

Developing a Theoretical Approach for Accurate Determination of the Density and Thermochemical Properties of Energetic Ionic Liquids

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Abstract: Energetic ionic liquids (EILs) are novel explosives and propellants which are useful for a variety of military and industrial applications. The physicochemical properties of EILs play an important role in determining their performance in practical applications. In this study, a combination of *ab initio* and empirical methods has been developed to accurately predict the key properties of EILs: a) temperature-dependent heat of formation (ΔH_f°), entropy (S) and heat capacity (C_p) of cation/anion pairs in the gas phase; b) 298 K density (ρ) and heat of formation (ΔH_f°) of EILs in the condensed phase. *Ab initio* methods were selected based on comprehensive validations of the thermochemical properties of closed shell molecules (glyoxal), open shell radicals (vinylperoxy), triplet carbines (oxoethylidene), and the densities of various simple salts (LiF, NaF, KF, MgF₂, CaF₂, LiCl, NaCl, KCl, MgCl₂, CaCl₂). The CBS-APNO/G3/G4//M06-2X/6-311++G(d,p) level of theory was selected for the calculation of geometries, frequencies, energies, etc., and the

CBS-APNO level of theory was chosen for calculating the *original* volumes of cations and anions. The proposed methods/approach calculated: a) the gas-phase thermochemistry of the cation/anion pairs of simple salts (Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, F⁻ and Cl⁻) and six triazolium-based energetic salts (ESs) or EILs representatives (3-azido-1,2,4-triazolium, 1-methyl-3-azido-1,2,4-triazolium, 1,4-dimethyl-3-azido-1,2,4-triazolium, nitrate and perchlorate), b) the condensed-phase density, lattice energy and heat of formation of ESs/EILs (3-azido-1,2,4-triazolium nitrate, 3-azido-1,2,4-triazolium perchlorate, 1-methyl-3-azido-1,2,4-triazolium nitrate, 1-methyl-3-azido-1,2,4-triazolium perchlorate, 1,4-dimethyl-3-azido-1,2,4-triazolium nitrate and 1,4-dimethyl-3-azido-1,2,4-triazolium perchlorate). In comparison with experimental and theoretical results in literature, excellent agreement was observed for all properties. Overall, discrepancies were less than 10%, a clear indication of the reliability of proposed methods/approach.

Keywords: Energetic ionic liquids (EILs) · Density · Heat of formation · Thermochemistry · Quantum chemistry

1 Introduction

Ionic liquids (ILs), or molten salts, are normally defined as ionic pairs with a melting point below 100 °C. In 1914, Paul Walden reported the very first IL (ethyl-ammonium nitrate) by neutralizing ethylamine with concentrated HNO₃ [1]. Due to their low volatility, high thermal stability, ionic conductivity, structural design-ability, and solubility in a wide range of chemical species, ILs have received significant attention in recent decades. This report summarizes a list of recently published review papers on the topic of ILs, covering the physical, chemical and biological properties of different types of ILs, with applications ranging from the laboratory to the industrial level (Table S1 of Supplementary Material 1). Of these, the energetic ionic liquids (EILs) are those which store large amounts of chemical energy for both military and civilian applications. The design ability of ionic liquids, enabling a choice of cations and anions for specific application, makes them extremely versatile. In the review paper published by Zhang *et al.* [2], he concludes that, a better understanding of hypergolicity and the ignition process will be great service in the design of new EIL-

based propellant systems, particularly in discovering what is responsible for hypergolicity and finding the chemical pathways in the combustion process.

As a new class of energetic materials, the physicochemical properties of EILs play an important role in determining performance in practical applications. Some of the critical properties that could be tailored by the proper selection of molecular structure are polarity, viscosity, heat of formation, density, thermal stability and combustion properties like hypergolicity and ignition delays. Density (ρ) is a primary metric to determine the energy performance of energetic materials, especially as an explosive. Even in a

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Supporting information for this article is available on the WWW under <https://doi.org/10.1002/prep.202000071>

wide range of propellants, density is vital in volume-limited applications. In general, the density of an EIL is closely related to the size, shape and structure of its component cation/anion pair, and the interaction between ionic pairs. Heat of formation (ΔH_f) is another important property closely related to the combustion and detonation performance of an EIL. In addition to controlling the stability of the compound, the magnitude of the heat of the formation is crucial to determining the adiabatic flame temperature. Other important properties include the melting point (T_m), glass transition temperature (T_g), decomposition temperature (T_d), viscosity (η), ignition delay time (IDT) and oxygen balance (OB), etc. However, the accurate determination of density and thermochemical properties of EILs often requires experimental data, both expensive and hazardous. These factors make a strong case for computing thermochemical properties—and thereby predicting sensitivity, hazardous characteristics and performance of energetic formulations—well in advance. Because EILs have built-in designability, understanding these properties could help formulate/synthesize new structures and predict the thermophysical properties that are not reported for molecules that are already prepared or predicted.

