

Valence Bond Study of Dissociation Behavior and Spectroscopic Constants for the Ground States of LiF and NaF*

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Ab initio VB calculations were used to determine the accurate spectroscopic parameters of the ground states of LiF and NaF. A set of potential energy curves corresponding to the ground states including ionic and covalent interactions, pure ionic interaction and covalent interaction were generated using the VBSCF method. Curve crossing in the dissociation processes of LiF and NaF was discussed. The optimized VB wave functions suggest that LiF and NaF are of high ionicity, and their ionic weights are 86.2% and 94.6%, respectively. NaF has a higher ionicity. The main difference between atom F and ion F⁻ and the effect of the proper description of this difference on dissociation energies were investigated.

Keywords VBSCF, Spectroscopic constant, Curve crossing

Introduction

The alkali halide diatomic molecules provide a typical curve crossing problem^[1]. The outstanding nonadiabatic behavior of the chemical ionization process $M + X \longrightarrow M^+ + X^-$ for alkali halides has been found. The ground states of these molecules are all $(1)^1$ of predominant ionicity. The dissociation limit corresponding to ions $M^+(^1S) + X^-(^1S)$ is always above that of the ground states $M(^2S) + X(^2P)$ because all the ionization potentials (I.P) of metal atoms are greater than any electron affinity (E.A) of a halogen atom. The energy difference between ionic and atomic dissociation limits is determined by $\Delta E = I.P(M) - E.A(X)$. The combination $M(^2S) + X(^2P)$ can give rise to a covalent $(2)^1$ molecular state. At large internuclear distances, the $(1)^1$ potential curve arising from the interaction of the ions will behave as $\Delta E - 1/R$ (relative to the atomic dissociation limit), while the covalent $(2)^1$ potential curve varies very slowly. Hence, all alkali halides show at least one crossing point at $R^* = 1/\Delta E$ if the interaction between the ionic and covalent states is ig-

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nored. However, when the interaction is concerned and the electronic structures are described by optimal mixing of ionic and covalent configurations, the crossing is always avoided, and a sharp change in the potential curve and electronic configuration takes place at about $R_x^{[2]}$.

J. J. Ewing, *et al.*^[3] reported a systematic study of the primary dissociation process of the alkali halide molecules in argon. For fluorides, CsF, RbF and KF dissociate essentially completely to ions, LiF dissociates completely to atoms, and NaF probably dissociates to mixtures of ions and atoms. L. R. Kahn *et al.*^[2] performed *ab initio* calculation on the four lowest $^1 \Sigma^+$ states of LiF. A set of adiabatic and diabatic potential curves were generated. Recently theoretical investigations on the dissociation energies and electronic structures of the ground states of the alkali fluorides have been carried out^[4-6]. However, there have been very few theoretical modes and calculations capable of reproducing reasonable dissociation energies.

Compared with molecular orbital (MO) theory, valence bond (VB) theory is closer to chemical intuition and provides a more pictorial tool for understanding the nature of chemical bonds and related phenomena. Although the so-called N! problem still exists in VB theory, *ab initio* VB calculations have recently become more and more active in the study of structures, reactions and excited states of molecules^[7-10]. The present work aims at generating reasonable dissociation potential curves of LiF and NaF using a very simple wave function of VB to form the corresponding ionic, covalent and the optimal mixing configurations, respectively, and probing nonadiabatic behavior for the dissociation processes of LiF and NaF in the adiabatic approximation.

Methodology

In the VB theory, a spin-free state wave function of a system can be expressed as the linear combination of a set of VB functions $\{\Psi(k)\}$

$$\Psi = \sum_k c_k \Psi(k) \quad (1)$$

For a system with N electrons and spin quantum number S , the VB function can be defined as^[11, 12]

$$\Psi(k) = A_k e^{[\lambda]} \Psi_0(k) = A_k e^{[\lambda]} [\mathcal{Q}(1) \dots \mathcal{Q}_{1(i-1)} \mathcal{Q}(i) \dots \mathcal{Q}_{N-2S} \dots \mathcal{Q}(N)] \quad (2)$$

where A_k is a normalization factor, \mathcal{Q} is a set of one-electron basis functions. The VB function defined by eq. 2 represents a VB structure where two orbitals ($\mathcal{Q}_i, \mathcal{Q}_j$) overlap to form a bond or a lone electron pair ($\mathcal{Q}_i = \mathcal{Q}_j$) and the last $2S$ orbitals are unpaired. $e^{[\lambda]}$ is a standard projection operator defined as

$$e^{[\lambda]} = (f^N N!)^{1/2} \sum_p D_{11}^{[\lambda]}(P) P \quad (3)$$

where $[\lambda] = [2^{N/2-1} 1^{2S}]$ is an irreducible representation of symmetric group S_N , $D_{11}^{[\lambda]}(P)$ is the matrix element of the standard orthogonal representation $[\lambda]$ of permutation P .

