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Simple Estimation of Electron Correlation Energies for Alkali Metal Diflouride Molecules

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The transferable properties of pair correlation energies of the F_2 component are investigated in the alkali metal diflouride molecules MF_2 (M = Li, Na, K). The F_{2^-} correlation energy contributions in MF_2 molecules are discussed and compared with the sum of pair correlation energies of the F_2 molecule and F_2^- anion. A simple method is proposed to estimate the correlation energy for ionic crystal compounds. This method can be used for the prediction and estimation of the correlation energy for large ionic molecules requiring much less computation work.

Introduction

The efficient calculation of accurate energy for a substance is very important in modern material science to investigate the structures, properties, and applications of the materials. Although the very accurate full configuration interaction (CI) method can provide the exact solution of the Schrödinger equation for some lowest lying states, it is practical only for very small molecules because of its high computing power demand. The approximate Hartree−Fock self-consistent field (HF method) method provides about 99% of the total energy of the system for the ground state energy of a molecule. However, the neglect of correlations between electrons leads to rather poor description in the chemical sense because the energy of the chemical bonds is comparable to that 1% error of the HF method. Therefore, the efficient calculation of correlation energy plays very important part in both the theoretical study and the application science. With the development of the material science and the wide applications of MF (Li, Na, and K) optical crystal materials, the properties and structures of MF molecules have been studied theoretically and experimentally. A considerable experimental work showed that X_2^- is one of the essential species in point defects in (solid) alkali halides and many other solids.[1] Using the crossed molecular beam technique,[2−5] EPR spectra,[5] and infrared and Raman spectra,[6−8] chemists have confirmed the existence of MF_2 “molecules”. Maessen and Cade[9,10] carried out their theoretical studies on electronic structures of MX_2 and pointed out that MX_2 systems form stable molecules with triangular geometry and can be described as highly ionic MX_2 systems. They also suggested that the electron correlation effects are important for accurate calculations of dissociation energies and electron affinities especially of the halogen molecules X_2, but they did not work on this problem. In recent years, Ju and co-workers[11] published their calculated results on the study of intrapair and interpair correlation energies of $NaCl_2$, LiF_2, and NaF_2. However, what they were emphasizing was to correct “high level correction” (HLC) of G1 and G2 theories.[12,13] They did not further investigate the detailed rules of the transferable properties of pair correlation energies for these ionic crystal compounds and did not work on the pair correlation energies for F_2, F_2^-, and KF_2 molecules. In this paper, we calculate the pair correlation energies for F_2, F_2^-, LiF_2, NaF_2, and KF_2 molecules using MP2/6-311++G(d) basis set and discuss the transferable property of some pair energies in these F_2-containing molecules. On the basis of the transferability of these pair correlation energies in this series compounds, we discuss the correlation energy from the viewpoint of the correlation contribution of F_2 component. The most practical purpose of the present paper is to propose a useful method to estimate the correlation energy for an ionic crystal compound from the sum of the correlation energies of its constituent ions. This simple method can be used to predict and estimate the accurate molecular energies for large crystal materials requiring much less computation work.

Computation Method

The method used is basically the same as that outlined in the previous work on $NaCl_2$ by Ju and Davidson.[11e]

The electron correlation energy is calculated by

$$E_c = \langle \Psi_{HF} | H - E_{HF} | \Psi \rangle \tag{1}$$

where Ψ_{HF} is the Hartree-Fock wave function with energy E_{HF} and Ψ is the exact wave function (in intermediate normalization $\langle \Psi | \Psi_{HF} \rangle = 1$). The exact wave function may be expanded in a series of configurations Ψ_{ij}^{ab} ..., with electrons excited from orbitals *ij*... to orbitals *ab*..., i.e.

$$\Psi = \Psi_{HF} + \Sigma C_i^a \, \Psi_i^a + \Sigma C_{ij}^{ab} \, \Psi_{ij}^{ab} + ... \tag{2}$$

Inserting eq 2 into eq 1 obtains:

$$E_c = \sum \epsilon_i + \sum_{i<j} \epsilon_{ij} \tag{3}$$

where

$$\epsilon_i = \sum_a \langle \Psi_{HF} | H | \Psi_i^a \rangle C_i^a \tag{4}$$

$$\epsilon_{ij} = \sum_{ab} \langle \Psi_{HF} | H | \Psi_{ij}^{ab} \rangle C_{ij}^{ab} \tag{5}$$

