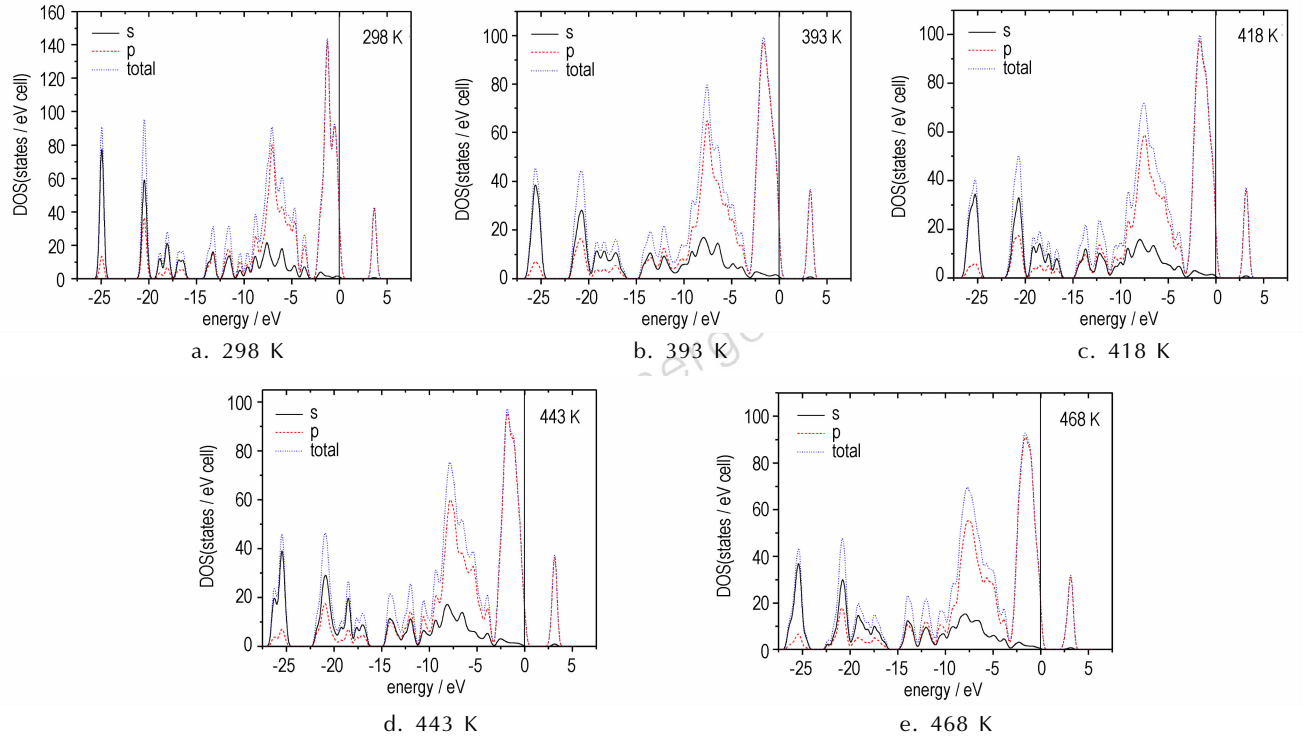
实际使用的含能材料很少是化合物,而多是混合物或复合物。对高能复合材料的广义结构-性能关系研究,显然难用量子化学(QC)、而宜用分子动力学(MD)方法。经典 MD 适用于较大较复杂体系的模拟,利于寻求近似的结构、性能的统计平均递变规律。

如何研究高能复合材料的感度理论判别? 先前从未见任何报导。建议重点关注其中易爆燃组分,关注其它组分对其相互作用所造成的结构、能量和性质的变化,借以关联材料的引发分解、起爆和感度。

4.1 易爆燃组分引发键的最大键长判据

优化高氯酸铵(AP)力场参数,建立修正的 MPCFF 力场,对 HMX/AP 二组分体系在不同配比和不同温度下进行 MD 模拟;因为在引发键键长最大时该键最弱,最易断裂,故首次提出以 HMX 引发键(N—NO_2)最大键长(R_{max})关联热解、起爆和感度性质;发现 7 种配比下的 R_{max} 与热和撞击感度实验值之间存在良好的线性关系;发现 R_{max} 随温度升高而单调递增,与感度随温度升高而增大的实验事实良好相符[96,97]。

