Vol 14 No 2, February 2005
1009-1963/2005/14(02)/0317-06
Chinese Physics
© 2005 Chin. Phys. Soc.
and IOP Publishing Ltd

New analytical potential energy function for doubly charged diatomic molecules*

Wang Fan-Hou(王藩侯)[a)†], Yang Chuan-Lu(杨传路)[b)],
Zhu Zheng-He(朱正和)[c)], and Jing Fu-Qian(经福谦)[d)]

[a)] *Institute of Computational Physics, Yibin University, Yibin* 644007, *China*
[b)] *Yantai Normal University, Yantai* 264000, *China*
[c)] *Institute of Atomic and Molecular Physics, Sichuan University, Chengdu* 610003, *China*
[d)] *Southwest Institute of Fluid Physics, Mianyang* 621900, *China*

(Received 8 June 2004; revised manuscript received 1 November 2004)

A new analytical potential function for doubly charged diatomic ions is proposed as

$$V(R) = \left(\sum_{n=0}^{k} a_n R^{n-1}\right)\exp(-a_{k+1}R) + \frac{C}{R},$$

where a_n, a_{k+1} and C are parameters, and R is the nuclear distance. This function can be used to describe the potential curves for doubly charged diatomic ions with both potential minimum and maximum, or without any stationary point. As examples, potential functions of this form for ground states of BH^{2+}, He_2^{2+} and HF^{2+} have been derived. The calculations using the theoretical method QCISD with basis set 6-311++G* have shown that the potential minimum of $BH^{2+}$is at $R_{\min}$=0.147nm, the maximum at $R_{\max}$=0.185nm, and $\Delta E = E_{\max} - E_{\min}$=0.062 eV; for He_2^{2+} $R_{\min}$=0.0736nm, $R_{\max}$=0.105nm, and $\Delta E = E_{\max} - E_{\min}$=0.71 eV. It is found that the potential curve for HF^{2+} is one with a singly repulsive branch. The force constants and spectroscopic data for BH^{2+} and He_2^{2+} have also been worked out.

Keywords: potential energy function, dication, dissociation limit, spectroscopic data
PACC: 1240Q, 9530E, 3310

1. Introduction

Pauling[1] discovered a volcanic potential energy curve for the He_2^{2+} system, which signals the beginning of series of publications on the doubly charged diatomics. The study of potential curves, dissociative channels, vertical double-ionization potentials and transition rates for small dications has received growing attention. Although the experimental and theoretical researches on this class of ions are rather interesting, very few investigations on analytical potential functions necessary for undertaking the molecular reaction dynamics had been reported before Professor Zhu *et al*[2] reported their work. For almost all neutral and singly charged diatomic molecules, the ground state has only one stationary point, namely that at the minimum. The extended Rydberg function[3−6] is the most satisfactory theoretical method for describing accurately the behaviour of these neutral diatomics in the equilibrium region. The Murrell–Sorbie function has subsequently been extended successfully to represent singly charged diatomic ions.[7] However, the extended Rydberg function is not satisfactory for doubly charged diatomic ions because this kind of molecules possess some features that the potential curves may have both potential minimum and maximum or singly repulsive branch.[8−10] In 2001, Borges Jr *et al*[11] reported a potential energy curve for $A^1\Pi$ state of a CO molecule with potential maximum by employing the extended-Hartree–Fock approximate correlation energy model for diatomics with inclusion of the united-atom limit (EHFACE2U).[12]

To rationalize and relate the experimental and theoretical numerical data, Professor Zhu *et al*[2] proposed an analytical potential function for doubly

*Project supported by the Youth Science and Technology Foundation of Sichuan Province, China (Grant No 03ZQ026-061).
†E-mail: Fanhou-wang@sohu.com

charged ions in 1997, which can be expressed as

$$V(R) = \frac{a_1}{\rho - a_2} - \frac{a_3}{(\rho - a_4)^2}, \quad (1)$$

where $\rho = R - R_0$; a_1, a_2, a_3, a_4 are parameters, and R is the nuclear distance.