Therefore, the scope of this study aims to develop a reliable theoretical approach for predicting the key properties:

- Temperature-dependent heat of formation (ΔH_f), entropy (S) and heat capacity (C_p) of cation/anion pairs in the gas phase
- 298 K density (ρ) and heat of formation (ΔH_f) of EILs in the condensed phase

2 *Ab initio* Method Selection for Gas-Phase Thermochemistry Calculation

In this section, various sets of *ab initio* methods were selected for calculating the gas phase heat of formation (ΔH_f) at 298 K. Table 1 shows nine methods, their corresponding parameters and the equations used for energy calculations. In all the methods, a density functional theory (DFT) M06-2X [3] with the 6-311 + G(d,p) [4,5] basis set was used for geometry optimization, vibrational frequency, zero point energies (ZPEs) and dihedral angle scan (1-D hindered internal rotation was treated for lower frequency modes). A coupled cluster theory CCSD(T)/cc-pVXZ or CCSD(T)/Aug-cc-pVXZ [6] (where X=D, T and Q) [7], with different complete basis set (CBS) extrapolation approaches, were adopted for the calculation of electronic single-point energies (SPEs) in methods one through eight. In method nine, combined compound methods CBS-APNO/G3/G4 [8–10] were used to directly calculate the zero Kelvin energies (ZKEs). All calculated energies (ZKEs = ZPEs + SPEs) were then used to derive the formation enthalpies at 0 K, using the atomization or isodesmic balanced reaction scheme, followed by statistical thermodynamic computation for the temperature-dependent heat of formation (ΔH_f), entropy (S) and heat ca-

Table 1. *Ab initio* methods and corresponding parameters and equations used for energy calculation.

Method	Method 1	Method 2	Method 3	Method 4	Method 5	Method 6	Method 7	Method 8	Method 9
Geometry, frequency and scan					M06-2X/6-311 + G(d,p)				
Scale factor for ZPEs					0.9698				
Scale factor for frequencies					0.983				
SPEs or ZKEs	CCSD(T)/cc-pVTZ CCSD(T)/cc-pVQZ	CCSD(T)/Aug-cc-pVTZ CCSD(T)/Aug-cc-pVQZ	CCSD(T)/cc-pVQZ CCSD(T)/cc-pV5Z	CCSD(T)/Aug-cc-pVQZ CCSD(T)/Aug-cc-pV5Z	CCSD(T)/cc-pVDZ CCSD(T)/cc-pVTZ CCSD(T)/cc-pVQZ	CCSD(T)/Aug-cc-pVDZ CCSD(T)/Aug-cc-pVTZ CCSD(T)/Aug-cc-pVQZ	CCSD(T)/cc-pVTZ CCSD(T)/cc-pVQZ CCSD(T)/cc-pV5Z	CCSD(T)/Aug-cc-pVTZ CCSD(T)/Aug-cc-pVQZ CCSD(T)/Aug-cc-pV5Z	CBS-APNO G3 G4
CBS extrapolation for SPEs or ZKEs	$E_{\text{CCSDM}/X-QZ} + (E_{\text{CCSDM}/X-TZ} - E_{\text{CCSDM}/X-QZ}) * 4^4 / (5^4 - 4^4)$	$E_{\text{CCSDM}/X-QZ} + (E_{\text{CCSDM}/X-TZ} - E_{\text{CCSDM}/X-QZ}) * 5^4 / (6^4 - 5^4)$	$E_{\text{CCSDM}/X-SZ} + (E_{\text{CCSDM}/X-QZ} - E_{\text{CCSDM}/X-SZ}) * 5^7 / (6^4 - 5^4)$	$(E_{\text{CCSDM}/X-TZ} - E_{\text{CCSDM}/X-QZ}) / (1/e^3 - 1/e) - (E_{\text{CCSDM}/X-QZ}) / (1/e^3 - 1/e)$ $-(e^2 - 1) / (1/e^3 - 1/e)$	$(E_{\text{CCSDM}/X-TZ} - E_{\text{CCSDM}/X-QZ}) / (1/e^7 - 1/e) - (E_{\text{CCSDM}/X-QZ}) / (1/e^7 - 1/e)$ $-(e^2 - 1) / (1/e^7 - 1/e)$	$(E_{\text{CCSDM}/X-QZ} - E_{\text{CCSDM}/X-TZ}) / (1/e^8 - 1/e^4) - (E_{\text{CCSDM}/X-TZ}) / (1/e^8 - 1/e^4) - (e^{2*} E_{\text{CCSDM}/X-SZ}) / ((e^2 - 1) / (1/e^8 - 1/e^4)) - (E_{\text{CCSDM}/X-TZ}) / (1/e^{14} - 1/e^4) - (e^2 - 1) / (1/e^{14} - 1/e^4)$	$(E_{\text{CCSDM}/X-QZ} - E_{\text{CCSDM}/X-TZ}) / (1/e^8 - 1/e^4) - (E_{\text{CCSDM}/X-TZ}) / (1/e^8 - 1/e^4) - (e^{2*} E_{\text{CCSDM}/X-SZ}) / ((e^2 - 1) / (1/e^8 - 1/e^4)) - (E_{\text{CCSDM}/X-TZ}) / (1/e^{14} - 1/e^4) - (e^2 - 1) / (1/e^{14} - 1/e^4)$	$(E_{\text{CCSDM}/X-QZ} - E_{\text{CCSDM}/X-TZ}) / (1/e^8 - 1/e^4) - (E_{\text{CCSDM}/X-TZ}) / (1/e^8 - 1/e^4) - (e^{2*} E_{\text{CCSDM}/X-SZ}) / ((e^2 - 1) / (1/e^8 - 1/e^4)) - (E_{\text{CCSDM}/X-TZ}) / (1/e^{14} - 1/e^4) - (e^2 - 1) / (1/e^{14} - 1/e^4)$	$(E_{\text{CBS-APNO}} + E_{\text{G3}} + E_{\text{G4}}) / 3$

Table 2. Target species in three different types.

Name	Formula	Structure	Formula	Structure
Glyoxal	trans-C ₂ H ₂ O ₂		cis-C ₂ H ₂ O ₂	
Vinylperoxy	trans-C ₂ H ₃ O ₂		cis-C ₂ H ₃ O ₂	
Oxoethylidene	trans-C ₂ H ₂ O		cis-C ₂ H ₂ O	

capacity (C_p). All *ab initio* calculations and thermodynamic computations were performed using the Gaussian 09 [11] and THERMO module of MultiWell [12] solvers, respectively. All calculated gas phase thermochemical properties (enthalpy of formation, entropy and heat capacity) are reported as a function of temperature (298–2000 K); these values were fitted to NASA polynomials [13] using the Fitdat utility in ANSYS CHEMKIN-PRO [14].