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TABLE 1: Negative of Pair Correlation Energy E_{Ij} (mh) for the F_2 Molecule[a]

	$1a_g$	$2a_g$	$3a_g$	$1b_{3u}$	$1b_{2u}$	$1b_{1u}$	$2b_{1u}$	$1b_{2g}$	$1b_{3g}$
	$1s_F$	$2s_F$	$2p_{zF}$	$2p_{xF}$	$2p_{yF}$	$1s_F$	$2s_F$	$2p_{xF}$	$2p_{yF}$
$1a_g$	6.74								
$2a_g$	1.06	8.43							
$3a_g$	0.82	17.08	59.41						
$1b_{3u}$	1.01	10.05	17.44	9.32					
$1b_{2u}$	1.01	10.05	17.44	14.68	9.32				
$1b_{1u}$	14.37	1.05	0.83	1.01	1.01	6.74			
$2b_{1u}$	1.25	10.08	20.64	11.28	11.28	1.27	8.66		
$1b_{2g}$	1.15	11.05	26.04	22.34	16.43	1.16	13.58	13.08	
$1b_{3g}$	1.15	11.05	26.04	16.43	22.34	1.16	13.58	20.46	13.08

[a] In Tables 1−5, the orbitals in second row indicate the corresponding main component of RHF MOs of the above orbitals.

TABLE 2: Negative of Pair Correlation Energy E_{Ij} (mh) for the F_2^- Anion

	$1a_g$	$2a_g$	$3a_g$	$1b_{3u}$	$1b_{2u}$	$1b_{1u}$	$2b_{1u}$	$3b_{1u}$	$1b_{2g}$	$1b_{3g}$
	$1s_F$	$2s_F$	$2p_{zF}$	$2p_{xF}$	$2p_{yF}$	$1s_F$	$2s_F$	$2p_{zF}$	$2p_{xF}$	$2p_{yF}$
$1a_g$	6.76									
$2a_g$	1.08	6.93								
$3a_g$	0.77	12.85	38.77							
$1b_{3u}$	0.97	9.88	20.20	9.46						
$1b_{2u}$	0.97	9.88	20.20	16.05	9.46					
$1b_{1u}$	14.42	1.09	0.77	0.97	0.97	6.76				
$2b_{1u}$	1.17	11.33	15.90	10.69	10.69	1.15	7.45			
$3b_{1u}$	0.59	5.08	9.79	9.94	9.94	0.59	5.79	0.00		
$1b_{2g}$	1.05	10.41	26.55	24.27	17.18	1.05	11.86	11.49	11.03	
$1b_{3g}$	1.05	10.41	26.55	17.18	24.27	1.05	11.86	11.49	19.27	11.03

In all calculations, the 6-311++G(d) split-valence polarization basis set is used. The electron correlation calculations are performed using the MP2−OPT1 method.[14,15] All geometries of the systems we study are optimized by Gaussian94 or Gaussian98 programs[16,17] at the 6-311++G(d) level. The molecular orbitals used are the ROHF canonical orbitals described in ref 14. All calculations of pair electron correlation energies are performed using the MELD suite of electron code developed by Davidson and co-workers.[18] To compare the results of the calculation of F_2-containing systems, all of the calculated results are arranged in the same kind of table for convenient comparison.

Computation Results and Discussion

1. Pair Correlation Energies of F_2, F_2^-, LiF_2, NaF_2, and KF_2. Tables 1−5 give the pair correlation energies of F_2, F_2^-, LiF_2, NaF_2, and KF_2. As it can be seen in Tables 1−5, the intrapair correlation energies of $1s_F^2$ remains the same in all of the above systems (−6.77 mh for LiF_2, NaF_2, and KF_2, −6.76 mh for F_2^-, and −6.74 mh for F_2). The interpair correlation energies of $1s_F^2 \rightarrow 1s_F^2$ are almost a constant (−14.43 mh for NaF_2 and LiF_2, −14.42 mh for F_2^- and KF_2, and −14.37 mh for F_2). The sum of the interpair energies of $1s_F^2 2s_F^2 + 1s_F^2 2p_F^2$ are −14.94, −15.01, 15.06, −14.81, and −15.29 mh in F_2, LiF_2, NaF_2, KF_2, and F_2^-, respectively. These values differ little in all of the above systems. All of these pair correlation energies are transferable in F_2-containing compounds. However, both the intrapair and interpair correlation energies of the valence shell electrons differ a lot in different molecules, and these pair correlation energies are not transferable in this series compounds. Analyzing the intrapair correlation energies of the bonding orbital electrons in LiF_2, NaF_2, and KF_2, we note that the intrapair energies of the bonding orbitals of $5a_1^2$ in LiF_2, $7a_1^2$ in NaF_2, and $9a_1^2$ in KF_2 are −38.09, −38.28, and −37.79mh, respectively. These three values are very close to −38.77 mh of the intrapair correlation energy of bonding orbital electrons in F_2^- anion but differ a lot from −59.41 mh of F_2 molecule. This indicates that the MF_2 molecules are strong ionic crystal compounds. The result agrees well with Maessen and Cade's conclusion that MX_2's are highly ionic $M^+X_2^-$ systems.