Later, Huang and Zhu[13] proposed another new analytical potential function, including an ionic Coulomb repulsion term and a Murrell–Sorbie function term, as follows:

$$V(R) = \frac{K}{R} - D_0(1+a_1\rho+a_2\rho^2+a_3\rho^3)\exp(-a_1\rho), \quad (2)$$

where $\rho = R - R_0$, a_1, a_2, a_3, D_0 and R_0 are parameters, and K is the coefficient of Coulomb potential.

Our recent work shows that neither Zhu's function nor Huang's function could describe accurately the potential energy curves of doubly charged diatomic ions over the entire inter-atomic distance space. In the present paper, we propose a new analytical potential function, including an ionic Coulomb repulsion term and a Varandas potential term,[12] which can be used to describe the diatomic ions with both potential minimum and maximum or without any stationary point. Based on ab initio calculations, the potential energy function has been obtained in our proposed form for the ground states for $B\mathrm{H}^{2+}$, He_2^{2+} and HF^{2+}, and the fitting is better than that by using either Zhu's or Huang's function.

2. Analytical potential function

Doubly charged diatomic ions, e.g. AB^{2+} molecule, have more competitive dissociation channels than neutral or singly charged molecules, like $A^{2+}+B$ or $A^+ + B^+$. The dissociation limits of molecule AB^{2+} are determined by the relation between single- and double-adiabatic- ionization potentials (IP^+ and IP^{2+}, respectively). For the ground-state species, if:

(a) IP^{2+} (A or B)>IP^+ (A)+IP^+(B), thus AB^{2+} might show either a metastable or a repulsive character, constantly dissociating into $A^+ + B^+$ or

(b) IP^{2+} (A or B)<IP^+ (A)+IP^+(B), thus AB^{2+} can be stable and its dissociation limit must be $A^{2+} + B$.

The majority of the AB^{2+} ions reported so far belongs to group (a), with several $A^+ + B^+$ channels lying below $A^{2+}+B$, because the former would be the optimum energy process. Therefore, it is reasonably assumed that there will be rather strong Coulomb repulsion between A^+ and B^+, with the exception of chemical bond force and nuclear repulsion. The doubly charged diatomic ions will be unstable without any stationary if the ionic Coulomb repulsion and nuclear repulsion are always dominant, or stable with both a potential minimum due to the balance of nuclear repulsion and chemical bond forces and a potential maximum caused by the balance of chemical bond forces and ionic Coulomb repulsion. For the doubly charged diatomic ions with both potential minimum and maximum, there are two repulsive branches, and an attractive branch.

In order to describe the potential curves for diatomic ions with both potential minimum and maximum or without any stationary point, we propose a new function as follows:

$$V = V_{\mathrm{Var}} + V_{\mathrm{Coul}}, \quad (3)$$

where V_{Var} is the Varandas potential term, a special case of the extended-Hartree-Fock approximate correlation energy model for diatomics suggested by Varandas,[12] and V_{Coul} is the Coulomb potential term. They can be written as

$$V_{\mathrm{Coul}} = \frac{C}{R} \quad (3a)$$

and

$$V_{\mathrm{Var}} = \left(\sum_{n=0}^{k} a_n R^{n-1}\right)\exp(-a_{k+1}R), \quad (3b)$$

where a_n, a_{k+1} and C are parameters to be determined, and R refers to the nuclear distance. In this paper, k=3.

This potential energy function has the correct physical significance. When the bond distance R is large enough, $V \approx V_{\mathrm{Coul}}$ because the Varandas potential term converges much more rapidly than the Coulomb potential term V_{Coul} as R increases. This function also has the correct dissociation limit for $V \to 0$, as R approaches infinity; and V tends to infinity as $R \to 0$.

The quadratic, cubic and quartic force constants $f_n\left(f_n = \dfrac{\mathrm{d}^n V}{\mathrm{d}R^n}, n = 2,3,4\right)$ could be derived from Eqs.(3) at their minima

$$f_2 = \sum_{n=0}^{3} a_n[(n-1)(n-2)R^{n-3} - 2a_4(n-1)R^{n-2} + a_4^2 R^{n-1}] \times \exp(-a_4 R) + \frac{2C}{R^3}, \quad (4)$$

$$f_3 = \sum_{n=0}^{3} a_n[(n-1)(n-2)(n-3)R^{n-4} - 3a_4(n-1)(n-2)R^{n-3} + 3a_4^2(n-1)R^{n-2} - a_4^3R^{n-1}] \times \exp(-a_4R) - \frac{6C}{R^4}, \quad (5)$$

$$f_4 = P_4\exp(-a_4R) + \frac{24C}{R^5}, \quad (6)$$

where

$$P_4 = \sum_{n=0}^{3} a_n[(n-1)(n-2)(n-3)(n-4)R^{n-5} - 4a_4(n-1)(n-2)(n-3)R^{n-4} + 6a_4^2(n-1)(n-2)R^{n-3} - 4a_4^3(n-1)R^{n-2} + a_4^4R^{n-1}].$$