The structural weight of a VB structure in the state Ψ_i can be defined as

$$W_i(k) = \frac{C_{ik}C_{il}}{\sum_{l=1} C_{ik}C_{il}} \Psi(k) \Psi(l) \quad (4)$$

Obviously, the weights satisfy the following normalization condition

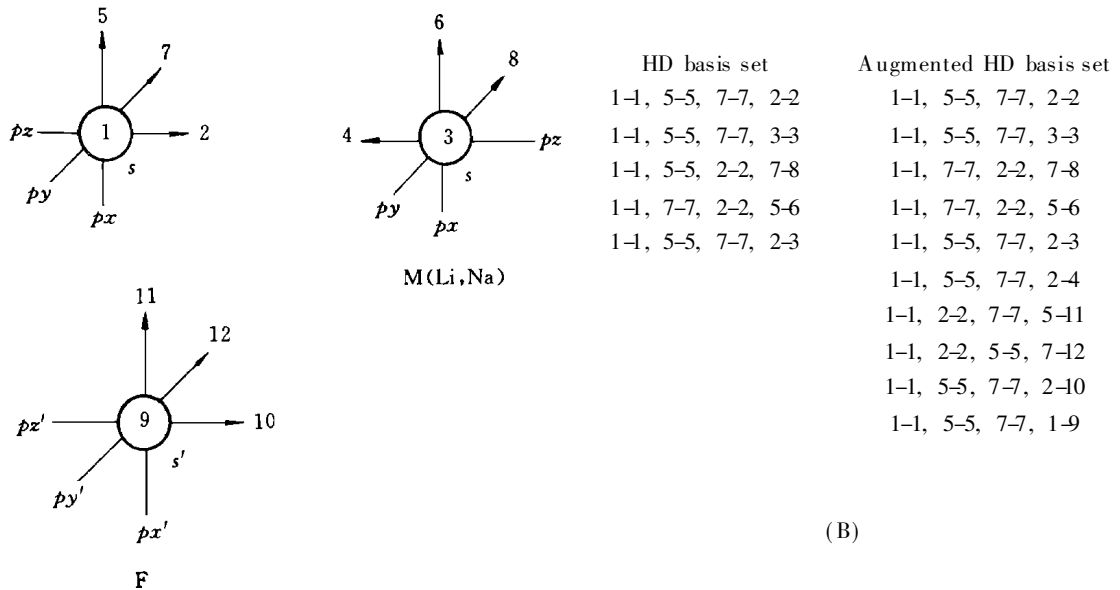
$$\sum_{k=1} W_i(k) = 1 \quad (5)$$

The weight $W_i(k)$ can be interpreted as the contribution of the VB structure $\Psi(k)$ to the state Ψ_i . From a collection $\{W_i(k)\}$ we can obtain a visual bonding picture arising from the atomic orbital overlap corresponding to the state Ψ_i .

In the VB theory, the evaluation of Hamiltonian and overlap matrix elements formed by nonorthogonal orbitals is a central problem. We make use of the permanent algorithm^[13] during the VB calculation. Orbital optimization employed in the present work is simple and traditional and is also based on the Davidson-Fletcher-Powell (DFP) family of variable metric methods^[14].

Computational Details

The one-electron basis functions in this work are atomic hybrid orbitals. In order to ensure an unambiguous definition of a covalent or an ionic bonding, the atomic hybrid orbital here is restricted to expand within the space constructed by the symmetry-adapted primitive functions from one atom. For LiF, two basis sets are employed, one is Dunning/Hay^⑦ (DH) double zeta $(10s, 5p)/(3s, 2p)$ ^[15], the other is based on DH basis set and augmented by one s ($\alpha = 0.076492$) and p ($\alpha = 0.073438$) primitive functions (contracted as $(4s, 3p)$) obtained from the calculation of the 2P state of F. For NaF, the basis set of F is the same as that of F in LiF, and the basis set of Na is based on Huzinaga^⑧ 21 split valence basis set



(A)

Fig. 1 The schematic drawing of bonded orbitals in atom F and M(Li, Na)(A) and

Valence bond structures(B)

(MIDI)^[16] and adding one p primitive function ($\alpha = 0.162797$) (contracted as $4s, 2p$) obtained by minimizing the energy of 2S state of Na.