From Table 6, it is obvious to see that the total interpair correlation energy predominates in all of the F_2-containing compounds and the total correlation energy increases rapidly and nearly linear with the increase of total electron number of the system.

2. Correlation Contributions of F_2 Component to LiF_2, NaF_2, and KF_2. As a well-known fact, the electron correlation energy of a system is roughly proportional with the electron number of the system. Therefore, it is very difficult to get the exact total correlation energy for a large system because thousands and thousands of basis functions are used to build Hamilton matrix which requires unimaginable calculation work. In fact, the very accurate full-CI method is practical only for very small molecules because of its high computation work demand. Can we calculate the correlation energy for a large molecule from partitioning it into simple calculations? From the above analysis about the transferable property of some pair correlation energies, it is informative to us that the total correlation energy of a system consists of the correlation energy contributions of its constituent atoms. Thus, we can calculate the correlation energy for a large molecule from the sum of the correlation contributions of its constituent atoms. First, we define the correlation energy contribution of the A constituent atom to the total correlation energy of the MA molecule is A-correlation contribution:

$$\begin{aligned} E_{\mathrm{corr}}(\mathrm{A}^{\delta-}) = {} & k_1 \Sigma E_{\mathrm{corr1}}(\text{nonbonding A orbital}) + \\ & k_2 E_{\mathrm{corr2}}(\text{intrapair of bonding orbital}) + \\ & k_3 \Sigma E_{\mathrm{corr3}}(\text{interpair of bonding orbital with A orbital}) + \\ & k'_3 \Sigma E'_{\mathrm{corr3}}(\text{interpair of bonding orbital with M orbital}) + \\ & k_4\, \Sigma E_{\mathrm{corr4}}(\text{interpair of inner A orbital with inner M orbital}) \end{aligned} \tag{6}$$

where $E_{\mathrm{corr}}(\mathrm{A}^{\delta-})$ is the correlation contribution of A component and δ^- is Mulliken charge of A component. In the MA molecule, we consider that all nonbonding molecular orbitals are respectively corresponding to M or A atomic orbitals except for the bonding molecular orbital of MA. Thus, to get the correlation contribution of the A component, the intrapair and interpair correlation energies in different molecular orbitals give different contribution parts to the A-correlation contribution. In eq 6, $\Sigma E_{\mathrm{corr1}}$(nonbonding A orbital) is the total pair energy of nonbonding A orbital electrons; because the two electrons in each nonbonding A orbital completely belong to the A component, all of these pair correlation energies of nonbonding A orbitals give to A-correlation contribution and the coefficients of these correlation energy terms $k_1 = 1.00$. E_{corr2}(intrapair of bonding orbital) is the intrapair energy of bonding orbital electrons; from the distribution of Mulliken charge of the $\mathrm{M}^{\delta+}\mathrm{A}^{\delta-}$ molecule, it can be considered that in this bonding molecular orbital there are $(1 + |\delta^-|)$ electron contents for the A component, whereas there are $(1 - |\delta^-|)$ electron contents for the M component; therefore, the coefficient of this intrapair correlation energy term is $k_2 = (1 + |\delta^-|)/2$. $\Sigma E_{\mathrm{corr3}}$(intrerpair of bonding orbital with A orbital) is the total interpair energy of bonding orbital electrons with A orbital electrons; to get the coefficient of the interpair correlation energy term between the bonding orbital and an A orbital, it is considered that among the four electrons in these two orbitals there are (1 + 1 + 1 +