The expressions relating the force constants f_n with the spectroscopic constants ω_e, $\omega_e\chi_e$, B_e, α_e and $R_e = R_{min}$ for diatomic molecules may be found as follows:[14,15]

$$f_2 = 4\pi^2\mu_A\omega_e^2c^2, \quad (7)$$

$$f_3 = -\frac{3f_2}{R_{min}}\left(1 + \frac{\alpha_e\omega_e}{6B_e^2}\right), \quad (8)$$

$$f_4 = \frac{f_2}{R_{min}^2}\left[15\left(1 + \frac{\alpha_e\omega_e}{6B_e^2}\right)^2 - \frac{8\omega_e\chi_e}{B_e}\right], \quad (9)$$

where c is the velocity of light, μ_A is the reduced mass for individual atoms, and B_e is given by

$$B_e = \frac{h}{8\pi^2c\mu_AR_{min}^2} = \frac{h}{8\pi^2cI_e}. \quad (10)$$

Based on the description by Murrell *et al*[4] one can learn about the potential energy surface either by analysing some experimental data (e.g., spectroscopy, molecular-beam scattering and reaction kinetics), or calculate the potential energy by the first principles from Schrödinger equation. The former of these approaches runs into what is generally called the inversion problem, and the latter, based on the first principles, is called the forward procedure. The theoretical derivation is quite accurate for small atomic systems.

3. Application

In the present paper, we take BH^{2+}, He_2^{2+} and HF^{2+} as examples, and calculate their potential curves, i.e. $V(R)$, and then make the least-squares fit to Eqs.(3) to find parameters a_n, a_{k+1} and C. Force constants f_2, f_3 and f_4 can be worked out from Eqs.(3) in terms of the values of a_n, a_{k+1} and C. It is straightforward to calculate ω_e, $\omega_e\chi_e$, α_e and B_e from Eqs.(7)–(10).

For the calculation and description of full potential curves for diatomic molecules or ions, first and foremost we must determine the reasonable dissociation limits.[16,17] So, we derive the dissociation limits of BH^{2+}, He_2^{2+} and HF^{2+} first. For BH^{2+}, the optimum energy dissociation will be $BH^{2+} \rightarrow B^+ + H^+$. If B^+ and H^+ are in their ground states ^1S_g, then the representation ^1S_g of the atomic group is resolved into that of $D_{\infty h}$ (BH^{2+}), i.e. $\sum^+$, its direct product $\sum^+ \otimes \sum^+ = \sum^+$. Therefore, the dissociation limit of BH^{2+} is

$$BH^{2+}(X^1\Sigma^+) \rightarrow B^+(^1S_g) + H^+(^1S_g).$$

Following the same theoretical method, we have

$$He_2^{2+}(X^1\Sigma_g^+) \rightarrow 2He^+(^2S_g)$$

and

$$HF^{2+}(X^3\Sigma^-) \rightarrow H^+(^1S_g) + F^+(^3P_g).$$

In the present work, the theoretical method QCISD[18] with basis set denoted as 6-311+G* has been used to calculate the ground states of BH^{2+}, He_2^{2+} and HF^{2+}. This method takes a quadratic CI (configuration interaction) calculation including single and double substitutions with a triples contribution to the energy added. The potential minimum of BH^{2+} is at R_{min}=0.147nm, the maximum at R_{max}=0.185nm, and $\Delta E = E_{max} - E_{min}$=0.062eV, which are comparable to those reported in Ref.[19] The potential minimum of He_2^{2+} is at R_{min}=0.0736nm, the maximum at R_{max}=0.105nm, and $\Delta E = E_{max} - E_{min}$=0.71eV. Nicolaides and Valtazanos[20] showed that the potential minimum of He_2^{2+} is at R_{min}=0.0705nm, the maximum at R_{max}=0.115nm. Our calculation indicates that the potential energy curve of HF^{2+} is repulsive. All the calculated results are summarized in Table 1.