In the VB and CASSCF calculations, the $1s$ orbitals of F and Li and $1s, 2s$ and $2p$ electrons of Na are frozen to reduce computational effort. The number of VB functions selected (including ionic M^+F^- , M^-F^+ and covalent $M-F$ structures) is 5 for the DH basis set and 10 for the extended DH or MIDI basis set, respectively, during the VB calculation. The serial numbers of the orbitals and valence bond structures constructing VB wave functions are shown in Fig. 1. For LiF, the active space forming CASSCF wave function is composed of four doubly occupied and eight virtual molecular orbitals with lower energy, namely, 8 electrons and 12 active orbitals. The number of active orbitals constructing the CASSCF wave function of NaF is 10 (four doubly occupied and six virtual molecular orbitals, namely, 8 electrons and 10 active orbitals). Gamess 95^[17] is used for CASSCF calculation.

Results and Discussion

1 Properties of the Ground States

Table 1 presents partial spectroscopic parameters for the ground states of LiF and NaF obtained with VB and CASSCF methods. For comparison, the experimental and theoretical spectroscopic parameters from other high level calculations are incorporated in Table 1. Although the agreement between the different theoretical methods and experiments to determine the equilibrium separations and vibrational frequencies is generally good, significant discrepancies for dissociation energies can be found. The VB calculation gives the underestimated dissociation energy of LiF at the level of DH basis set. This is due to the poor description of F^- for the DH basis set. When one $3s$ and $3p$ primitive functions are implemented in the DH basis set for F, a reasonable dissociation energy D_0 of 5.99 eV is predicted by the VB method, this result is superior to other theoretical calculations with large basis sets augmented with several d and f functions. The VB calculation on NaF reproduces an excellent dissociation energy D_0 of 5.33 eV, compared with the experimental value^[19]. These results imply that the VB method with relatively small and proper basis set suggested in the present work can generate the accurate potential energy curves of LiF and NaF and describe correctly the dissociation processes.

Table 1 Spectroscopic parameters of the ground states of LiF and NaF^a

Method	r_e	ω_e	$D_e(D_0)^b$	Contracted basis M/F
LiF				
exp. ^[18]	0.157	910	5.97(5.91)	
present				
VB	0.161	919	3.83(3.77)	$3s2p/3s2p$
VB	0.164	968	6.05(5.99)	$3s2p/4s3p$
CASSCF	0.163	896	5.02(4.97)	$3s2p/3s2p$
CASSCF	0.164	821	5.19(5.14)	$3s2p/4s3p$
MRCI PS ^[5]	0.157	903	5.68(5.62)	$4s5p1d1f/7s5p4d3f$
CI(SD) ^[4]	0.157	919	6.12(6.06)	$6s8p6d2f/6s5p4d2f$

Method	r_e	ω_e	$D_e(D_0)^b$	Contracted basis M / F
NaF				
exp. ^[19]	0.193	536	(5.33)	
present				
VB	0.197	504	5.36(5.33)	4s2p / 4s3p
CASSCF	0.196	500	4.40(4.37)	4s2p / 4s3p
MRCI PS ^[5]	0.194	523	4.66(4.62)	6s4p 2d 1f / 7s5p 4d3f
CI(SD) ^[4]	0.192	538	(4.99)	8s6p 4d 2f / 6s5p 4d2f

a . r_e in nm, ω_e in cm^{-1} and $D_e(D_0)$ in eV; b . D_0 has been computed as $D_e - \omega_e/2$.

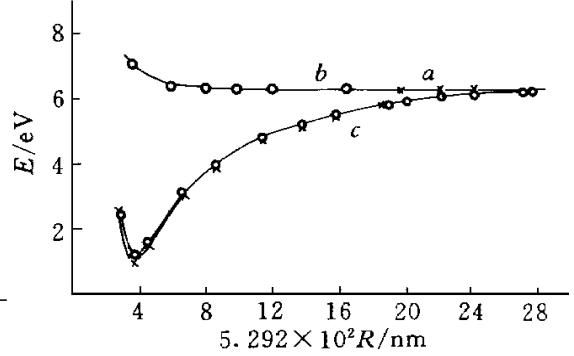
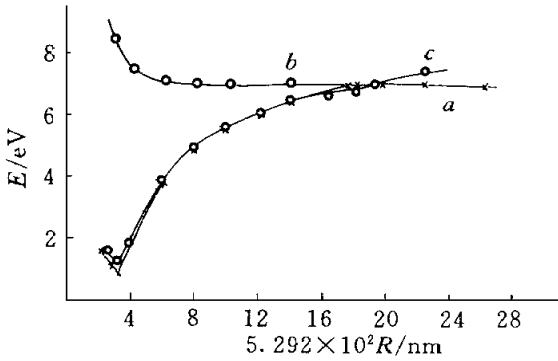


Fig. 2 Potential energy curves of LiF corresponding to different interactions.