TABLE 3: Negative of Pair Correlation Energy E_{Ij} (mh) for the LiF_2 Molecule

	$1a_1$	$2a_1$	$3a_1$	$4a_1$	$5a_1$	$1b_1$	$1b_2$	$2b_2$	$3b_2$	$4b_2$	$1a_2$
	$1s_F$	$1s_{Li}$	$2s_F$	$2p_{zF}$	$2p_{yF}$	$2p_{xF}$	$1s_F$	$2s_F$	$2p_{zF}$	$2p_{yF}$	$2p_{xF}$
$1a_1$	6.77										
$2a_1$	0.00	14.89									
$3a_1$	1.07	0.16	6.90								
$4a_1$	0.98	0.39	9.85	9.66							
$5a_1$	0.80	0.00	12.74	21.50	38.09						
$1b_1$	0.97	0.09	9.72	16.30	19.83	9.44					
$1b_2$	14.43	0.00	1.08	0.98	0.80	0.97	6.77				
$2b_2$	1.17	0.05	11.24	10.89	15.85	10.61	1.15	7.50			
$3b_2$	0.86	0.00	10.10	24.89	25.09	16.90	0.86	11.51	13.80		
$4b_2$	0.60	0.05	5.02	10.16	9.33	9.81	0.60	5.77	11.26	0.00	
$1a_2$	1.06	0.02	10.31	17.65	27.26	24.07	1.06	11.83	18.91	11.61	11.12

TABLE 4: Negative of Pair Correlation Energy E_{Ij} (mh) for the NaF_2 Molecule

	$1a_1$	$2a_1$	$3a_1$	$4a_1$	$5a_1$	$6a_1$	$7a_1$	$1b_1$	$2b_1$	$1b_2$	$2b_2$	$3b_2$	$4b_2$	$5b_2$	$1a_2$
	$1s_{Na}$	$1s_F$	$2s_{Na}$	$2p_{zNa}$	$2s_F$	$2p_{zF}$	$2p_{yF}$	$2p_{xNa}$	$2p_{xF}$	$1s_F$	$2p_{yNa}$	$2s_F$	$2p_{zF}$	$2p_{yF}$	$2P_{xF}$
$1a_1$	12.00														
$2a_1$	0.00	6.77													
$3a_1$	1.82	0.00	3.38												
$4a_1$	0.51	0.11	9.69	8.22											
$5a_1$	0.07	0.96	1.49	3.45	5.79										
$6a_1$	0.00	0.97	0.15	1.29	8.86	9.95									
$7a_1$	0.00	0.79	0.00	1.17	11.50	20.32	38.28								
$1b_1$	0.57	0.00	11.28	15.53	2.46	0.28	0.00	10.76							
$2b_1$	0.00	0.97	0.01	1.06	8.76	16.25	20.00	0.01	9.45						
$1b_2$	0.00	14.43	0.00	0.11	0.97	0.97	0.79	0.00	0.97	6.77					
$2b_2$	0.56	0.00	11.04	15.24	2.49	0.39	0.00	17.66	0.11	0.00	10.37				
$3b_2$	0.00	1.15	0.16	1.41	9.90	10.72	15.67	0.26	10.52	1.14	0.40	7.31			
$4b_2$	0.00	1.04	0.06	1.20	9.26	24.82	26.61	0.09	17.14	1.04	0.20	11.61	10.89		
$5b_2$	0.00	0.60	0.01	0.52	4.51	9.91	9.53	0.01	9.86	0.60	0.06	5.70	11.37	0.00	
$1a_2$	0.00	1.05	0.00	1.08	9.26	17.42	26.56	0.00	24.19	1.05	0.09	11.66	19.16	11.46	10.99