Three different types of target species were selected for testing/validating the methods above:

- Closed shell molecule: glyoxal
- Open shell radical: vinylperoxy
- Triplet carbene: oxoethylidene

These species represent three different types of electronic structures; their small sizes (four to five heavy atoms) enabled high-level calculations for SPEs, shown in Table 1. Reliable thermodynamic properties can also be obtained from the following well-known databases:

- Thermochemical Data of Organic Compounds (TDOC) by Pedley *et al.* [15]: Experiments
- Active Thermochemical Tables (ATcT): refs. [16–18]
- Goldsmith *et al.* [19]: RQCISD(T)/cc-pVT,QZ//B3LYP/6-311++G(d,p), with bond additivity correction

Table 2 illustrates the structure of three species, with trans- and cis- isomers identified for each. The T1 diagnostic [20] for 60 SPEs calculations were found to be ≤ 0.037 , with only six showing values greater than 0.040 (Table S2 in Supplementary Material 1), indicating the reliability of single-reference methods for describing the wave functions.

Figure 1 shows a comparison of 298 K heat of formation (ΔH_f) for four species/isomers: trans-C₂H₂O₂, cis-C₂H₂O₂, cis-C₂H₃O₂ and trans-C₂H₂O. X-axis stands for nine methods used in this study; y-axis represents the difference between the calculated results and data from the literature with the kcal/mol unit. It can be seen that methods one through eight predicted the heat of formation by 0.7–3.5 kcal/mol, while Method 9 slightly under predicted the value by less

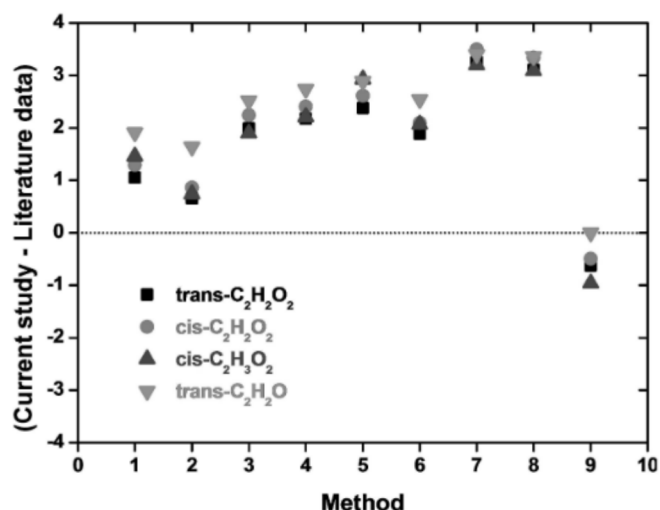


Figure 1. Comparison of 298 K heat of formation (ΔH_f). Unit: kcal/mol.

than 1 kcal/mol, less than a 2% difference. This clearly indicates that Method 9 (CBS-APNO/G3/G4//M06-2X/6-311++G(d,p)) was the most reliable method for accurately predicting gas phase thermochemistry, with a significantly cheaper calculation load. More detailed comparison, including entropy and heat capacity properties, can be found in Table S3 in Supplementary Material 1.

3 *Ab initio* Method Selection for Density Calculation

On the molecular level, the density of an EIL is closely related to the structure of its component cation and anion, which is further related to the size, shape and proximity of the two ions. In the literature, the density of EILs is usually

experimentally measured by X-ray, or calculated using an empirical formula [21]. Today, greater efforts are dedicated to developing computational methods—such as group contribution and quantum mechanical theory—to predict the densities of EILs with maximum accuracy. Of these, a simple volume parameter approach was recently developed for the rapid and accurate estimation of densities of EILs at room temperature [22], in which the density can be calculated by the equation:

$$\rho = MW/(0.6022 \cdot MV)$$

where ρ is the density, and MW and MV are the molecular weight and volume of an EIL, respectively.

Further, for a given EIL: $M_p N_q$, its molecular volume can be estimated as the sum of the volumes of its contained cation and anion [23]:

$$MV = p \cdot V_{M+} + q \cdot V_{N-}$$

where $M+$ and $N-$ denote the cation and anion respectively, and p and q are the corresponding electron charges. V_{M+} and V_{N-} represent the corrected volume of the two ions respectively, which can be further calculated using the following equation:

$$V_{\text{corrected}} = V_{\text{original}} - [0.6763 + 0.9418 \cdot X_{\text{H-atom}}]$$

where $V_{\text{corrected}}$ and V_{original} represent the corrected and the original volume of a species, respectively, and $X_{\text{H-atom}}$ is the number of hydrogen atoms in the species.

The above approach demonstrates that the original volume of the content cation/anion pairs was sufficient to predict the density of their corresponding EILs; the method's reliability has been tested in recent studies [24–27]. However, the key point of this approach is that it predicts the original volume of an ion, which remains unclear regarding the selection of a proper *ab initio* method. To this end, the intent is to systematically evaluate different *ab initio* methods regarding the ability to accurately predict the original volume of an ion.