细致考察了典型炸药及其为基 PBXs 引发键键长统计分布,均呈近似对称 GAUSS 型[8]。例如图 13 所示的 RDX(001)在 295 K 的键长分布。



a. 298 K　b. 393 K　c. 418 K

d. 443 K　e. 468 K

图 12　不同温度下 ε-CL-20 晶体的态密度

Fig. 12　Electronic DOS of crystalline ε-CL-20 at different temperatures

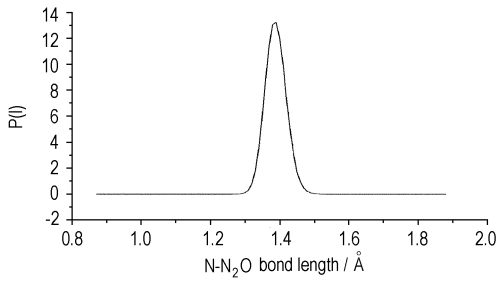


图 13　RDX(001)在 295 K 的键长分布

Fig. 13　Bond length distribution of RDX(001) at 295 K

RDX(001)引发键 N—NO_2 的平均键长 R_{ave}(1.389Å)与最可几键长(1.390Å)几乎相等,且与 RDX 晶体中 N—N 键长实验值(1.413Å)很接近。R_{ave}随温度或其它组分的含量(如粘结剂)变化很不敏感。有趣的是,最大键长(R_{max} =1.570Å)虽在体系中出现几率很小,约为 10^{-8},但 R_{max}随温度升高而显著地单调地递增。在各类 PBX 键长分布中亦大体如此。例如在 RDX(001)/PS(聚苯乙烯)中,引发键 N—NO_2键长分布见表 4。随温度升高 R_{ave}变化很小,但 R_{max}递增明显,所以易爆燃组分引发键的最大键长确可用作 PBX 感度相对大小的理论判据[8]。

由五组分体系推进剂 MD 模拟结果(表 5)可见,随粘结剂与 AP、HMX 配比变化,易爆燃组分(NG, BTTN 和 HMX)的引发键(O—NO_2 和N—NO_2)的平均键长(R_{ave})几无变化,但最大键长(R_{max})变化显著。

表 4　RDX(001)/PS 在不同温度的 N—NO_2 键最大(R_{max})和平均键长(R_{ave})

Table 4　Max bond length (R_{max}) and average bond length (R_{ave}) of RDX(001)/PS at different temperatures

T/K	195	245	295	345	395
R_{max}/Å	1.542	1.561	1.592	1.614	1.624
R_{ave}/Å	1.388	1.389	1.390	1.391	1.391

表 5　不同质量比(PEG/NG/BTTN)/AP/HMX 五组分体系的平均和最大键长

Table 5　Max bond length (R_{max}) and average bond length (R_{ave}) of (PEG/NG/BTTN)/AP/HMX with different mass ratios　(Å)

mass ration	R_{ave} (NG)	R_{max} (NG)	R_{ave} (BTTN)	R_{max} (BTTN)	R_{ave} (HMX)	R_{max} (HMX)
2.5:4.1:1.4	1.036	1.419	1.307	1.430	1.373	1.507
2.5:3.9:1.9	1.036	1.426	1.307	1.434	1.374	1.508
2.5:3.5:2.3	1.036	1.450	1.307	1.461	1.371	1.540
2.5:2.9:2.9	1.036	1.429	1.306	1.441	1.373	1.516
2.5:2.3:3.5	1.036	1.421	1.305	1.434	1.371	1.509
2.5:1.9:3.9	1.035	1.421	1.307	1.434	1.371	1.507
2.5:1.4:4.4	1.037	1.430	1.307	1.430	1.371	1.520

根据易爆燃组分引发键最大键长判据,应可预示质量比(PEG/NG/BTTN):AP:HMX=2.5:3.5:2.3时,其热和撞击感度将最大[8]。

4.2 键连引发键的双原子作用能判据、内聚能密度[98]