By iterating a system of normal equations based on the least-squares fit, the parameters a_n, a_{k+1} and C of function (3) have been worked out for He_2^{2+}, BH^{2+} and HF^{2+} (Table 2); from these it is easy to derive f_2, f_3 and f_4, and then calculate spectroscopic data ω_e, $\omega_e\chi_e$, B_e and α_e using equations (7)–(10), see Tables 3 and 4 respectively. The calculated and reproduced potential curves for BH^{2+}, He_2^{2+} and HF^{2+} are shown in Fig.1. The dots in Fig.1 refer to the results of ab initio calculations, and the curves are the fitted results. One can see that our curves agree well with the results of ab initio calculations.

Table 1. The calculated potential minima and maxima for the ground state of He_2^{2+} and BH^{2+} molecules.

Molecules	R_{min}/nm	R_{max}/nm	$\Delta E = E_{max} - E_{min}$/ eV
$BH^{2+}(X^1\Sigma^+) \rightarrow B^+(^1S_g)+H^+(^1S_g)$	0.147	0.185	0.062
	0.148[19]	0.182[17]	0.044[19]
$He_2^{2+}(X^1\Sigma_g^+) \rightarrow 2He^+(^2S_g)$	0.0736	0.105	0.71
	0.0705[20]	0.115[18]	

Table 2. The parameters of the analytic potential function (3).

Molecules	a_0/eV·nm	a_1/eV	a_2/eV·nm^{-1}	a_3/eV·nm^{-2}	a_4/nm^{-1}	C/eV·nm
$BH^{2+}(X^1\Sigma^+)$	10.47	–265.10	4418.53	–50419.73	35.08	1.42
$He_2^{2+}(X^1\Sigma_g^+)$	397.62	–23774.89	500616.21	–3988859.01	78.77	1.44
$HF^{2+}(X^3\Sigma^-)$	9.33	–244.05	1447.58	–3208.98	23.37	1.42

Table 3. The derived force constants for BH^{2+} and He_2^{2+}.

Molecules	f_2/eV·nm^{-2}	$-f_3$/eV·nm^{-3}	f_4/eV·nm^{-4}
$BH^{2+}(X^1\Sigma^+) \rightarrow B^+(^1S_g)+H^+(^1S_g)$	356.02	32711.70	1552885.20
$He_2^{2+}(X^1\Sigma_g^+) \rightarrow 2He^+(^2S_g)$	4361.56	637182.25	60614764.16

Table 4. The derived spectroscopic data for BH^{2+} and He_2^{2+}.

Molecules	ω_e/cm^{-1}	$\omega_e\chi_e$/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}
$BH^{2+}(X^1\Sigma^+)$	1025	221.8	8.465	1.469
$He_2^{2+}(X^1\Sigma_g^+)$	2434.492	228.165	15.546	1.539