Table 3 shows the 16 *ab initio* methods selected for evaluation, it includes different levels of theories: a density functional theory (DFT), a composite, Møller-Plesset (MP) correlation, and a coupled cluster theory, with different types of methods for each theory. Different sizes of basis sets were also comprehensively employed: 6-311++G(D,P), cc-pVXZ and aug-cc-pVTZ (where X=D, T, Q and 5). To evaluate these methods, the simplest cations and anions were selected, based on the elements in the first three rows of the periodic table: Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , F^- and Cl^- , which can form ten of the simplest salts: LiF, NaF, KF, MgF_2 , CaF_2 , LiCl, NaCl, KCl, MgCl_2 and CaCl_2 . The simple structures and the well-known densities of these salts made them good candidates for the evaluation.

Table 3. *Ab initio* methods selected for evaluation.

Method type	Method number	Method name
Density functional theory (DFT) methods	1	B3LYP/6-311++G(D,P)
	2	M062X/6-311++G(D,P)
	3	wB97XD/6-311++G(D,P)
	4	B2PLYPD3/6-311++G(D,P)
Composite methods	5	CBS-QB3
	6	CBS-APNO
	7	G3
	8	G4
Møller-Plesset (MP) correlation methods	9	MP2/aug-cc-pVTZ
	10	MP3/aug-cc-pVTZ
	11	MP4(SDQ)/aug-cc-pVTZ
Coupled cluster theory methods	12	CCSD(T)/cc-pVDZ
	13	CCSD(T)/cc-pVTZ
	14	CCSD(T)/cc-pVQZ
	15	CCSD(T)/cc-pV5Z
	16	CCSD(T)/aug-cc-pVTZ

Table 4 shows the densities calculated for ten simple salts using 16 different *ab initio* methods. The salts were selected based on their ionic structures, which are similar to those of EILs. The sizes and charges of ionic components varied across the sample set selected. The “-” designation in the table indicates that the basis sets: cc-pVXZ and aug-cc-pVTZ (where X=D, T, Q and 5) were not available for the calculation of K and Ca elements in Gaussian. Compared against experimental values, the density of most salts is under predicted by *ab initio* calculations by about 2.5%–53%. The relatively lower level DFT methods (method 1, 2, 3 and 4) showed the greatest discrepancies, with an average error of 26%–36%. The composite method CBS-APNO showed the greatest accuracy with an average error of 9.2%, and in terms of calculation load, it was much cheaper than the coupled cluster theory methods, with large basis sets. For these reasons, CBS-APNO was recommended for the prediction of the original volumes of ions. The calculated volume values for all cations and anions are summarized in Table S4 in the Supplementary Material 1.

4 Gas-Phase Thermochemistry and Method Validation for Simple Salts

This section validates the method (CBS-APNO/G3/G4//M06-2X/6-311++G(d,p)) proposed in Section 1, to predict the thermochemistry of representative simple salts selected in the previous section. Data from the literature were chosen from the NIST Chemistry WebBook [28] and Gao *et al.* [29] for comparison.

Tables 5 and 6 compare the 298 K heat of formation (ΔH_f°) and entropy (S) of all ions and salts against the data from NIST and Gao *et al.*, respectively. Excellent agreement was achieved for all cations, anions and salts, with less than a 5% difference for both 298 K heat of formation (ΔH_f°) and

Table 4. Density comparisons of simple salts. Unit: g/cm³.

Method	LiF	NaF	KF	MgF ₂	CaF ₂	LiCl	NaCl	KCl	MgCl ₂	CaCl ₂
1	1.22	1.99	1.63	1.63	1.66	1.23	1.69	1.52	1.47	1.51
2	1.51	2.01	2.23	1.69	1.76	1.36	1.67	1.86	1.47	1.53
3	1.34	1.85	2.29	1.72	1.59	1.29	1.61	1.91	1.50	1.45
4	1.46	1.98	2.17	1.74	2.00	1.43	1.76	1.92	1.60	1.76
5	2.20	2.67	2.37	2.52	2.87	1.28	1.58	1.63	1.42	1.59
6	1.86	2.84	2.98	2.40	2.33	1.58	2.12	2.31	1.84	1.88
7	2.42	2.63	2.73	2.89	3.12	1.23	1.47	1.66	1.38	1.53
8	1.69	2.19	1.96	2.19	2.27	1.34	1.64	1.62	1.55	1.65
9	1.54	1.99	—	1.92	—	1.22	1.50	—	1.40	—
10	1.21	1.81	—	1.51	—	1.39	1.82	—	1.61	—
11	1.45	2.05	—	1.74	—	1.65	2.06	—	1.85	—
12	2.06	2.68	—	2.48	2.65	1.59	1.97	—	1.79	1.93
13	1.75	2.25	—	2.14	1.98	1.53	1.85	—	1.74	1.70
14	1.38	2.17	—	1.84	1.85	1.33	1.80	—	1.58	1.62
15	1.47	2.30	—	1.90	1.87	1.22	1.65	—	1.42	1.46
16	1.49	2.10	—	1.87	—	1.53	1.93	—	1.76	—
Experiment	2.63	2.56	2.48	3.15	3.18	2.06	2.17	1.98	2.32	2.15

Table 5. 298 K heat of formation (ΔH_f) and entropy (S) comparison for cations and anions.

Ions	ΔH_f at 298 K/kcal mol ⁻¹			S at 298 K/cal K ⁻¹ mol ⁻¹		
	Current study	NIST	Gao <i>et al.</i>	Current study	NIST	Gao <i>et al.</i>
Li ⁺	161.73	—	161.30	31.77	31.79	—
Na ⁺	143.17	—	139.82	35.34	35.36	—
K ⁺	119.77	—	119.77	36.92	36.95	—
Mg ²⁺	555.49	—	551.08	35.50	—	—
Ca ²⁺	452.78	—	455.69	36.99	—	—
F ⁻	-60.57	-59.54	-61.74	34.77	34.79	—
Cl ⁻	-53.00	-54.34	-55.04	36.63	36.65	—

Table 6. 298 K heat of formation (ΔH_f) and entropy (S) comparison for salts.