TABLE 5: Negative of Pair Correlation Energy E_{Ij} (mh) for the KF_2 Molecule

	$1a_1$	$2a_1$	$3a_1$	$4a_1$	$5a_1$	$6a_1$	$7a_1$	$8a_1$	$9a_1$	$1b_1$	$2b_1$	$3b_1$	$1b_2$	$2b_2$	$3b_2$	$4b_2$	$5b_2$	$6b_2$	$1a_2$
	$1s_K$	$1s_F$	$2s_K$	$2p_{zK}$	$3s_K$	$2s_F$	$3p_{zK}$	$2p_{zF}$	$2p_{yF}$	$2p_{xK}$	$3p_{xK}$	$2p_{xF}$	$1s_F$	$2p_{yK}$	$2s_F$	$3p_{yK}$	$2p_{zF}$	$2p_{yF}$	$2p_{xF}$
$1a_1$	23.54																		
$2a_1$	0.00	6.77																	
$3a_1$	2.97	0.00	2.31																
$4a_1$	2.40	0.00	5.32	3.54															
$5a_1$	0.31	0.00	1.12	1.88	8.18														
$6a_1$	0.00	1.06	0.00	0.01	0.09	6.81													
$7a_1$	0.04	0.00	1.19	1.65	8.82	0.29	19.94												
$8a_1$	0.00	0.96	0.02	0.03	0.27	9.79	1.32	10.41											
$9a_1$	0.00	0.78	0.00	0.00	0.06	12.55	0.87	20.58	37.79										
$1b_1$	2.40	0.00	5.33	6.35	1.89	0.01	1.97	0.04	0.00	3.54									
$2b_1$	0.04	0.00	1.20	1.99	9.08	0.05	27.75	0.65	0.05	1.65	20.55								
$3b_1$	0.00	0.97	0.00	0.00	0.04	9.71	0.37	16.12	19.91	0.00	0.11	9.43							
$1b_2$	0.00	14.42	0.00	0.00	0.00	1.08	0.00	0.96	0.78	0.00	0.00	0.97	6.77						
$2b_2$	2.40	0.00	5.33	6.35	1.88	0.01	1.97	0.04	0.00	6.35	1.99	0.00	0.00	3.54					
$3b_2$	0.00	1.16	0.00	0.00	0.02	11.18	0.23	10.87	15.50	0.00	0.00	10.60	1.15	0.00	7.41				
$4b_2$	0.04	0.00	1.20	1.99	9.01	0.1	27.66	0.77	0.22	1.99	28.14	0.10	0.00	1.64	0.03	20.42			
$5b_2$	0.00	0.82	0.00	0.00	0.00	10.04	0.13	30.38	23.44	0.00	0.00	16.78	0.82	0.00	11.50	0.00	14.12		
$6b_2$	0.00	0.60	0.00	0.00	0.02	5.00	0.23	9.91	9.42	0.00	0.05	9.88	0.60	0.00	5.75	0.09	11.31	0.00	
$1a_2$	0.00	1.05	0.00	0.00	0.00	10.25	0.28	17.52	26.24	0.00	0.00	24.18	1.05	0.00	11.76	0.01	18.77	11.49	11.00

TABLE 6: Intrapair, Interpair, and Total Correlation Energies (mh) for F_2, F_2^-, LiF_2, NaF_2, and KF_2 Systems

	F_2	F_2^-	LiF_2	NaF_2	KF_2
E_{intra}	134.80	107.65	124.93	150.94	216.06
E_{inter}	368.67	430.70	430.23	526.15	619.58
E_{total}	503.46	538.35	555.16	677.10	835.64

$|\delta^-|$) electron contents for the A component, so the coefficient $k_3 = (1 + 1 + 1 + |\delta^-|)/4$. $\Sigma E'_{corr3}$(intrerpair of bonding orbital with M orbitals) is the total interpair energies of bonding orbital electrons with M orbital electrons; according to the distribution of Mulliken charge of $M^{\delta+}A^{\delta-}$, there are $(1 + |\delta^-|)$ electron contents for the A component among the four electrons of the bonding orbital and a M nonbonding orbital, and thus, the coefficients of these terms are $k'_3 = (1 + |\delta^-|)/4$. ΣE_{corr4} (interpair of inner A orbital with inner M orbital) is the total interpair energies of inner A orbital electrons with inner M orbital electrons; for these interpair correlation energies between an inner A orbital and an inner M orbital, the coefficients of these terms are $k_4 = (1 + 1)/4 = 0.50$. In this way, according to eq 6, we can accurately calculate the A-correlation contribution to the total correlation energy of the MA molecule. The basic assumptions of the above equation are as follows: the correlation contribution of one component in a molecule is the sum of the pair correlation energies including those of it's own orbital electrons of this component and these pair correlation energies including it's own orbital electrons can be estimated from the partial charge of this component.

