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To understand matter from a point of view of clusters

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Abstract. We present an optimum valence bond scheme to study important stable geometric structures of clusters, by combining the characteristics of frontier molecular orbitals and the first-principle molecular dynamics simulation. It is interesting to note that even for small size clusters it has already provided clues in some macroscopic properties of the second- and the third-row elements in the period table (e.g. melting and boiling point).

PACS. 36.40.-c Atomic and molecular clusters

1 Introduction

Clusters can be regarded as stable aggregates of several atoms (molecules) up to more than 10^4 atoms (molecules); They should play roles as bridges between isolated atoms (molecules) and bulk materials. There are recent interests to study novel properties and their corresponding geometric structures of such clusters [1]. In order to elucidate the dependence of such cluster's electronic properties and corresponding geometric structures with the cluster size (i.e., the number of atoms), it requires theoretical methods which can efficiently provide quantitative descriptions of such cluster systems. We present an optimum valence bond scheme [2,3] to study important stable geometric structures of clusters, by combining the characteristics of frontier molecular orbitals and the first-principle molecular dynamics simulation. With limited computational efforts, we can obtain the properties of cluster X_m with m as large as possible, and the properties of all clusters X_i ($i < m$), e.g., their stable geometric structures, electronic properties, etc. We here present our results about electronic structures and the corresponding geometric structures of all important clusters (X_n, $n \leq 4$) for the second- and the third-row elements in the period table. It is interesting to note that even for small size clusters it has already provided clues in some macroscopic properties of the second- and the third-row elements in the period table (e.g. melting and boiling point).

2 Theoretical method and calculation result

In the present paper, we present an optimum valence bond scheme to determine the electronic structures and the geometric structures of the important clusters [2,3]. Our calculations of electronic structures of clusters are carried out based on Density Functional Theory (DFT) [4] because of its success to achieve, with less computational efforts, enough accuracy almost comparable with expensive post-SCF methods such as, Møller-Plesset perturbation theories (MP) [5], configuration interaction methods (CI) [6], coupled-cluster methods (CC) [7], and complete-active-space multiple-configuration self-consistent-field methods (CAS-MC-SCF) [8]. After solving the electronic Hamiltonian self-consistently, the forces exerting on the atomic nuclei can be calculated based on the Hellmann-Feynman theorem. Therefore, a stable geometric structure of clusters can be determined according to classical mechanics so that there are no forces exerting on the atomic nuclei. We adopt the Gaussian 03 program [9] to perform such first-principle molecular dynamics calculations. A problem to determine the important stable cluster structures is to exhaust all possible initial starting atomic coordinates of clusters; the number of all possible initial coordinates will increase exponentially with the number of atoms which form various clusters. We present an optimum valence bond scheme [2,3]; firstly, to determine a minimum set of initial coordinates based on the picture of the frontier molecular orbitals [10] (i.e., the highest occupied molecular orbital, HOMO, and the lowest unoccupied molecular orbital, LUMO) and then to calculate all important stable clusters by the first-principle molecular dynamics method. More specifically, starting with O_3 clusters which have three types of structures given in Table 1 (trivial for monomer and dimmer), we can find out appropriate initial coordinates for 4-oxygen clusters based on combinations of the HOMO or the LUMO of the O_3 cluster and the corresponding unoccupied atomic valence orbital or the corresponding

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Table 1. Important 3- and 4-atom clusters of the second- and the third-row elements.