Salts	ΔH_f at 298 K/kcal mol ⁻¹		S at 298 K/cal K ⁻¹ mol ⁻¹	
	Current study	NIST	Current study	NIST
LiF	-81.83	-81.45	47.86	47.85
NaF	-69.04	-69.42	51.96	52.01
KF	-75.99	-78.10	54.10	54.16
MgF ₂	-172.60	-173.70	59.66	61.29
CaF ₂	-186.75	-187.50	63.54	65.43
LiCl	-46.40	-46.79	50.83	50.89
NaCl	-43.74	-43.36	54.86	54.92
KCl	-53.42	-51.31	57.09	57.14
MgCl ₂	-94.90	-93.80	65.33	66.20
CaCl ₂	-113.46	-112.70	70.95	69.37

entropy (S), clearly indicating the reliability of the method proposed in Section 1. Notably, the temperature dependent heat of formation, entropy and heat capacity were systematically calculated in this study, filling the blanks in the literature data and providing a full picture of thermodynamic properties of ions and salts (summarized in Tables S5 and S6 in the Supplementary Material 1).

5 Condensed Phase Heat of Formation and Method Validation for Simple EILs

The heat of formation of EILs in the condensed phase can be determined using the gas phase heat of formation and heat of phase transition (lattice energy: ΔH_L), according to Hess's law of constant summation: Born–Haber energy cycle [29], as shown in Figure 2.

Based on Figure 2, the heat of formation of an EIL can be simplified by the following formula:

$$\Delta H_f^0(\text{EIL}, 298 \text{ K}) = \Delta H_f^0(\text{cation}, 298 \text{ K}) + \Delta H_f^0(\text{anion}, 298 \text{ K}) - \Delta H_L$$

where ΔH_L is the lattice energy of the EIL, for a given EIL: $M_p N_q$. It can be further predicted using the following equations, proposed by Jenkins *et al.* [30,31]:

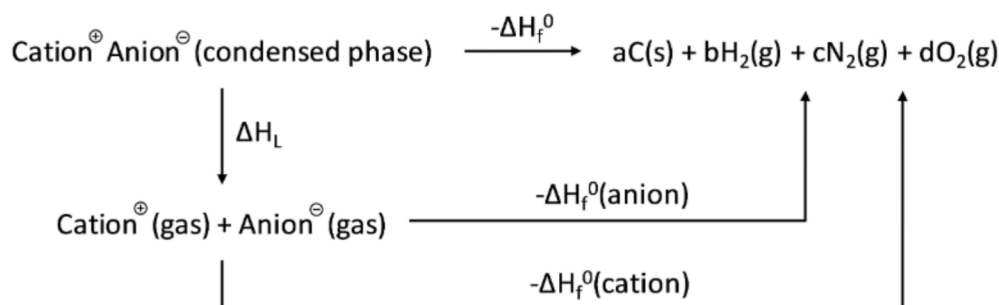


Figure 2. Born–Haber cycle for the formation of EILs.

$$\Delta H_L = U_{\text{POT}} + [p^*(X_M/2 - 2) + q^*(Y_N/2 - 2)]^*RT$$

where X_M and Y_N depend on the nature of both cation M^+ and anion N^- (3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions). R is the gas constant, which equals $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, and T is temperature in Kelvin. The lattice potential energy U_{POT} in the above equation can be estimated using one of the following equations [30,31]:

$$U_{\text{POT}} = 2I^*[\alpha^*(\rho/MW)^{1/3} + \beta]$$

$$U_{\text{POT}} = \gamma^*(\rho/MW)^{1/3} + \delta$$

where ρ and MW are density and molecular weight of the EIL mentioned in Section 2, α and β are appropriate fitted coefficients, chosen according to the stoichiometry of the EIL, and γ and δ can be calculated using the equations below:

$$\gamma = 2 \times 10^{-7} * I^* \alpha^* N_A^{1/3}$$

$$\delta = 2I^* \beta$$

where N_A is Avogadro's constant, and I is the ionic strength, for a given EIL: $M_p N_q$ can be derived by its charge ratio ($p:q$):

$$I = \frac{1}{2} * (pq^2 + qp^2)$$

Table 7 summarizes the typical values for α , β , γ , δ , proposed by Jenkins *et al.* [31]. Based on these values, both lattice potential energy (U_{POT}) and lattice energy (ΔH_L) can be simultaneously calculated, with the unit of kJ mol^{-1} . For the formula of EIL beyond the cases shown in the first column of the table ($U_{\text{POT}} > 5000 \text{ kJ mol}^{-1}$), γ and δ coefficients are given as:

$$\gamma = 10^{-7} * A^* I^* (2I^* N_A)^{1/3}$$

$$\delta = 0$$

Table 7. Typical values for α , β , γ , δ and I used for different EILs.

EILs	Ionic strength	$\alpha/\text{kJ mol}^{-1} \text{ nm}$	$\beta/\text{kJ mol}^{-1}$	$\gamma/\text{kJ mol}^{-1} \text{ nm}$	$\delta/\text{kJ mol}^{-1}$
MN (1:1)	1	117.3	51.9	1981.2	103.8
M ₂ N (1:2)	3	165.3	-29.8	8375.6	-178.8
MN ₂ (2:1)	3	133.5	60.9	6764.3	365.4
MN (2:2)	4	101.6	91.5	6864.0	732.0

where A represents the general electrostatic conversion factor, with the value of $121.4 \text{ kJ mol}^{-1}$, and ionic strength I can be given as:

$$I = \frac{1}{2} * \sum (n_i * z_i^2)$$

where n_i is the number of ions of type i in the formula unit with charge z_i .