早先我们基于苯硝基衍生物孤立分子的QC-CNDO/2计算,曾以键连引发键C—NO_2键的C与N之间的双原子作用能E_{C-N}与实验撞击感度进行相关;E_{C-N}越大,表明C—N键越强,越难以断裂引发分解,故相应的化合物感度便愈小[24]。而今在COMPASS力场框架下,对HMX及其为基、F_{2311}为粘结剂的PBX进行不同温度和不同浓度的MD模拟,由MD模拟提供键连引发键N—NO_2的双原子作用能E_{N-N}的统计平均值见表6和表7。HMX及其为基PBX的键连引发键N—NO_2的N与N之间的双原子作用能E_{N-N},随温度升高而减小,随粘结剂F_{2311}的浓度增大而变大,很好地阐明了感度随温度升高而增大、随粘结剂浓度增大而减小的实验事实。为此,建议基于MD模拟所得键连引发键的双原子作用能的统计平均值,可作为高能炸药及其为基复合材料的感度理论判据。

内聚能密度(CED)是由单位体积凝聚相变为其气态时所需能量。由表6可见,HMX(100)和HMX(100)/F_{2311}的CED随温度升高而单调递减,表明CED越小,感度越大,在此情况下CED亦可较好关联感度的相对大小,符合高能物质由晶相变为气相易、则便利于分解起爆的一般实验事实。然而,由表7可见,随粘结剂浓度增大,PBX的CED却依次减小,与感度随粘结剂增多而减小的实验事实不符。足见仅考虑聚结态变化所需能量的理论指标,在关联感度时有较大局限性。只有包括了引发键断裂所需能量的双原子作用能,才具有较大普适性。

4.3 力学性能与感度关系,感度影响因素的综合分析[8]

力学性能是含能材料最重要的性能之一,依赖于体系的组成、结构和相互作用,影响体系的安全性。先前只有单体炸药的MD模拟报导[99-101]。从2004年起,我们以"切割分面"、"吸附包覆"和"渗透添加"等模型,率先对PBX进行MD模拟,通过力学分析,求得TATB和HMX等常用炸药为基的PBXs的弹性力学性能[102-104],此后又扩展到CL-20、双环HMX等HEDC为基PBXs和推进剂、发射药等多组分体系的MD研究,还关联了稳定性、相容性、爆炸性和热膨胀等多种性能以及用于HEDM的理论设计[105-132]。

MD研究表明,少量高聚物粘结剂的加入,使PBXs的工程模量(即拉伸、体积和剪切模量)与基炸药的工程模量相比,均有显著下降,亦即使体系的刚性下降,强度变弱,使体系变得钝感亦即更安全了。表8给出不同粘结剂浓度下PBXs的工程模量,由表8可见,各模量值均随浓度增大而呈单调下降趋势,与随粘结剂浓度增大PBXs的感度减小的实验事实相一致。由此可见,以PBXs工程模量大小判别其感度的相对高低是合理可行的。

表6 不同温度下HMX(100)和HMX(100)/F_{2311}的双原子作用能E_{N-N}和内聚能密度(CED)

Table 6 Energy E_{N-N} and Cohesive energy density CED of HMX(100) and HMX(100)/F_{2311} at different temperatures

T/K	E_{N-N}/kJ·mol^{-1}		CED/kJ·mol^{-1}	
	HMX(100)	HMX(100)/F_{2311}	HMX(100)	HMX(100)/F_{2311}
245	156.0	150.4	0.8987	0.73986
295	154.8	149.8	0.8778	0.72732
345	154.1	149.2	0.85272	0.71478
395	153.2	148.4	0.82764	0.70224
445	152.6	147.1	0.80256	0.68552

表7 不同F_{2311}浓度下HMX/F_{2311}中N与N之间的双原子作用能E_{N-N}和内聚能密度(CED)

Table 7 Energy E_{N-N} and Cohesive energy density CED of HMX/F_{2311} for different concentrations

consistence/%	E_{N-N}/kJ·mol^{-1}	CED/kJ·mol^{-1}
4.2	149.8	0.727
8.1	150.6	0.723
11.7	150.9	0.736
15.0	151.6	0.719
18.0	152.9	0.702