TABLE 7: F_2-Correlation Energy Contributions in LiF_2, NaF_2, and KF_2 Molecules (mh)

MF_2	Mulliken charge	$\sum E_{corr1}$	E_{corr2}	k_2	$\sum E_{corr3}$	k_3	$\sum E'_{corr3}$	k'_3	$\sum E_{corr4}$	k_4	$\sum E_{corr(F2)}$
LiF_2	0.65	368.21	38.09	0.83	133.20	0.91	0.00	0.41	0.76	0.50	521.41
NaF_2	0.83	358.09	37.59	0.91	131.54	0.96	1.26	0.46	19.81	0.50	529.06
KF_2	0.90	373.18	37.79	0.95	139.21	0.975	1.20	0.475	5.41	0.50	538.33

TABLE 8: $E_{corr}(M^+) + E_{corr}(F_2^-)$ and $E_{corr}(MF_2)$ in MF_2 Molecules (mh)

MF_2	$E_{corr}(M^+)$	$E_{corr}(F_2^-)$	$E_{corr}(M^+) + E_{corr}(F_2^-)$	$E_{corr}(MF_2)$	absolute error	relative error
LiF_2	14.83	538.35	553.18	555.16	−1.98	0.36
NaF_2	138.89	538.35	677.24	677.10	0.14	−0.02
KF_2	293.02	538.35	831.37	835.64	−4.27	0.51

TABLE 9: $E_{corr}(M^+) + E_{corr}(A^-)$ and $E_{corr}(MA)$ in KF and K_2F_2 Molecules (mh)[a]

MA	$E_{corr}(M^+)$	$E_{corr}(F^-)$	$E_{corr}(M^+) + E_{corr}(F^-)$	$E_{corr}(MA)$	absolute error	relative error
KF	265.69	251.94	517.63	518.73	−1.11	0.21
K_2F_2	265.69	251.94	1035.26	1038.33	−3.07	0.30

[a] The correlation energies of KF and K_2F_2 are calculated by Gaussian98 (MP2(full)/6-311++G(d)).

According to the above equation, we take $F_2^{\delta-}$ as a complex ion in F_2-containing molecules to calculate the correlation contributions of F_2 component in LiF_2, NaF_2, and KF_2 and list the relative results in Table 7.

From this table, it can be seen that the correlation contribution of the F_2 component increases with the increase of the ionic bond strength from LiF_2 to NaF_2 to KF_2. The F_2-correlation contribution from LiF_2 to NaF_2 to KF_2 is gradually nearer to the total correlation energy of F_2^- anion. Furthermore, the F_2-correlation contribution of KF_2 is approximately equal to the total correlation energy of the F_2^- anion. This is because the stronger the ionic bond the more negative the charge of the F_2 component, so there is more electron content around $F_2^{\delta-}$, which gives more electron correlation energy to it. Therefore, this result shows that in MF_2 compounds the stronger the ionic bond strength of the compound the larger the correlation contribution of F_2 component. With a comparison of these correlation contributions with the correlation energies of F_2(−503.46 mh) and F_2^- (−538.35 mh), it can be further concluded as follows: in MF_2 molecules, the correlation contribution of the F_2 component increases with the increase of the ionic bond strength of the compound, and this contribution value is always less than the correlation energy of F_2^- anion and always larger than that of F_2 molecule. These results indicate that the definition of eq 6 is reasonable and helpful for us to estimate the correlation energy for F_2-containing ionic compounds.

3. $E_{corr}(M^+) + E_{corr}(F_2^-)$ and $E_{corr}(MF_2)$. From the above analysis, it is shown that in highly ionic MF_2 molecules the correlation contributions of the F_2 component in MF_2 are very close to the correlation energy of F_2^-. This result illuminates us that we could estimate the correlation energy of MF_2 from the sum of the pair correlation energies of the F_2^- and M^+ ions. We calculate the sum of the correlation energies of the F_2^- and M^+ ions for LiF_2, NaF_2, and KF_2 and give these results in Table 8.

Table 8 shows the relationship of $E_{corr}(M^+) + E_{corr}(F_2^-)$ and $E_{corr}(MF_2)$. It is interesting to compare the sum of $E_{corr}(M^+) + E_{corr}(F_2^-)$ with the value of $E_{corr}(MF_2)$. As it can be seen in the above table, the differences between the sum of $E_{corr}(M^+) + E_{corr}(F_2^-)$ and $E_{corr}(MF_2)$ in LiF_2, NaF_2, and KF_2 are very small. That is because in ionic molecules most of the second-order interpair contributions between the anion and the cation are very small and some of them are even zero, so the correlation between the two ions in an ionic molecule is too small. This is the reason that MF_2 (M = Li, Na, and K) is the approximation of the ionic systems of $M^+ + F_2^-$. This result gives us an idea that we can estimate the value of $E_{corr}(MF_2)$ from the sum of $E_{corr}(M^+) + E_{corr}(F_2^-)$ for an ionic molecule introducing only a small error. On the basis of these analyses, we propose a very simple method to estimate the correlation energy for ionic compounds that the total correlation energy of an ionic compound is the sum of the pair correlation energies of its constituent ions. This simple method can be indicated in the following equation:

