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**Vibronic
Coupling
Density**
Understanding
Molecular
Deformation



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Understanding Molecular Deformation

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Preface

Nobel laureate Roald Hoffmann pointed out, “Understanding and Explaining and their Strong-Tie to Teaching” in the memorial lecture at the Kenichi Fukui 100th birthday anniversary 2018 in Kyoto.¹ He sketched a possible path to coexistence, way from theory and understanding through simulation and then back again to understanding. We want to quote his sketches. He gave the process of understanding, insight, and explanation, and then prediction. Understanding is often tacit, or silent, a state of mind. It is usually qualitative, though it may have quantitative aspects. Quantitative reinforces qualitative. And simulation is around the corner. An explanation is inherently more pedagogic and storytelling. More useful to science are hypotheses, alternative narratives. An explanation comes to us through stories, chemical stories. Prediction is the conceptual passage between understanding and simulation and is the practical counterpart of contemplative understanding, “I know how” instead of “I know why.”

A molecule can be regarded as a system of electrons in a framework of nuclei, that is, a molecular structure. Chemists are interested in molecular motions under the interactions of other molecules or an electromagnetic field. The motion of a molecule is decomposed into translational, rotational, and vibrational modes. An intramolecular motion, i.e., molecular deformation, is expressed as a combination of vibrational modes.

Exactly speaking, vibrations and motions of electrons cannot be separated. Therefore, any change of an electronic state gives rise to a molecular deformation. The couplings among vibrations and electrons are called vibronic coupling (VC). The magnitude of deformation depends on the strength of VCs, vibronic coupling constants (VCCs). The direction of deformation depends on the relative values of the VCCs of vibrational modes. Thus, if we can understand the reason for the relative strength and magnitude of VCCs, we can explain the molecular deformation under a certain interaction. Vibronic coupling density (VCD), a density form of a VCC,

¹Roald Hoffmann, “Simulation versus Understanding: A tension, and not just in Quantum Chemistry,” the lecture in the Memorial Symposium of “Kenichi Fukui 100th birthday anniversary,” Kyoto, 2018.

enables us to explain such a reason. In this monograph, we will give the instructive path to the VCD and the VCC analyses.

Chemistry in alchemy was just aimed at getting gold without understanding. Modern chemistry emerged with the concept of atoms and molecules. After the quantum study, the electron behavior circulating nuclei was led to the principal concept underlying all explanations in chemistry. Many textbooks have given the plausible explanations to clarify the molecular structure. And the frontier molecular orbital concepts were proposed to visualize the path of a chemical reaction. The conventional explanations have provided students with a considerable familiarity with the molecular structure in terms of the electronic state. However, the more rational and more convincing ways should be given. Here the VCD and the VCC analyses are introduced. They are starting from the *ab initio* molecular Hamiltonian, and systematic, rational ways to understand chemical phenomena, and which can give the quantitative evaluation of the force applied under the chemical deformation process. We offer the guidelines to integrate the traditional “hand-waving” approach of chemistry with more rational and general VCD and VCC alternative. Further outlooks for the newly functionalized chemical systems. Thus, through the visualization by VCD and the evaluation by VCC, the study of chemistry by molecular orbital theory is brought into the domain of substantial science, where qualitative concepts can be rendered quantitatively and tested rigorously against the quantum theory.

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Acronyms

AO	Atomic Orbital
AVCC	Atomic Vibronic Coupling Constant
CASSCF	Complete Active Space Self-consistent Field
DFT	Density Functional Theory
EVCD	Effective Vibronic Coupling Density
HOMO	Highest Occupied Molecular Orbital
irrep	irreducible representation
JT	Jahn–Teller
JTE	Jahn–Teller Effect
LUMO	Lowest Unoccupied Molecular Orbital
MO	Molecular Orbital
OVCC	Orbital Vibronic Coupling Constant
OVCD	Orbital Vibronic Coupling Density
PJTE	Pseudo-Jahn–Teller Effect
QVCC	Quadratic Vibronic Coupling Constant
QVCD	Quadratic Vibronic Coupling Density
SOMO	Singly Occupied Molecular Orbital
TDMD	Transition Dipole Moment Density
VB	Valence Bond
VC	Vibronic Coupling
VCC	Vibronic Coupling Constant
VCD	Vibronic Coupling Density
VSEPR	Valence Shell Electron Pair Repulsion