表8 不同浓度HMX/F_{2311}的工程模量

Table 8 Mechanical properties of HMX/F_{2311} with different consistence of F_{2311}

consistence /%	tensile modulus /GPa	bulk modulus /GPa	shear modulus /GPa
0.0	12.6	10.4	4.8
4.2	7.4	6.9	2.8
8.1	7.3	6.5	2.5
11.7	7.6	6.4	2.4
15.0	7.3	6.4	2.4
18.0	6.8	6.2	2.2

然而,从不同温度下PBXs的MD模拟求得的力学性能(表9)可见,随温度升高,它们的工程模量单调递减,表明PBXs刚性减弱,即变"软"了,有利于感度下降。但若以模量大小为判据,则导致随温度升高PBXs感度下降的结论,与实验事实却不符!

表 9 不同温度下 RDX/PS 的工程模量

Table 9 Mechanical properties of RDX/PS at different temperatures

T/K	tensile modulus /GPa	bulk modulus /GPa	shear modulus /GPa
195	6.0	6.1	2.2
245	5.0	5.2	1.9
295	3.0	4.1	1.1
345	2.9	4.3	1.1
395	1.5	3.3	0.5

这是因为影响感度的因素较多较复杂,必须加以综合分析和考量。随温度升高,PBXs 中基炸药(易爆燃组分)引发键的最大键长 R_{max} 增大,有助于断开引发键(A—B)的双原子作用能 $E_{A—B}$ 减小,即表明随温度升高,分子被"活化"了,易于引发分解起爆,使感度变大;而且此时结构、能量的变化变成影响感度的主导因素,超过了模量减小使体系变软、变得钝感的影响因素,亦即力学性能此时已成为次要因素。

在另一些情况下,如在相同温度下,高聚物与基炸药的相互作用,虽使 PBX 中引发键的最大键长增大,使之超过了基炸药中引发键最大键长。但是,由于 PBX 的工程模量小于基炸药的相应值,使体系变"软"、变"钝",加之高聚物热容较大,吸热作用明显;其包覆基炸药造成的隔热作用也较大。这些效应综合起来成为主导因素,超过了结构(R_{max} 增大的)效应,决定了 PBX 较基炸药钝感,亦此时结构因素便成为影响感度的次要因素,而力学性能等变成了判别稳定性和感度的主导因素。总之,判别体系的感度大小和安全性,必须综合分析诸多影响因素,还要分清主次,抓住个别情况下的主导和决定性因素,才能得出正确的结论。

5 结 论

近 30 年来,从分子、晶体到复合材料的多层次结构-感度关系的微观理论研究,得到如下结论:

(1) 我国对含能材料撞击感度的微观理论判据研究,起步早,原创性强;形象直观,物理意义清晰;从热力学发展到动力学,适用面很广;确实处于国际先进水平,且在诸多方面起到了引领作用。

(2) 要始终抓住影响感度的关键和本质。如在前人从实验中提炼出来的"热点"理论和"引发键"思想的基础上,融进相关的结构、能量、反应和力学性能等重要参量,便能形成简单而直观的理论判据。

(3) 要以一把钥匙开一把锁,与时俱进,不断选择最先进适用的理论方法,促使感度理论研究更深入系统,结论更可靠,以便经得起历史的检验。

(4) 要以多尺度(微观、介观和宏观)方法相结合,全面地研究解决含能材料多层次结构、性能和设计问题;对于至关重要的安全性课题更应当如此。

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Theoretical Studies on Sensitivity Criterion of Energetic Materials——From molecules, crystals, to composite materials

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Abstract: For nearly three decades, many microcosmic theoretical criterions on impact sensitivity of energetic materials at home and abroad have been suggested by using quantum chemistry calculations and molecular dynamics simulations. In this article, we mainly present some work on thermal decomposition mechanisms and sensitivity criterions of energetic molecules, crystals, and composite materials by our research group. Among them, some studies and criterions on impact sensitivity of energetic crystals and composite materials are reported for the first time.

Key words: quantum chemistry; energetic materials; thermal decomposition mechanism; sensitivity; quantum chemistry; molecular dynamics

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