Valence bond study on excited states of molecules*  
---Bonding features of the low-lying states of molecule $B_2$

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Abstract Based on the correspondence of the molecular orbital theory and valence bond theory to the description of chemical bonds, the $ab$ $initio$ valence bond (VB) calculations of the low-lying states of diatomic molecules are realized. The calculation results for the low-lying states of $B_2$ show that the VB calculation has clear-cut physical significance, and its simulation of the behavior of the potential energy surface about the equilibrium position is superior to that of the molecular orbital theory. The valence bond calculation involving only a few bonded tableaus can correctly reflect the effect of electronic correlation.

Keywords: excited states, VB theory, $B_2$.

Excited states, as a status of a molecule existing in the special process and condition, are increasingly noticed with the development of modern experimental technology and theoretical methodology. At present, studies on low-lying states by the post-SCF methods including CI, MCSCF, MP, CC based on the molecular orbital (MO) theory have become relatively mature. Large scale post-SCF calculations for small systems can reproduce excellent spectroscopic constants. However, they cannot give a clear chemical bonding picture familiar to chemists, and it is difficult to extend them to the study of Rydberg states. Valence bond (VB) theory played a great role in development of chemistry before, and much attention has been paid to the methodology and application of modern VB theory$^{[1-6]}$. Up to now, molecular symmetry has not been explicitly imposed to the VB calculation, and it is not easy to classify and assign the low-lying electronic states, which hinders the VB study of excited states. In the present work, using the bonded-tableau unitary group approach (BTUGA) of modern VB theory, based on the correspondence between electronic configurations and resonance among VB structures, we realized the VB description of excited states. Several low-lying states of $B_2$ were investigated, and bonding features of boron were discussed.

1 Basic theory and computational methods

1.1 Multiconfigurational self-consistent field (MCSCF) and multi-bonded tableau self-consistent field (MBTSCF) methods

For a multi-electron system with $N$ electrons and spin $S$, its state can be described as

$$\Psi = \sum_{\Lambda} C_{\Lambda} \Phi_{\Lambda}. \quad (1)$$

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In the MCSCF method, $\Phi_A$ is a configuration function, usually, a Slater determinant constructed by a set of MOs occupied by electrons in some pattern. Here the MOs $|\phi_k\rangle$ can be expanded with basis functions $|\chi_{\nu}\rangle$, i.e.

$$\phi_k = \sum_{\nu} C_{\nu k} \chi_{\nu}. \quad (2)$$

The expected value of the energy and MCSCF wavefunction of the system can be obtained by optimizing $|C_A, C_{\nu k}|$. If the MCSCF wavefunction is derived from all the possible excitations of all the electrons in a given active space, it is called the complete active space self-consistent field (CASSCF) method.

In modern VB calculation, $\Phi_A$ is a VB structure function or bonded tableau. The bonded tableau can be defined as

$$\Phi_{\text{BT}}(I) = A_I e_{11}^{[\lambda]} \Phi_0(I), \quad (3)$$

where $A_I$ is a normalization factor, $e_{11}^{[\lambda]}$ is a standard project operator, and $[\lambda] = [2N/2-S12S]$ is an irreducible representation of group $S_N$. $\Phi_0(I)$ is a multiplication of basis orbitals $|\zeta_k\rangle$. The basis orbitals are generally taken from atomic orbitals, atomic hybrid orbitals or overlap-enhanced orbitals (AOEs), represented by

$$\zeta_k = \chi_k + \sum_{\nu \neq k} C_{\nu k} \chi_{\nu}. \quad (4)$$

In the MO theory, if only one term in eq. (1) is considered, it is the usual SCF method, and when multiple terms are involved, it is the MCSCF. Similarly, in the VB calculation, if only one or several bonded tableaus corresponding to the single Slater determinant are involved, we can call it the bonded tableau self-consistent field (BTSCF) method; and when more bonded tableaus are considered and the coefficients of the bonded tableaus and basis orbitals are optimized simultaneously, one can call it the MBTSCF. For the details of BTUGA, refer to references [7—9].

1.2 Description of one-electron (1e) bond, two-electron (2e) bond, and three-electron (3e) bond

According to the MO theory, the bonding between atoms can be described with bonding electrons and anti-bonding electrons in the MOs, but in the VB theory chemical bond is derived from resonances between the VB structures$^{[10]}$. There exists the following correspondence between the both (table 1):

<table>
<thead>
<tr>
<th>Method</th>
<th>1e-bond</th>
<th>2e-bond</th>
<th>3e-bond</th>
<th>lone pair</th>
</tr>
</thead>
<tbody>
<tr>
<td>MO</td>
<td>$H_2$</td>
<td>$H_2$</td>
<td>$He_2^+$</td>
<td>$He_2^-$</td>
</tr>
<tr>
<td>VB</td>
<td>$</td>
<td>H^+ H, HH^-</td>
<td>$, $</td>
<td>H^+ H^-, HH^+</td>
</tr>
<tr>
<td>BT</td>
<td>$</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

In table 1, 1 and 2 indicate 1s orbitals. For a typical covalent bond with 2 electrons (e.g. H-H), the ionic structures (H$^+$H$^+$ or H$^+H^-$) can be ignored if semi-localized orbitals as shown by eq.