Symbols

\mathbf{x}	Cartesian coordinate in the three-dimensional space
x, y, z	x, y, z -components of \mathbf{x} , relative coordinates (Chap. 2.2)
X, Y, Z	Coordinates of the center of mass (Chap. 2.2)
\mathbf{r}	A set of spatial coordinates of all electrons
i, j	Labels of electrons, Labels of atom (Chap. 2.2)
l_i	Bond length of atom i and $i + 1$
φ_i	Bond angle of atom $i - 1, i, \text{ and } i + 1$
χ_i	Dihedral angle of atom $i - 1, i, i + 1, \text{ and } i + 2$
\mathbf{r}_i	Spatial coordinate of electron i
x_i, y_i, z_i	x, y, z -components of \mathbf{r}_i
$\boldsymbol{\omega}$	A set of spin coordinates of all electrons
ω_i	Spin coordinate of electron i
\mathbf{R}	A set of spatial coordinates of all nuclei
A, B	Labels of nuclei
\mathbf{R}_A	Spatial coordinate of nucleus A
X_A, Y_A, Z_A	x, y, z -components of \mathbf{R}_A
\mathbf{R}^0	Reference nuclear configuration
\mathbf{R}_A^0	Spatial coordinate of nucleus A in the reference nuclear configuration
X_A^0, Y_A^0, Z_A^0	x, y, z -components of \mathbf{R}_A^0
$\Delta\mathbf{R}$	Displacement of all nuclei from \mathbf{R}^0
$\Delta\mathbf{R}_A$	Displacement of nucleus A from \mathbf{R}_A^0
$\Delta X_A, \Delta Y_A, \Delta Z_A$	x, y, z -components of $\Delta\mathbf{R}_A$
\mathbf{Q}	A set of all mass-weighted vibrational coordinates
α, β	Labels of vibrational modes
Q_α	Mass-weighted vibrational coordinate of mode α
q_α	Vibrational coordinate of mode α in the real space
\mathbf{u}_α	Vibrational vector of mode α in the mass-weighted space
\mathbf{v}_α	Vibrational vector of mode α in the real space
μ_α	Reduced mass of mode α
ω_α	Frequency of mode α
$v_\alpha(\mathbf{x})$	Linear potential derivative with respect to vibrational mode α

$w_{\alpha\beta}(\mathbf{x})$	Quadratic potential derivative with respect to vibrational modes α, β
$w_{\alpha_1 \dots \alpha_k}(\mathbf{x})$	k -th-order potential derivative with respect to vibrational modes $\alpha_1 \dots \alpha_k$
m, n	Labels of electronic states
$\Psi_m(\mathbf{r}, \mathbf{R})$	m -th total electronic wave function at the nuclear configuration \mathbf{R}
$E_m(\mathbf{r}, \mathbf{R})$	m -th total electronic energy at the nuclear configuration \mathbf{R}
$\rho_m(\mathbf{x})$	Electron density in the m -th electronic state
$\Delta\rho_m(\mathbf{x})$	Electron density difference between the reference and the m -th electronic states
$\rho_{mn}(\mathbf{x})$	Overlap density between m -th and n -th electronic states
$\rho_{ab}(\mathbf{x})$	Overlap density between a -th and b -th molecular orbitals
$V_{mn,\alpha}$	Linear vibronic coupling constant between m -th and n -th electronic states with respect to vibrational mode α
$W_{mn,\alpha\beta}$	Quadratic vibronic coupling constant between m -th and n -th electronic states with respect to vibrational modes α, β
$W_{mn,\alpha_1 \dots \alpha_k}$	k -th-order vibronic coupling constant between m -th and n -th electronic states with respect to vibrational modes $\alpha_1 \dots \alpha_k$
$\eta_{mn,\alpha}(\mathbf{x})$	Linear vibronic coupling density between m -th and n -th electronic states with respect to vibrational mode α
$\eta_{mn,\alpha\beta}(\mathbf{x})$	Quadratic vibronic coupling density between m -th and n -th electronic states with respect to vibrational modes α, β
$\eta_{mn,\alpha_1 \dots \alpha_k}(\mathbf{x})$	k -th-order vibronic coupling density between m -th and n -th electronic states with respect to vibrational modes $\alpha_1 \dots \alpha_k$
$V_{ab,\alpha}$	Linear orbital vibronic coupling constant between a -th and b -th molecular orbitals with respect to vibrational mode α
$W_{ab,\alpha\beta}$	Quadratic orbital vibronic coupling constant between a -th and b -th molecular orbitals with respect to vibrational modes α, β
$W_{ab,\alpha_1 \dots \alpha_k}$	k -th-order orbital vibronic coupling constant between a -th and b -th molecular orbitals with respect to vibrational modes $\alpha_1 \dots \alpha_k$
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