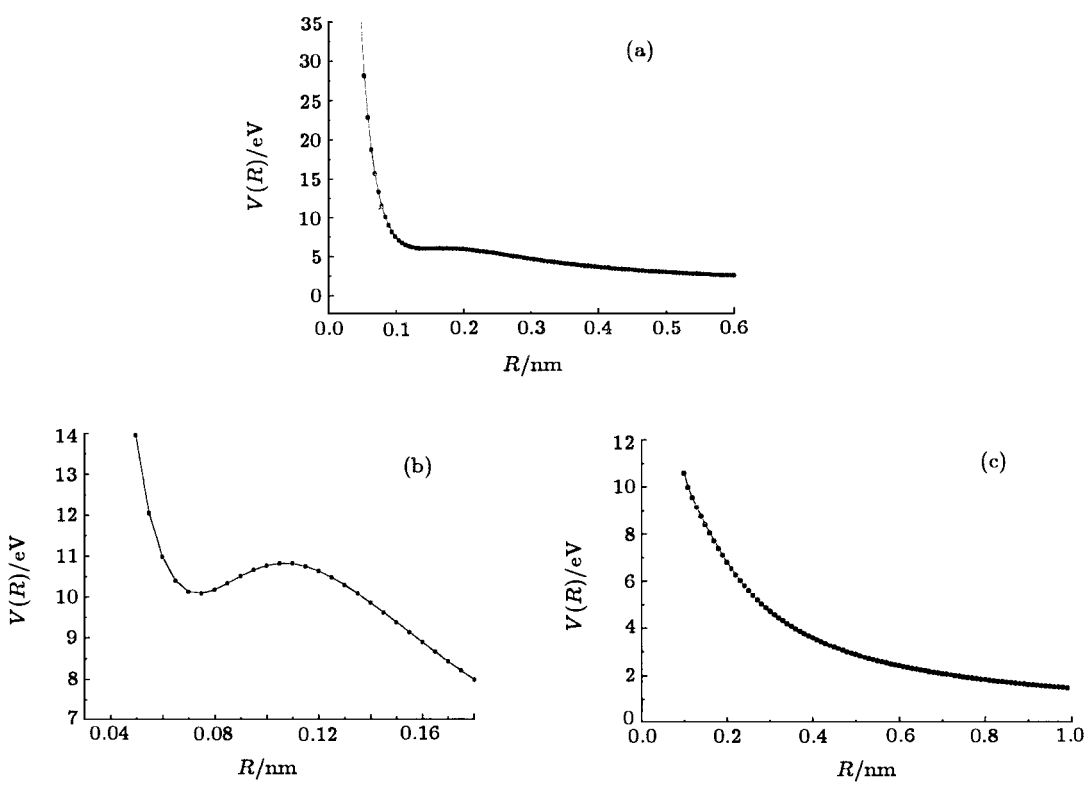


Fig.1. The potentials for (a) $BH^{2+}(X^1\Sigma^+)$, (b) $He_2^{2+}(X^1\Sigma_g^+)$ and (c) $HF^{2+}(X^3\Sigma^-)$.

Figures 2(a) and 2(b) are the fitted potential curves for the ground state of He_2^{2+} by using Zhu's model and Huang's model, respectively. As in Fig.1, the dots in Fig.2 refer to the results of ab initio calculations, and the curves are the fitted results. One can see that the fitted curve either by employing Zhu's function or Huang's function deviates from the calculated points obviously. In particular, the Zhu-model curve could not provide a reliable extension of the data beyond the fitting region. Although the number of fitting parameters in function (3) and the number of those in Huang's model are identical, the fitting by using function (3) is better than that by using Huang's model.

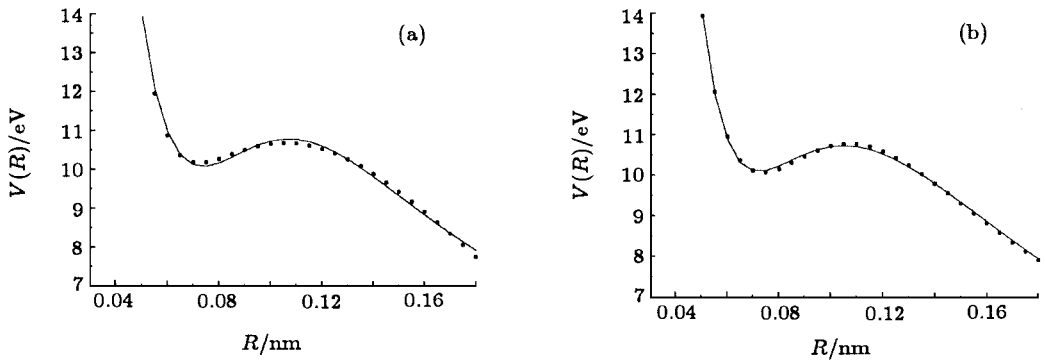


Fig.2. The potential curves for He_2^{2+}: (a) Zhu's model; (b) Huang's model.

4. Discussion

It is well known that there are three different types of potential maximum for diatomic molecules or ions: i.e., the potential maximum results from pre-dissociation, the van der Waals interaction, and the non-crossing of potential curves of two electronic states with the same irreducible representation for a given molecular group. The present work gives an eloquent proof that the fourth type of potential maximum exists as well, which is due to the Coulomb repulsion between an ionic pair with the same charge.[2] The Coulomb repulsive potential is related closely to inter-ionic distance and is proportional to the product of ionic charges.