To validate the complete approach and method developed thus far, six typical triazolium-based energetic salts (ESs) were selected as representatives:

- 3-Azido-1,2,4-triazolium Nitrate (Tri-1)
- 3-Azido-1,2,4-triazolium Perchlorate (Tri-2)
- 1-Methyl-3-azido-1,2,4-triazolium Nitrate (Tri-3)
- 1-Methyl-3-azido-1,2,4-triazolium Perchlorate (Tri-4)
- 1,4-Dimethyl-3-azido-1,2,4-triazolium Nitrate (Tri-5)
- 1,4-Dimethyl-3-azido-1,2,4-triazolium Perchlorate (Tri-6)

As shown in Table 8, the six ESs were formulated by the cross-combination of three cations (3-azido-1,2,4-triazolium, 1-methyl-3-azido-1,2,4-triazolium and 1,4-dimethyl-3-azido-1,2,4-triazolium) and two anions (nitrate and perchlorate), the corresponding melting points of each ESs indicate that Tri-3, Tri-4, Tri-5 and Tri-6 belong to the EILs, while Tri-1 and Tri-2 have slightly higher melting point than 100°C .

Table 9 shows calculated gas phase heat of formation (ΔH_f°) at 298 K for three cations and two anions, results were compared with the data obtained from ATcT [16–18], Gao *et al.* [29] and Gutowski *et al.* [32]. The differences were less than 0.5%, clearly proving the reliability of the *ab initio* method proposed in Section 1.

Table 8. Structures of two sets of cations and anions.

Name	Abbreviation	Cation	Anion	Melting point/°C
3-Azido-1,2,4-triazolium Nitrate	Tri-1			147
3-Azido-1,2,4-triazolium Perchlorate	Tri-2			123
1-Methyl-3-azido-1,2,4-triazolium Nitrate	Tri-3			66
1-Methyl-3-azido-1,2,4-triazolium Perchlorate	Tri-4			55
1,4-Dimethyl-3-azido-1,2,4-triazolium Nitrate	Tri-5			98
1,4-Dimethyl-3-azido-1,2,4-triazolium Perchlorate	Tri-6			68

Table 10 shows the calculated 298 K density, lattice energy and heat of formation for the two ESs and four EILs in the condensed phase, compared with results from available literature from Xue *et al.* [33] and Gao *et al.* [29]. It is notable that the density values from Xue *et al.* were ex-

perimental data, measured in a gas pycnometer at 25 °C, based upon which Gao *et al.* derived both lattice energy and heat of formation theoretically. However, this study uses a fully computational approach (experimental data unnecessary) to conduct density, lattice energy and heat of

Table 9. 298 K heat of formation (ΔH_f) and entropy (S) comparison for cations and anions.

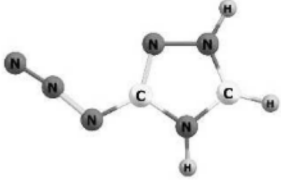
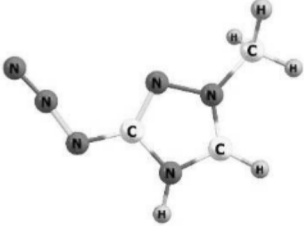
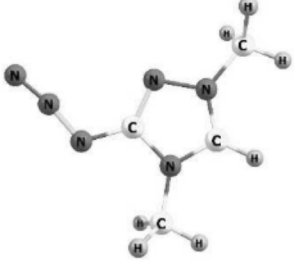
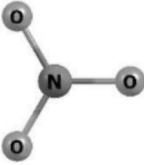
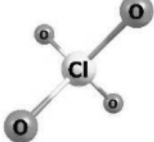
Name	Structure	ΔH_f at 298 K/kcal mol ⁻¹			
		Current study	ATcT	Gao et al.	Gutowski et al.
3-Azido-1,2,4-triazolium		277.1	–	280.1	282.8
1-Methyl-3-azido-1,2,4-triazolium		267.0	–	269.0	273.1
1,4-Dimethyl-3-azido-1,2,4-triazolium		260.0	–	260.4	265.8
Nitrate		–73.5	–73.3	–73.6	72.4
Perchlorate		–65.3	–65.0	–66.4	66.0

Table 10. 298 K density, lattice energy and heat of formation comparison for EILs in condensed phase.

ESs/ EILs	$\rho/\text{g cm}^{-3}$		$\Delta H_f/\text{kcal mol}^{-1}$		$\Delta H_f/\text{kcal mol}^{-1}$	
	Current study	Xue <i>et al.</i>	Current study	Gao <i>et al.</i>	Current study	Gao <i>et al.</i>
Tri-1	1.73	1.76	128.0	128.6	75.6	78.0
Tri-2	1.89	–	124.4	–	87.3	–
Tri-3	1.61	1.63	123.0	120.1	70.5	72.0
Tri-4	1.76	1.66	120.1	114.4	81.6	84.4
Tri-5	1.56	1.58	119.8	120.1	66.6	66.7
Tri-6	1.71	1.67	117.2	116.6	77.4	77.5

formation for the ESs/EILs simultaneously. Excellent agreement was found for all three properties, with less than 6%, 4% and 5% differences, respectively, once again validating

the accuracy of the computational approach and theory proposed here.

Notably, the thermodynamic properties (ΔH_f , S and C_p) of above cations and anions, and the physicochemical properties of above EILs have been summarized in Table S7 and S8 respectively in the Supplementary Material 1.