	Li	Be	B	C	N	O	F
3-atom cluster*	$^4(0.25)D_{3h}$ $^2(1.25)D_{\infty h}$ $^2(1.43)C_{2v}$	$^1(0.73)D_{\infty h}$ $^3(0.88)C_{2v}$ $^1(1.38)D_{3h}$	$^2(5.65)D_{\infty h}$ $^4(7.13)C_{2v}$ $^2(8.45)D_{3h}$	$^3(12.9)D_{3h}$ $^1(13.7)D_{\infty h}$	$^2(8.77)C_{2v}$ $^2(10.4)D_{\infty h}$	$^1(4.33)D_{3h}$ $^3(4.80)C_{2v}$ $^1(5.74)C_{2v}$	$^4(0.14)C_{2v}$ $^4(0.64)D_{3h}$
4-atom cluster	$^5(0.14)D_{\infty h}$ $^5(0.87)T_d$ $^1(1.87)D_{\infty h}$ $^3(2.19)D_{2d}$ $^1(2.53)D_{2h}$	$^5(0.66)D_{\infty h}$ $^1(2.11)C_{2v}$ $^1(2.21)D_{4h}$ $^3(2.68)D_{4h}$ $^3(2.89)D_{2h}$ $^1(4.19)T_d$	$^1(9.39)D_{\infty h}$ $^3(10.2)T_d$ $^1(11.2)C_{2v}$ $^3(12.5)D_{4h}$ $^1(13.8)D_{2h}$	$^3(5.92)D_{2d}$ $^1(10.7)T_d$ $^1(18.4)D_{2h}$ $^3(19.9)D_{\infty h}$	$^3(11.2)D_{2d}$ $^1(11.5)T_d$ $^1(11.6)D_{2h}$	$^3(4.59)C_s$ $^1(5.28)D_{3h}$ $^3(5.54)C_s$ $^1(5.55)D_{2d}$ $^1(7.69)C_{2h}$ $^1(8.46)D_{2h}$ $^3(8.95)C_{2h}$ $^3(9.40)D_{2h}$	$^1(2.76)D_{\infty h}$
	Na	Mg	Al	Si	P	S	Cl
3-atom cluster	$^4(0.11)D_{3h}$ $^2(1.10)D_{\infty h}$ $^2(1.13)C_{2v}$	$^3(-0.64)C_{2v}$ $^1(0.34)D_{\infty h}$ $^1(0.58)D_{3h}$	$^2(2.75)D_{\infty h}$ $^4(3.03)C_{2v}$ $^2(3.19)D_{3h}$	$^3(6.72)D_{3h}$ $^1(6.92)C_{2v}$	$^2(4.92)C_{2v}$ $^2(5.66)D_{\infty h}$	$^3(5.09)C_{2v}$ $^1(5.65)D_{3h}$ $^1(6.15)C_{2v}$	$^4(0.14)D_{\infty h}$ $^4(1.25)D_{3h}$ $^2(2.20)C_{2v}$
4-atom cluster	$^5(0.10)D_{\infty h}$ $^5(0.36)T_d$ $^3(1.25)D_{\infty h}$ $^3(1.70)D_{2d}$ $^1(1.926)C_{2h}$ $^1(1.928)D_{2h}$	$^3(0.37)D_{2h}$ $^1(0.53)D_{\infty h}$ $^1(0.80)C_{2v}$ $^1(1.55)T_d$	$^1(3.85)C_s$ $^3(4.13)D_{\infty h}$ $^5(4.43)T_d$ $^1(4.65)C_{2v}$ $^1(4.75)C_{2h}$ $^3(4.93)D_{2h}$	$^1(8.86)T_d$ $^3(9.58)D_{2d}$ $^1(10.80)D_{2h}$	$^3(7.87)C_{2v}$ $^1(8.06)C_{2v}$ $^1(8.33)D_{2h}$ $^1(8.60)D_{2h}$ $^3(9.04)D_{2d}$ $^1(10.30)C_{2v}$ $^1(17.73)T_d$	$^1(7.26)D_{3h}$ $^1(7.74)C_{2v}$ $^1(7.62)D_{2d}$ $^1(8.28)C_{2v}$ $^1(8.43)D_{2h}$ $^3(9.06)C_{2v}$	$^1(4.12)D_{\infty h}$

* $^{(2S+1)}(BE)\ Sym$; S: the total spin, BE: the binding energy (eV), Sym: point symmetry group.

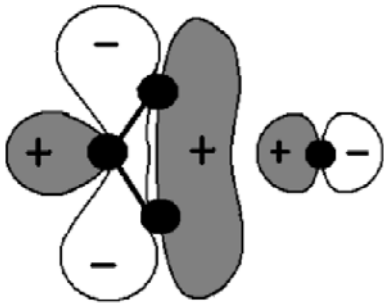

Fig. 1. An initial coordinate of 4-oxygen clusters.

occupied atomic valence orbital of the oxygen atom respectively. As shown in Figure 1, based on the HOMO of the ground-state O_3 with a C_{2v} symmetry and the unoccupied $2p$ orbital of O, an initial coordinate for 4-oxygen clusters can be selected with a favor phase matching condition of electron wave-functions [10]. It is one of four possible initial coordinates for the ground-state O_3 plus one oxygen. Adding one oxygen atom to three types of O_3 clusters, we can find out a minimum set of initial coordinates for 4-oxygen clusters. With the minimum set of initial coordinates of 4-oxygen clusters, we can perform the first-principle molecular dynamics calculations to determine all important stable O_4 clusters given in Table 1. Sometimes different initial coordinates lead to a same O_4 structure. It may reduce computational efforts. Note that in the first-principle calculations one should try various total spin multiplicities in order to take into accounts possible Jahn-Teller instabilities [2,11]. Based on an inductive-type procedure, we can continue to determine all important stable clusters X_{n+1} with the knowledge of all important stable clusters X_n by plus one atom X. Here the important stable clusters are define to be formed by electron valence orbitals without involving any Rydberg molecular orbitals [2]. Therefore, with limited computational efforts, we can obtain the properties of cluster X_m with m as large as possible, and the properties of all clusters X_i $(i < m)$, e.g., their stable geometric structures, electronic properties, etc. Table 1 lists all important stable structures up to 4-atom clusters for the second-row and the third-row elements in the period table. We would like to conclude by making the following comments; the optimum valence bond scheme should be applied to any combinations of a cluster A and another cluster B by considering combinations of the generalized higher occupied molecular orbitals (GHOMOs) or the general lower unoccupied molecular orbitals (GLUMOs) of the cluster A and the corresponding GLUMOs or GHOMOs of the cluster B respectively. Because the density of states is very high for larger clusters, one should consider several relevant occupied MOs below the HOMO, i.e., GHOMOs and several relevant unoccupied MOs just above the LUMO, i.e., GLUMOs.