In consideration of the point charge approximation, the coefficient of Coulomb potential can be written as

$$K = \frac{q_A q_B}{4\pi\varepsilon_0},$$

where q_A and q_B are the charges of ions A^+ and B^+, respectively. ε_0 is the dielectric coefficient in vacuum. A doubly charged diatomic molecule could be dissociated into two singly charged ions, then $q_A = q_B = e = 1.602 \times 10^{-19}$ Coulomb, $K = 1.4399$eV·nm. From Table 2 one can see that C for He_2^{2+}, HF^{2+} and BH^{2+} is very close to this value.

5. Conclusion

The present method for expressing the analytic potential function is not only reasonable to establish either one (for repulsive state) or three (for metastable state) different inter-atomic distances for a given potential energy, but also quite flexible for application. If one has derived a potential curve by ab initio calculations, it is easy to obtain the parameters a_k, a_{k+1} and C by a least-squares fit, and then derive f_2, f_3 and f_4 from function (3) and the spectroscopic constants from Eqs.(7)–(10).

Based on the ab initio calculations, the potential energy functions have been fitted to our proposed form for He_2^{2+}, BH^{2+} and HF^{2+}. The force constants and spectroscopic data for BH^{2+} and He_2^{2+} have also been worked out. The fitted parameters C are approximately equal to those in the point approximation, indicating that the function proposed in this paper is reasonable. We believe that the present analytical potential energy function of these doubly charged diatomic ions will be helpful to our understanding of their structure, spectroscopy and reaction dynamics.

Acknowledgement

We thank Jing Xu and Lan Pu for their help with the computations of some of the data.

References

[1] Pauling L 1933 *J. Chem. Phys.* **1** 56

[2] Zhu Z H, Wang F H, Cheng B, Tan M L and Wang H Y 1997 *Mol. Phys.* **92** 1061

[3] Murrell J N and Sorbie K S 1974 *J. Chem. Soc. Faraday Trans.* **2** (70) 1552

[4] Murrell J N, Carter S, Farantos S C, Huxley P and Varandas A J C1984 *Molecular Potential Energy Functions* (London: Wiley)

[5] Huxley P and Murrell J N 1983 *J. Chem. Soc. Faraday Trans.* **2** (79) 323

[6] Zhu Z H, Shen S Y, Mou W M and Li L 1984 *J. Mol. Sci.* **2** (79) 79

[7] Wang F H, Jiang D L and Zhu Z H 1997 *J. Sichuan Univ.* **34** 198 (in Chinese)

[8] Wang F H, Zhu Z H and Jing F Q 1998 *J. Mol. Struct. (THEOCHEM)* **453** 71

[9] Mao H P, Wang H Y, Tang Y J, Zhu Z H and Zheng S T 2004 *Acta Phys. Sin.* **53** 37 (in Chinese)

[10] Wang F H, Zhu Z H, Yang C L and Jing F Q 1998 *Chin. Phys. Lett.* **15** 715

[11] Borges Jr. I, Caridade P J S B and Varandas A J C 2001 *J. Mol. Spectrosc.* **209** 24

[12] Varandas A J C 1988 *Adv. Chem. Phys.* **74** 255

[13] Huang Z and Zhu Z H 2000 *J. Mol. Struct.* **525** 123

[14] Dunham J L 1932 *Phys. Rev.* **41** 721

[15] Mills I M 1974 *Theoretical Chemistry* **1** 110

[16] Zhu Z H 1996 *Atomic and Molecular Reaction Statics* (Beijing: Science Press) (in Chinese)

[17] Zhu Z H and Yu H G 1997 *Molecular Structure and Molecular Potential Energy Function* (Beijing: Science Press) (in Chinese)

[18] Pople J A, Head-Gordon M and Raghavachri K 1987 *J. Chem. Phys.* **87** 5968

[19] Nicolaides C A, Chrysos M and Valtazanos P 1990 *J. Phys.* B **23** 791

[20] Nicolaides C A and Valtazanos P 1990 *Chem. Phys. Lett.* **174** 489