The total energy of the ground state at the equilibrium geometry is $-107.049\ 606$ hartree at the level of $3s2p/4s3p$ basis set.

- a. Ground state potential;
- b. $(2)^1 +$ covalent potential;
- c. pure ionic potential.

Fig. 3 Potential energy curves of NaF corresponding to different interactions.

The total energy of the ground state at the equilibrium geometry is $-260.468\ 676$ hartree at the level of $4s2p/4s3p$ basis set.

- a. Ground state potential;
- b. $(2)^1 +$ covalent potential;
- c. pure ionic potential.

From the optimized VB wave functions of the ground states for LiF and NaF we can see that LiF and NaF are predominant ionicity, the ionic weights in LiF and NaF are 86.2% and 94.6%, respectively, and NaF has a higher ionicity than LiF. This is in agreement with the experiment^[20]. The ionic VB structures formed by exciting $(2s, 2p)$ electrons to $(3s, 3p)$ of F^- have a significant contribution to the ground state. This suggests that when an electron is transferred from the metal atom M (Li or Na) to F, an electron relaxation from $(2s, 2p)$ to $(3s, 3p)$ takes place in F^- of $M^+ F^-$, which may be important for the theoretical methods to determine the dissociation energy. The electron relaxation reflects a main difference between atom F and ion F^- .

2 Potential Energy Curves

Figs. 2 and 3 show the potential energy curves corresponding to the ground states $(1)^1 +$ (including ionic and covalent interactions), covalent molecular state $(2)^1 +$ and pure ionic interactions in LiF and NaF. In our calculations the VB and CASSCF methods can give the correct atom dissociation limit $M(^2S) + F(^2P)$, while single Slater determinant Hartree-Fock method leads to ionic dissociation limit $M(^2S) + F(^2S)$. The covalent molecular

states $(2)^1 +$ of LiF and NaF are unstable states. The potential of $(2)^1 +$ varies very slowly at large internuclear distances, approaching that of the separated atoms.

For LiF, a less covalent interaction (13.8%) exists at the equilibrium separation r_e , at large internuclear separations there is only ionic interaction. At the distance of 17.5 bohr (0.926 nm) a sharp change of the electronic structure from ionic $\text{Li}^+ \text{F}^-$ to covalent configuration Li-F takes place. Thus we can expect that nonadiabatic behavior occurs at 17.5 bohr (0.926 nm). This value is close to 14 bohr (0.741 nm) at which the simple Coulomb curve would cross the energy of the separated atoms^[3]. From Fig. 2 we can see that the pure ionic potential cross the covalent potential curve at the distance 19.5 bohr (1.032 nm), and the distance is greater than 14 bohr (0.741 nm) and 17.5 bohr (0.926 nm). This is due to more polarization that is involved when only the ionic wave function is optimized compared with the potential of the ground state.

For NaF, there is only a covalent weight of 5.4% at the equilibrium position, and the covalent contribution to the ground state will gradually vanish as the internuclear distance increases. At the internuclear distance of 19.5 bohr (1.032 nm) the sharp changes of the electronic structure from ionic $\text{Na}^+ \text{F}^-$ to covalent configuration Na-F and energy can be seen in Fig. 3. We expect that at this distance 19.5 bohr (1.032 nm) nonadiabatic behavior occurs in the adiabatic approximation. This separation is also close to 16 bohr (0.847 nm) obtained with the simple Coulomb curve^[3]. However, the pure ionic potential curve varies slowly at large distances, and cross the covalent potential of $(2)^1 +$ at about a larger separation of 27 bohr (1.429 nm). Compared with the case of LiF, the intersection between the ionic and covalent potential curves is postponed for NaF. This phenomenon can be owed to a greater polarization existing in NaF. The behavior of ionic potential energy curve of NaF may be the reason why NaF probably dissociates into the mixtures of ions and atoms^[3].

Conclusions

The theoretical spectroscopic parameters for the ground states of LiF and NaF, and potential energy curves corresponding to different interactions have been calculated using *ab initio* VB and CASSCF methods. The results show that VB method with a compact VB wave function can not only describe correctly entire dissociation processes of LiF and NaF, but reproduce sufficiently accurate spectroscopic parameters, especially, the dissociation energies. The main difference between atom F and ion F^- in MF is the electron relaxation existing in F^- resulted from exciting electrons ($2s, 2p$) to ($3s, 3p$). This is very important for VB method to determine correctly the dissociation energy. The sharp change of VB wave function corresponding to different VB structures can reflect directly the nonadiabatic behavior in the adiabatic approximation. LiF and NaF are high ionicity, the ionic weights are 86.2% and 94.6%, respectively, at the equilibrium separations.

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