Table 2. Melting and boiling points of the element X and the dissociation energies (DE) of the ground-state clusters X_n based on their binding energies (BE).

atomic element X	melting point K	boiling point K	$BE\ \epsilon_2$ of X_2 (eV)	$BE\ \epsilon_3$ of X_3 (eV)	$BE\ \epsilon_4$ of X_4 (eV)	DE $\epsilon_3 - \epsilon_2$ (eV)	DE $\epsilon_4 - \epsilon_3$ (eV)	DE $\epsilon_4 - 2\epsilon_2$ (eV)
Li	453.7	1615	0.90	1.43	2.53	0.53	1.10	0.73
Be	1560	2745	0.18	1.38	4.19	1.20	2.81	3.83
B	2300	4275	2.58	8.45	13.80	5.87	5.35	8.64
C	4100	4470	5.09	13.74	19.93	8.65	6.19	9.75
N	63.14	77.35	9.74	10.43	11.58	0.69	1.15	–7.90
O	50.35	90.18	5.18	5.74	9.40	0.56	3.66	–0.96
F	53.48	84.95	1.38	0.64	2.76	–0.74	2.12	0.00
Na	371	1156	0.77	1.13	1.93	0.36	0.80	0.39
Mg	922	1363	0.14	0.58	1.55	0.44	0.97	1.27
Al	933	2793	1.19	3.19	4.93	2.00	1.74	2.55
Si	1685	3540	3.06	6.95	10.80	3.89	3.85	4.68
P	317.3	550	4.75	5.66	17.73	0.91	12.07	8.23
S	388.4	717.8	4.12	6.15	9.06	2.03	2.91	0.82
Cl	172.2	239.1	2.06	2.20	4.12	0.14	1.92	0.00

Note that $\epsilon_5 - \epsilon_4 = -5.03$ eV; $\epsilon_5 - \epsilon_3 - \epsilon_2 = 2.29$ eV for phosphor.

3 Conclusion

Based on the optimum valence bond scheme, the electronic structures and the corresponding geometric structures of all important clusters (X_n, $n \leq 4$) for the second- and the third-row elements X can be determined with limited computational efforts, as shown in Table 1. Although some uncertainty to determine approximate energy functionals in DFT still exists, adequate accuracy for the binding energies of the calculated clusters can be achieved, e.g., good agreements [2] with the available experimental data [12] for the ground-state dimmers. Before applying DFT to an unknown system, validity and accuracy of various energy functionals must be taken care of. More specifically, we adopt the B3LYP energy functional [13] for the second- and third-row elements except for Na and Mg. For the cluster systems of Na and Mg, we adopt the PBEPBE energy functional [14]. Table 2 lists the binding energies of the ground-state 3-atom and 4-atom clusters for the second- and the third-row elements. It is interesting to note that even for small size clusters it has already provided clues in some macroscopic properties of corresponding elements (e.g. melting and boiling point) [15]. More specifically, the dissociation energies of the clusters, especially for the dissociation of the 3-atom clusters into a dimmer plus an atom and the 4-atom clusters into the dimmer pairs given in the last third and the last columns of Table 2, vary accordingly with the melting points and the boiling points for the second- and the third-row elements except for phosphor. Note that the dissociation energy of P_5 into P_4 plus P is -5.03 eV. Therefore, It is a special case for phosphor since the bulk phosphor material consists of the very stable clusters P_4. In the last column of Table 2, the dissociation energies of the 4-atom clusters X_4 into a pair of dimmers X_2 are -7.90, -0.96 and 0.00 eV for the elements, N, O and F respectively. It indicates that the bulk phase of such elements, N, O and F, are gases consisting of diatomic molecules, N_2, O_2 and F_2 respectively. It is also interesting to note that the dissociation energies of X_4 into X_3 plus X (1.15, 3.66, 2.12 eV) vary accordingly with the differences of the boiling- and melting points (14.21, 39.83, 31.47 K) for such elements (N, O, F) in gas phase respectively. Finally, we would like to conclude; the optimum valence bond scheme should be applied to any combinations of larger clusters by considering combinations of the GHOMOs or the GLUMOs between clusters respectively. It deserves further studies in the properties of matter from physical pictures of clusters.

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