6 Conclusions

This work reported a systematic approach for predicting the key physicochemical properties of EILs, including: a) the temperature dependent gas phase thermochemistry (heat of formation, entropy and heat capacity) of cations and anions; b) 298 K density and heat of formation of EILs in the condensed-phase. The *ab initio* methods used in this ap-

proach were developed on the basis of comprehensive validations; the entire approach can be summarized as follows:

- *Ab initio* calculation at the CBS-APNO/G3/G4//M06-2X/6-311 + G(d,p) level of theory for the geometries, frequencies, energies, etc. of cations and anions
- 298 K ΔH_f calculation using atomization, or isodesmic, chemically balanced reaction schemes for cations and anions (gas phase)
- Temperature dependent ΔH_f , S and C_p calculation using statistical thermodynamics theory for cations and anions (gas phase)
- *Ab initio* calculation at the CBS-APNO level of theory for the original volumes of cations and anions
- ρ calculation using $\rho = MW/V_{corrected}$ and $V_{corrected} = V_{original} - [0.6763 + 0.9418 * X_{H-atom}]$ equations for EILs (condensed phase)
- U_{POT} calculation using the $U_{POT} = 2I^*[\alpha^*(\rho/MW)^{1/3} + \beta]$ or $U_{POT} = \gamma^*(\rho/MW)^{1/3} + \delta$ equations for EILs (condensed phase)
- ΔH_L calculation using the $\Delta H_L = U_{POT} + [p^*(X_M/2-2) + q^*(Y_N/2-2)] * RT$ equation for EILs (condensed phase)
- 298 K ΔH_f calculation using the Born-Haber cycle for EILs (condensed phase)

In comparison with available experimental and theoretical results in the literature, the above approach and *ab initio* methods involved proved to effectively predict the key properties of EILs with high accuracy; the overall discrepancy was proven to be less than 10%. Moreover, the advantage of this approach is its pure theoretical background, requiring no experimental input/data. Finally, considering application and future work, by using the proposed approach, the physicochemical properties' database of common and novel EILs can be created consistently, a significant advantage in understanding the combustion and detonation behaviors of EILs.

Acknowledgements

The authors acknowledge the KAUST Supercomputing Laboratory (KSL) for providing the computing resources and technical supports. This work was supported by the KAUST Office of Sponsored Research with funding to the Clean Combustion Research Center.

References

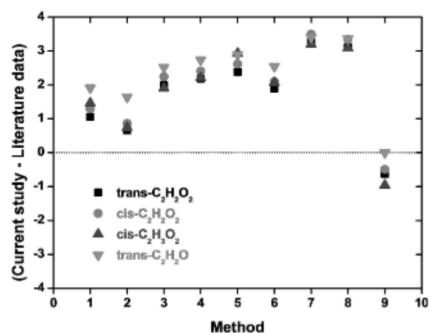
- [1] P. Walden, Ueber die Molekulargröße und Elektrische Leitfähigkeit Einiger Geschmolzenen Salze, *Bull. Acad. Imp. Sci. St. Petersburg, VI Ser.* **1914**, *8*, 405–422, <http://mi.mathnet.ru/eng/izv6491>.
- [2] Q. Zhang, J. M. Shreeve, Energetic Ionic Liquids as Explosives and Propellant Fuels: A New Journey of Ionic Liquid Chemistry, *Chem. Rev.* **2014**, *114*, 10527–10574. DOI: 10.1021/cr500364t.
- [3] Y. Zhao, D. G. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, non-covalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals, *Theor. Chem. Acc.* **2008**, *120*, 215–241. DOI: 10.1007/s00214-007-0310-x.
- [4] A. D. McLean, G. S. Chandler, Contracted Gaussian basis sets for molecular calculations. I. Second row atoms, Z=11–18, *J. Chem. Phys.* **1980**, *72*, 5639–5648. DOI: 10.1063/1.438980.
- [5] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions, *J. Chem. Phys.* **1980**, *72*, 650–654. DOI: 10.1063/1.438955.
- [6] G. D. Purvis, R. J. Bartlett, A full coupled-cluster singles and doubles model: The inclusion of disconnected triples, *J. Chem. Phys.* **1982**, *76*, 1910–1918. DOI: 10.1063/1.443164.
- [7] T. H. Dunning, Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen, *J. Chem. Phys.* **1989**, *90*, 1007–1023. DOI: 10.1063/1.456153.
- [8] J. W. Ochterski, G. A. Petersson, A complete basis set model chemistry. V. Extensions to six or more heavy atoms, *J. Chem. Phys.* **1996**, *104*, 2598–2619. DOI: 10.1063/1.470985.
- [9] L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, J. A. Pople, Gaussian-3 (G3) theory for molecules containing first and second-row atoms, *J. Chem. Phys.* **1998**, *109*, 7764–7776. DOI: 10.1063/1.477422.
- [10] L. A. Curtiss, P. C. Redfern, K. Raghavachari, Gaussian-4 theory, *J. Chem. Phys.* **2007**, *126*, 084108. DOI: 10.1063/1.2436888.
- [11] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *Gaussian 09*, Gaussian, Inc., Wallingford CT, **2016**.
- [12] J. R. Barker, T. L. Nguyen, J. F. Stanton, C. Aieta, M. Ceotto, F. Gabas, T. J. D. Kumar, C. G. L. Li, L. L. Lohr, A. Maranzana, N. F. Ortiz, J. M. Preses, J. M. Simmie, J. A. Sonk, P. J. Stimac, *Multi-Well Software Suite*, University of Michigan, Ann Arbor, Michigan, USA, **2016**; <http://clasp-research.engin.umich.edu/multi-well/>.
- [13] S. Gordon, B. J. McBride, *Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations*; Report No. NASA SP-273; National Aeronautics and Space Administration: Washington, DC, **1976**.
- [14] ANSYS Chemkin-Pro 17.2, ANSYS, Inc.: San Diego, **2016**.
- [15] J. B. Pedley, *Thermochemical Data of Organic Compounds*, Springer Netherlands, **2012**.
- [16] B. Ruscic, R. E. Pinzon, M. L. Morton, G. von Laszewski, S. J. Bittner, S. G. Nijsure, K. A. Amin, M. Minkoff, A. F. Wagner, Introduction to Active Thermochemical Tables: Several "Key" Enthalpies of Formation Revisited, *J. Phys. Chem. A* **2004**, *108*, 9979–9997. DOI: 10.1021/jp047912y.
- [17] B. Ruscic, R. E. Pinzon, G. von Laszewski, D. Kodeboyina, A. Burcat, D. Leahy, D. Montoy, A. F. Wagner, Active Thermochemical Tables: thermochemistry for the 21st century, *J. Phys.: Conference Series* **2005**, *16*, 561.