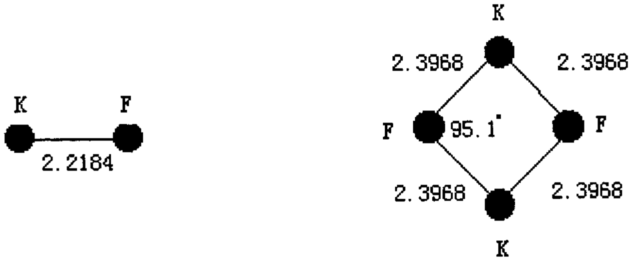

Figure 1. Molecular geometries of KF and K_2F_2.

$$E_{corr}(MA) \approx E_{corr}(M^+) + E_{corr}(A^-) \qquad (7)$$

where MA is a highly ionic compound, $E_{corr}(MA)$ is the correlation energy of MA, and $E_{corr}(M^+)$ and $E_{corr}(A^-)$ are the correlation energies of M^+ and A^- ions, respectively. By using this equation we can estimate the correlation energy for strong ionic systems which can reach chemical accuracy but require much less computation work. It is reasonable to infer that for an analogue or a large complex system containing the same kind of ions we can get the total correlation energy by summarizing those energies of its component parts within a small error.

To test our simple method, we calculated the correlation energies of K^+, F^-, KF, and K_2F_2 at the HF/6-311++G(d)//MP2(full)/6-311++G(d) level shown in Table 9. These calculations were done with Gaussian98.[17] The optimized geometries of KF and K_2F_2 are given in Figure 1. It is shown that K_2F_2 is a diamond configuration and can be considered as an approximation of the $2K^+ + 2F^-$ ionic system. The Mulliken charges of K in KF and K_2F_2 are 0.79 and 0.90, respectively. As can be seen in Table 9, the difference between $E_{corr}(KF)$ and $E_{corr}(K^+) + E_{corr}(F^-)$ for KF is −1.1 mh (−0.69 kcal/mol) and the difference for K_2F_2 is -3.07 mh (-1.93 kcal/mol). If we consider that K_2F_2 is a dimer of KF molecule and estimate the correlation energy of K_2F_2 from the correlation energy of KF, the error is only -0.87 mh (-0.55 kcal/mol). These results can reach the chemical accuracy within 2 kcal/mol but require much less calculation work. From the above analysis, it can be confirmed that this method is very useful to estimate the electron correlation energy for ionic crystal compounds. That is of particular importance to estimate and predict the accurate molecular energies for large ionic material systems.

Conclusions

The principle conclusions obtained from our discussions are as follows:

In F_2-containing molecules, the $1s_F^2$ intrapair energy and $1s_F^2 \rightarrow 1s_F^2$ interpair correlation energies of inner shell electrons of the F atom remain almost the same. The sum of the interpair energies of $1s_F^2 2s_F^2 + 1s_F^2 2p_F^2$ differ little in F_2, F_2^-, LiF_2, NaF_2, and KF_2. All of these pair correlation energies are transferable in F_2-containing compounds. However, the pair correlation energies of the valence shell electrons are large and differ a lot in all of these F_2-containing molecules. These results are helpful to estimate the correlation energy for F_2-containing ionic compounds.

On the basis of the analysis of the intrapair and interpair energies of this series compounds, it is confirmed that MF_2 (M = Li, Na, and K) are approximations of the ionic systems of $M^+ + F_2^-$. In MF_2 molecules, the F_2-correlation energy contributions increase with the increase of the ionic bond strength of the molecules. Furthermore, these contribution values are always less than the correlation energy of the F_2^- anion but larger than that of the F_2 molecule.

On the basis of our calculated results, we propose a very simple method to estimate the correlation energy for strong ionic compounds. In a strong ionic compound, the total electron correlation energy can be estimated from the sum of correlation energies of its constituent ions only introducing an acceptable small error. This method is very useful to predict and estimate the correlation energies for ionic crystal compounds.

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