Nature of Chemical Bonds in Excited States

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I shall discuss the nature of chemical bonds coexisting together with huge electronic-state fluctuation in highly excited states of boron clusters.

The total electronic state $\Psi(\mathbf{r},\mathrm{t};\mathbf{R}(\mathrm{t}))$ for the electronic coordinates $\mathbf{r}$ at time *t* and a nuclear position $\mathbf{R}(\mathrm{t})$ is expanded in basis state functions such as the *I*th adiabatic state $\Phi_I(\mathbf{r};\mathbf{R})$ as $\Psi(\mathbf{r},\mathrm{t};\mathbf{R}(\mathrm{t}))=\sum_I C_I(t)\Phi_I(\mathbf{r};\mathbf{R})\big|_{\mathbf{R}=\mathbf{R}(\mathrm{t})}$. Starting from a pure adiabatic state, I=300 with $C_{300}(0)=1.0$, for instance, the time-dependent state soon begins to behave like a diffusion in the entire *I*-space with the distribution functions $\left|\mathrm{C}_I(t)\right|^2$. This is due to the dense quasi-degeneracy among the electronic states and continual and intensive nonadiabatic transitions. Here the notion of adiabatic states and the associated potential energy surface (PES) lose the sense, and the Landau-Zener one-dimensional theory for nonadiabatic transition through a well isolated crossing is far from practical. The electronic wavefunction are highly correlated and essentially complex-valued. Yet, the chemical bonds persist under the huge electronic-state fluctuation. We study the nature of the relevant chemical bonds and identify the origin of and quantify the electronic fluctuation in a simple one-electron picture with our developed Energy Natural Orbitals [1]. The present challenge provides us with a basic theoretical scheme useful also in general studies on excited state chemistry.

Prior to the boron clusters, I will begin my talk with the nature of chemical bonds of a couple of low-lying excited states of hydrogen molecules as a fundamental matter. [2]

[1] K. Takatsuka and Y. Arasaki, J. Chem. Phys. **154**, 094103 (2021). “Energy natural orbitals.”
[2] Y. Arasaki and K. Takatsuka, J. Chem. Phys. **156**, 234102 (2022). “Nature of chemical bond and potential barrier in an invariant energy-orbital picture.”
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