- [18] B. Ruscic, D. Feller, K. A. Peterson, Active Thermochemical Tables: dissociation energies of several homonuclear first-row diatomics and related thermochemical values, *Theor. Chem. Acc.* **2013**, *133*, 1415. DOI: 10.1007/s00214-013-1415-z.
- [19] C. F. Goldsmith, G. R. Magoon, W. H. Green, Database of Small Molecule Thermochemistry for Combustion, *J. Phys. Chem. A*, **2012**, *116*, 9033–9057. DOI: 10.1021/jp303819e.
- [20] T. J. Lee, P. R. Taylor, A diagnostic for determining the quality of single-reference electron correlation methods, *Int. J. Quantum Chem.* **1989**, *36*, 199–207. DOI: 10.1002/qua.560360824.
- [21] S. Tamari, A. Aguilar-Chávez, Optimum design of the variable-volume gas pycnometer for determining the volume of solid particles, *Meas. Sci. Technol.* **2004**, *15*, 1146–1152. DOI: 10.1088/0957-0233/15/6/015.
- [22] C. Ye, J. M. Shreeve, Rapid and Accurate Estimation of Densities of Room-Temperature Ionic Liquids and Salts, *J. Phys. Chem. A* **2007**, *111*, 1456–1461. DOI: 10.1021/jp066202k.
- [23] B. M. Rice, J. J. Hare, E. F. C. Byrd, Accurate Predictions of Crystal Densities Using Quantum Mechanical Molecular Volumes, *J. Phys. Chem. A* **2007**, *111*, 10874–10879. DOI: 10.1021/jp073117j.
- [24] A. F. Jalbout, Z. Y. Zhou, X. Li, M. Solimannejad, Y. Ma, Molecular connectivity relationships to electrostatic potential derived parameters, *J. Mol. Struct.: THEOCHEM* **2003**, *664-665*, 15–19. DOI: [https://doi.org/10.1016/S0166-1280\(03\)00476-7](https://doi.org/10.1016/S0166-1280(03)00476-7).
- [25] L. Qiu, H. Xiao, X. Gong, X. Ju, W. Zhu, Crystal density predictions for nitramines based on quantum chemistry, *J. Hazard. Mater.* **2007**, *141*, 280–288. DOI: <https://doi.org/10.1016/j.jhazmat.2006.06.135>.
- [26] J.-F. Pan, Y.-W. Lee, Crystal density prediction for cyclic and cage compounds, *Phys. Chem. Chem. Phys.* **2004**, *6*, 471–473. DOI: 10.1039/B315038K.
- [27] N. Bouhaida, N. E. Ghermani, Elusive contribution of the experimental surface molecular electrostatic potential and promolecule approximation in the empirical estimate of the crystal density, *J. Chem. Phys.* **2005**, *122*, 114101. DOI: 10.1063/1.1862238.
- [28] P. J. Linstrom, W. G. Mallard, The NIST Chemistry WebBook: A Chemical Data Resource on the Internet, *J. Chem. Eng. Data* **2001**, *46*, 1059–1063. DOI: 10.1021/je000236i.
- [29] H. Gao, C. Ye, C. M. Piekarski, J. M. Shreeve, Computational Characterization of Energetic Salts, *J. Phys. Chem. C* **2007**, *111*, 10718–10731. DOI: 10.1021/jp070702b.
- [30] H. D. B. Jenkins, H. K. Roobottom, J. Passmore, L. Glasser, Relationships among Ionic Lattice Energies, Molecular (Formula Unit) Volumes, and Thermochemical Radii, *Inorg. Chem.* **1999**, *38*, 3609–3620. DOI: 10.1021/ic9812961.
- [31] H. D. B. Jenkins, D. Tudela, L. Glasser, Lattice Potential Energy Estimation for Complex Ionic Salts from Density Measurements, *Inorg. Chem.* **2002**, *41*, 2364–2367. DOI: 10.1021/ic011216k.
- [32] K. E. Gutowski, R. D. Rogers, D. A. Dixon, Accurate Thermochemical Properties for Energetic Materials Applications. II. Heats of Formation of Imidazolium-, 1,2,4-Triazolium-, and Tetrazolium-Based Energetic Salts from Isodesmic and Lattice Energy Calculations, *J. Phys. Chem. B* **2007**, *111*, 4788–4800. DOI: 10.1021/jp066420d.
- [33] H. Xue, Y. Gao, B. Twamley, J. M. Shreeve, New Energetic Salts Based on Nitrogen-Containing Heterocycles, *Chem. Mater.* **2005**, *17*, 191–198. DOI: 10.1021/cm048864x.

Manuscript received: March 27, 2020

Revised manuscript received: August 20, 2020

Version of record online: ■■■, ■■■■



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Developing a Theoretical Approach
for Accurate Determination of the
Density and Thermochemical Prop-
erties of Energetic Ionic Liquids

